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CATALYTIC OXIDATION OF OLEFINS OVER MODIFIED COPPER OXIDE CATALYSTS

By

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ABSTRACT

The vapor phase air oxidation of propene and 2-methylpropene to acrolein and methacrolein was investigated in an isothermal integral flow reactor at atmospheric pressure between 300 and 500°C. The skeleton catalyst (copper oxide) supported on pumice stone or inactivated alumina was modified in a constant and continuous supply of trace amounts of selenium, sulfur, bromine, chlorine and iodine, all having the electronegativities higher than that of copper.

The effect of various process variables, namely the weight ratio of modifier to olefin in the feed, the feed ratio of oxygen to olefin, reaction temperature and the reciprocal of space velocity, on the conversion of olefin and the product distribution was determined by gas chromatography.

It was found that in 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.

The catalytic oxidation of methacrolein over the same catalyst in the presence and absence of a chlorine modifier was also studied. The results indicate that the promotional effect of the modifier is mainly due to its successfully suppressing the further oxidation of aldehyde to the undesired products.

The active phase of the catalyst for the selective oxidation of olefin was found to be cuprous oxide by X-Ray diffraction studies.

The Electronic Theory of Catalysis has been modified to explain the results and a mechanism is proposed. It has been suggested that the charged oxygen and olefin are selectively adsorbed 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 the optimum conditions.

Out of the several models proposed for the oxidation of 2-methylpropene over chlorine modified copper oxide catalyst, the most suitable one appears 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 be expressed by the equation

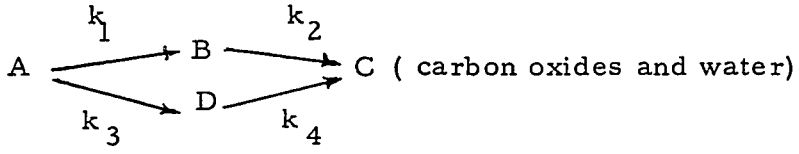
$$r = \frac{K_S K_H P_H}{1 + K_H P_H + K_M P_M} \cdot \frac{K_O P_O}{1 + K_O P_O}$$

Where K_S, K_H and K_M are temperature dependent constants.

I. INTRODUCTION

In recent years, the controlled oxidation of olefins and dienes to useful intermediate products has attracted wide attention. It has now been possible to obtain many valuable oxygenated carbon compounds, as well as dienes from the plentiful 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 naphthalene to phthalic anhydride.

Though 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 B 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 k's 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.

The broader features of the mechanisms of non-catalysed reactions of hydrocarbons and oxygen are now well established, though in no case is there a complete understanding of all the aspects of the reaction. These oxidations are free-radical chain processes[66] whose kinetics are dependent upon the interplay of four groups of elementary steps - initiation, propagation, branching and termination. However, in the heterogeneous catalytic oxidation, the competition between reactants and partial oxidation products for the active sites of the catalyst as well as the surface properties (surface defects etc.) of the solid make a similar kinetic expression more complicated.

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 variables available 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 copper oxide catalyst for methacrolein production always decreases with increasing conversions as required for a consecutive reaction. Similar results have been reported for propene oxidation over bismuth molybdate catalyst[1]. The selectivity of the reaction can be improved even at high conversions by using a suitable catalyst and modifying it with some dopents (modifiers).

A variety of solids can act as heterogeneous catalysts for the partial oxidation of hydrocarbons. The most common catalysts are transition metal oxides which are usually semiconductors. Though generally p-type semiconductor oxides (copper oxide, nickel oxide, mangenese oxide etc.) are much more active oxidation catalysts, they by themselves seldom show little or no selectivity to particular intermediate products. On the other hand, n-type semiconductors (molybdenum oxide, vanadium oxide etc.) show good selectivity but have little or no activity.

Copper oxide (p-type) and molybdenum oxide (n-type) 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.

Some efforts have been made in the past to achieve high selectivity and activity of the catalyst by modifying the skeleton catalyst with different additives. Unfortunately most of the work is covered in the patents, and details are not available. In general, the most active and selective catalysts are combinations of highly active oxides, e.g., oxides of copper, nickel, cobalt, mangenese, iron, chromium and tin with oxides of more negative moderating elements, e.g., oxides of phosphorous, arsenic, antimony, bismuth, selenium, tellurium and halogen.

Most oxidation catalysts are semiconductors. There have been numerous attempts to correlate catalytic properties of oxides with their semiconductivity[13,22,71,95]. One of the

most widely used theory to explain the reactions on semiconductors is the Electronic Theory of Catalysis on Semiconductors. The fundamental hypothesis of the theory is that all heterogeneous catalytic reactions are either acceptor reactions (n-type) or donor reactions (p-type). An acceptor reaction is catalyzed by free electrons, and the donor reaction is catalyzed by positive holes. The activity of a semiconductor catalyst is determined by its Fermi level at the catalyst surface. This theory has been capable of explaining many empirical correlations such as decomposition of nitrogen oxides[13, 20, 92], oxidation of carbon monoxide over doped catalyst [23, 70, 80]. In the present study, this theory with slight modifications was used to investigate the oxidation of olefins over modified copper oxide catalysts.

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 difficulty in a precise analysis because of the low concentration of products in the gas stream. On the other hand, the integral method is not restricted to a small conversion and the analytical accuracy is greater. However, it is much more difficult to integrate the rate equations since there are several hidden parameters which may diminish the value of the experimental data[52].

All of the modifiers generally used to enhance the activity and selectivity of the skeleton catalyst have been found to be unstable at the reaction temperature. Since these modifiers continuously escape from the catalyst surface, a batch reactor would not be suitable for catalyst modification study.

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

The Objects of the Present Work

(1) To set up the apparatus to investigate the olefin oxidation over copper oxide catalyst in a constant and continuous supply of modifiers in different forms, and to study their promotional effects and the optimum amount which could be used in selective oxidation.

(2) To study the effect of process variables on the conversion and product distribution over the most suitably modified catalyst.

(3) To identify the active component of the catalyst for the selective oxidation.

(4) To propose a hypothesis which could explain the promotional effect of these modifiers in olefin oxidation, and

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

II. LITERATURE SURVEY

Although the oxidation of olefins to unsaturated carbonyl compounds has been of great industrial importance, 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 exothermicity 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 types 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-methylpropene to methacrolein.

This chapter includes a summary of the published literature on the two well known catalysts - copper oxide and bismuth molybdate. Emphasis is placed on the reaction kinetics, evidence regarding the influence of catalyst composition, the reaction mechanisms and the yield of corresponding unsaturated aldehydes. Also included is the oxidation of olefins over some other less commonly used oxide catalysts and recent developments in the catalyst modification in order to enhance the selective oxidation.

(A) Copper Oxide as a Catalyst

Although the supported copper oxide catalysts have been used most frequently, the use of the bulk metal in the form of powder, gauze, film, shavings or even as the material of the reaction tube has been reported[39,45,85].

Gorokhovatskii et al.[31] investigated the influence of the supports, porous glass, silcon carbide and alumina on the catalytic oxidation of olefins. They found that pore structure and chemical composition influenced the oxidation. The increase in surface area or a decrease in the pore size of the supports was accompanied by a decrease in the specificity.

Isaev and Margolis[41] made a kinetic study of the air oxidation of propene at atmospheric pressure in a dynamic unit. The copper-catalyzed reaction yielded acrolein, carbon dioxide, water and a small quantity of acetaldehyde. These investigators found that the propene oxidation rate was proportional to oxygen concentration and was independent of propene concentration. They obtained an apparent activation energy of 30 kcal/gm-mole for carbon dioxide formation over a silite supported copper catalyst and 23-25 k cal/gm-mole over a pumice supported catalyst. Similarly, the acrolein oxidation rate was found to be proportional to oxygen concentration and independent of acrolein concentration. They suggested that the presence of propene reduced considerably the acrolein oxidation rate.

Popova, Mil'man and Latysheva[74] studied 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, at 350 - 370°C. They used a 2-methylpropene/oxygen ratio of 5.6 over a wide range of space velocities. 3.8% of the 2-methylpropene was converted to carbonyl compounds: 82.5% of which was methacrolein, 7.2% propionaldehyde, 6.2% acetaldehyde and 4.1% acrolein.

Enikeev, Isaev and Margolis[25] studied the oxidation of propene to acrolein on pumice supported copper oxide catalyst. From experimental data on oxygen and propene adsorption and results obtained while investigating the nature of the intermediates by an isotope method, they proposed a stage scheme for the oxidation of propene to acrolein. Oxygen in either atomic or molecular form is first adsorbed on the surface of the catalyst. Next propene is 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 decomposes into acrolein and water. The adsorbed acrolein interacts with oxygen from the gas phase giving a charged intermediary complex, which decomposes into carbon dioxide, water and a hydrocarbon radical adsorbed on the surface. The latter reacts again with oxygen. By analogy, they postulated that propene might be 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 decomposes into carbon dioxide, water and a hydrocarbon radical with a smaller number of carbon and hydrogen atoms. Also, they observed that 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. They were able to establish 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.

Belousov and co-workers[9] used the recirculating flow method with high propene/acrolein ratios to study the oxidation of propene over copper oxide catalyst. They suggested that carbon dioxide came largely from a parallel oxidation of propene and that rates could be described as

$$\text{acrolein production rate} = \frac{k_1 (O_2)}{1+b\,(\text{products})}$$

$$\text{carbon dioxide production rate} = \frac{k_2 (O_2)}{(C_3H_4O)^{0.7} (C_3H_6)^{0.2}}$$

Further study of the effect of steam on the oxidation of propene was made by Gorokhoratskii and Popova[30], over a copper oxide catalyst of low concentration, supported on silicon carbide. They used steam up to 60% of the feed and found that the rates for acrolein and carbon dioxide production could be expressed as

$$\text{acrolein production rate} = \frac{k_1 (O_2)^{0.8} (C_3H_6) [1+(H_2O)]^{0.5}}{[1+b' (C_3H_4O)][1+b_1 (H_2O)]}$$

$$\text{carbon dioxide production rate} = \frac{k_2 (O_2) (C_3H_6)}{[1+b'' (C_3H_4O)][1+b_2 (H_2O)]}$$

They observed that at high steam concentrations, the rate is approximately first order in propene and in oxygen as well.

Lakshmanan and Rouleau[53] studied the air oxidation of propene to acrolein over a cement pasted copper oxide catalyst in a continuously stirred reactor between 375° and 450°C. They found that 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

$$\text{acrolein production rate} = \frac{k_s K_1 (C_3H_6) (O_2)}{[1+K_1 (C_3H_6) + K_2 (C_3H_4O)]^2}$$

A very different picture of propene oxidation kinetics over a copper oxide catalyst was presented by Billingsley and Holland[12], who studied the reaction in a differential reactor at 240°C. They concluded that the reaction was limited by mass transfer of the oxygen and proposed the following rate equations

$$\text{acrolein production rate} = \frac{0.72\, k (C_3H_6) (O_2)}{0.72 (C_3H_6) + 4.5 (O_2)}$$

$$\text{carbon dioxide production rate} = \frac{3 k (O_2)^2}{0.72 (C_3H_6) + 4.5 (O_2)}$$

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 the most workers.

Dowden and Caldwell[21] studied the effect of reactant ratio, contact time and temperature on the conversion and yield of 2-methylpropene oxidation. They claimed that by 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, a conversion of 17% per pass with a 95% yield of methacrolein could be obtained at 400°C.

The kinetics of 2-methylpropene oxidation to methacrolein was studied by Popova and Milman [73] in a conventional flow reactor. The rates of methacrolein and carbon dioxide formation were found to be first and zero order with respect to oxygen and olefin respectively. The same orders were reported by Mann and Rouleau[57] for the overall oxidation in a static system between 360° and 400°C.

Mann and Rouleau[58] also published data on the 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

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

They suggested that the rate controlling step was the surface reaction between adsorbed 2-methylpropene and gaseous oxygen or weakly adsorbed oxygen.

Shapovalova and co-workers[83] studied the same reaction using the recirculating flow method at 330 - 385°C with 2-13% oxygen, 7-80% 2-methylpropene, 0.25 - 1.11% methacrolein and 0.30 - 1.85% carbon dioxide. Their results were similar to those obtained in propene oxidation, and suggested the following rate equations

$$\text{methacrolein production rate} = \frac{k_1 (O_2) (C_4H_8)^{0.1}}{1+b_1 [(H_2O + C_4H_6O)]}$$

$$\text{carbon dioxide production rate} = \frac{k_2 (O_2)^{0.8}}{1+b_2 [H_2O]}$$

Belousov and co-workers[8] passed pulses of mixed olefins (propene and 2-methylpropene) over a copper oxide catalyst and concluded from the inhibition of the oxidation of one olefin by another that the olefins compete in adsorption on the surface and they suggested that olefin adsorption is a necessary step in the formation of the activated complex.

Hearne and Adams[35] have studied the oxidation of several olefins over copper oxide catalyst. They have suggested that the reaction is not necessarily a direct substitution in the allylic position but may also involve a hydrogen elimination from the allyl position and a shift of the double bond, since methyl vinyl ketone and not crotonaldehyde is made from both butene-1 and butene-2.

Further insight into the mechanism of propene oxidation was given by Voge, Wagner and Stevenson[90] who located the carbon isotope in acrolein from propene labelled in the methyl group. They observed that half of the heavy carbon in the acrolein product was in the carbonyl group and isomerization of the unreacted propene was negligible and suggested that the only plausible mechanism to be the initial removal of a hydrogen atom from the methyl group to form an allyl intermediate which subsequently reacts at either end with equal probability. They also pointed out that carbon dioxide is largely formed from complete oxidation of the acrolein.

The confirmation and extension of this scheme was made by Adams and Jennings[2]. They reported 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. They have suggested that the mechanism of propene oxidation was the same over both catalysts.

(B) Bismuth Molybdate as a Catalyst

A catalyst containing bismuth and molybdenum oxides was used many years ago by Tanner for the oxidation of acetylene[87], but only recently similar catalysts have been employed for the oxidation of mono-olefins. Sometimes bismuth phosphomolybdate catalysts are also mentioned.

Veatch et. al. [89] reported that a composition $Bi_9Mo_{12}O_{52}$, either supported on silica gel or unsupported, gave high conversions of propene with high specificity to acrolein. They studied the reactions at high temperature between 350 and 500° C, using the equal weight of the active phase and support (silica gel), and a reactant ratio propene : air : steam of 1 : 5 : 6.3. They found that the presence of steam was beneficial and the optimum specificity was 60% at about 375° C, and the maximum propene conversion was 55%. They also observed that by variation of the air-propene feed ratio from 3 to 12, the selectivity to acrolein was only slightly affected, and at temperatures higher than 450° C, the propene conversion declined.

A laboratory study of the oxidation of propene to acrolein, and of 2-methylpropene to methacrolein, using bismuth molybdate

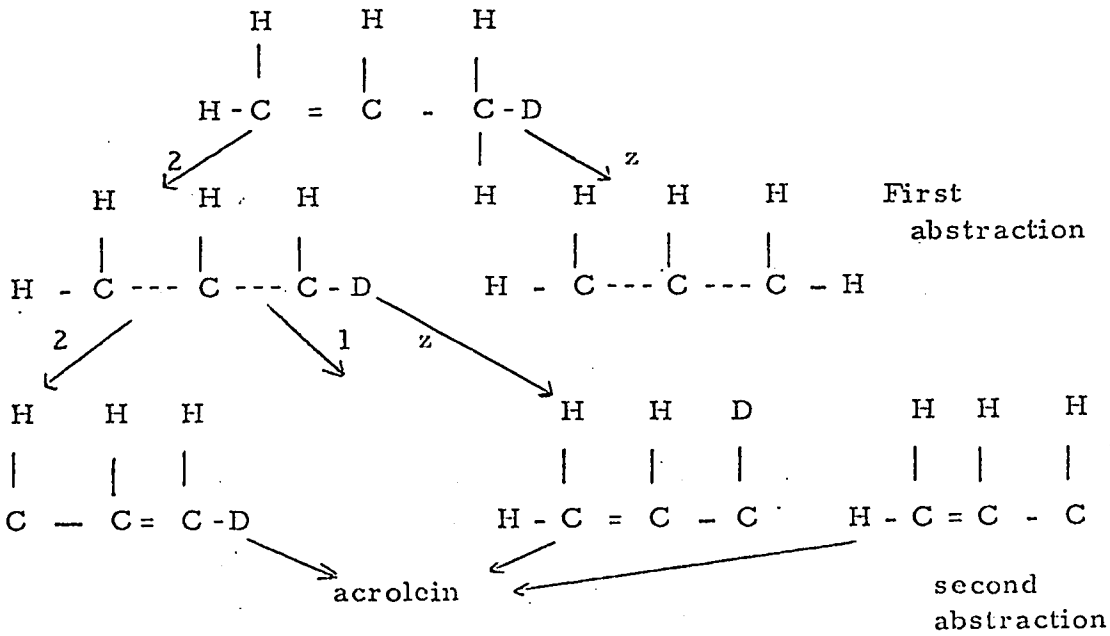
catalyst has been described by Adams and co-workers[3]. They found that the reactions were quite selective and the main side reaction is the total combustion to carbon dioxide. 2-methylpropene gave methacrolein with 80% selectivity. They also reported that there was a pronounced effect of temperature on the selectivity, and a maximum value was observed in the region 450 to 550° C, in the oxidation both of propene and 2-methylpropene. They found that there was no effect on the activity or selectivity when steam was added to the feed.

Kinetics of the oxidation of propene and of the four butenes over bismuth molybdate was also investigated by the Adams' group They found that the reaction was first order with respect to olefin and independent of oxygen and products. Relative reactivities of olefins were determined by them 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 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.

Uchijima and Oda[88] 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, and concluded that the same mechanism is involved in the formation of the aldehydes. However, 2-methylpropene was more readily oxidized than propene, the ratio of the two oxidation rate constants ($k_{\text{methacrolein}} / k_{\text{acrolein}}$) at 450° C was found by them as 4.5/ 13.2. Also, they found that 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 k cal/g-mole respectively.

Evidence on the mechanism of oxidation over bismuth molybdate has come 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 isotropic compositions of the products were in good agreement with those obtained over cuprous oxide, indicating that the same mechanism is inherent with both catalysts. The mechanism was proposed to be the initial abstraction of an allylic hydrogen to form a symmetric π-allyl intermediate, followed next by hydrogen abstraction from either end of this intermediate and by the hetero atom (oxygen) incorporation. The model is illustrated by the following scheme for 1-propene-3 d.



Here the numbers show the relative probability of the preceding species reacting along the indicated path, where z is the discrimination isotope effect (k_D/k_H) related to the different reactivities of the C - D and C - H bonds. They have also assumed that these abstractions were irreversible and that the discrimination isotope effect was the same in each abstraction. A value of z was calculated from the deuterium content of each product. The same value (0.55 - 0.57) was obtained from both 1-propene-3d and 1-propene-1d for the acrolein product, although the two olefins gave different amounts of deuterated products. They have postulated that further attack occurred though the hydrogen (or deuterium) atoms and that the probability of attack was proportional to the reactivity of these atoms.

Sachtler[77] and Sachtler and de Boer[78] also found evidence for a symmetric intermediate from the oxidation of propene containing radioactive carbon over bismuth molybdate. When the C^{14} was at either end of the propene molecule, half of it was found in the carbonyl group of the product acrolein. When it was in the middle carbon, no C^{14} was found in the carbonyl group.

McCain, Gough and Godin[65] found the same results using a bismuth phosphomolybdate supported on silica for propene oxidation.

Batist and co-workers[7] have studied the atomic ratio (Bi/Mo) in the bismuth molybdate catalyst for olefin oxidation in order to find the reasons for the markedly different catalytic behavior of bismuth molybdate relative to bismuth and molybdenum oxide. They found that the most active region was 40 - 70 atomic % bismuth, but some irregularities were noted, depending on the preparations and heat

treatment of the catalysts. Maximum activity was found to be near Bi/Mo = 1 provided the catalyst was not heated over about 500° C.

Margolis and co-workers[62] reported that the best selectivity was obtained for a mixed bismuth-molybdenum oxide that contained about 30 atomic % bismuth. The electronic work function was found to be a maximum at about this concentration.

(C) Other Oxides

Kutseva and Margolis[51] investigated the oxidation of propene over vanadium oxide and molybdenum oxide and mixtures of these alone and with additives. An approximately 50-fold excess of propene, relative to oxygen was used. They found the reaction to be first and zero order with respect to oxygen and propene respectively. In each case, the selectivity to acrolein was less than 30%. The selectivity with vanadium oxide was poorer to that with molybdenum oxide but its activity was much greater. Saturated aldehydes, carboxylic acids and carbon monoxide were formed in quantities comparable with those of acrolein and carbon dioxide.

Kitahara and Moriya[46] investigated the catalytic oxidation of 2-methylpropene to methacrolein over various metal oxides and their mixtures. They found that a vanadium oxide - molybdenum oxide - phosphorous oxide catalyst supported on an Al-sponge was the most effective catalyst for oxidation. They studied 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. Several undesirable by-products, i. e., ketones and acids besides methacrolein were obtained in the liquid products.

Several patents [6, 11, 91] mentioned that antimony oxide especially when used in conjunction with tin oxide gave a fairly good specificity to acrolein. The tin may be replaced by tungsten, uranium or molybdenum. The mixtures of molybdenum and tin oxides also gave comparable yields of acrolein and acrylic acid.

Wakabayashi et al. [93] studied the oxidation of propene over tin-antimony oxide catalysts in a flow system. They found that optimum catalyst composition for acrolein formation was a mixture containing a 3 : 1 atomic ratio of tin/antimony. X-Ray studies of the catalyst suggested that antimony oxide is dissolved in tin oxide giving solid solution. They also reported that the electrical conductivity of the catalyst increased markedly up to 3 atomic % antimony and then only slightly affected for the mixture containing more than 3 atomic % antimony. An increase in the initial rate of acrolein formation was observed when the concentration of the quasi-free electrons on the catalyst surface increased on addition of antimony oxide to tin oxide.

In a study directed primarily at the synthesis of methacrylonitrile, Brill and Finley[14] oxidized 2-methylpropene using oxygen/2-methylpropene ratio of 2 in a tube coated with α-alumina and molybdenum oxide and obtained a 40% selectivity to methacrolein for 34% conversion. Besides methacrolein, carbon dioxide and carbon monoxide were formed.

Zhiznevskii et al. [99] 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 and 420° C. They found that an increase in the percentage of

tellurium (up to 30%) increased the selectivity, and an increase in molybdenum up to 22-35% raised the specific activity. The best results were obtained with the catalyst having the composition iron: molybdenum : tellurium = 1 : 1 : 0.85..

The kinetics of the oxidation of 2-methylpropene into methacrolein over iron-molybdenum-tellurium catalyst in the presence of steam was studied by Zhizneskii et al. in the range 360 - 420°C. They have reported the rates of formation as

$$W_{C_4H_6O} = \frac{k_1 \, C_{O_2} \, C_{H_2O}^{0.4}}{1 + b \, C_4H_6O} \quad \text{mole/sec/}\ell$$

$$W_{CO_2} = \frac{k_2 \, C_{O_2} \, C_{H_2O}^{0.25}}{1 + b \, C_4H_6O} \quad \text{mole/sec/}\ell$$

$$W_{CO} = k_3 \, C_{O_2} \, C_{H_2O}^{0.25} \quad \text{mole/sec/}\ell$$

They reported that the formation of carbon oxides 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 k cals for methacrolein, carbon dioxide and carbon monoxide respectively.

(D) Modified Catalysts

Many attempts have been made in the past to achieve high selectivity and activity of the catalyst by modifying the skeleton catalyst with different additives. Unfortunately, most of the work is covered in the patents, and details are not available. In general,

the most active and selective catalysts for olefin oxidation are combinations of highly active oxides, e. g., oxides of copper, nickel, cobalt, manganese, iron, vanadium, molybdenum and tin with oxides of more negative moderating elements, e. g., oxides of phosphorous, arsenic, antimony, bismuth, selenium, tellurium and halogens.

The effect of several additives upon the catalytic activity and selectivity of metal oxides for ethene and propene oxidation has been investigated by Margolis et al.[62], and Ostrovskii et al.[69]. Margolis et al. have made measurements of the work function changes which occur on the surface (silver oxide and copper oxide) when the reactants and products are adsorbed, and when promoters are added to the catalyst. They showed that propene and also acrolein, lowered the work function of cuprous oxide and were therefore adsorbed as electron donors, on the other hand, oxygen and carbon dioxide were electron acceptors, and water a weak electron donor. They also postulated that carbon dioxide was only adsorbed on an oxygen covered surface, probably as a $CO_3^=$ complex. The results of Margolis et al. agree with the conductivity measurements of Lyubarskii[55], who also found that oxygen was an electron acceptor.

Margolis et al. also measured the work function changes which followed on doping the copper oxide catalyst with various additives. These were incorporated by impregnating the oxide with a solution of a suitable salt. The impregnated oxide, containing 2 atomic % of the modifier was obtained by calcination. Work function measurements showed that electropositive elements (Iron, chromium or lithium) all lowered the work function, thereby increasing the oxygen adsorption. Whereas these additives considerably

lowered the activation energy for carbon dioxide, they increased it for acrolein formation. The specificity for the production of acrolein also decreased, though not as much as the changes in activation energies. The electronegative elements (chlorine, sulfur) increased the work function and thereby the selectivity for acrolein formation.

Ostrovskii et al.[69] prepared catalysts containing labelled selenium, tellurium and sulfur and varied the proportion of additives between 10^{-5} to 10^{-1} atomic %. Small amounts of the additive were found to improve both the activity and selectivity, but with larger amounts the activity declined. However with sulfur the selectivity declined also. They concluded from the radioactivity measurements that the additives became concentrated on the surface under the reaction conditions and that selenium and tellurium, unlike chlorine were retained by the catalyst. They suggested that the change in the activity of the modified catalysts was due to a change in the bond energy of adsorbed oxygen and that traces of halogen compounds must be continuously added to the reactor feed in order to maintain the high selectivity of the catalysts.

Kominami et al.[49] and Kruzhalov et al.[50] studied the oxidation of propene over copper oxide catalysts in the presence of selenium. Both of them found that selenium drastically influenced the copper-catalyzed oxidation reaction and a high selectivity for acrolein formation was obtained even at complete conversion of propene.

While Kominami et al. postulated that the formation of copper selenite (the intermediate) during the reaction is responsible for the high selectivity for acrolein, Kruzhalov et al. proposed that selenium

is chemisorbed on the oxide surface and thus blocked the active sites for the complete oxidation. They also suggested that during the formation of acrolein, selenium assisted the decomposition of allyl hydroperoxide radical, resulting thereby in increased yield of acrolein. They found that in the presence of selenium, the reaction order with respect to propene changed from zero to first.

Many patents concerning the partial oxidation of propene and other olefins to acrolein and higher unsaturated aldehydes in the presence of selenium have been granted between 1950 and 1960 to Hadley and co-workers at Distillers Company Limited. The process was carried out in the vapor phase over various supported copper oxide catalysts either impregnated with elemental selenium [32] or by introducing the selenium as vapor in the feed itself [32]. They claimed that in either case, selenium lengthened the life of the copper catalyst and increased the yield of unsaturated aldehydes. These patents mostly refer to the passing of 25 liters of gas mixture (98% air and 2% olefin by volume) per hour over 8 to 10 grams of catalyst between 200 and 400° C in the presence of 0.0008 gram of selenium vapor per liter of feed.

During the past few years, though several patents [10,14,15,18] have appeared describing the use of sulfur, halogen and their compounds in conjunction with a skeleton catalyst (copper phosphate) with the purpose of obtaining improved catalysts for olefin oxidation, none of these give any information regarding the kinetics of the reaction or the role of such additives and its optimum amount required to enhance the activity of the catalyst.

Popova et al.[75] have investigated the introduction of a small amount of molybdenum and tungsten to copper oxide catalyst for oxidizing propene. They found that though the addition of molybdenum and tungsten oxides did not affect the reaction order with respect to propene and oxygen and the activation energy of acrolein formation, it increased the activation energy for carbon dioxide formation.

Kolchin et al.[11] studied the effect of several modifiers added to the bismuth molybdate catalyst for the oxidative ammonolysis of propene. They found that in the presence of additives such as oxides of potassium, lithium, barium, cobalt and nickel, there was a change in the phase composition of the catalyst. $Bi_2O_3 \cdot 2MoO_3$ was converted to $Bi_2O_3 \cdot 3MoO_3$ and $Bi_2O_3 \cdot MoO_3$. Though this change in catalyst composition decreased the rate of formation of acrolein, it did not affect the rate of formation of carbon dioxide. Addition of oxides of alumium, iron, chromium and copper did not influence the activity of the catalyst. Addition of $SO_4^=$, $PO_4^=$ and Cl^- did not affect the rate of acrolein formation, but decreased the rate of side reaction, resulting thereby an increase in selectivity for acrolein.

Arsenic modified catalysts prepared from several oxides was used by Ishikawa and co-workers[43] for propene and 2-methyl-propene oxidations. They found that fairly large amount of arsenic is needed for best results in the oxidation of olefin to aldehydes. Combinations of iron, manganese, vanadium and molybdenum-alumina with arsenic proved to be effective for improving selectivity. A selectivity of 80% with a conversion of 18% was obtained by using a catalyst containing arsenic/iron in an atomic ratio of 1.4 to 1 for propene oxidation at 410°C. They also found that these catalysts, like

those obtained by addition of selenium to copper oxide, operated best at high oxygen / olefin ratios.

Recently, the catalytic oxidation of 2-methylpropene over selenium dioxide and sulfur dioxide modified copper oxide catalysts was investigated by Mann and Yao[59,60]. They found that in the presence of an optimum amount of these oxides, the selectivity of the catalyst for methacrolein was much improved, and they also suggested[61] 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 would be expected. They have postulated that the partial oxidation of 2-methylpropene to methacrolein is a p-type reaction (reaction rate is accelerated with the increase in positive hole concentrations on the catalyst surface) and its further oxidation to carbon oxides is an n-type reaction(reaction rate is accelerated with the increase in concentration of free electrons on the catalyst surface) under optimum conditions.

III. EXPERIMENTAL

A. Reactants and Chemicals Used for Making Catalysts and Modifiers

(1) Propene

C. P. grade propene gas (Matheson Co.) with a minimum purity of 99% was used. The gas was received in cylinders containing liquified propene at a pressure of 136 psig (70° F).

(2) 2-Methylpropene

C. P. grade compressed 2-methylpropene gas (Matheson Co.) with a minimum purity of 99% was used. The gas was received in cylinders containing liquified 2-methylpropene at a pressure of 25 psig (70° F).

(3) Air

Compressed air (Linde Co.) in cylinders at a pressure of 2500 psig was used as the source of oxygen. The gas chromatograms of air showed that it contained 20.95% oxygen, 79.00% nitrogen and 0.05% carbon dioxide. Any water vapor was removed by passing it through a tube containing indicating drierite.

(4) Cupric nitrate $Cu(NO_3)_2 \cdot 3H_2O$

Reagent grade cupric nitrate meeting the A. C. S. specification was obtained from Baker Chemical Co. (Lot No. 704802).

(5) Mangenese (ous) 50% nitrate solution $Mn(NO_3)_2$

Fisher certificated (Lot No. 762191).

(6) Nickel (ous) nitrate $Ni(NO_3)_2 \cdot 6H_2O$

Fisher certificated (Lot No. 701611).

(7) Methacrolein

Reagent grade methacrolein was obtained from K and K Rare Chemicals (Lot No. 3903) in its purest form. The gas chromatogram showed that it contained 98% minimum methacrolein with acrolein as the main impurity.

(8) Selenium dioxide

Reagent grade selenium dioxide was obtained from Matheson Coleman and Bell Company with a minimum purity of 99%.

(9) Sulfur dioxide

Compressed sulfur dioxide gas (minimum purity 99.95%) was obtained from Matheson Company.

(10) Methyl bromide

Compressed methyl bromide gas from Matheson Co. (minimum purity 99.5%) at a pressure of 17 psig was used as the source of bromine modifier.

(11) Tetrachloroethylene

Spectroscopic grade tetrachloroethylene (minimum purity of 99.5%) from Fisher Scientific Co. was used as the source of chlorine modifier.

(12) Propyl iodide and Methyl iodide

Spectroscopic grade methyl iodide and propyl iodide (minimum purity 99%) obtained from Matheson Coleman and Bell Co., were used as the source of iodine modifiers.

(13) n-Heptane

Research grade n-heptane (minimum purity of 99+ mole %) obtained from Phillips Petroleum Co. was used as the diluent of chlorine and iodine modifiers.

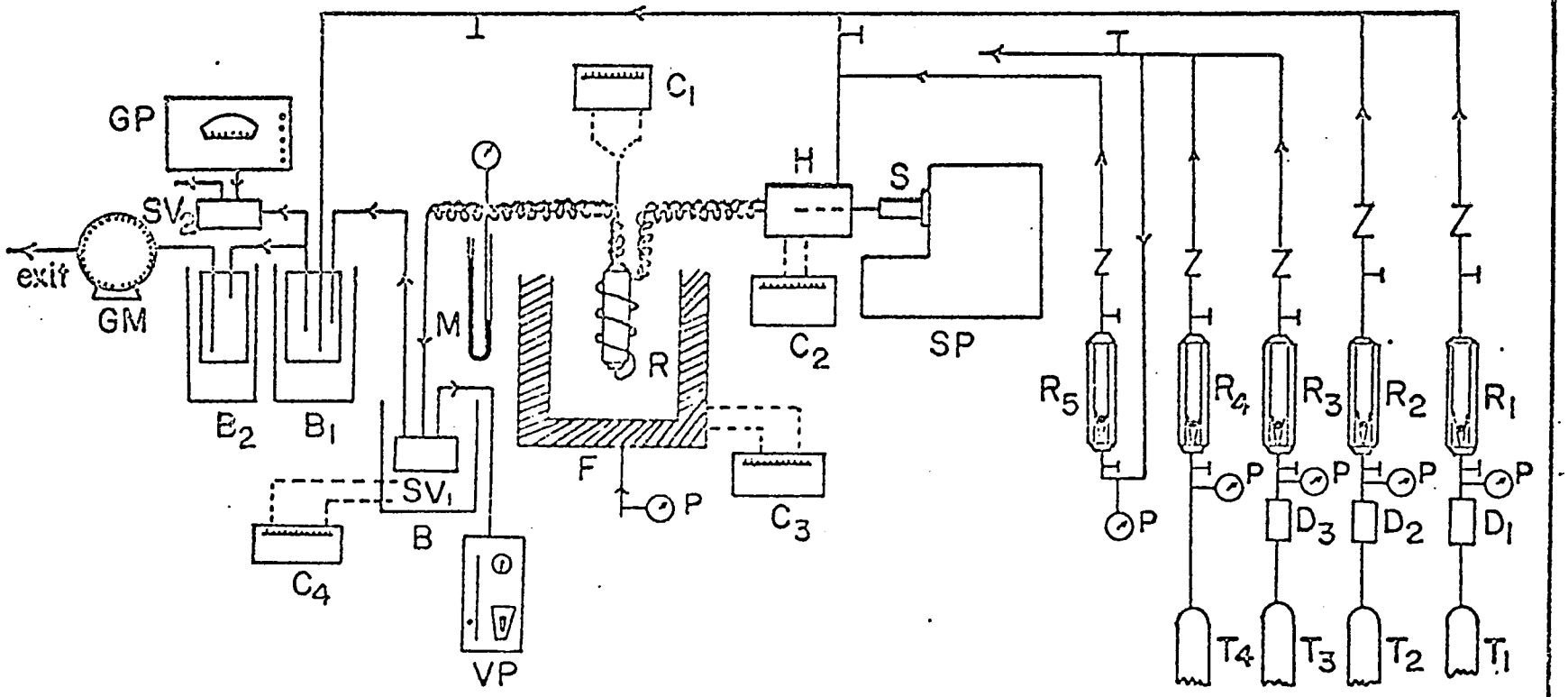
B. Apparatus

The selective oxidation of olefins to corresponding aldehydes was investigated in a flow system. The equipment, constructed in the Department, was made of 316 stainless steel throughout. The apparatus was designed to investigate the kinetics of oxidation reactions under a constant and continuous supply of trace amounts of modifiers in different forms. A schematic diagram of the experimental apparatus used in this study is shown in Figure 1.

The apparatus comprised of three main units - (i) Feed preparation and doping unit; (ii) Reaction unit and; (iii) Products separation unit.

(i) Feed preparation and doping unit

The feed preparation unit consisted of five gas streams. While the first and second lines transported reactants for the oxidation, the other three were used for introducing the modifiers.



B : oil bath
B1 : ice trap
B2 : liquid nitrogen trap
C1 - C4 : temperature controller
D1 - D3 : drying tubes
F : furnace
P : pressure controllers
GM : gas test meter
GP : gas partitioner
H : hot inlet
M : manometer
R : reactor
R1 - R5 : rotameters
S : syringe
SP : syringe pump
SV1,2 : sampling valves
T1 , T3 : air tank
T2 : 2-methylpropene tank
T4 : SO_2 (CH_3Br) tank
VP : vapor fractometer

Figure 1- Schematic Diagram of the Apparatus

The reactants, compressed air and C. P. grade olefin (propene or 2-methylpropene) were obtained from high pressure cylinders, through a series of diaphram type pressure regulators, whereby the pressure of air and olefin were reduced to 20 psig. Trace amounts of moisture were removed by passing the gases through the drying tubes. The gas lines used in this section were made of $\frac{1}{8}$" O. D. stainless steel tubing. Both valves and fittings except the fine metering valves were made by Autoclave Engineering Inc., Erie, Pa., and were capable to withstand pressures up to 5000 psi.. Fine metering valves for regulating the gas flow rates were supplied by Nupro Co., Cleveland, Ohio. The flow rates of air and olefin were measured by Brooks rotameters. The inlet gas lines were immersed in a circulatory constant temperature bath (Haake Instrument Co., West Germany) prior to their passing through the rotameters. Each rotameter was connected with a mercury manometer so that the pressure and temperature effect on the gas flow rates could be corrected.

In the case where selenium was used for doping, a constant temperature vaporizer containing selenium dioxide was used, the amount of selenium in the feed was controlled by changing the temperature of the vaporizer and the air flow rate through the rotameter R_3.

In the case where sulfur was used for doping, the compressed sulfur dioxide gas was first measured with a calibrated rotameter, R_4 and was well diluted with a stream of air, the flow rate of which was measured by another rotameter R_3; while a small amount of

the controlled air-sulfur dioxide gas mixture was admitted into the reactor system through rotameter R_5, the rest of the gas mixture was vented into the atmosphere through a needle valve.

In the case where bromine was used for doping, the compressed methylbromide gas was used as the source. The amount of bromine in the methylbromide - air mixture was controlled by the partial pressure of methylbromide. The mixture was prepared in a static blending system shown in Figure 2. An empty nitrogen gas cylinder from Linde Co. was first purged several times with compressed air, then the methylbromide gas was admitted, the equilibrium gauge pressure shown in the attached manometer was observed with the kathetometer and was adjusted by the find metering valve, the accuracy of pressure reading is ± 0.1 mm Hg. The measured methylbromide gas was further diluted by compressed air through a two-stage high pressure regulator (Matheson Co. model 2), the final equilibrium pressure was measured by the Test Gauge 0-600 psi (Mansfield and Green Inc.) which is calibrated within an accuracy of $\pm \frac{1}{4}$ psi. The mixture (41.4 ml/min) was admitted to the preheater through the rotameter R_3.

When chlorine and iodine were used as modifiers, the spectroscopic grade tetrachloroethylene or propyliodide was dissolved in research grade n-heptane and introduced continuously and precisely from a gas tight syringe (Hamilton Co., Whittby, California) driven by a motorized syringe pump (Harvard Apparatus Inc., Mills, Mass.) into a hot inlet, where it was vaporized and carried away by a hot air stream from the preheater. The gas tight syringe with teflon coated plunger and tip could stand pressure

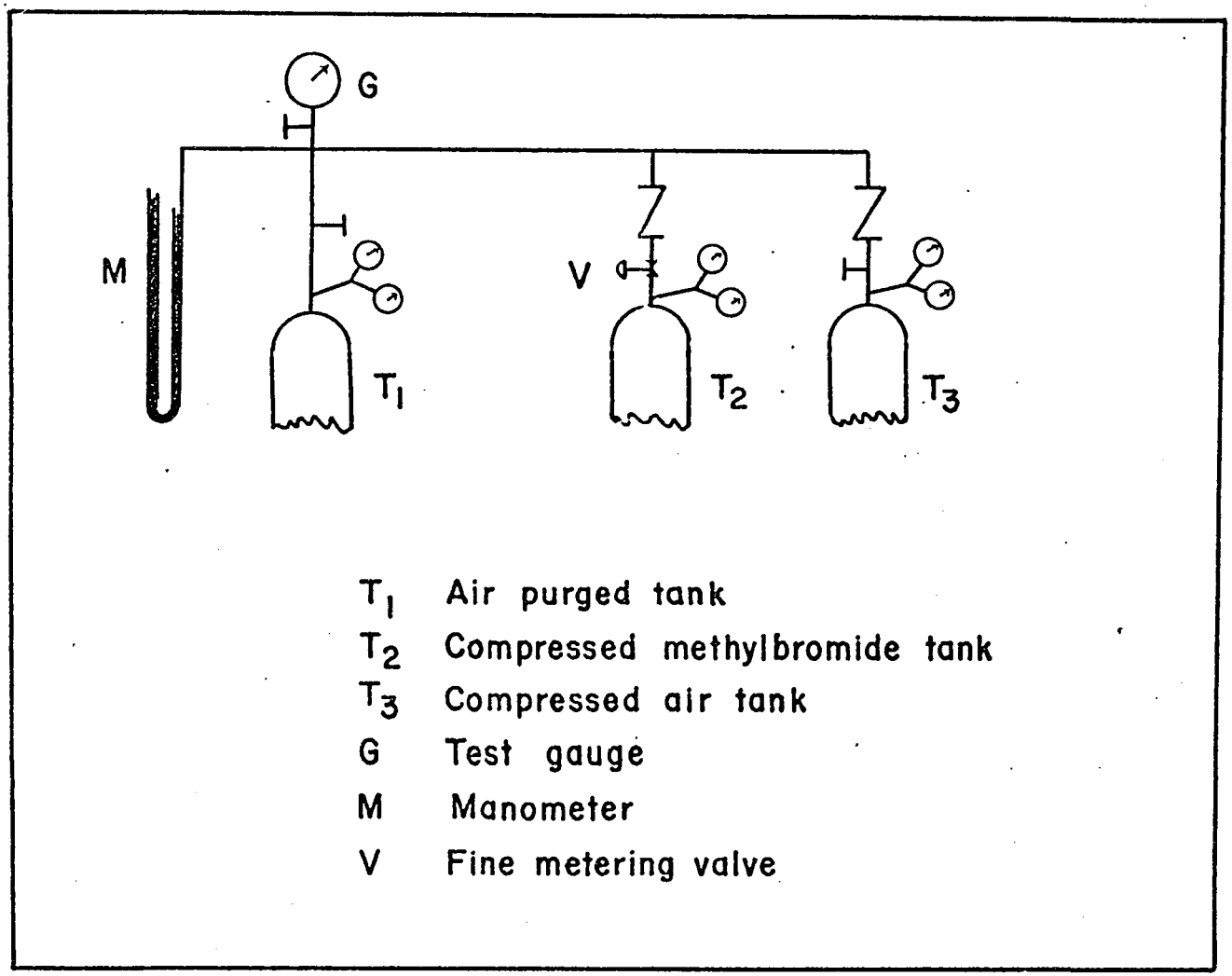


Figure 2- Static Blending System for Bromine-Air Mixture

up to 20 psig without any leakage. The syringe pump was equipped with synchronous motor and a gear train with knob for selecting twelve exact speeds. Reproducibility was within 0.5%.

The hot inlet was supplied by Hamilton Co. (Catalogue No. 86800). The outer body was made of heavy aluminum which evenly distributed the heat from the cartridge heater and eliminated cold spots. A high velocity preheated gas stream continuously washed the septum area and restricted flashback. The gas passed to the reactor through a 1 mm I. D. glass vaporizer. The temperature of the hot inlet was well controlled by a Honeywell pyrovane temperature controller at 120 $\pm$ 1°C.

In the case where the effect of steam on the catalytic oxidation of olefin over modified and unmodified catalyst or the catalytic oxidation of methacrolein was investigated, an extra portable syringe pump with another vaporizer was equipped prior to the entrance of reaction unit.

Between the vaporizer and the preheating section, the line was heated by a heating tape with an energy regulator (Fisher Catalogue 28-450). The temperature was maintained a little higher than the vaporizer in order to prevent the possibility of condensation of the modifiers in the line.

(ii) Reaction unit

The reactor with the preheating section wound around it was immersed in a constant temperature fluidized bed furnace. The reactor was made of 6 foot long $\frac{1}{8}$" O. D. 316 stainless steel tubing. The preheated reactants with modifiers entered the reactor

from the bottom of the reactor. Details of the preheating section and reactor are given in Figure 3.

A porous stainless steel plate, supplied by Pall Trinity Micro Corp., Cortland, New York, was inserted at the bottom of the reactor. The grade D plate had mean pore size of 65 microns, a normal thickness of $\frac{1}{16}$ inch and produced a pressure drop of approximately 0.1 psig per 180 cfm/sq. ft. of air. An autoclave reducer was used below the porous plate and attached to the feed line from the feed preparation unit.

The top of the reactor was fitted with a Swagelok "T" connection. A stainless steel tubing, $\frac{1}{16}$ inch O. D. containing two iron-constantan thermocouples was inserted through this connection to a level just above the top of the porous plate. The first thermocouple in the protection tube being connected with temperature controller C_1 for controlling the catalyst bed temperature, the second going to a potentiometer (Honeywell, model 2745) for measuring the temperature during the reaction. The thermocouples were supplied by Thermoelectric Canada Ltd., Brampton, Ont.

The temperature of the reactor was controlled by a Honeywell Pyrovane temperature controller. It was used with transducers such as thermocouples that generated a milivolt 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 $\pm 2°C$.

The fluidized bed furnace was made from a 1 foot long, 5 inch O. D. and $\frac{1}{4}$ inch thickness steel cylinder with a porous

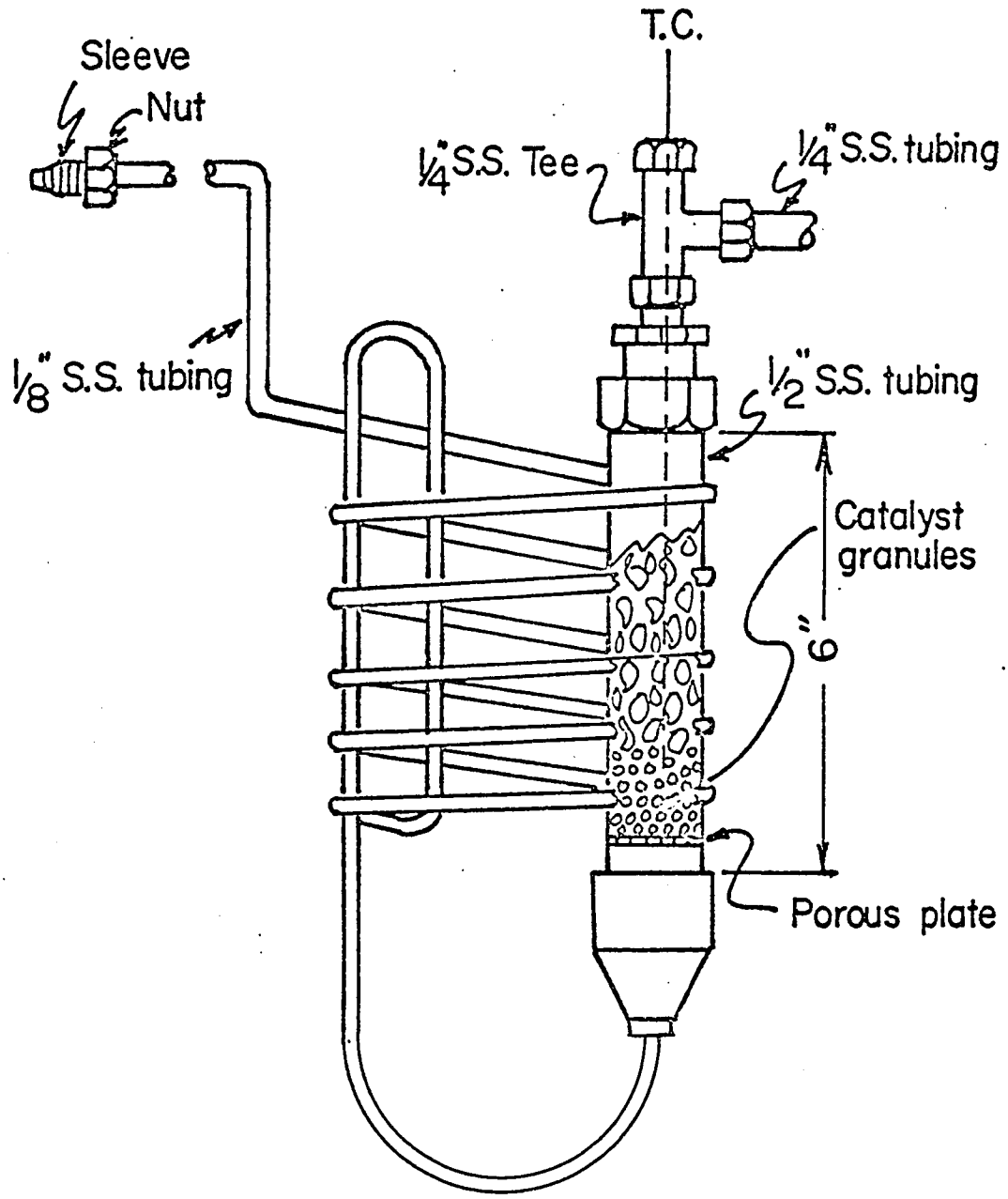


Figure 3- Reactor and Preheater

stainless steel plate inserted at the bottom, and was covered tightly by a 1 foot long 5 inch I. D. ceramic core (Norton Co., Hamilton, Ont.). The nicrome wire with a resistance of 25 ohm was wrapped around the groove of the ceramic core and was connected to a 10 ampere powerstat then to temperature controller C_1. A steel funnel 5 inches wide at the top, tapering to $\frac{1}{4}$ inch at the bottom welded to the base of the steel cylinder below the porous plate and attached to the compressed air line.

Silicon carbide, mesh size 100-150 (supplied by Cole-Palmer Co., Chicago) was used as the heating medium of the fluidized bed, and was placed in the container on top of the porous plate. The reactor was held upright in the center of the bed, while the vessel was almost completely filled with silicon carbide. During operation, the compressed air from the Departmental air compressor first passed through a filter to remove oil and moisture, the pressure was adjusted to 5 psig by a pressure regulator (supplied by Matheson Co., model 73) and its flow rate was adjusted by a Brooks flowmeter.

The asbesto cement was mixed with a small amount of water and applied in a 1" thick layer to the heating wires for insulation and also to fix the wires in position. Another booster heater, made of Ceram-A-Flex beaded heating wire (Chemical Rubber Co., Cleveland, Ohio) with a resistance of about 50 ohms, was wrapped inside a quartz tube and immersed in the fluidized bed. The wire was connected to a 10 ampere powerstat and was left on all the time. The powerstat was set in such a way as to produce sufficient heat to overcome the heat losses to surroundings.

An iron constantan thermocouple was used to measure the temperature of the fluidized bed, the difference in temperature was found never to exceed $\pm 1°C$ throughout the bed.

The reactor and fluidized bed were then placed in an outer steel cylinder, one foot long in diameter, resting 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 steel cylinder and the bed was packed with vermiculate. The surface of the outer cylinder was coated with a layer of fiber glass and asbestos cloth 4" thick for further insulation.

(iii) Product separation unit

This unit consisted of a condenser, three traps, a drying tube, two gas chromatographs with two gas sampling devices for analyzing the unreacted reactants and reaction products. Two chart recorders for recording gas chromatograms, 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 vapor.

The water condenser was made of a 10" x 3" O. D, acrylic pipe. A 6' x $\frac{1}{8}$" O. D. stainless steel tubine was used as the cooling coil. 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 psig pressure without any leakage. A sampling loop (4. 5 ml volume) was attached to the valve. The bath oil was heated by an immersion heater (Fisher Catalogue 11-463-18V4) with a variac powerstat. A constant bath temperature was maintained by

temperature controller C_4 (a Yellow Springs Thermistor temperature controller model 71), having a controlled deviation within $\pm 0.01°C$. The liquid bath, 10" x 10" O. D. (Pyrex-Corning Glass Works, Corning, New Jersey) was well insulated with asbestos cements and glass wool to reduce the heat losses to the surroundings, the temperature of the sampling gas, essentially the reaction pressure, was controlled at 830 mm Hg. by adjusting the needle valve in the exit line.

The Perkin-Elmer model 154-D vapor 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 Phillips chart recorder PR 2216, with various multi-range unit was connected to the vapor fractometer to record the peak composition of the effluent stream. A Phillips PT 1600 integrator was used to obtain the area under each peak. Two readings were taken from the integrator, one prior to the start of a peak and another immediately after the completion of this peak. The difference between these two readings was a measure of the area under this peak.

The exit gas from the high temperature sampling valve V_1 was led to the condenser and 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" x 1" O. D. pyrex was packed with 10-20 mesh indicating drierite (anhydrous calcium sulfate), and pieces of stainless steel gauge wire of 100 mesh were placed at either end to stop the small drierite particles from escaping into the gas stream.

All traces of moisture from the gaseous reaction products which could damage the column were removed prior to their analysis in the Fisher Gas Partitioner by the condenser and drying tube.

The product stream after the removal of water was led to the Fisher Gas Partitioner through a six-way linear gas sampling valve supplied by Aerograph Co. The sampling gas passed through the sampling loop (0. 25 ml) and then 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 simultaneously connected with the carrier gas. Using this scheme, it was possible to flush reproducible sample volumes into the separating columns of the gas partitioner.

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

A zero suppressor (supplied by Fisher Scientific Co.), 0-10 mv, was used to connect the gas partitioner and the chart recorder (Texas Instrument Inc., Texas Model Servo/ritter II) from which the recorder input signal exceeded 1 mv could be suppressed.

C. Preparation and Properties of the Catalysts

(1) Copper oxide supported on pumice

The pumice supported copper oxide catalyst (16% by weight of copper) was prepared by impregnating 20-40 mesh crushed pumice stones (supplied by Fisher Scientific Co.) with copper nitrate solution. Pumice stones were 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. The pumice granules were dried in an oven at 105°C for about 10 hours. Copper nitrate solution containing 15.21 gms of $Cu(NO_3)_2 \cdot 3H_2O$ or equivalent to 4 gms of copper was mixed with 21 gms of pumice granules in a crucible. The mixture was vigorously stirred for one hour and slowly evaporated to dryness for 6 hours at room temperature, 12 hours at 40°C and 6 hours at 105°C. It was then calcinated at 450°C for about 6 hours in a muffle furnace. A weighed amount of the catalyst was charged into the reactor and activated by passing air over it for 12 hours at 450°C.

(2) Copper oxide supported on α-alumina

The catalyst, containing 10% by weight of copper, was prepared by impregnating the known weight of inactivated alumina with copper nitrate solution. Alumina in the shape of $\frac{1}{4}$" spheres was supplied by Norton Ceramic Co., Hamilton, Ont. The spheres were crushed to 20-40 mesh, washed and dried by heating for 12 hours at 105°C before being impregnated. The rest of the procedure was the same as in the preparation of pumice supported catalyst.

(3) Nickel oxide supported on α-alumina

Nickel oxide supported on the inactivated alumina was prepared in the same manner as in the preparation of alumina supported copper oxide catalyst except that the nickel nitrate solution was used instead of copper nitrate solution as the starting material.

(4) Copper oxide-manganese dioxide supported on α-alumina

The alumina supported copper-manganese oxide catalyst (8% copper, 2% manganese) was prepared by impregnating 20-40 mesh crushed inactivated alumina and following a procedure similar to the one used in making the alumina supported copper oxide catalyst.

The physical properties of the α-alumina supported copper oxide catalyst are given in Table I.

TABLE I Physical Properties of Catalyst

particle diameter (Dp)	=	0.56 mm
particle density (ρ_p)	=	1.2473 gm/cc.
apparent density (ρ_a)	=	1.1056 gm/cc.
Thermal conductivity of catalyst (Kc)	=	116 cal/hr/cm/°C
Thermal conductivity of support (Ks)	=	26.76 cal/hr/cm/°C
Specific surface area (A_m)	=	0.84 m^2/gm

The particle diameter (Dp) was determined by measurement with a micrometer. A random sample of 25 granules was taken and the diameter of each measured with a micrometer. An arith-

metic average of these measurements gave the value of the particle diameter as 0.56 mm.

The particle density (ρ_p) was determined by measuring the weight and volume occupied by 100 granules of the catalyst. Since the granules were relatively small, the sphericity was taken as 0.9.

The specific surface area of the catalyst (Am), as determined with the standard BET apparatus was 0.84 m^2/gm.

The color of the catalyst was black prior to use. The X-ray diffraction pattern (Figure 18-A) indicated that the active components were α - alumina and cuprous oxide. Both the surface area measurements and X-ray diffraction studies were carried in the Applied Chemistry Division, National Research Council, Ottawa, Ont.

The activity of the catalyst was verified periodically by passing a specified mixture of olefin and air mixture and determining the percentage conversion of olefin. The change in catalytic activity was found to be negligible.

The chlorine modified copper oxide catalyst appeared to be highly selective and much more stable. In addition, the products are rather clear - methacrolein, water and carbon dioxide, the concentration of the acids, carbon monoxide and other aldehydes in the products was found to be too low to affect the material balance. In view, therefore, of the stability and selectivity of the catalyst, it was used throughout in the kinetic investigation of the reaction except where stated otherwise.

D. Experimental Procedure

(1) Leakage test

The system was tested at 50 psig for any possible leaks in the following way:

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

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

(iii) Every accesible connection part was tested with snoop.

(2) Calibration of equipment

Flow rates of the gas streams were measured by calibrated rotameters, the temperature of the inlet gases being maintained at 25°C. The pressure was maintained at 1160 mm Hg by the manual adjustment of the fine metering valves in the exit of rotameters. The volumetric flow rates were checked by both the soap bubble method and wet test gas meter supplied by American Instrument Co. Since both calibration and experimental runs were under same operating temperatures and pressures, consequently, the correction for temperature and pressure variations were unnecessary. Calibration curves for the flow rates of air, olefin, carbon dioxide and carbon monoxide are given in Appendix B.

The feed rates of chlorine, iodine modifier and methacrolein were controlled by the speed of the syringe pump, which in turn was

calibrated by weighing the distilled water pumped for a certain time. The results of calibration for the syringe pump is given in Appendix B.

The thermocouples were calibrated by inserting them into the fluidized bed furnace and an ASTM thermometer (0 - 400°C) was attached to it. A calibration curve of temperature against millivolts is given in Appendix B.

Synthetic mixtures, similar to the actual samples, were used to calibrate the Gas Partitioner and the Vapor Fractometer, with the time and order of elution of the components based on previous injections of the pure components.

The gas samples were separated on the Fisher Gas Partitioner. A synthetic mixture of both gases was prepared from the feed preparation unit through the bypass of the reactor. Mixtures of oxygen, carbon dioxide, propene, 2-methylpropene and carbon monoxide with nitrogen in 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 preparation unit. Mixtures of water, acrolein and methacrolein of known composition were injected into the Perkin-Elmer Model 154-D Vapor Fractometer from the feed preparation unit. The calibration curves, both for the Gas Partitioner and Vapor Fractometer, are given in Appendix B.

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 height 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 the method of measuring the areas under the peaks with an integrator, since the variations due to the differences in each sampling, especially when the sample quantities were very small.

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

(3) Analysis procedure

(i) Acids

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

(ii) 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 pressure of the sampling gas were well controlled.

The column used for separation was 15% by weight of carbowax 1500 (supplied by Gas Chromotographic Specialities, Brockville, Ont.) coated on columnpak T (Teflon Powder). Methyl chloride was used as

the solvent. Though the 6 ft long 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 gas chromatogram obtained from Vapor Fractometer is shown in Figure 4.

(iii) 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 $\frac{1}{4}$" O. D. copper tubing columns in series. The first column was packed with a 6 foot 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 foot long molecular sieve 5A followed by a 5 foot long uncoated celite diatomaceous silica and was used to separate oxygen, nitrogen and carbon monoxide. A typical analysis of the products from the Gas Partitioner is shown in Figure 5. Nitrogen gas was used as the key component for its chemical inertness.

(4) Operating procedure

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

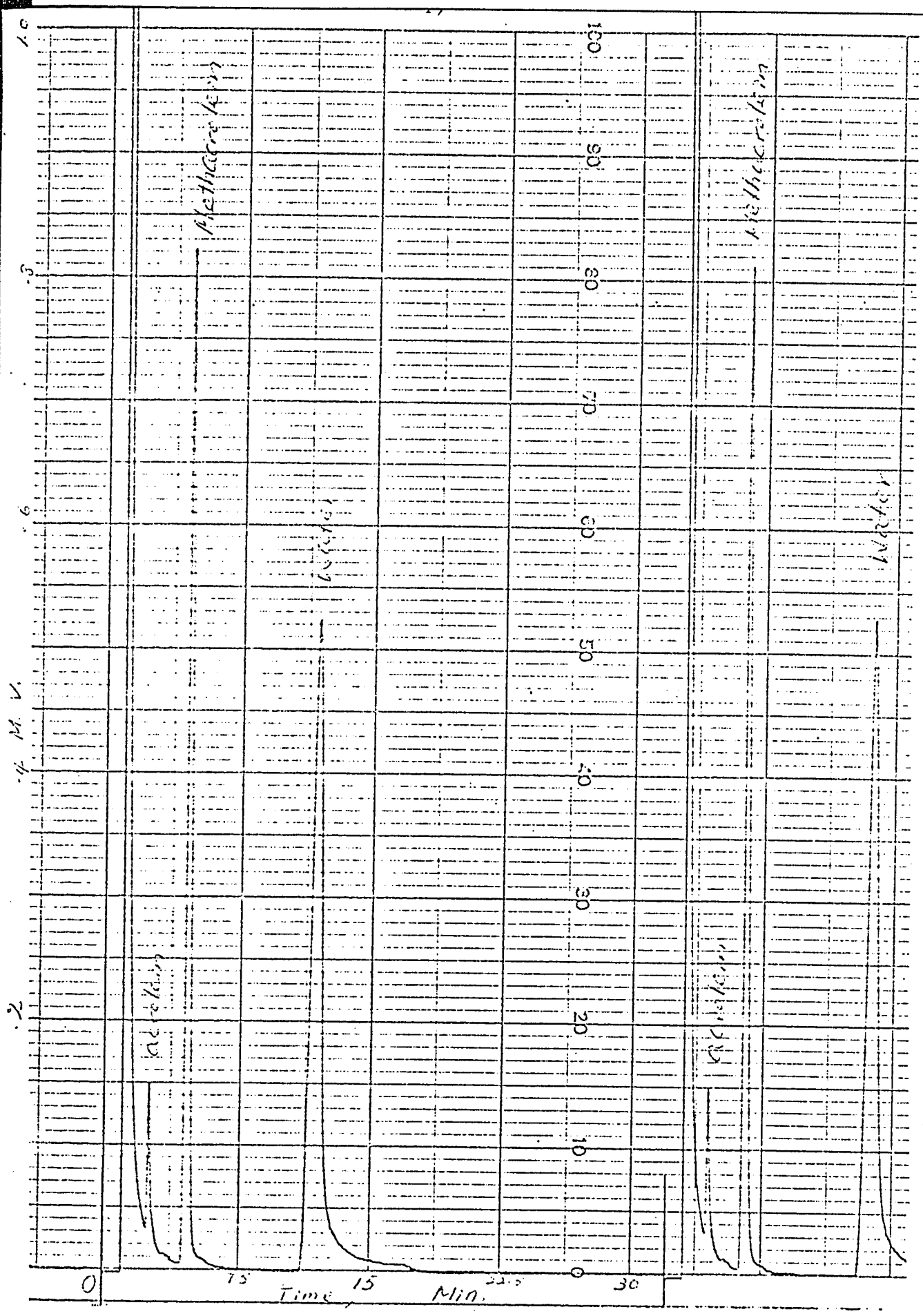


Figure 4- Typical Analysis of the Liquid Products

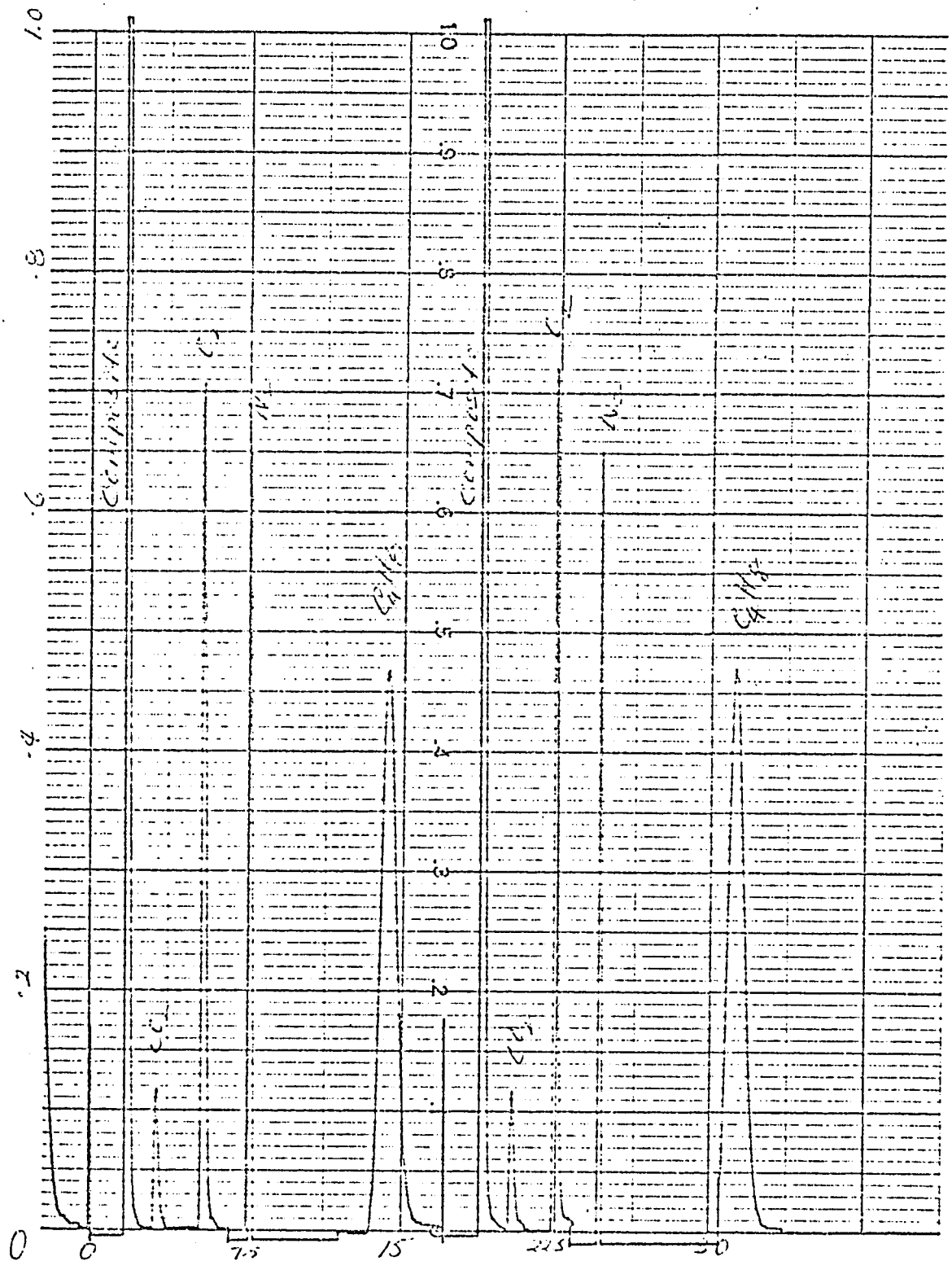


Figure 5- Typical Analysis of the Gaseous Products

(i) Start up

(a) Test the system for any leaks by pressuring the system with air to 50 psig.

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

(c) Turn the helium gas streams and the temperature controllers for the gas partitioner and vapor fractometer.

(d) Switch on the detectors and recorders for gas chromatographs in order to allow the base line to become straight and stable.

(e) Turn on the departmental compressed air to fluidize the furnace bed at 5 psig and a flow rate about 2 liter/min.

(f) 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.

(g) Switch on the various heating tapes used for preheating the air entering the evaporation chamber and maintaining the feed line leading to the reactor at 200° C.

(h) Turn on the "Variac" powerstats and the temperature controllers for

(i) The inlet gases
(ii) Fluidized bed furnace
(iii) Reactor
(iv) Sampling gas for vapor fractometer.

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

(ii) Run

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

(b) The modifier was introduced into the feed line. The amount of modifier was controlled by adjusting the dilution ratio of air-modifier, the speed of syringe pump or the size of syringe.

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

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

(e) 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 the samples in the two gas chromatograms show no change in composition thereby indicating that a steady-state has been reached.

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

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

(h) Drain the condensates from both traps.

(i) Periodically the gas chromatographs calibrations were checked to assure the stability of the columns.

IV RESULTS

The experimental data were obtained by means of a quasi-isothermal fixed bed reactor at atmospheric pressure. Steady state was not only realized from the operating conditions but also from the product analysis. The effects of various variables, namely weight ratio of dopents to olefin in feed, Z, (gm/hr/gm/hr), oxygen to olefin ratio in feed, $\bar{R}$, reaction temperature, T and the reciprocal of space velocity, W/F, on the conversion of olefins, X, yield of various products, Y, carbon dioxide, water and aldehydes and also the selectivity, S, of the catalyst for acrolein and methacrolein formation were investigated.

While conversion (X) is defined as the moles of olefin reacted per hour to the moles of olefin fed per hour, the yield (Y) is defined as the moles of various products formed per hour to the moles of olefin fed per hour. The ratio of the moles of acrolein or methacrolein produced per hour to the moles of olefins reacted per hour has been defined as selectivity (S).

During the experiments, though the rate of olefins charged into the reactor was maintained constant, different feed ratios were obtained by adjusting the air flow rate. While the reciprocal of space velocity was varied by changing the amount of catalyst, the different values of dopent to olefin ratios were obtained by adjusting the amount of modifiers in the feed which was in turn controlled by the dilution ratio or speed of the syringe pump and the size of the syringe.

The effect of different amounts of modifiers - selenium, sulfur, bromine, chlorine and iodine in the feed on the catalytic oxidation of 2-methylpropene at 400°C is shown in Figures 6 to 10 and the results are given in Appendix D (Tables A-D-1 to A-D-5).

A typical gas chromatogram which shows the promotional effect of doping the copper oxide catalyst in the propene oxidation is given in Figure 11. Chromatogram A indicates the comparative amounts of acrolein and water formed in the oxidation over the unmodified catalyst. Chromatogram B shows the marked increase in the selectivity for acrolein over the same catalyst and under the identical operating conditions ($W/F = 6.5$, $\bar{R} = 0.633$ and $T = 375°C$) but in the presence of an optimum amount of chlorine modifier. On stopping the continuous supply of chlorine, a gas chromatogram similar to A was obtained, indicating that a continuous supply of modifier was essential in obtaining a high selectivity for acrolein.

All of these modifiers (selenium, sulfur, bromine, iodine and chlorine) showed similar trends in the promotional effects on the copper oxide catalyst in aldehyde formation. The conversion of olefin and the yield of aldehyde increased with smaller amount of modifier and then declined with further increasing amounts of modifier, on the other hand, the carbon dioxide yield decreased rapidly with the increasing amounts of modifier in the beginning and then was only slightly affected by the further increasing amounts of modifier. The selectivity of the catalyst for aldehyde formation increased very fast in the beginning and then decreased with the further addition of modifier.

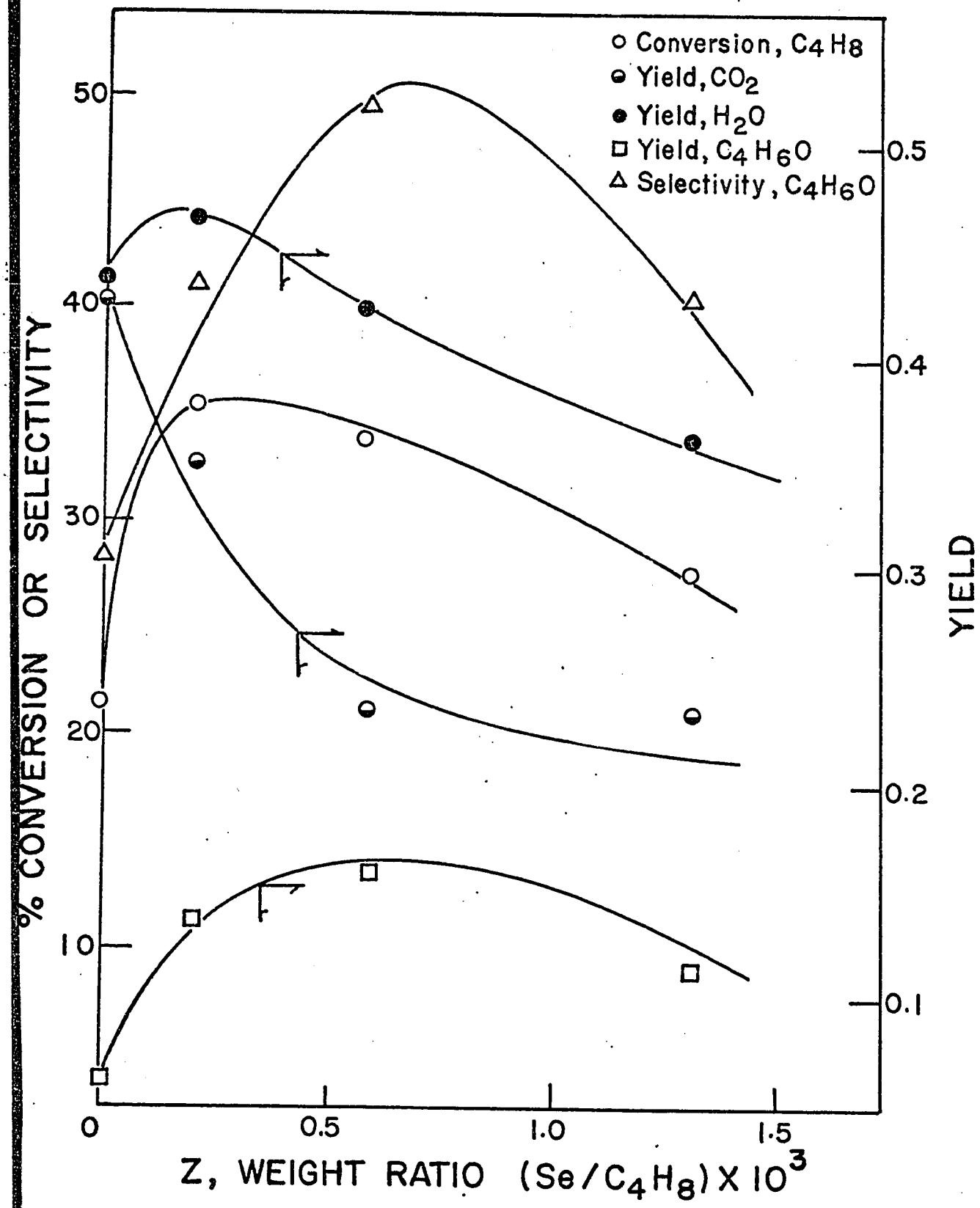


Figure 6- Effect of Selenium in the Feed on Conversion, Yields and Selectivity for Oxidation of 2-methyl-propene at 400 °C, W / F = 1.68, R = 0.9910

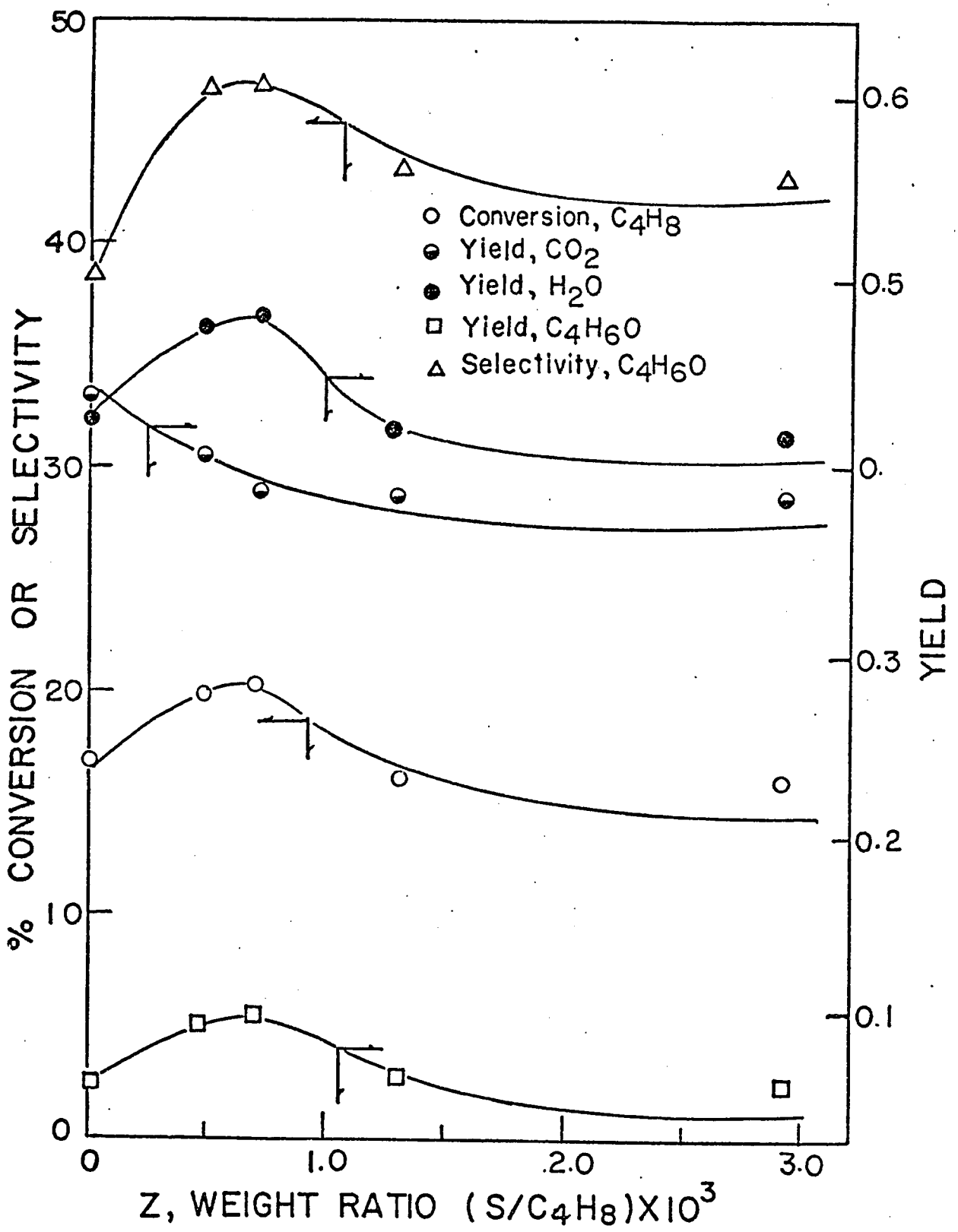


Figure 7- Effect of Sulfur in the Feed on Conversion, Yields and Selectivity for Oxidation of 2-methylpropene at 400 °C, W/F = 1.68, R = 0.6882

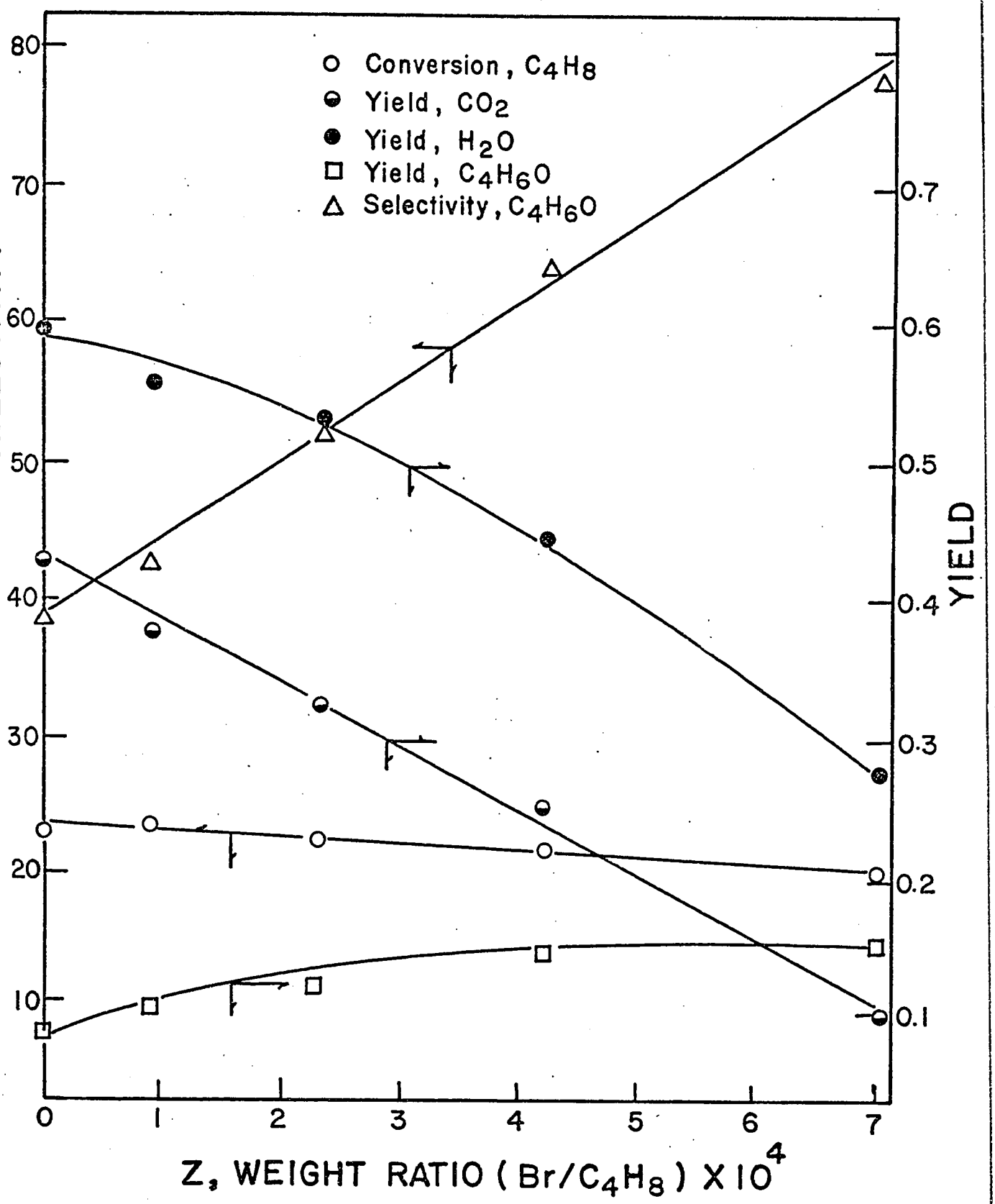


Figure 8- Effect of Bromine in the Feed on Conversion, Yields and Selectivity for Oxidation of 2-methyl-propene at 400 °C, W / F = 1.61, R = 0.8185

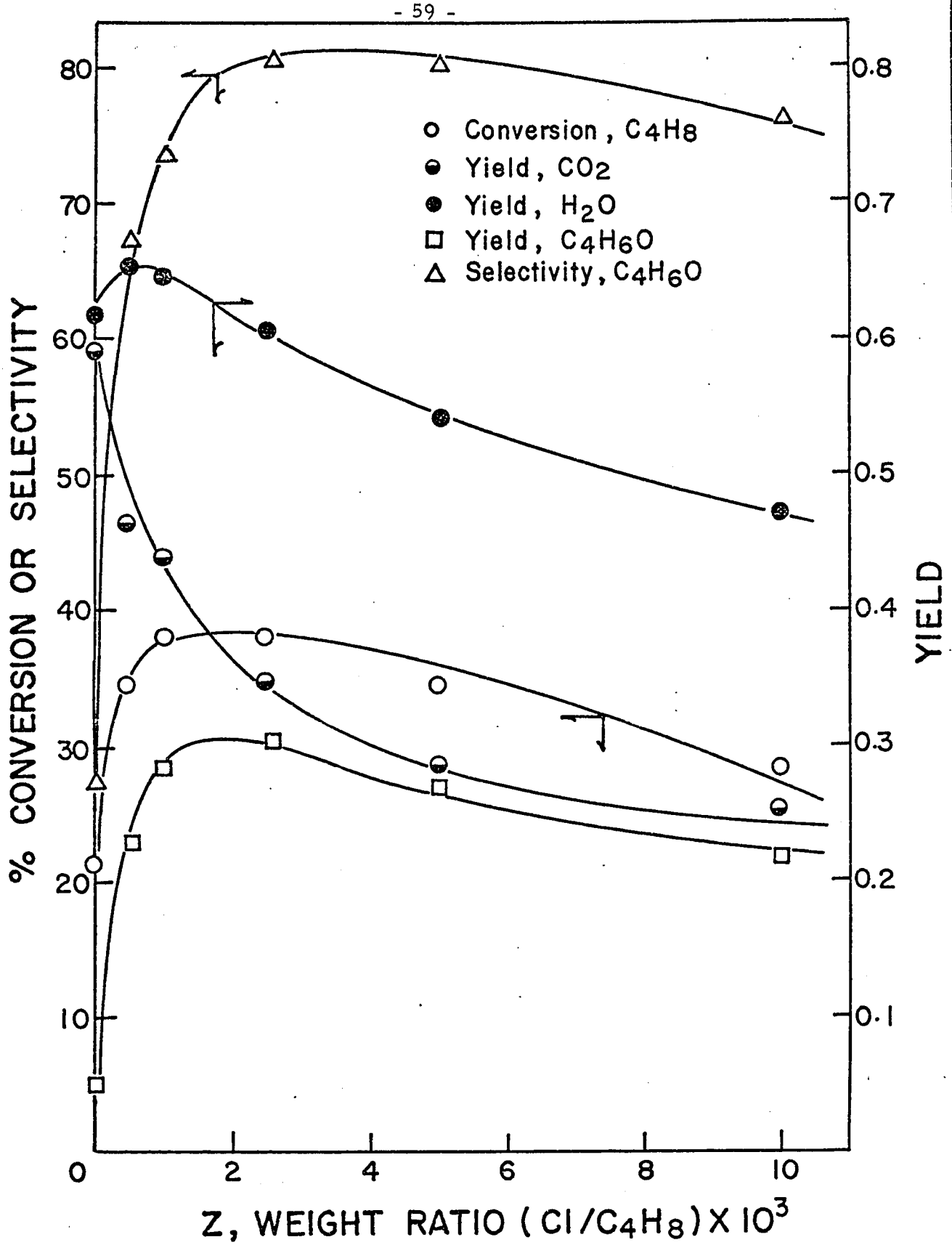


Figure 9- Effect of Chlorine in the Feed on Conversion, Yields and Selectivity for Oxidation of 2-methyl-propene at 400 °C, W / F = 5.27, R = 0.9543

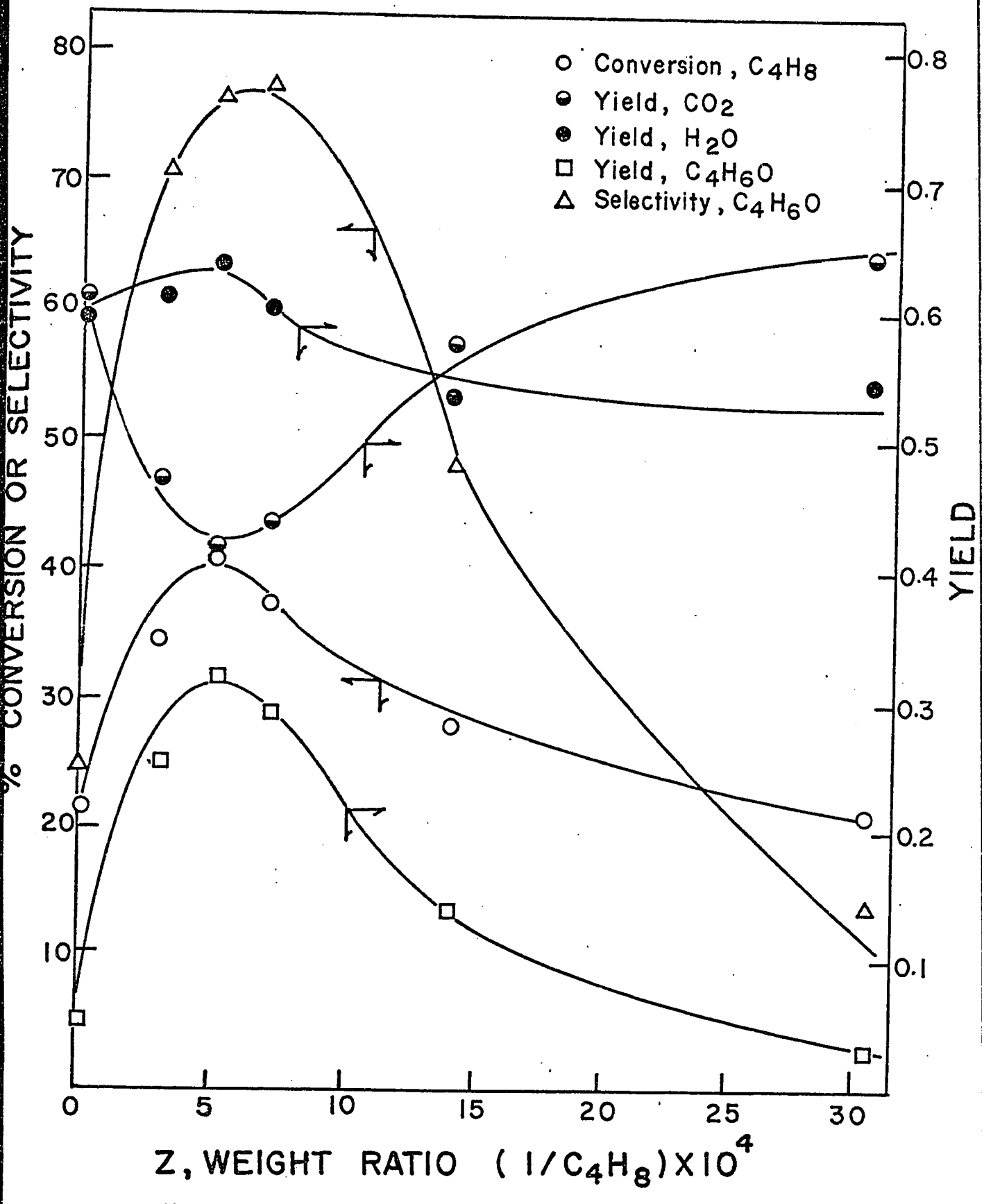


Figure 10- Effect of Iodine in the Feed on Conversion, Yields and Selectivity for Oxidation of 2-methylpropene at 400 °C, W / F = 5.27, R = 0.9543

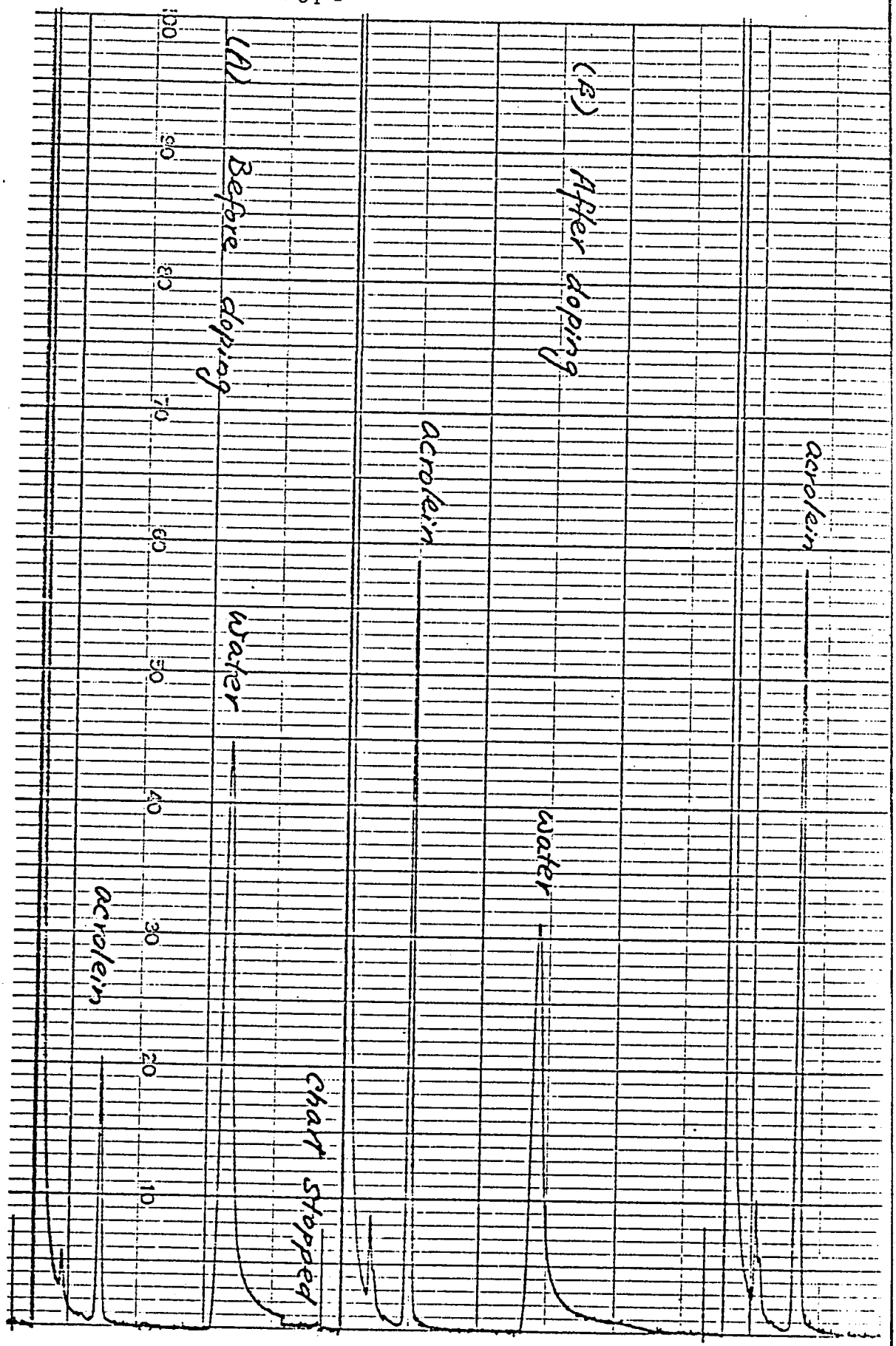


Figure 11- Gas Chromatogram Showing the Promotional Effect of Chlorine on Propene Oxidation

The results for different modifiers used with copper oxide catalysts in the oxidation of 2-methylpropene were compared with their electronegativities and are given in Table 2. It has been found that the optimum range of modifier/ 2-methylpropene weight ratio for methacrolein formation is about 0.0005 to 0.0015 . The increase in the selectivity (compared at the same conversion) is clearly due to the modifiers having electronegativies higher than that of the skeleton catalyst, copper. Also, the increase in selectivity for methacrolein is proportional to its electronegativities, excluding iodine.

TABLE 2

Modified Copper Oxide Catalysts for 2-Methylpropene Oxidation

Catalyst	Modifier	Electro-negativity (54)	Optimum weight ratio (modifier/olefin)	% Conv.	% Selectivity
Cu	-	1.75		29.08	33.80
	I	2.21	0.0005	29.00	57.00*
	S	2.44	0.0006	29.00	45.00*
	Se	2.48	0.0009	29.00	44.00*
	Br	2.74	0.0007	29.00	80.00**
	Cl	2.83	0.0015	29.34	81.34

* interpolated

** extrapolated

In addition to the above results, the following two anomalies were observed.

1) The copper oxide catalyst was found to be sensitive to sulfur dioxide, especially at the beginning of the induction period[60]. A continuous addition of sulfur dioxide to the reactants during the induction period poisoned the catalyst, and both the activity and selectivity declined. Since the catalyst was poisoned, it was difficult to restore its activity completely. However, constant promotional effect and stability of the catalyst in the presence of sulfur dioxide were obtained by introducing it intermittently into the reactor at the beginning of the induction period for about two hours. Subsequently when the surface of the catalyst was modified by the presence of sulfur dioxide, a continuous and constant supply of sulfur dioxide did not affect the stability of the catalyst. However, it definitely changed its performance.

2) The copper oxide catalyst was more sensitive to the presence of further iodine supply in the feed (from propyliodide). The yield and selectivity for methacrolein decreased very rapidly when the iodine in the feed exceeded its optimum amount (Z = 0.0005). On the other hand, the effect of increasing iodine in the feed on the yield of carbon dioxide was quite different from that obtained with chlorine, bromine, sulfur and selenium doping. Although initially the yield decreased with increasing amount of iodine, it increased when the added iodine in the feed exceeded its optimum amount. At this stage, a drastic decrease in the selectivity for methacrolein was observed. Similar results were also observed when methyliodide was used as the source of iodine. It was also found that either on reducing iodine concentration in the feed or increasing the 2-methylpropene charge to maintain the optimum iodine/2-methylpropene weight ratio, the yield of carbon dioxide again decreased and high selectivity was obtained.

The oxidation of methacrolein, the primary oxidative product in 2-methylpropene oxidation was also investigated in order to find whether carbon dioxide is formed from the further oxidation of unsaturated aldehydes or from the direct oxidation of olefins, and to obtain some insight concerning the promotional effect of the modifiers. The catalyst was the same as used in the olefin oxidation, in which chlorine was used as a modifier. It was found that in the absence of the modifier, methacrolein oxidation was quite sensitive to temperature and oxygen/methacrolein feed ratio. The reaction was almost complete at temperature higher than 350°C. On the other hand, when 2-methylpropene was mixed with air in the absence of the catalyst at 400°C, no reaction was observed.

The effect of different amount of chlorine in the feed on the catalytic oxidation of methacrolein for a feed ratio of 7.7 at 327°C is shown in Figure 12 and the results are given in Appendix D (Table A-D-6). The conversion of methacrolein declined with increased amounts of chlorine in the feed. The results were in agreement with 2-methylpropene oxidation over chlorine modified catalyst (Figure 9) and indicated that at temperature higher than 350°C, carbon dioxide originates mostly from the further oxidation of aldehyde.

The catalytic oxidation of propene was studied over the copper oxide catalyst at 375°C for an oxygen to propene ratio of 0.6332 and chlorine was used as the modifier. The results are given in Appendix D. (Table A-D-7) and are shown in Figure 13. The trends of the results were quite similar in behavior to those obtained in 2-methylpropene oxidation in the presence of iodine. The yield of carbon dioxide decreased first, and then increased with increasing amount

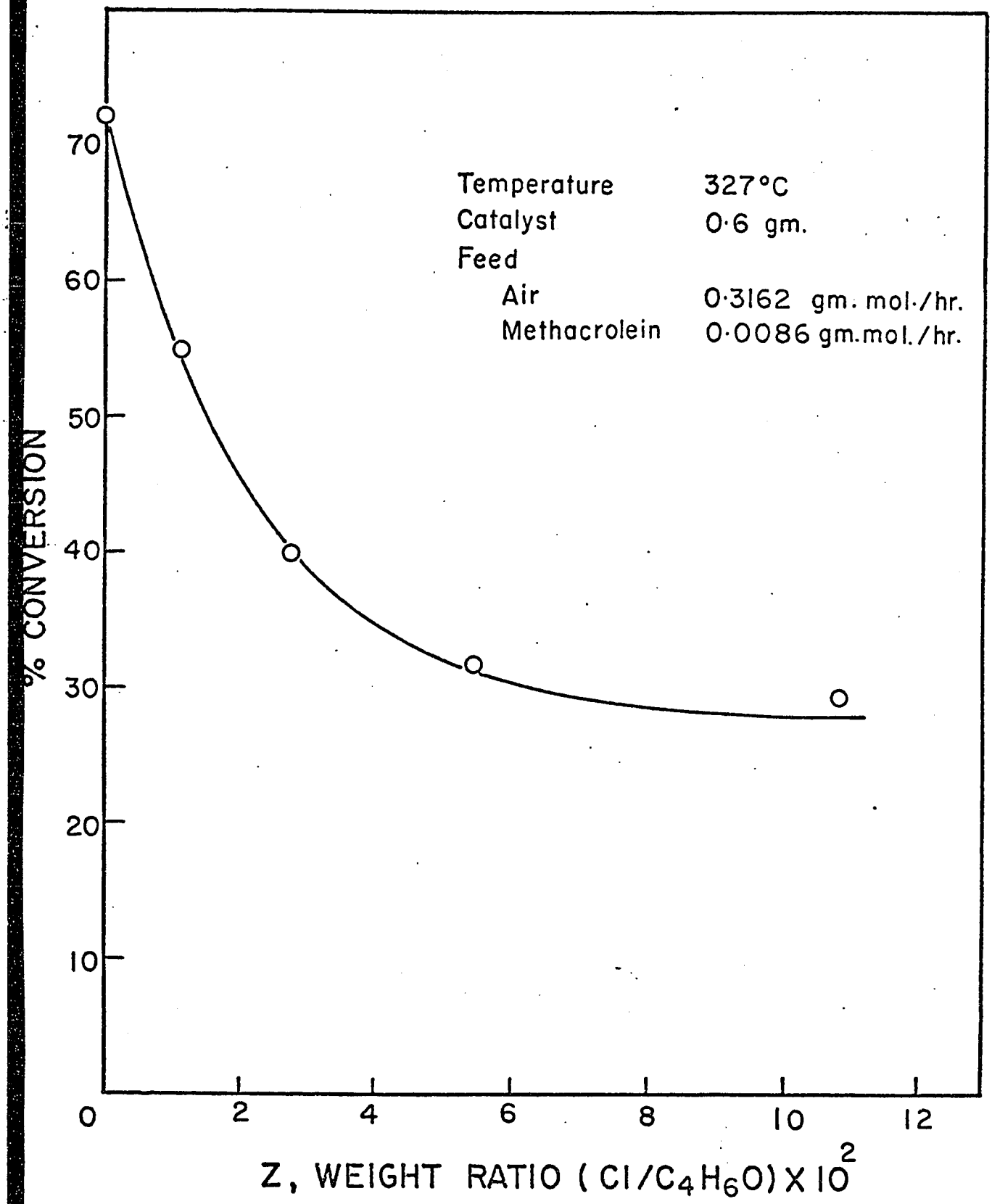


Figure 12- Catalytic Oxidation of Methacrolein over Chlorine Modified and Unmodified Copper Oxide at 327 °C

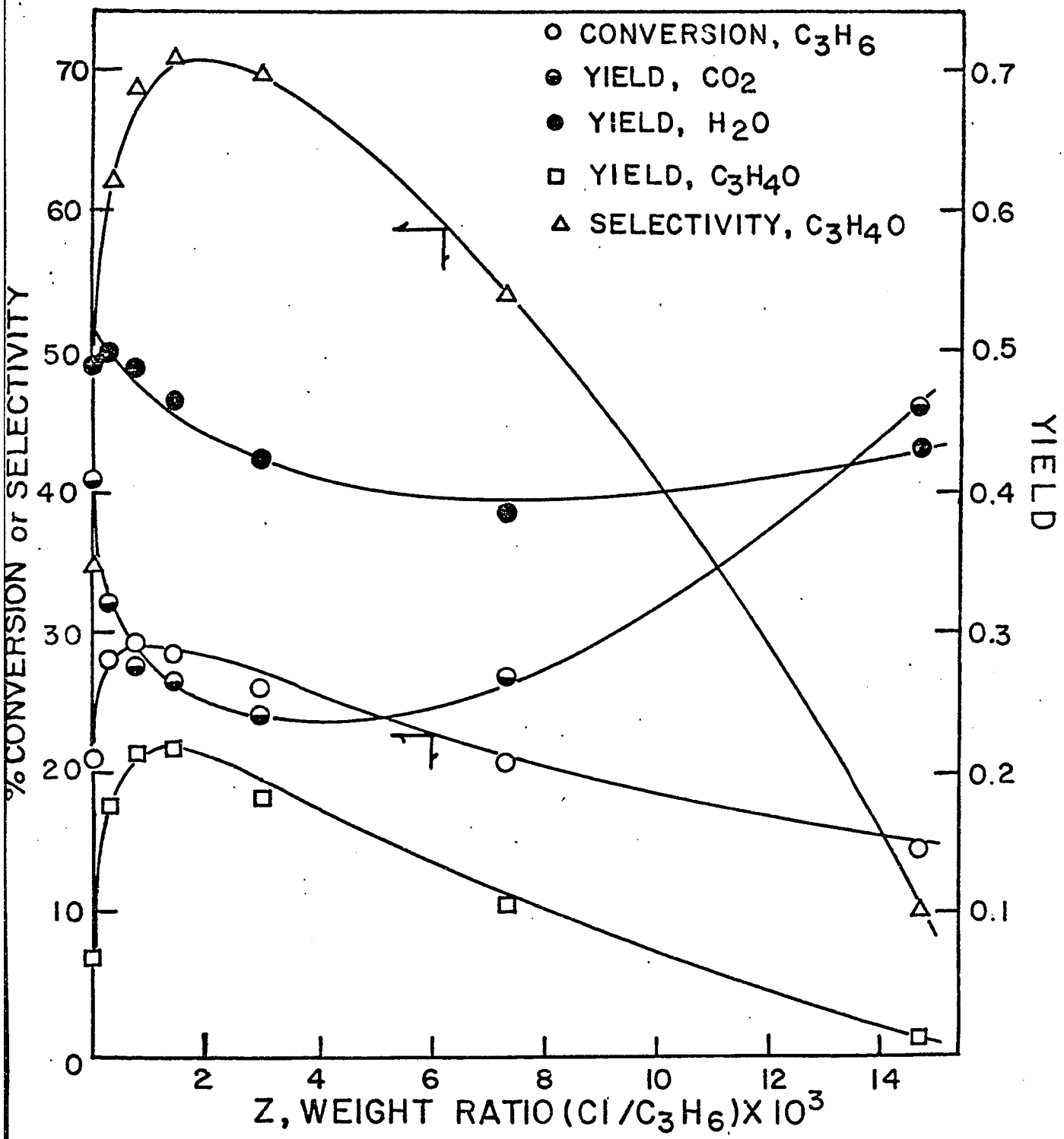


Figure 13 - Effect of Chlorine in the Feed on Conversion Yields and Selectivity for Propene Oxidation at 375°C, $W/F = 6.38$, $\bar{R} = 0.5332$

of chlorine in the feed, and there was a drastic decrease in yield of acrolein in an excess supply of chlorine. The optimum chlorine/propene weight ratio was about Z = 0.00075, which is comparatively less than that required in 2-methylpropene oxidation (Z = 0.0015).

The effect of feed ratio (oxygen/olefin) on the conversion, yields and selectivity for oxidation of 2-methylpropene over a bromine modified and unmodified copper oxide catalyst was investigated for a W/F ratio of 1.61 at 400°C. The results are shown in Figures 14 and 15 and are given in Appendix D (Table A-D-3). While the selectivity for methacrolein decreased with feed ratios in the absence of bromine, the presence of bromine did not appear to have any effect on the selectivity. The yield of methacrolein increased linearly with increasing feed ratios irrespective of the presence or absence of bromine. Though the yield of carbon dioxide increased with feed ratios in the absence of a modifier, it was not affected by feed ratios in the presence of bromine in the feed ratio range of 0.5 to 1.0.

The influence of temperature on the conversion, product distribution and selectivity for oxidation of 2-methylpropene over bromine modified catalyst was investigated in the range of 310-500°C. The results are given in Appendix D (Table A-D-8) and are shown in Figure 16. While both the conversion of 2-methylpropene and the yield of methacrolein increased steadily with increasing temperatures, the yield of carbon dioxide and water increased faster than methacrolein thereby decreasing the selectivity for methacrolein. Above 450°C, the conversion, yield, and selectivity all decreased. The best operating temperature for methacrolein production over the modified catalyst was found to be in the range of 350-450°C.

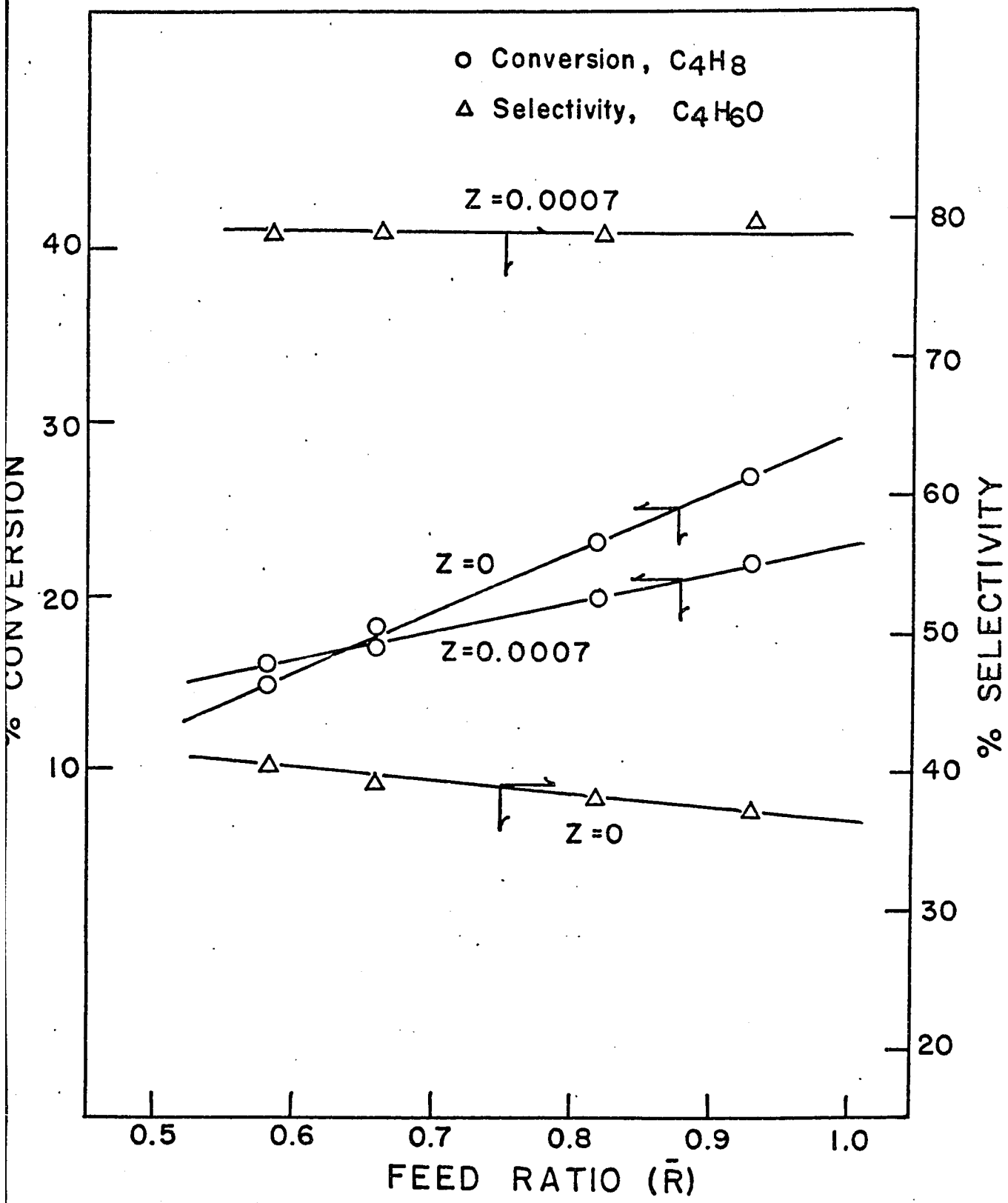


Figure 14- Effect of Feed Ratio on the Conversion and Selectivity for Oxidation of 2-methylpropene over Bromine Modified and Unmodified Copper Oxide Catalyst at 400°C

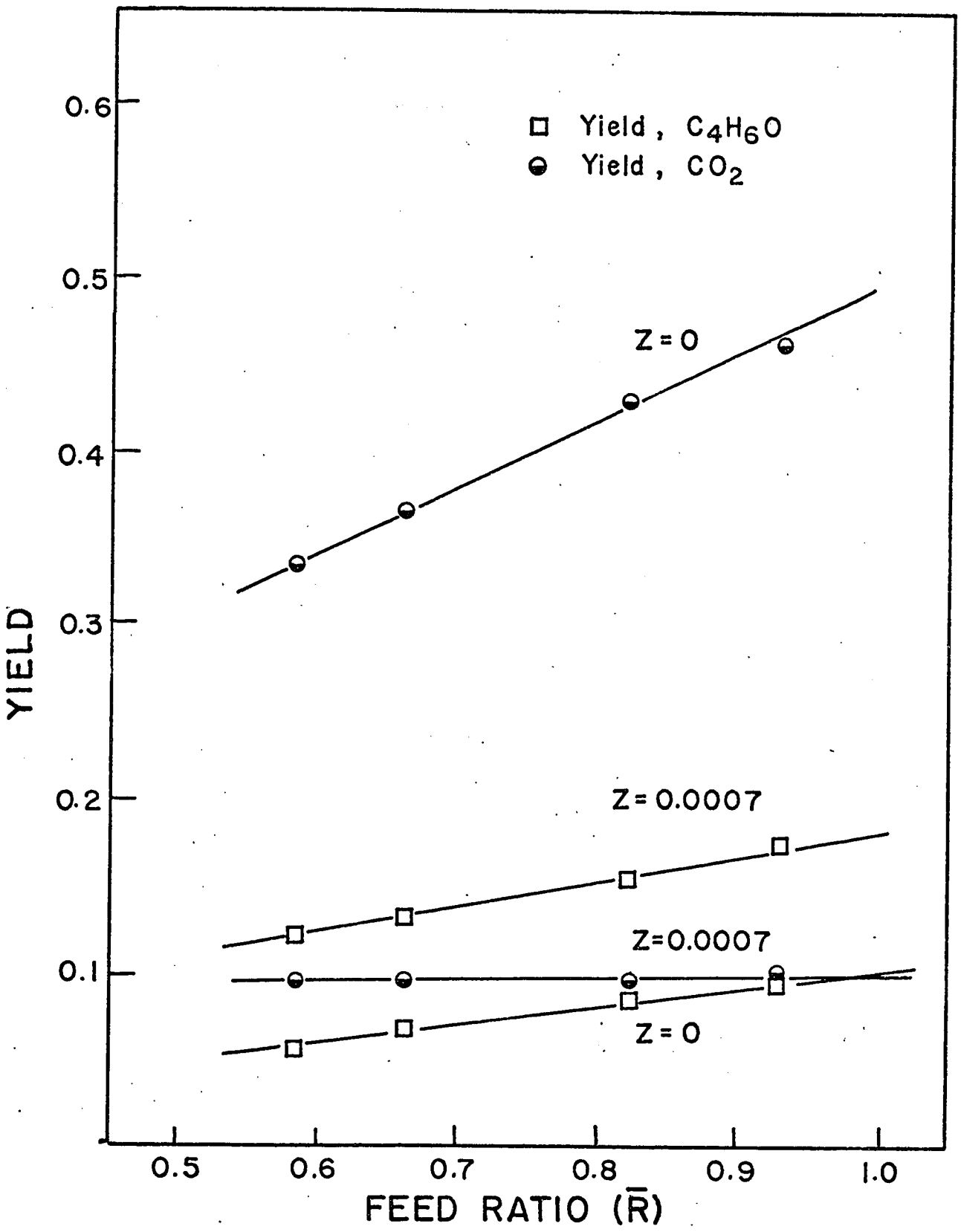


Figure 15- Effect of Feed Ratio on the Conversion

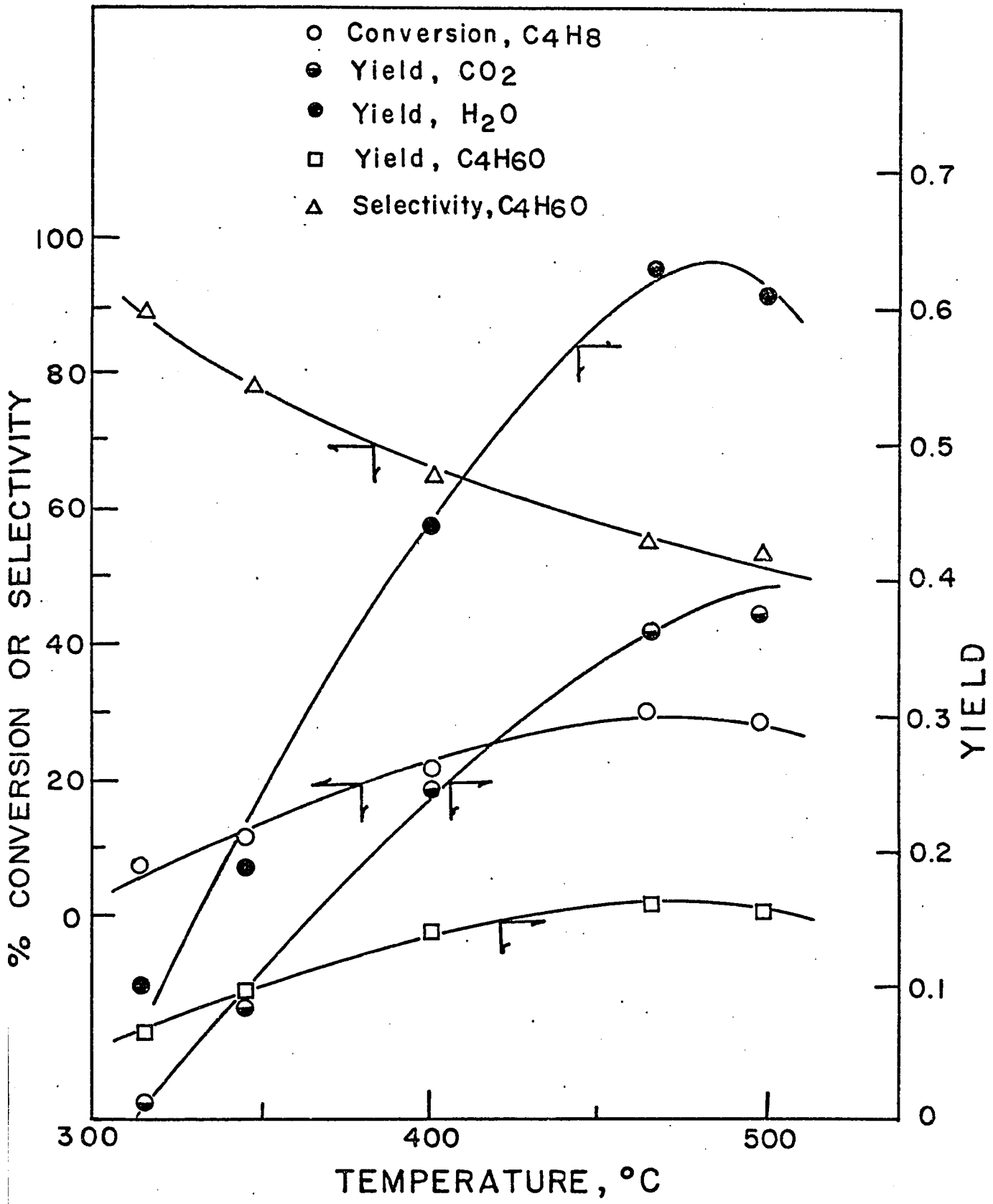


Figure 16 - Temperature Effect on Conversion, Yields and Selectivity for Oxidation of 2-Methylpropene over Bromine Modified Copper Oxide Catalyst

The effect of the reciprocal of space velocity on the conversion, yield and selectivity of a chlorine modified catalyst for the oxidation of 2-methylpropene at various feed ratios and temperatures is given in Figures 25 to 34 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 and was affected little in the range of shorter contact time.

The colour of the fresh catalyst was dull black and the modified catalyst discharged from the reactor was of a reddish-orange colour. The X-Ray diffraction patterns of the catalysts were studied in the Applied Chemistry Division, National Research Council, Ottawa. The results are given in Table 3 and are shown in Figures 17 and 18.

TABLE 3

X-Ray Diffraction Patterns of the Catalysts

Catalyst	Cu_2O	CuO	Unknown
1) fresh (Figure 17-A)	none	major	trace
2) used without modifier (Figure 17-B)	some	major	trace
3) used with optimum chlorine modifier (Figure 18-A)	major	none	trace
4) used with overdoped chlorine modifier (Figure 18-B)	major	some	some

O Al_2O_3
X Cu_2O
Δ CuO
. unknown

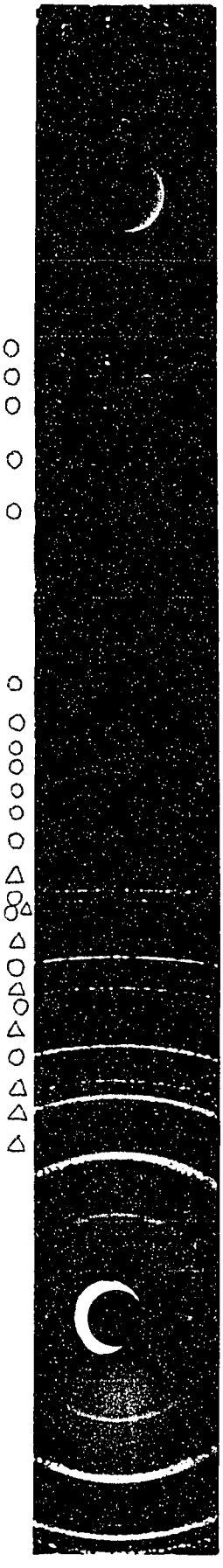


Figure A. Fresh Catalyst

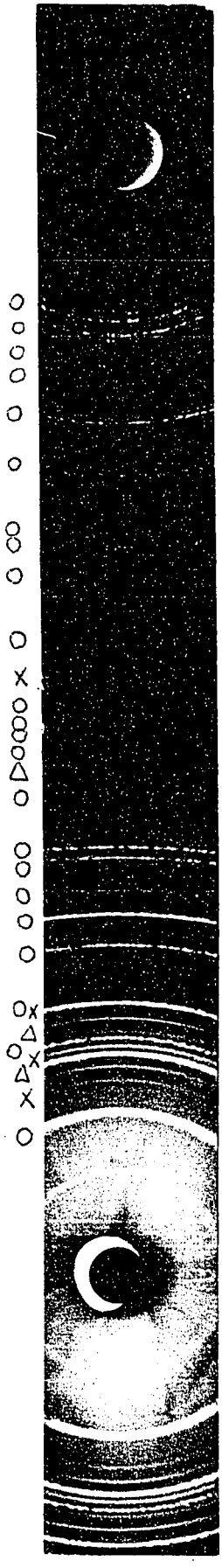


Figure B. Used Catalyst Without Modifier

Figure 17 - X-Ray Diffraction Patterns of the Catalyst

Figure 18 - X-Ray Diffraction Patterns of the Catalyst

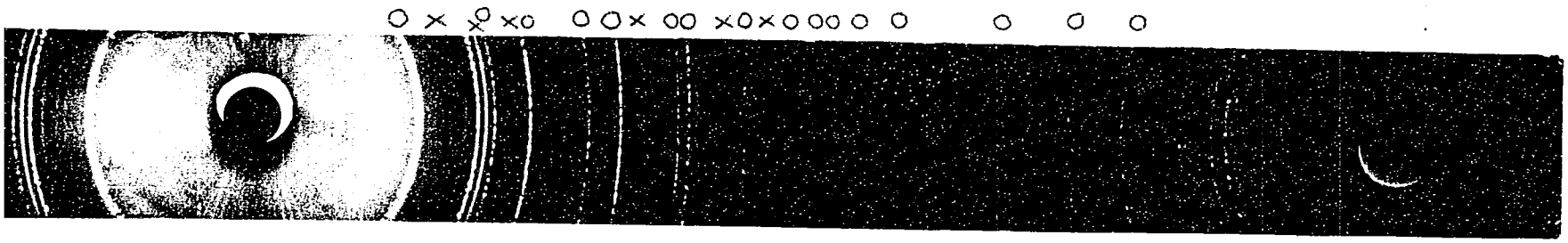


Figure A. Used Catalyst Modified With an Optimum Amount of Chlorine

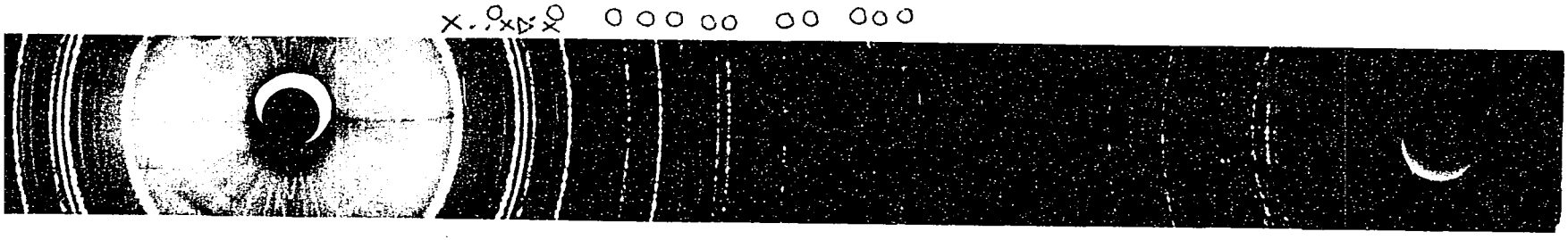


Figure B. Used Catalyst With Overdoped Chlorine Modifier

O Al_2O_3
X Cu_2O
Δ CuO
- Unknown

V KINETIC ANALYSIS OF DATA

The fundamental problem in the design of a catalytic process is the relationship between the reaction rate and the operating variables. The reaction rate, r, can be expressed as a function of conversion. It is customary to correlate and derive a rate expression in terms of partial pressures of reactants and products based on the well-known Langmuir-Hinshelwood theory[36].

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

(A) Rate Steps in Heterogeneous Catalysis

The overall catalytic process is the result of a series of reaction steps. For porous solid catalysts these steps are:

(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. In such cases two additional steps should be added to the list: (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.

The relative importance of these steps can vary greatly and depends 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 would be very complicated. The steps 1, 2, 6 and 7 are physical process which can be minimized or accounted for independently as will be described later. The chemical steps 3, 4, 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. Even inclusion of only these three steps results in equation of high complexity. Usually only one of these three steps offers a much higher resistance than the other two, and is therefore considered to be the rate controlling or rate-determining step, while the other two are considered to be at equilibrium.

(B) Factors Affecting the Rate Mechanism

Hougen[37] has pointed out that five serious sources of error could affect the evaluation of a rate equation and interpretation of rate data in flow reactions catalyzed by solids. These errors are:

(1) Variation in catalyst activity.

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

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

(4) Appreciable departure from plug flow.

(5) Neglect of pressure drop due to flow.

In order to derive a true rate equation, the above mentioned factors which may effect the mechanism significantly should be either eliminated or minimized.

1) Stability of the Catalyst

In this study, the activity of the catalyst remained fairly constant during the entire run of experiments. This was confirmed by repeating a standard run at several times in the experimental program, the results are given in Appendix D (Table A-D-10). In addition, the excellent constancy of syringe pump speed provided a precise supply of chlorine modifiers in the feed.

2) Internal Diffusion and Effectiveness Factor

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

(i) 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 A° 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 (Table A-F-2) and represented in Figure 19. The constancy of conversion indicates that molecular diffusion was negligible.

(ii) Knudsen diffusion - it occurs in small catalyst pores, i.e., at atmospheric pressure, when the mean pore radius is < 200 A°.

The effective Knudsen diffusivity is given as

$$D_{K,\,eff} = 19,400 \frac{\beta^2}{\tau S_g \rho_p} \sqrt{\frac{T}{M}} \qquad (5\text{-}1)$$

where β = porosity of catalyst

τ = tortuosity of catalyst

S_g = specific surface area of catalyst

ρ_p = catalyst particle density

T = absolute temperature

M = molecular weight of the gas mixture

The effectiveness factor of a catalyst used to evaluate the effect of Knudsen diffusion is defined as the ratio of the actual rate of reaction per unit mass of catalyst to the rate which would exist

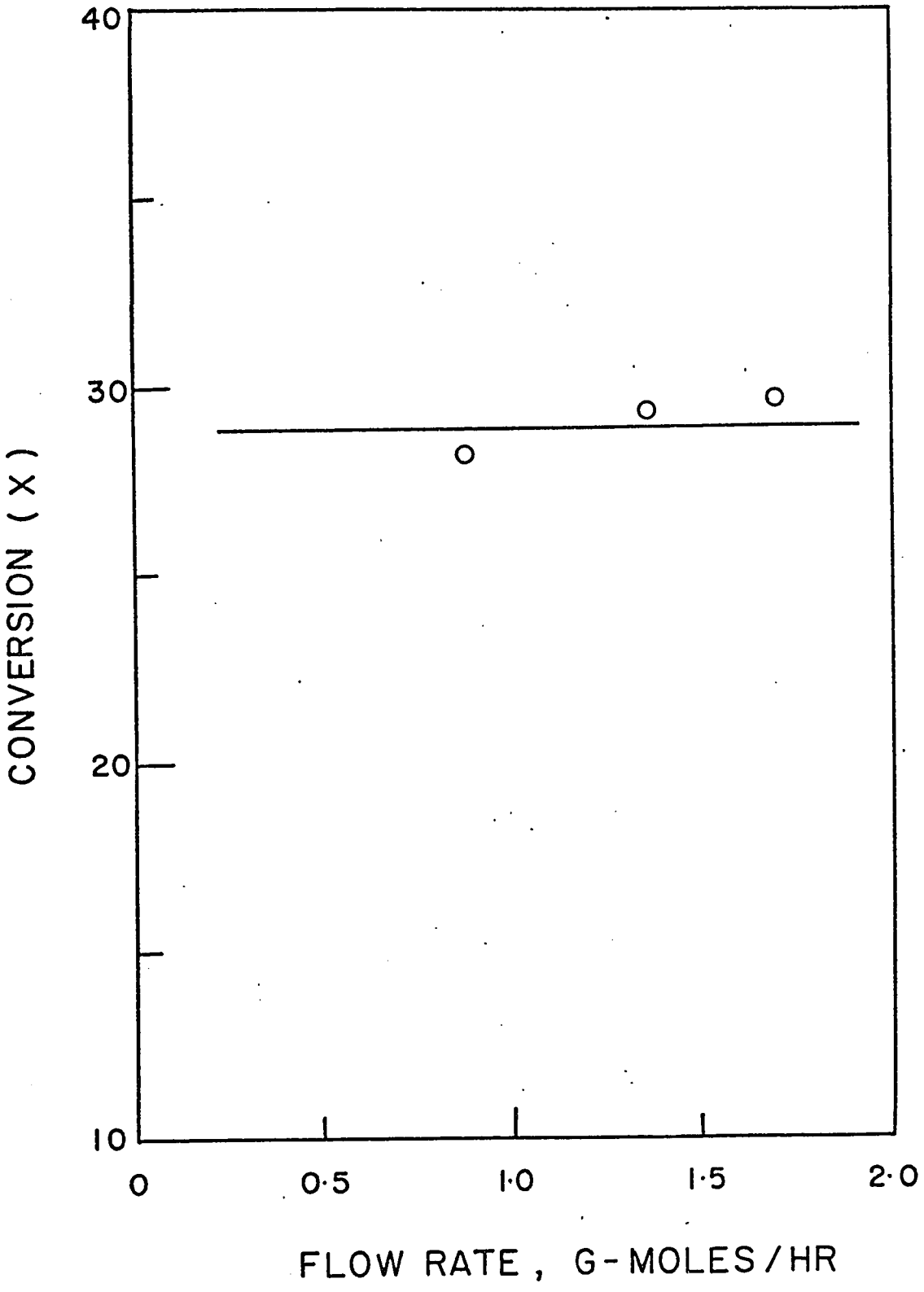


Figure 19- Effect of Feed Velocity on Conversion for Oxidation of 2-methylpropene

if the concentration at all interior interfaces were the same as those at the gross exterior interface.

Although much effort has been spent on the correlation of the effectiveness factor with the physical properties of the system, the success was not great. Only relatively simple cases have been treated. An estimate of the effectiveness factor for the catalyst used in this study was calculated by using a modified Thiele method [79]. A value of nearly unity was obtained. The detailed calculation is shown in Appendix F.

A common method of determining the importance of Knudsen diffusion is to examine the effect of decreased catalyst particle size on the reaction rate. If pore diffusion effects are significant, a decreased particle size results in increased reaction rate, due to the shorter average pore length in the smaller particle. The catalyst used throughout this study was prepared by crushing the support and consisted of a -20 + 40 mesh screen fraction. The average diameter of the particle was 0.56 mm. The catalyst selected for evaluating the magnitude of Knudsen diffusion consisted of a -40 + 70 mesh screen fraction with an average diameter of 0.32 mm. As shown in Appendix F (Table A-F-1), the particle size of catalyst has no significant effect on the conversion rate, thereby implying that the Knudsen diffusion effect was not rate-determining and hence could be neglected.

3) External Resistances to Mass and Heat Transfer

In the rate equations for reactions catalyzed by solid surfaces the partial pressures and temperature should represent

values at the gas-solid interface. These values could be significantly different from those in the ambient stream because of resistances imposed by heat and mass transfer. It is desirable to eliminate these resistances to simplify the correlation of experimental data with reaction rates.

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

$$r_{m_A} = k_{G_A} a_m \varphi (P_A - P_{A_i}) \tag{5-2}$$

and

$$g_{m_A} = r_{m_A} \Delta H_A = h_G a_m \varphi (T - T_i) \tag{5-3}$$

where

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

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

k_{G_A} = mass transfer coefficient for component A

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

a_m = external surface area of the catalyst per unit mass

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

P_A = partial pressure of component A in the ambient stream

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

T = temperature of the ambient stream

T_i = temperature of the catalyst.

Values of dimensionless Chilton-Colburn[19], j factors are related to heat and mass transfers by the following relation for gases

$$j_D = \left(\frac{k_G \, p_{f_A}}{G_m}\right)\left(\frac{\mu}{\rho \, D_{AM}}\right)_f^{2/3} \tag{5-4}$$

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

where

P_{f_A} = film pressure factor, defined by Equation (5-11)

μ = viscosity of the gas

ρ = density of the gas

D_{AM} = average diffusion coefficient of component A

C_p = specific heat of the gas

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

K = thermal conductivity of the gas

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

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

subscript f = properties at average condition of the gas film

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

j_h and j_D can be obtained from Gamson, Thodes and Hougen's[27] equations

$$j_h = 1.06 \left(\frac{D_p G_m}{\mu}\right)^{-0.41} \quad (5\text{-}6)$$

$$j_D = 0.99 \left(\frac{D_p G_m}{\mu}\right)^{-0.41} \quad (5\text{-}7)$$

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

j_h and j_D can be obtained by Wilke and Hougen's[94] equations

$$j_h = 1.95 \left(\frac{D_p G_m}{\mu}\right)^{-0.51} \quad (5\text{-}8)$$

$$j_D = 1.82 \left(\frac{D_p G_m}{\mu}\right)^{-0.51} \quad (5\text{-}9)$$

where

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

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

π = total pressure

a_p = average surface area per particle.

The term P_{f_A}, the film pressure factor for component A which accounts for the bulk flow of the fluid in equation (5-4) for the reaction

$$a\,A + b\,B \rightleftarrows r\,R + s\,S \tag{5-10}$$

is defined as

$$P_{f_A} = \frac{(\pi + \delta_A P_A) - (\pi + \delta_A P_{A_i})}{\ln\left(\frac{\pi + \delta_A P_A}{\pi + \delta_A P_{A_i}}\right)} \tag{5-11}$$

where

$$\delta_A = \frac{r + s + a + b}{a} \tag{5-12}$$

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

Yoshida et al.[98] have developed a method for calculating the drop in pressure and temperature between the bulk gas stream and the exterior surface of the catalyst, and even within the catalyst particle. The temperature and pressure gradient (ΔT and ΔY) can be easily determined from the charts proposed by them using calculated values of the modified Reynolds number and dimentionless Prandtl and Schmidt numbers. In essence, they can be represented by

$$\Delta T = Q\,(j_h)^{-1}\,(Pr)_f^{2/3} \tag{5-13}$$

and

$$\Delta Y_A = \frac{\Delta P_A}{P_A} = R\,(j_D)^{-1}\,Y_{f_A}\,(Sc)^{2/3} \tag{5-14}$$

where

ΔT = temperature drop across the film

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

$$Q = \frac{r \Delta H_A}{a_m \varphi C_p G_m} \qquad (5\text{-}15)$$

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

$$R = \frac{r_a}{a_m \varphi G_m} \qquad (5\text{-}16)$$

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

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

The j-factors are related to the modified Reynolds number $\left(\frac{G_m}{a_V \varphi \mu}\right)$ by the equations

(i) $$j_D = 0.84 \, Re^{-0.51} \text{ when } 0.01 < Re < 50 \qquad (5\text{-}17)$$

(ii) $$j_D = 0.57 \, Re^{-0.41} \text{ when } 50 < Re < 1000 \qquad (5\text{-}18)$$

and $$j_h = 1.076 \, j_D \qquad (5\text{-}19)$$

The data of many investigators have been correlated by this method. The gradients are found to fall in a narrow band on ΔY_A vs R or ΔT vs Q plot, indicating that R and Q are the most significant factors in controlling the pressure and temperature gradients respectively.

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

A sample calculation based on the method of Yoshida et al. for estimating the temperature and pressure drop from the bulk gas stream to the surface of the catalyst is shown in Appendix G. The highest partial pressure gradient thus, calculated was found to be of the order of 0.001 and the temperature at the catalyst surface was calculated to be 5°C higher than that of the main gas stream. Hence, these effects could be neglected.

4) Appreciable Departure from Plug Flow

In a steady-state flow reactor, the relationship between the reciprocal of space velocity, 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 $$F\,dX = r\,dW \qquad (5\text{-}20)$$

where

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

W = mass of catalyst in the reactor

F = feed rate, moles per unit time

X = conversion, moles per unit moles of feed.

Integration yields

$$W/F = \int_0^X \frac{dX}{r} \qquad (5\text{-}21)$$

When integrating equation (5-21), one must make the assumption that the gases are passing through the catalyst bed under conditions of plug glow, i.e., that the velocity profile across the width of the reactor is flat. The flow distribution in the packed bed was investigated by Smith et al.[81]. The flow patterns in the packed beds were affected by the packing shape, packing depth, the position of flow, the packing size, and the tube size. It was reported that the deviation from a uniform velocity profile is not very significant if the ratio of tube to pellet diameter is greater than 30. The ratio of reactor to catalyst diameter used in the present study is about 22. In addition, a porous stainless steel plate was inserted at the entrance of the reactor to brake the velocity pattern of the incoming gases. It appears that no appreciable errors were produced by assuming plug flow even though it rarely exists. Also the results of the effect of feed velocity on conversion (Figure 19) indicates that the assumption of the plug flow is quite reasonable, since the conversion of 2-methylpropene was not affected by the feed velocity.

5) Neglect of Pressure Drop Due to Flow

The pressure drop through a packed bed is given by Ergun's equation[26] for either laminar or turbulent flow. In this investigation, the pressure drop through the catalyst bed was measured experimentally. The maximum pressure drop never exceeded 10 mm Hg. Therefore, the outlet pressure of the reactor (830 mm Hg.) was employed for the reaction pressure.

(C) Correlation of Rate Equations

The diffusion steps (1, 2, 6 and 7) which are physical process, were found not to be rate controlling. The remaining steps (3, 4 and 5)

which are chemical processes, were examined in detail in order to determine which one offered the greatest resistance to the overall reaction. For each of the three chemical steps, namely adsorption of reactants, surface reaction, and desorption of products, several mechanisms can be postulated depending on whether one or both of the reacting substances are adsorbed on the catalyst surface.

1) Adsorption Isotherm

In postulating a reaction mechanism for a catalytic reaction and thereby obtaining a rate expression, adsorption of at least one of the reactants is considered a necessity. A knowledge of adsorption isotherms is therefore very essential. Three theoretical isotherms, those of Langmuir, Freundlich and Temkin, are well known. 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. Among these the Langmuir isotherm has been widely used for its simplicity. The assumptions underlying the Langmuir isotherm are: (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 nearby adsorbed molecules.

From either a kinetic or statistical approach[34], the Langmuir isotherm can be derived as follows

$$\theta_A = \frac{K_A P_A}{1 + \Sigma K_I P_I} \qquad (5\text{-}22)$$

where

θ_A = the fraction of the catalyst surface covered by A

K_A = the equilibrium adsorption constant of A

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

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

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

2) Langmuir - Hinshelwood Mechanism

The derivation of the Hougen-Watson type rate equations is based on the Langmuir-Hinshelwood theory of catalysis assuming that only one of the reaction steps is the rate-determining step, the rest of the steps are assumed to be at equilibrium. 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 an example, a rate equation is developed for a bimolecular reaction $A + B \rightleftarrows R + S$, since such type of reaction has been investigated in the present studies. The rate-controlling step of the reaction is assumed to be the surface reaction between adsorbed A and adsorbed B to give R and S. The forward reaction rate is proportional to the concentration of adjacently adsorbed AB pairs, C_{AB}

$$r_f = k\, C_{AB} \tag{5-23}$$

where

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

k = reaction velocity constant for surface reaction

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

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

$$C_{AB} = C_A \cdot S \cdot \theta_B = C_A \cdot S \cdot \frac{C_B}{L} = \frac{S}{L} C_A \cdot C_B \qquad (5\text{-}24)$$

where

L = total molal active sites per unit mass of catalyst

substituting equation (5-24) into equation (5-23) gives

$$r_f = \frac{kS}{L} C_A \cdot C_B = kSL \cdot \theta_A \cdot \theta_B$$

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

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

$$r = \frac{kSL\, K_A K_B (P_A P_B - P_R P_S/K)}{(1 + K_A P_A + K_B P_B + K_R P_R + K_S P_S)^2} \qquad (5\text{-}26)$$

where K = thermodynamic equilibrium constant for the overall reaction.

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

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

Equations of the form similar to equation (5-26) have been systematically developed and compiled by Hougen and Watson[38] and Yang and Hougen[97] for various reaction mechanisms with different rate controlling steps.

Following the Hougen-Watson approach, the possible reaction mechanisms for the catalytic air oxidation of 2-methylpropene to methacrolein can be 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 ($K_N P_N$) was not included in the rate equations, since according to Dowden[22], the chemisorption of nitrogen on copper oxide is negligible.

The rate equations derived using Hougen-Watson approach are listed in Table 4 . Where the subscript H, M and O represent 2-methylpropene, methacrolein and oxygen respectively.

3) Mechanisms Based on Two Types of Active Sites

(Modified Langmuir-Hinshelwood Mechanism)

One difficulty arises in the practical application of the Langmuir isotherm to the adsorption of a mixture of gases. The Langmuir equation predicts that the addition of one gas to a second gas will always decrease the amount adsorbed of the latter. Numerous cases of physical adsorption are known in which exactly the

TABLE 4

Rate Equations Derived From Hougen-Watson Method

(One Type of Active Site)

No.	Rate-Controlling Step	Mechanism	Rate Equation
1	Adsorption of 2-methylpropene	Surface reaction between adsorbed 2-methylpropene and oxygen	$r = \frac{K_s P_H}{1 + K_O P_O + K_M P_M}$
2	Adsorption of 2-methylpropene	Surface reaction between adsorbed 2-methylpropene and O_2 in gas phase	$r = \frac{K_s P_H}{1 + K_M P_M}$
3	Adsorption of oxygen	Surface reaction between adsorbed 2-methylpropene and oxygen	$r = \frac{K_s P_O}{1 + K_H P_H + K_M P_M}$
4	Adsorption of oxygen	Surface reaction between adsorbed oxygen and 2-methylpropene in gas phase	$r = \frac{K_s P_O}{1 + K_M P_M}$
5	Desorption of methacrolein	Surface reaction between adsorbed 2-methylpropene and oxygen	$r = \frac{k'_d \left(\frac{K P_H P_O}{P_W} - P_M \right)}{1 + K_H P_H + K_O P_O + K K_M \frac{P_M P_O}{P_W}}$

. . . continuation. . .

No.	Rate-Controlling Step	Mechanism	Rate Equation
6	Desorption of methacrolein	Surface reaction between adsorbed 2-methylpropene and oxygen in gas phase	$r = \dfrac{k'_d\left(\dfrac{K P_H P_O}{P_W} - P_M\right)}{1 + K_H P_H + K K_M \dfrac{P_H P_O}{P_W}}$
7	Desorption of methacrolein	Surface reaction between adsorbed oxygen and 2-methylpropene in gas phase	$r = \dfrac{k'_d\left(\dfrac{K P_H P_O}{P_W} - P_M\right)}{1 + K_O P_O + K K_M \dfrac{P_H P_O}{P_W}}$
8	Surface reaction	Surface reaction between adsorbed 2-methylpropene and adsorbed oxygen	$r = \dfrac{K_s K_H P_H K_O P_O}{(1 + K_H P_H + K_O P_O + K_M P_M)^2}$
9	Surface reaction	Surface reaction between adsorbed 2-methylpropene and oxygen in the gas phase	$r = \dfrac{K_s K_H P_H P_O}{1 + K_H P_H + K_M P_M}$
10	Surface reaction	Surface reaction between adsorbed oxygen and 2-methylpropene in the gas phase	$r = \dfrac{K_s K_O P_O P_H}{1 + K_O P_O + K_M P_M}$

opposite behavior is observed, i.e., where the second gas increases the adsorption of the first gas[16]. Some observations were also found on chemisorption[29] 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 having a negative adsorption coefficient in the 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

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

In the usual application of Langmuir-Hinshelwood approach this (experimental) result is considered to be physically impossible, and any reaction mechanism which leads to a negative adsorption coefficient is automatically discarded.

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

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

then for component A

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

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

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

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

Where superscript (I) and (II) refer to the type (I) and type (II) active sites respectively. Using this approach, the difficulty of having negative adsorption coefficients in the Langmuir isotherm is resolved since the adsorption is not restricted to competition for active sites.

This concept may be applied to the catalytic oxidation of olefins 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 olefin are to be selectively adsorbed, then the equilibrium fractions covered by oxygen and 2-methylpropene would be

$$\theta_O = \frac{K_O P_O}{1 + K_O P_O} \qquad (5\text{-}32)$$

and

$$\theta_H = \frac{K_H P_H}{1 + K_H P_H + K_M P_M} \qquad (5\text{-}33)$$

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

As an illustration of 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.

$$A + \square \xrightarrow{k_1} A^+ — \odot \tag{5-34}$$

$$B + \odot \xrightarrow{k_2} B^- — \square \tag{5-35}$$

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

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

$$r_1 = k_1 p_A \theta_\square \tag{5-36}$$

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

$$r_2 = k_2 P_B \theta_\odot \tag{5-37}$$

Where $\theta_\square$ and $\theta_\odot$ represent the fraction of active site being positive hole and free electron respectively.

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

also $\theta_\odot = 1 - \theta_\square$ (5-39)

substituting equations (5-37), (5-38) and (5-39) into equation (5-36) gives

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

and

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

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

TABLE 5

Rate Equations Derived From Modified Langmuir-Hinshelwood Mechanism

(Two Types of Active Sites)

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

(4) Correlation of Initial Rate Data

In a steady state flow reactor, the relationship between conversion, flow rate and reaction rate is given by the equation

$$F\,dX = r\,dW$$

which on integration yields

$$\int_o^W \frac{dW}{F} = \int_o^X \frac{dX}{r}$$

$$\frac{W}{F} = \int_o^X \frac{dX}{r}$$

Yang and Hougen[97], 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 mechanisms, 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 20 against the partial pressure of 2-methylpropene in the feed. From the charts of Yang and Hougen[97], which show the effect of feed composition upon initial rates for various mechanisms, and the information derived from Figure 20, it was concluded that desorption of product was definitely not rate controlling. The mechanism 5, 6 and 7 were therefore discarded.

(5) Correlation of Conversion Data

The results of Voge et al.[90] and the experimental results of the present investigation showed that in the oxidation of olefin to unsaturated aldehydes, carbon dioxide came mainly from the consecutive oxidation of aldehydes. On the basis that the oxidation of 2-methylpropene with air over a copper oxide 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

$$C_4H_8 + O_2 \rightleftharpoons C_4H_6O + H_2O \qquad (5\text{-}42)$$

$$C_4H_6O + 5O_2 \rightleftharpoons 4CO_2 + 3H_2O \qquad (5\text{-}43)$$

let X = moles of 2-methylpropene reacting per hour by reaction (5-42)/ moles of 2-methylpropene fed per hour

Z = moles of methacrolein reacting per hour by reaction (5-43)/ moles of 2-methylpropene fed per hour.

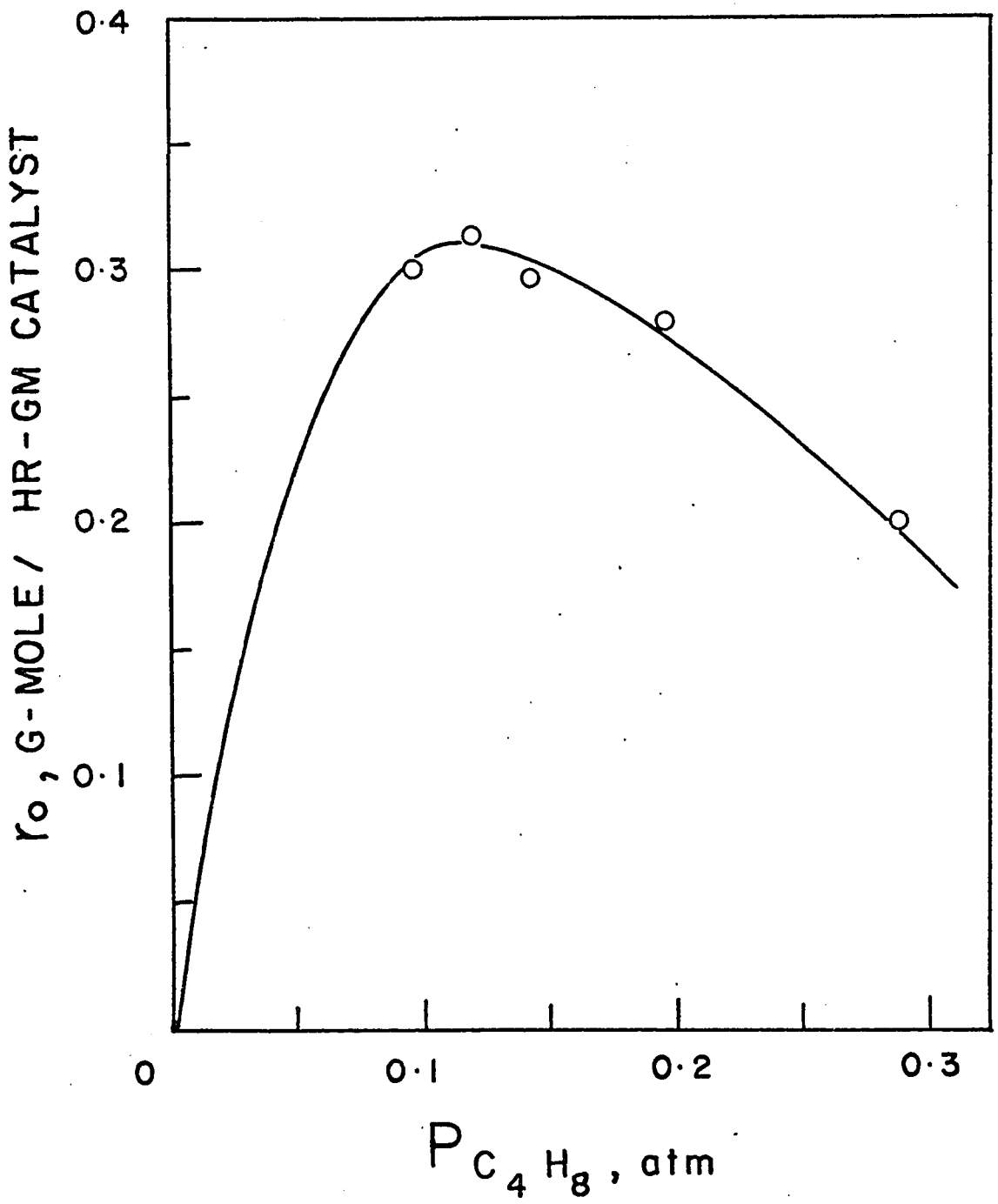


Figure 20 - Initial Rates (r_o) Versus $P_{C_4H_8}$ in Feed at 400 °C

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

$$Z = 1/4\ X_C \tag{5-44}$$

Where X_C = moles of carbon dioxide produced per hour/moles of 2-methylpropene fed per hour.

Values of X and $1/4\ X_C$ for different feed ratios at various temperature (Table A-D-9 in Appendix D) were plotted as shown in Figures 21 -24. From the curves in these figures, the following equation was derived

$$Z = 0.24\ X \tag{5-45}$$

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 $_oN_H$ = moles of 2-methylpropene in the feed

$_oN_O$ = moles of oxygen in the feed

Then, for any conversion, X

N_H = moles of 2-methylpropene in the product

$= {}_oN_H\,(1-X)$

N_M = moles of methacrolein in the product

$= {}_oN_H\,(X - Z) = 0.76\ (_oN_H)\ X$

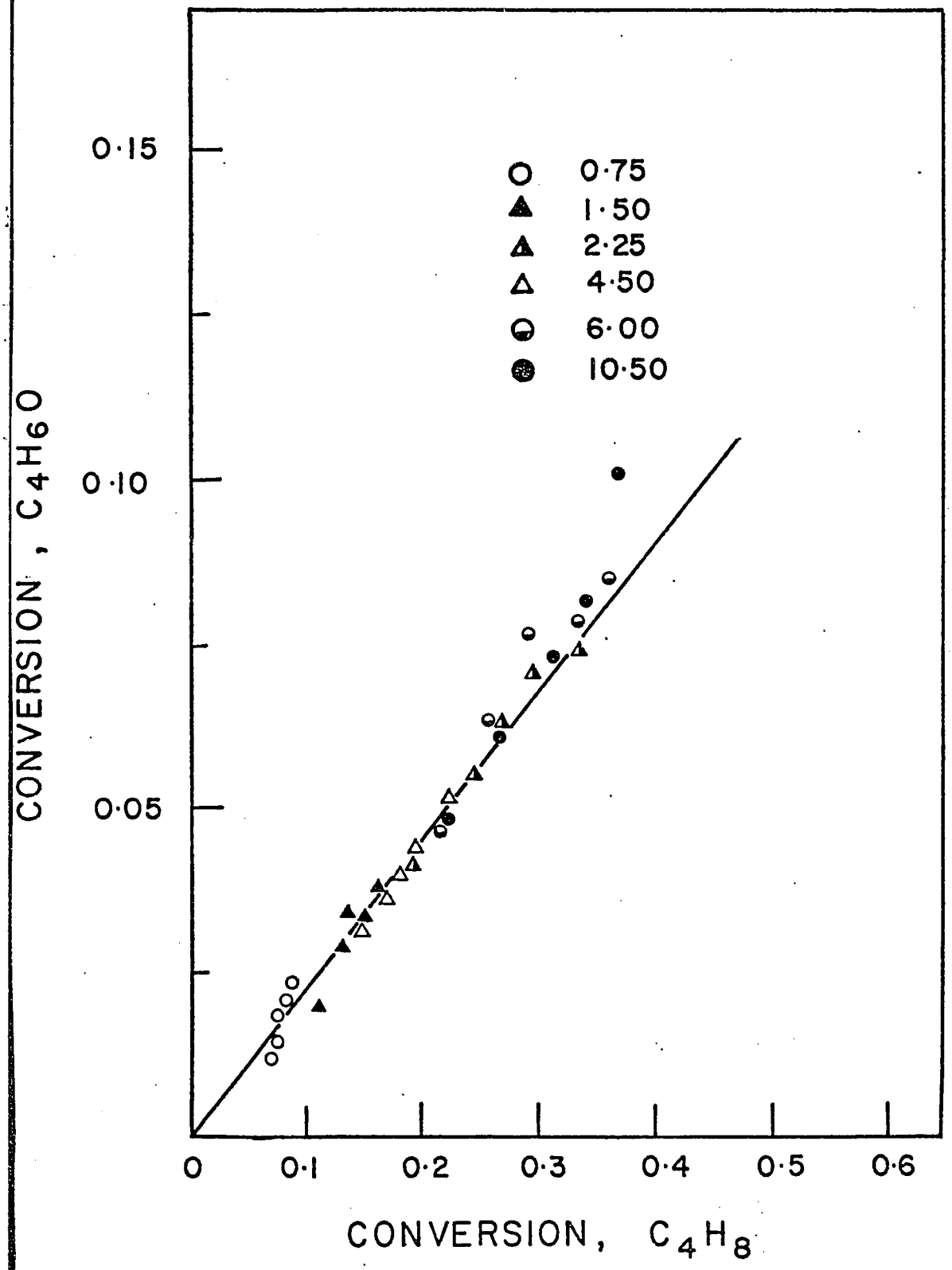


Figure 21 - Conversion of 2-methylpropene Versus Conversion of Methacrolein at 350°C

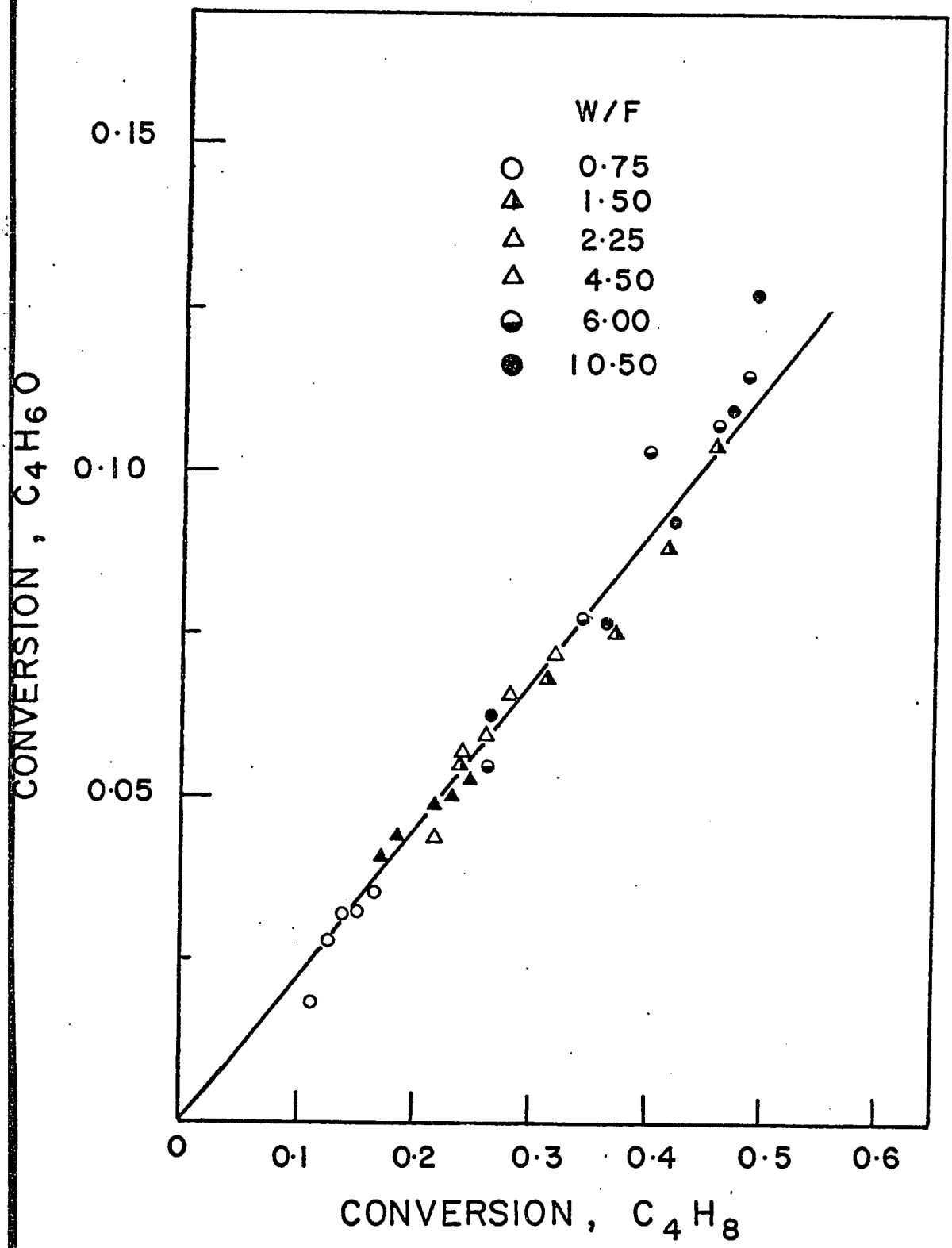


Figure 22- Conversion of 2-methylpropene Versus Conversion of Methacrolein at 375 °C

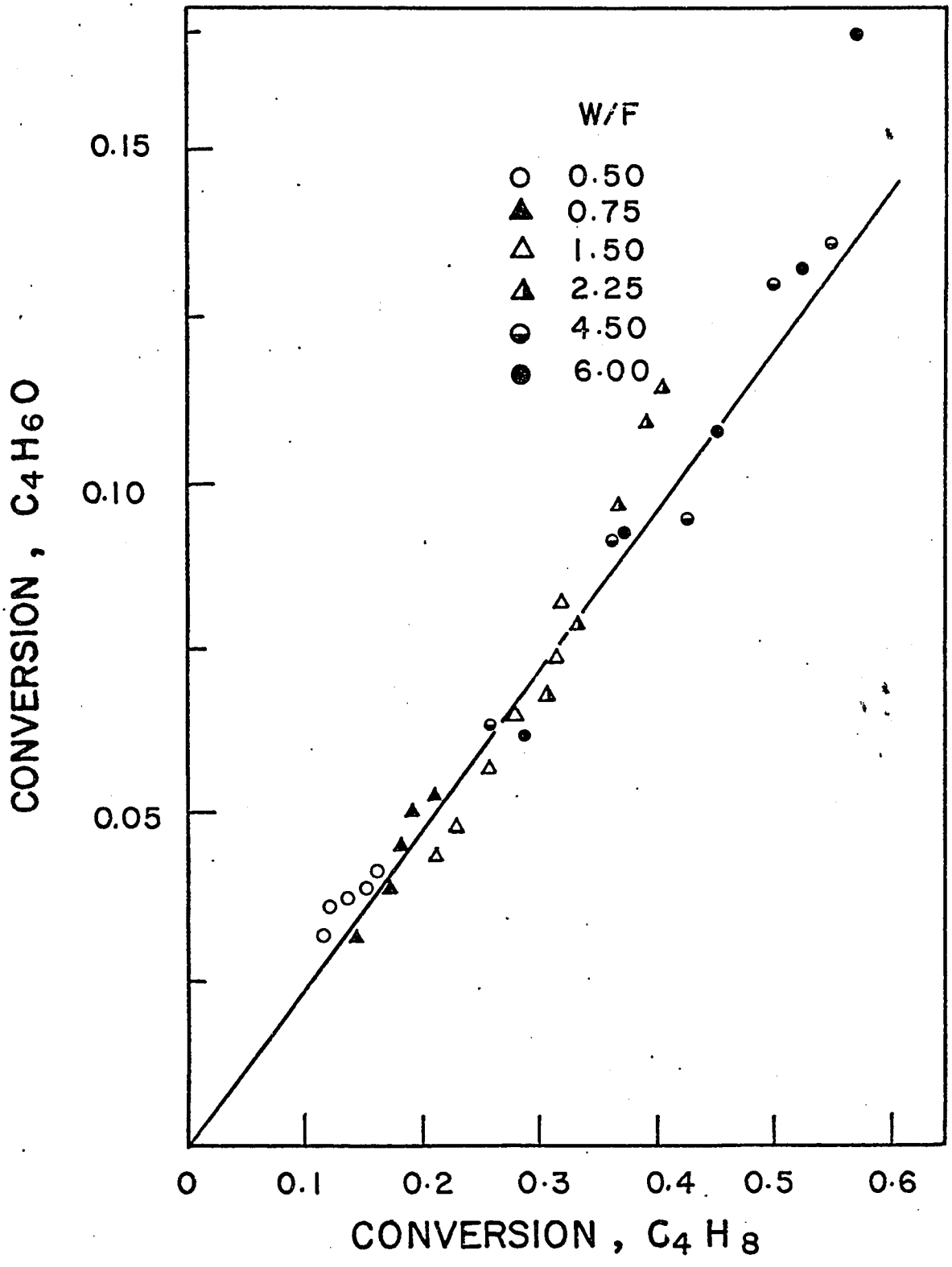


Figure 23- Conversion of 2-methylpropene Versus Conversion of Methacrolein at 400 °C

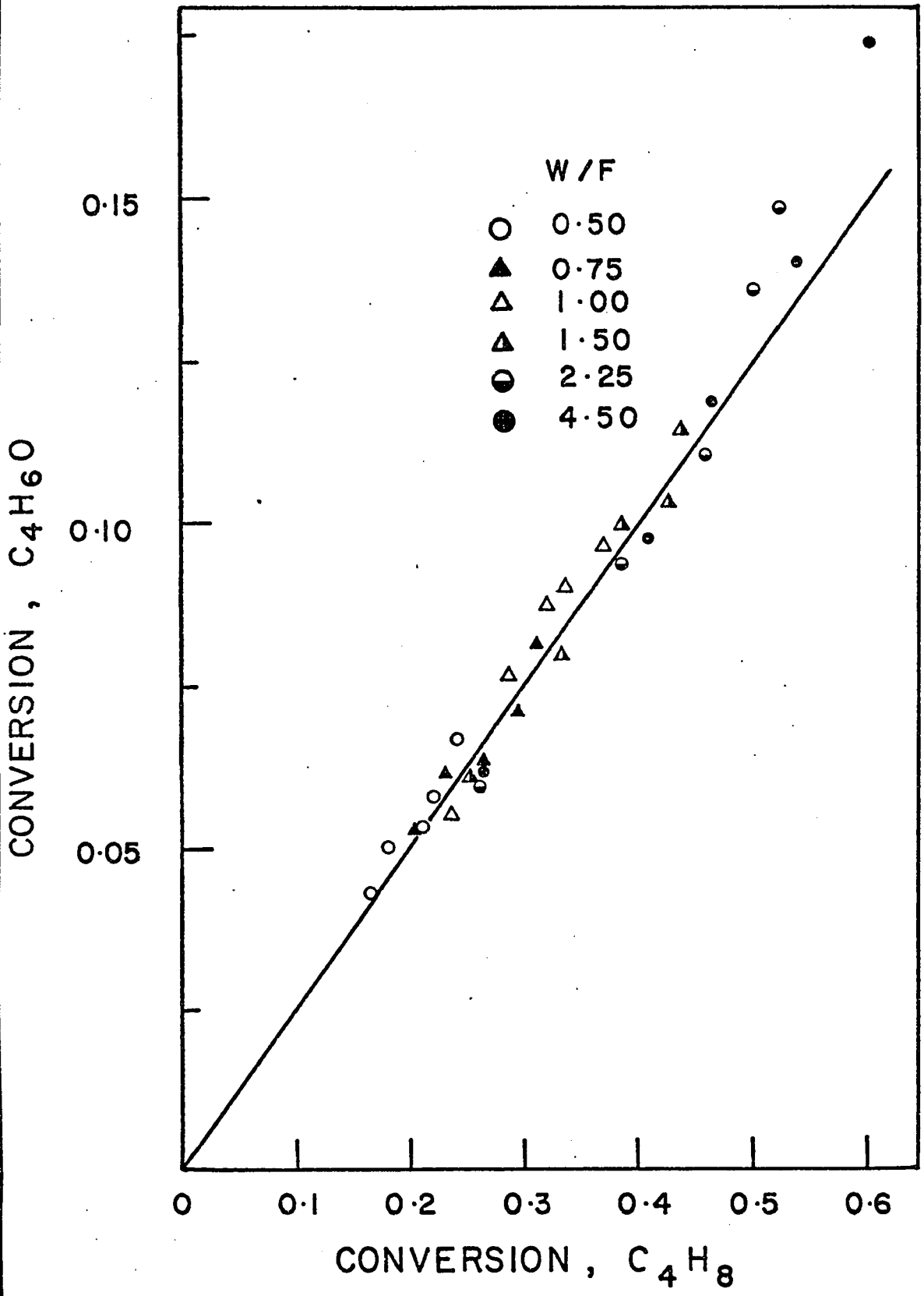


Figure 24- Conversion of 2-methylpropene Versus Conversion of Methacrolein at 425 °C

TABLE 6

Integrated Rate Equations

Mechanism	
1	$W/F = \left(\frac{1}{K_s}\right)\left[\frac{K_O(e-d) - K_M b - 1}{a} \ln(1-x) + \frac{K_O e - K_M b}{a} x\right]$
2	$W/F = \left(\frac{-1}{K_s}\right)\left[\frac{(1 + K_M b)}{a} \ln(1-x) + \frac{K_M b}{a} x\right]$
3	$W/F = \left(\frac{1}{K_s}\right)\left[\frac{(K_H a - K_M b)}{e} x - \frac{(e + K_H a (e-d) + K_M b d)}{e^2} \ln(1 - ex/d)\right]$
4	$W/F = \left(\frac{-1}{K_s}\right)\left[\frac{(e + K_M b d)}{e^2} \ln(1 - ex/d) + \frac{K_M b}{e} x\right]$
8	$W/F = \left(\frac{1}{K_O K_s}\right)\left[\left(\frac{K_H a}{e} - \frac{2 K_M b}{e} + \frac{K_M^2 b^2}{K_H a e}\right) x + \frac{K_M^2 b^2}{e^2} \ln(1-x) - \left(\frac{K_H a (e-d)}{e^2} + \frac{K_M^2 b^2 d^2}{K_H a e^2 (e-d)} - \frac{2 K_M b d}{e^2}\right) \ln(1 - ex/d)\right]$

. . . continuation. . .

Mechanism

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

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

11 $$W/F = \left(\frac{1}{K_s}\right)\left[\left(\frac{1}{K_O K_H a (e-d)} + \frac{K_M b d}{K_O K_H a e (d-e)} - \frac{1}{K_O e}\right) \ln (1 - ex/d) + \left(1 - \frac{K_M b}{K_H a}\right) \times \right.$$
$$\left. - \left(\frac{1}{K_O K_H a (d-e)} + \frac{1}{K_H a} + \frac{K_M b}{K_O K_H a (d-e)} + \frac{K_M b}{K_H a}\right) \ln (1-x)\right]$$

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

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

N_W = moles of water in the product

$= {}_oN_H (X + 3Z) = 1.72 ({}_oN_H) X$

N_C = moles of carbon dioxide in the product

$= ({}_oN_H) 4Z = 0.96 ({}_oN_H) X$

N_O = moles of oxygen in the product

$= {}_oN_O - {}_oN_H (X + 5Z) = {}_oN_O - 2.2 ({}_oN_H) X$

N_N = moles of nitrogen in the product

$= {}_oN_N$ = 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 ${}_oN_T$ was used. Now if one lets

$$({}_oN_H)(P_T/{}_oN_T) = a \tag{5-46}$$

$$0.76 ({}_oN_H)(P_T/{}_oN_T) = b \tag{5-47}$$

$$0.96 ({}_oN_H)(P_T/{}_oN_T) = c \tag{5-48}$$

$$({}_oN_O)(P_T/N_T) = d \tag{5-49}$$

$$2.2 ({}_oN_H)(P_T/N_T) = e \tag{5-50}$$

and P_T = reaction pressure (830 mm Hg. or 1.092 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;

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

$$P_O = d - eX \tag{5-52}$$

$$P_M = bx \tag{5-53}$$

$$P_W = cx \tag{5-54}$$

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 (mechanisms 1-4 and 8-13) are given in Table 6. Finally, a non-linear regression technique, developed by Marquart [63] 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 11 fitted the experimental data best. The rate equation based on this mechanism can be expressed as

$$r = \frac{K_S K_H P_H}{1 + K_H P_H + K_M P_M} \cdot \frac{K_O P_O}{1 + K_O P_O} \tag{5-55}$$

The values of K_S, K_H, and K_O between 350 and 525°C are listed in Table 7, since K_O value is small (0.459, 0.765, 0.691 and 0.535 respectively) it would not affect the donominator of equation (5-55) significantly, an average value of 0.60 is used.

TABLE 7

Temperature Effect on Rate Constants

°C	°K	$1/T \times 10^3$	K_O	K_H	K_M	K_S
350	623	1.605	0.60	66.8	355	1.27
375	648	1.543	0.60	45.6	249	2.90
400	673	1.486	0.60	46.6	180	3.34
525	698	1.433	0.60	37.4	117	7.44

(6) Temperature Effect on Rate Constants

The temperature dependence of K_S, K_H and K_M is shown in Figure 35. The mathematical expressions describing the temperature dependence of K_S, K_H and K_M are given in the following equations

$$\ln K_S = 6.39 - \frac{3.89 \times 10^3}{T} \quad (5\text{-}56)$$

$$\ln K_H = -0.37 + \frac{1.36 \times 10^3}{T} \quad (5\text{-}57)$$

$$\ln K_M = -2.12 + \frac{2.93 \times 10^3}{T} \quad (5\text{-}58)$$

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

The values of K's obtained from Table 7 were substituted into equation 8 of Table 6 to determine the W/F versus X relation, Figures 25-34 show the comparison between the experimental and predicted values of this relation. The solid lines in the figure refer to the curves predicted by substituting the appropriate values of K's in the relation; the circles represent the experimental data. A sample calculation is given in Appendix I.

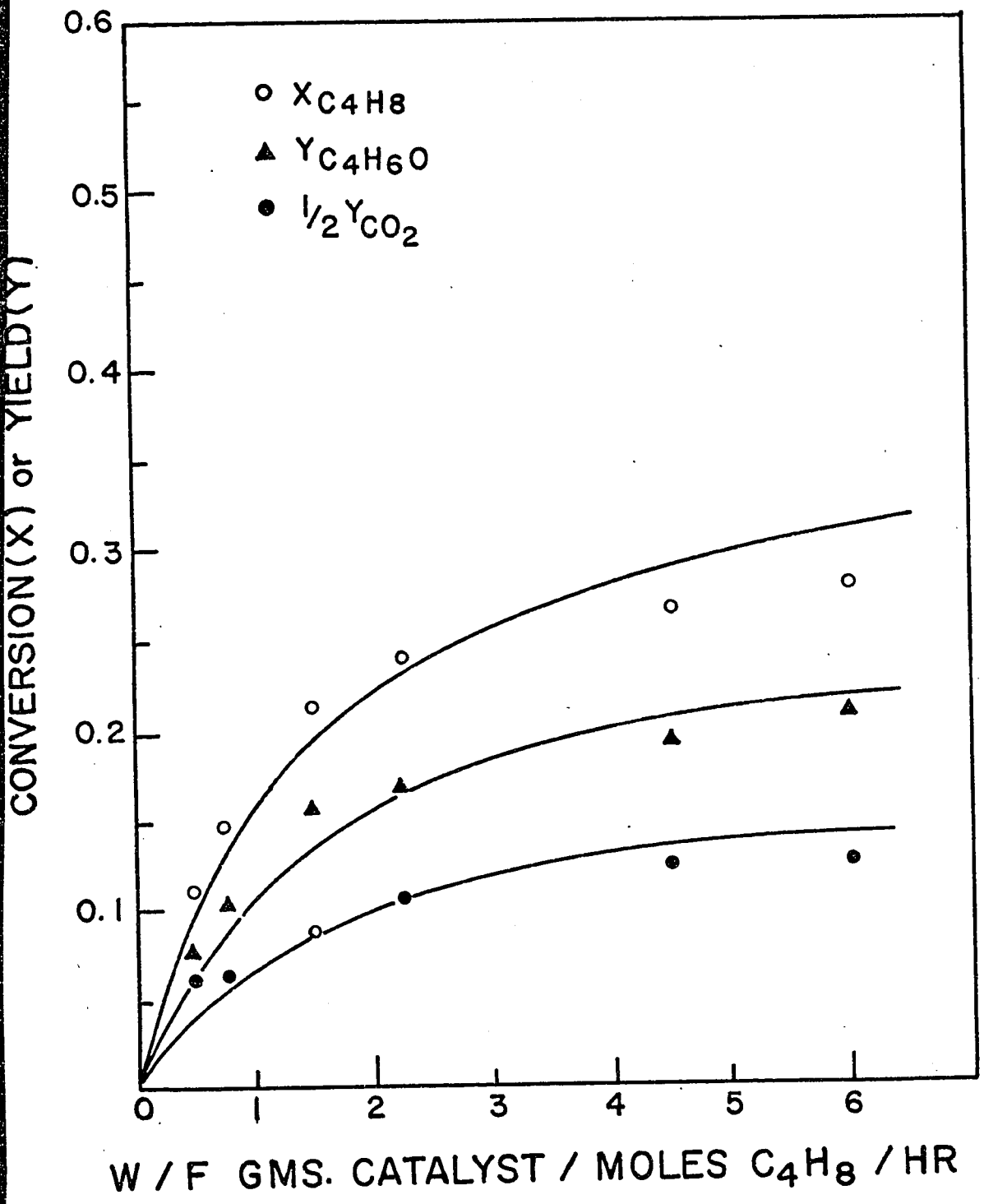


Figure 25- W/F Effect on Conversion and Yields for Oxidation of 2-methylpropene over Chlorine Modified Copper Oxide Catalyst at 400 °C, R = 0.5913

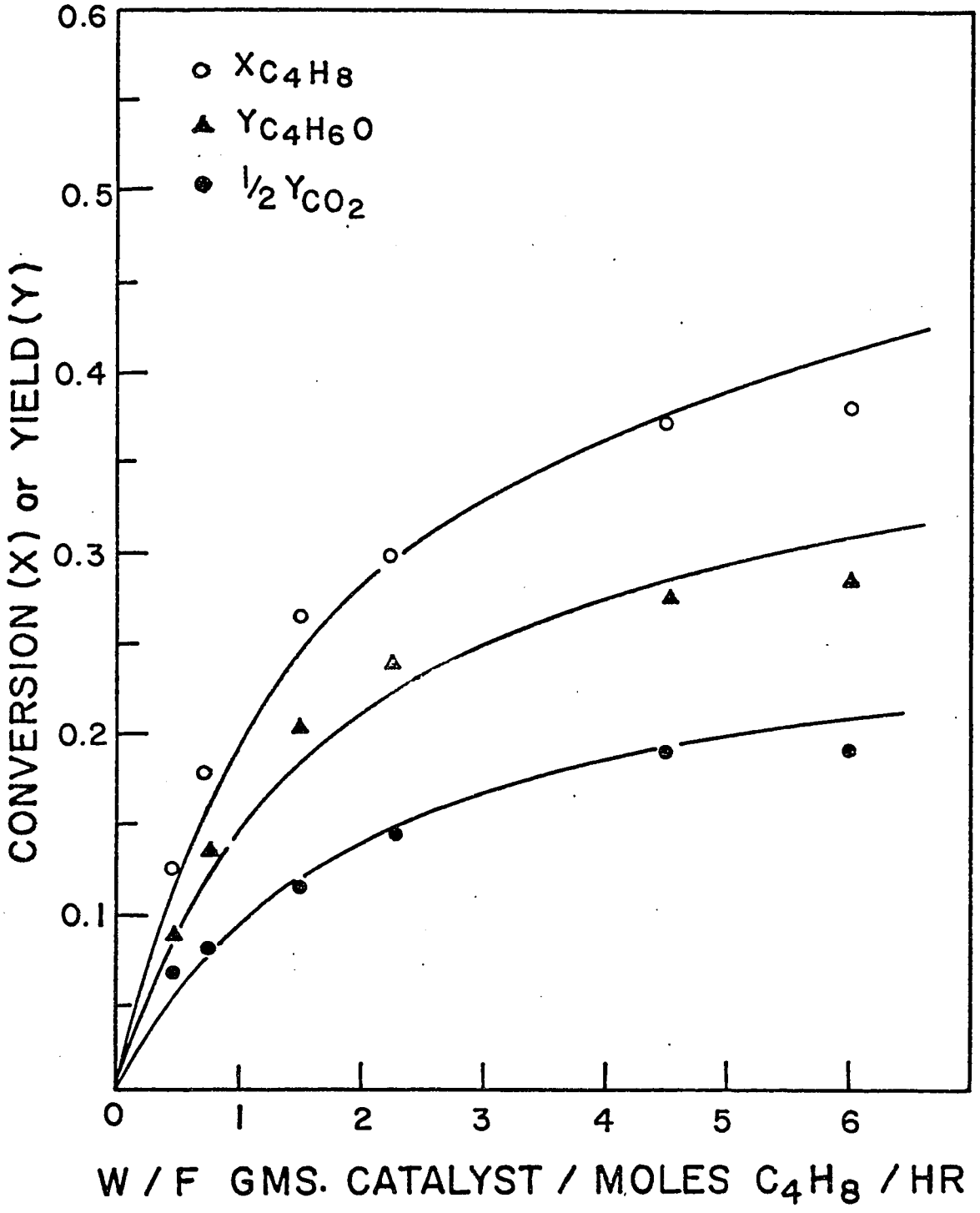


Figure 26- W/F Effect on Conversion and Yields for Oxidation of 2-methylpropene over Chlorine Modified Copper Oxide Catalyst at 400 ° C, R = 0.9710

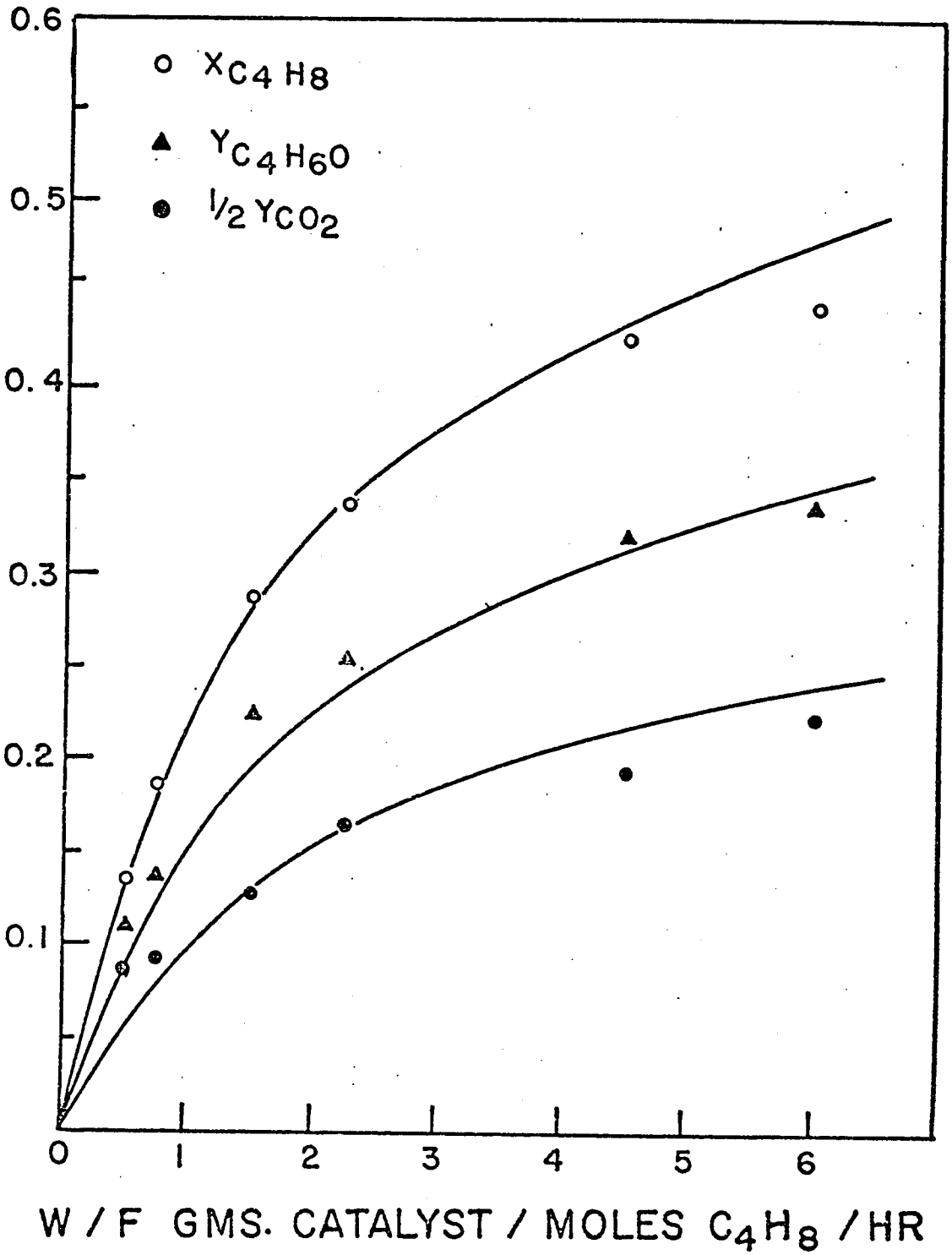


Figure 27- W/F Effect on Conversion and Yields for Oxidation of 2-methylpropene over Chlorine Modified Copper Oxide Catalyst at 400 °C, R = 1.3998.

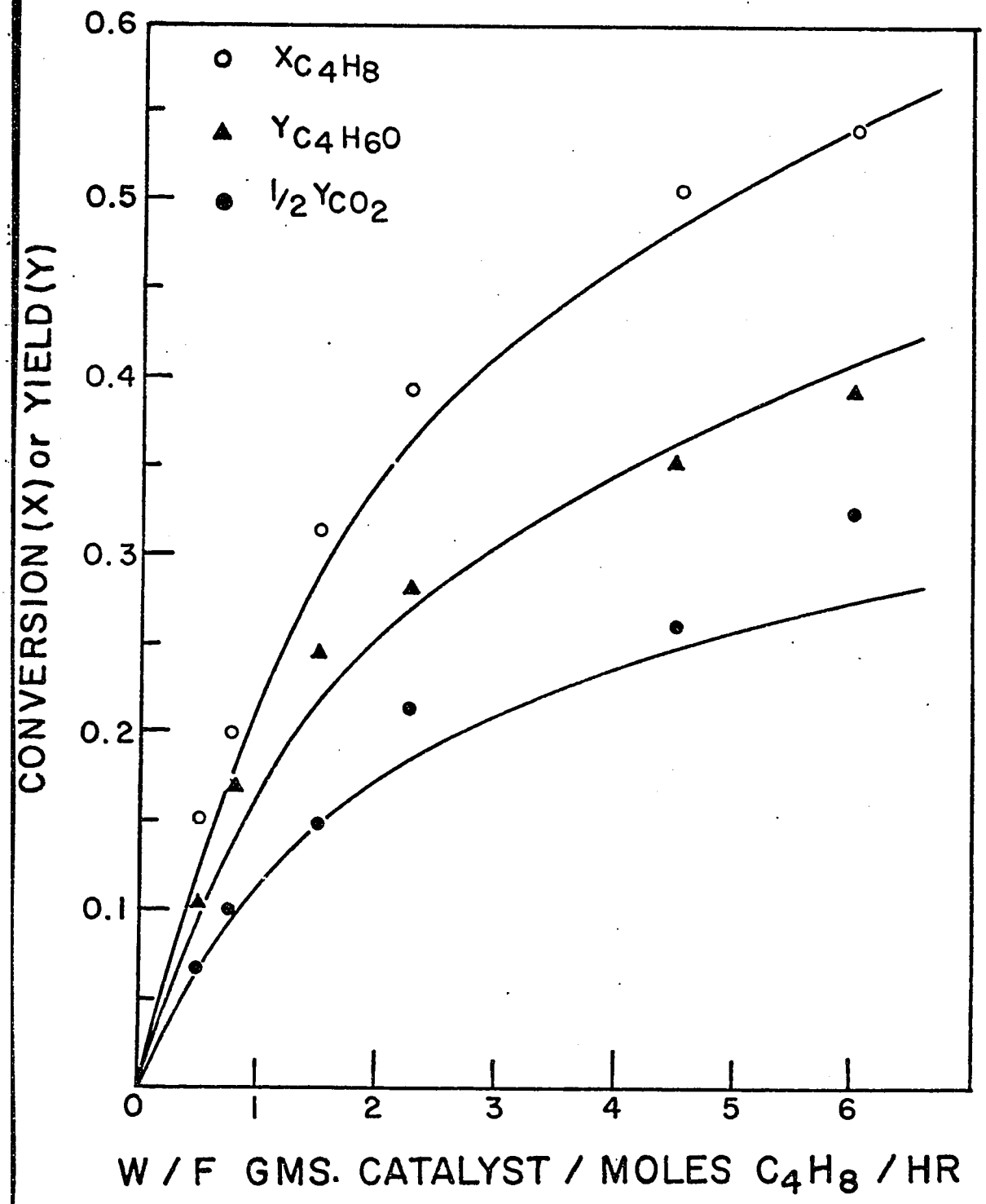


Figure 28- W/F Effect on Conversion and Yields for Oxidation of 2-methylpropene over Chlorine Modified Copper Oxide Catalyst at 400 °C, R = 1.7240

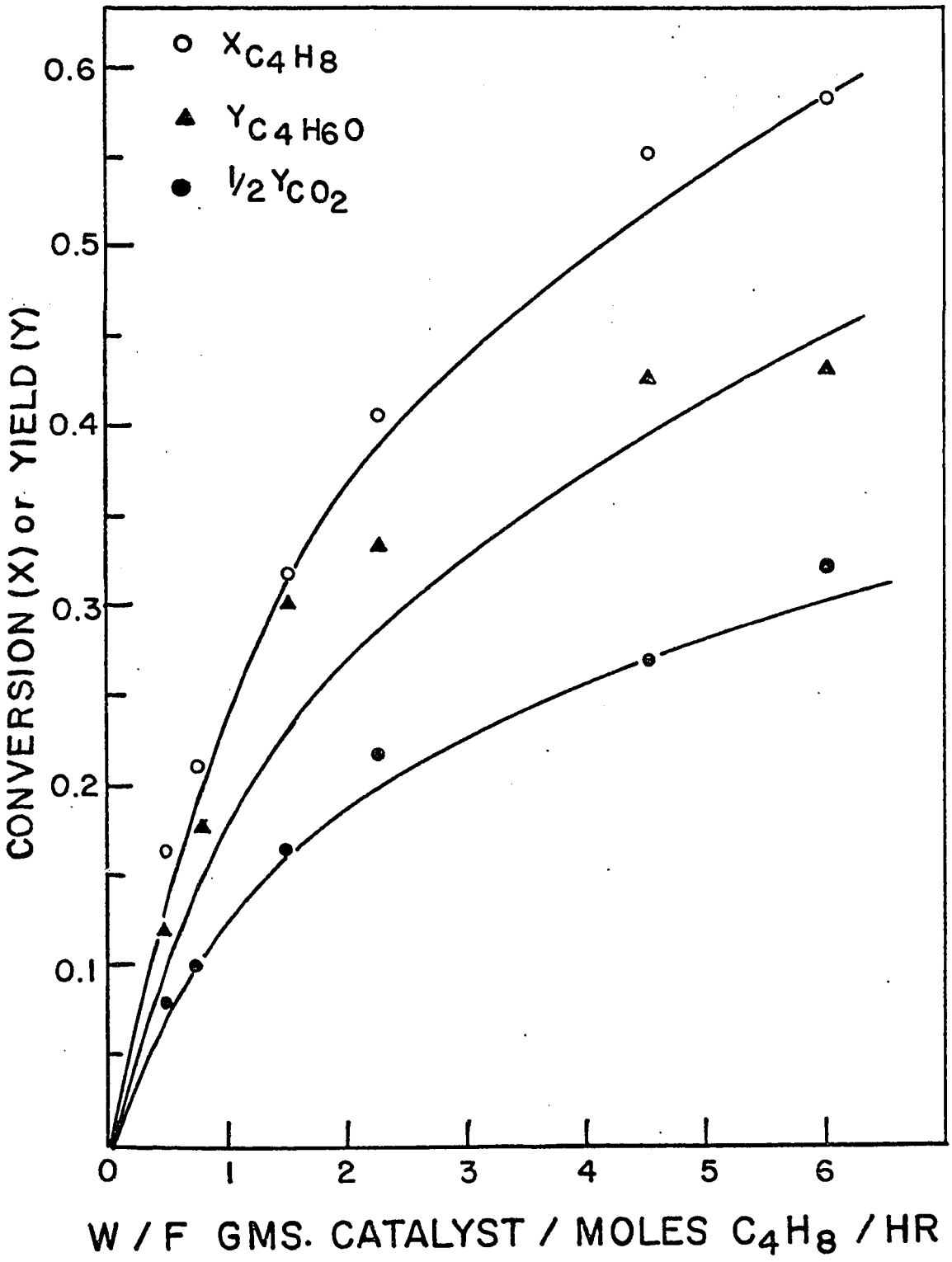


Figure 29- W/F Effect on Conversion and Yields for Oxidation of 2-methylpropene over Chlorine Modified Copper Oxide Catalyst at 400 °C, R = 2.2337

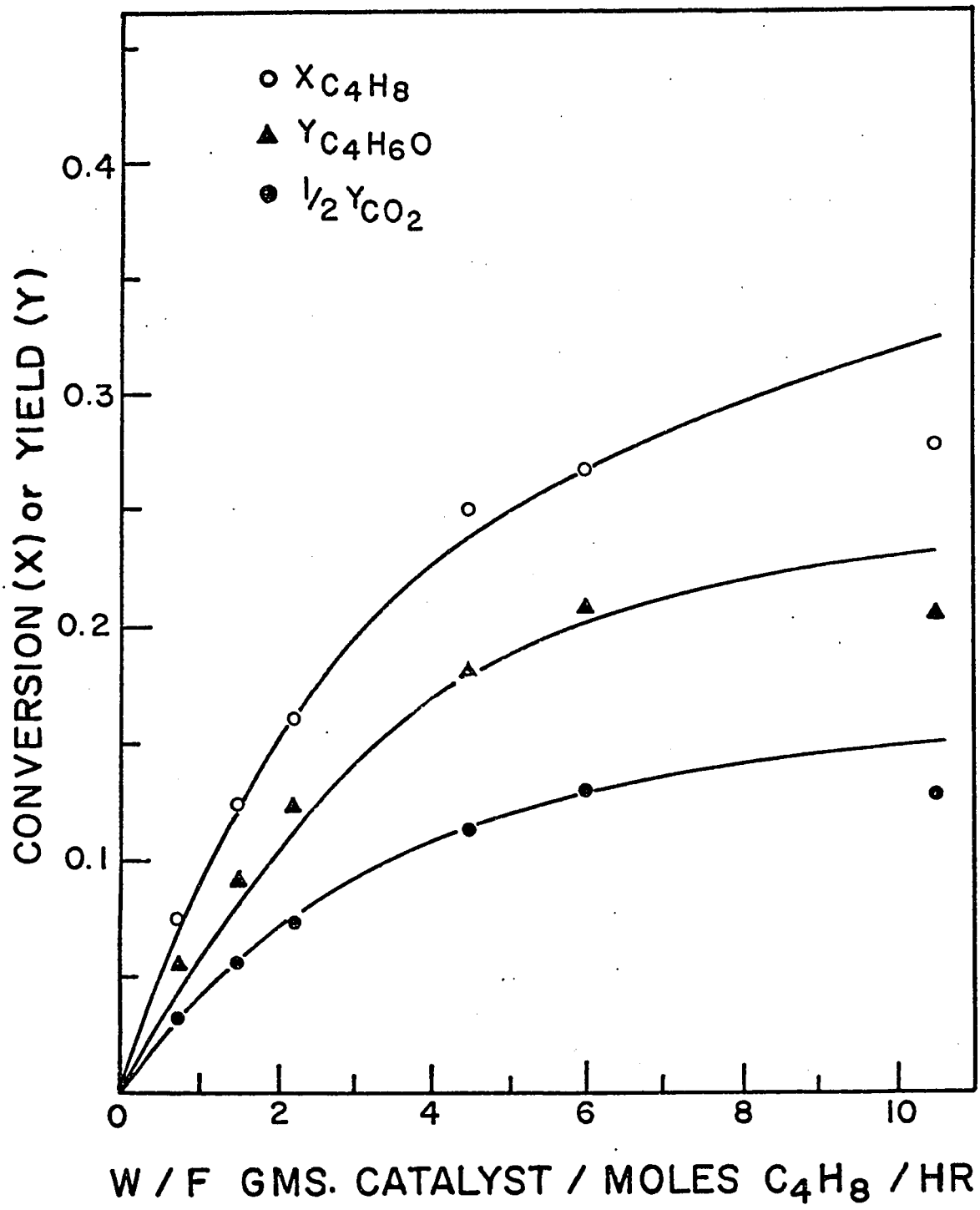


Figure 30- W/F Effect on Conversion and Yields for Oxidation of 2-methylpropene over Chlorine Modified Copper Oxide Catalyst at 350 °C, R = 0.9710

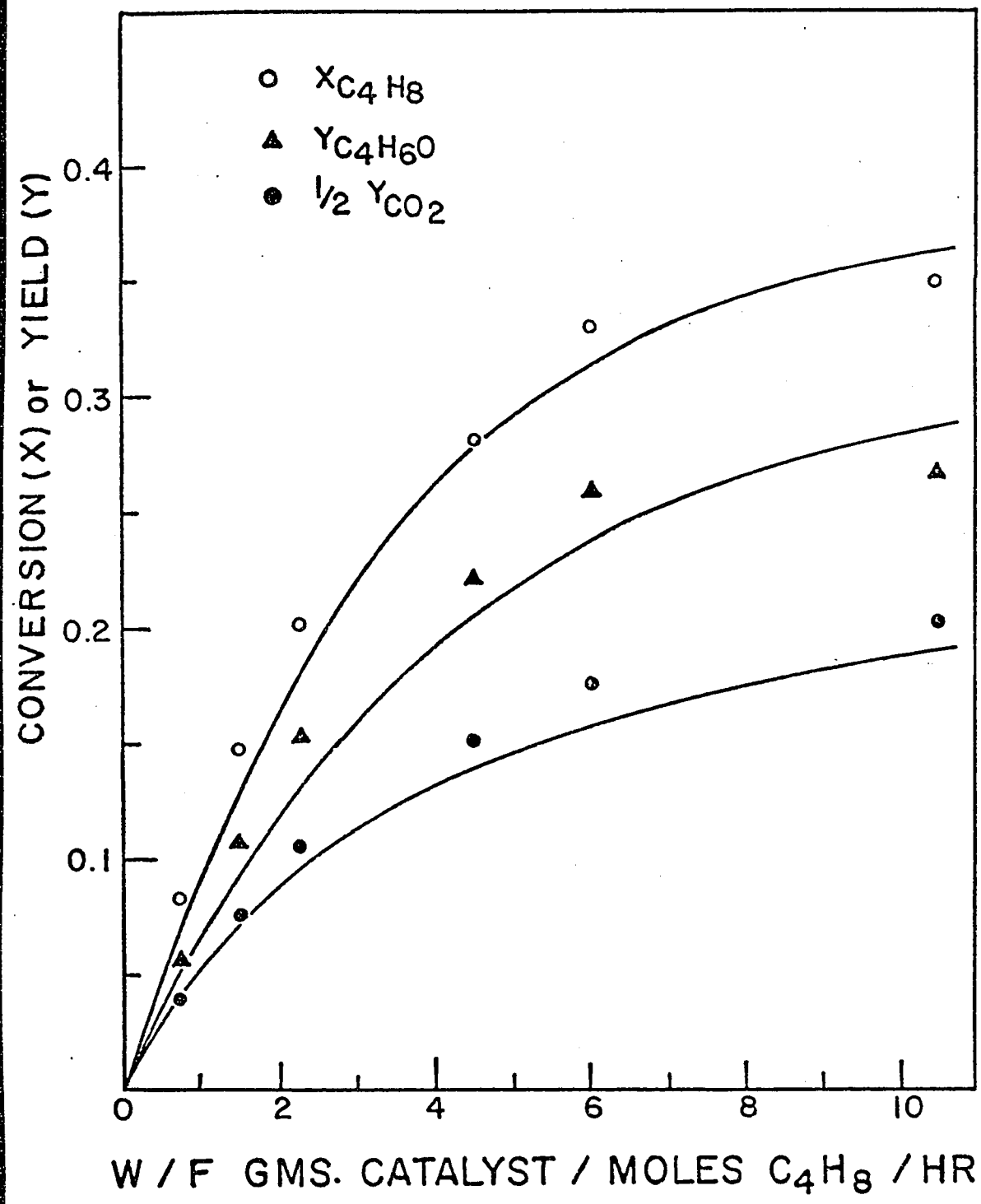


Figure 31- W/F Effect on Conversion and Yields for Oxidation of 2-methylpropene over Chlorine Modified Copper Oxide Catalyst at 350 °C, R = 1.7240

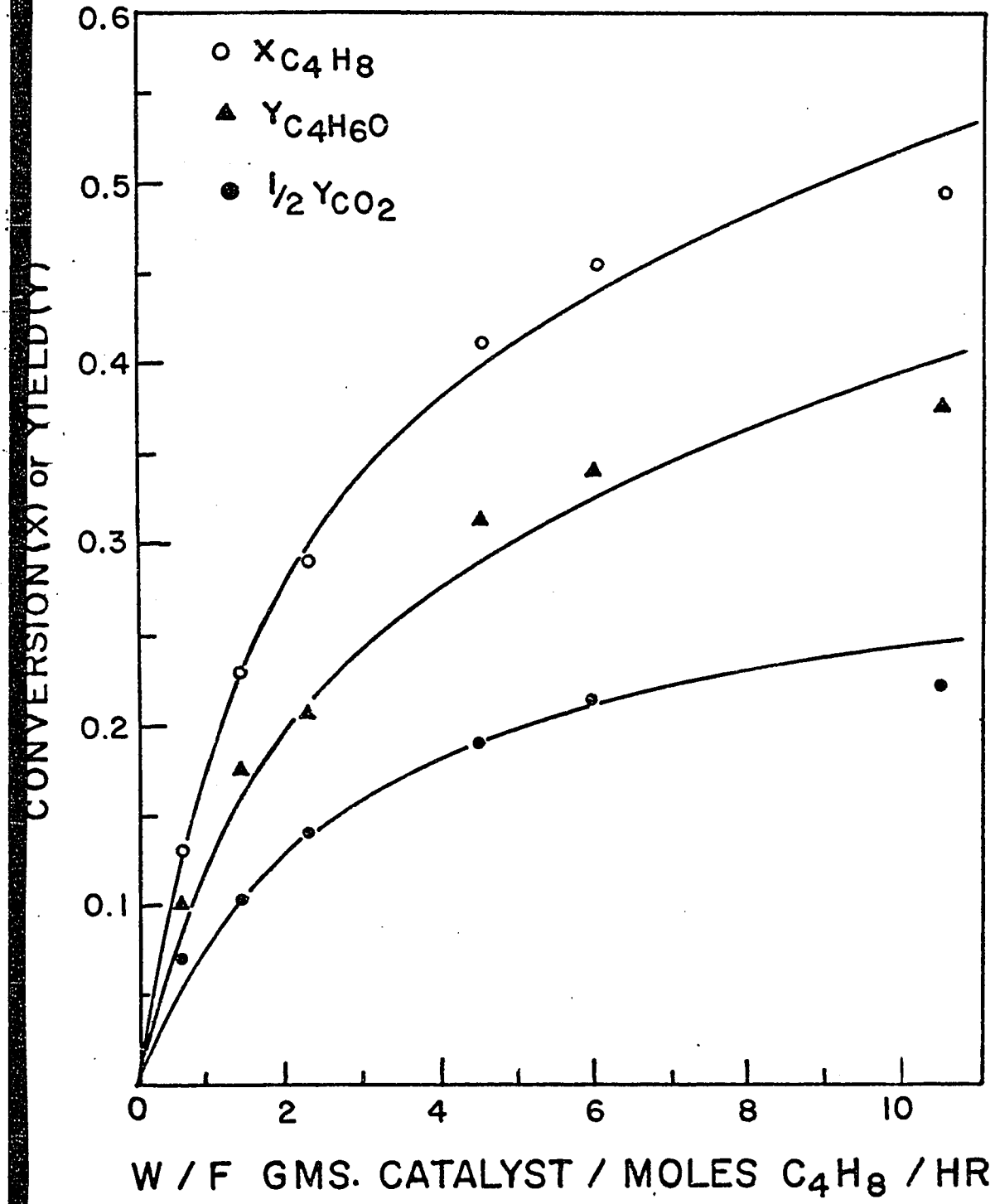


Figure 32- W/F Effect on Conversion and Yields for Oxidation of 2-methylpropene over Chlorine Modified Copper Oxide Catalyst at 375 °C, R = 1.7240

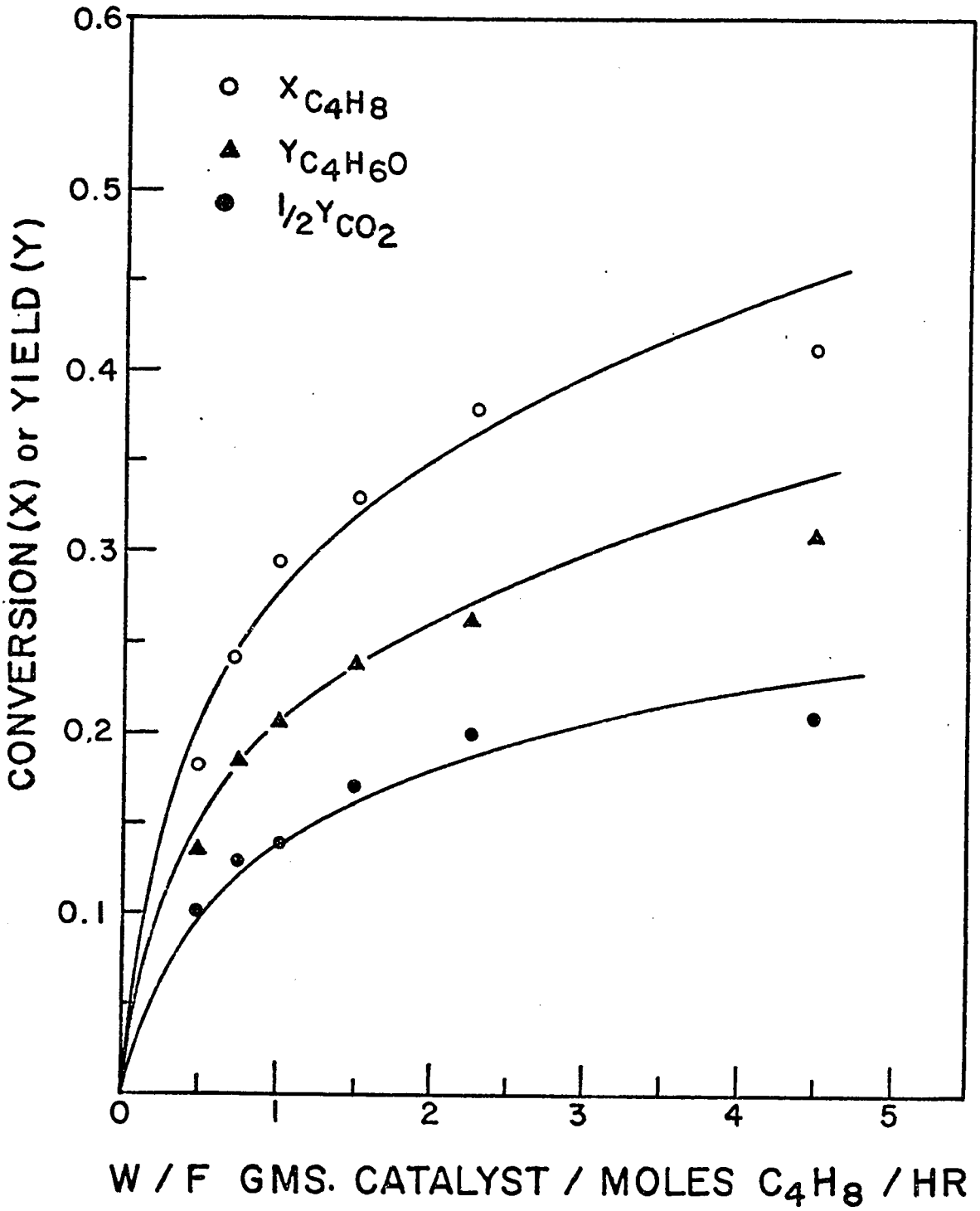


Figure 33- W/F Effect on Conversion and Yields for Oxidation of 2-methylpropene over Chlorine Modified Copper Oxide Catalyst at 425 °C, R = 0.9710

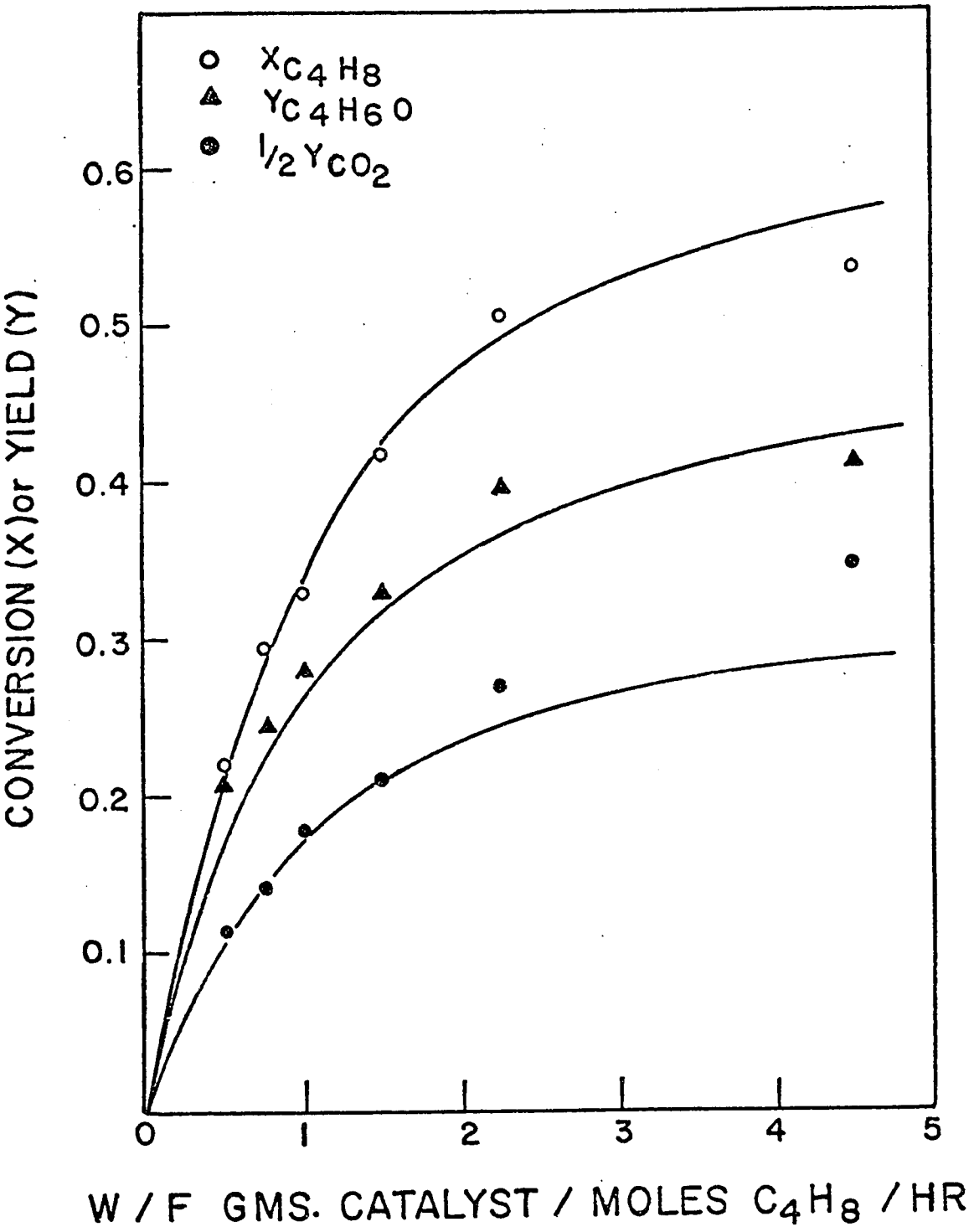


Figure 34- W/F Effect on Conversion and Yields for Oxidation of 2-methylpropene over Chlorine Modified Copper Oxide Catalyst at 425 °C, R = 1.7240

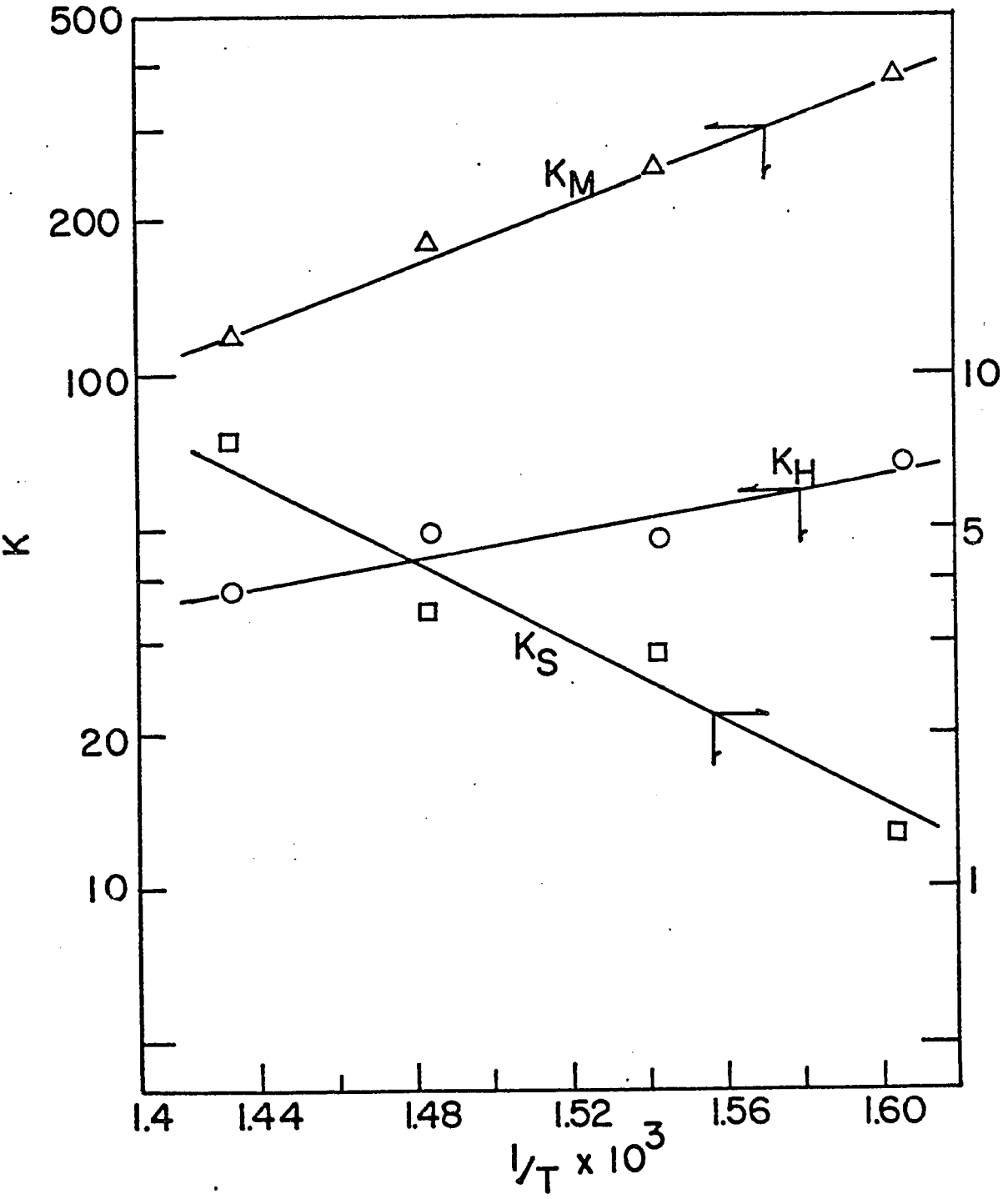


Figure 35- Temperature Effect on K_H, K_M and K_S

VI DISCUSSION

The yield of methacrolein in the catalytic oxidation of 2-methylpropene over copper oxide catalyst is generally limited as an increase in the olefin conversion is always accompanied with a decrease in the selectivity. Similar results are reported in the literature for the oxidation of propene over bismuth molybdate catalyst.

In the presence of several modifiers, i.e., selenium, sulfur, bromine, chlorine and iodine, all having the electronegativities higher than that of the skeleton catalyst (copper oxide), both the conversion of olefin and the yield of the corresponding aldehydes, increased with trace amounts of modifiers in the feed but decreased when larger amounts of these were added. The data obtained in the present research indicate that the function of the promoters used involves a modification in the surface properties of the catalyst rather than simply the catalyst poisoning or selective poisoning.

Furthermore, the results obtained from the oxidation of methacrolein over chlorine modified and unmodified copper oxide catalyst suggest that carbon dioxide originates mostly from the further oxidation of aldehyde at temperature over 350°C which is in agreement with the literature observations[40, 90]. The results also indicate that the promotional effect of these modifiers is mainly due to the successful suppression of the undesired oxidations.

Among the various operating variables, such as temperature, space velocity, amount of oxygen and olefin in the feed, it was found that for an optimum production of aldehydes, the amount of modifier in the feed is more closely related to the olefin charged

in the feed rather than other variables. This is concluded from the observations that in the oxidation of 2-methylpropene, as long as the optimum weight ratio of promoter to olefin in feed was kept constant, a variation in the feed ratio (oxygen/olefin), reaction temperature or space velocity would not affect the selectivity for methacrolein formation substantially, on the other hand, by keeping all the variables constant, a change in the modifier/olefin weight ratio significantly affected the selectivity for methacrolein formation.

A recent patent of Brill et al.[15] described the uses of polyhalides in conjunction with copper phosphate for the oxidation of 2-methylpropene to methacrolein. They found that a continuous supply of the organic halide (trimethylene bromide) with the reactants in feed tended to suppress the oxidation reaction and the production of methacrolein. They also noted that when a feed mixture containing 0.5 volume percent trimethylene bromide was passed through the reactor for about 3 hours and then the reactants were continuously fed into the reactor without the modifier, a much higher methacrolein yield (79.8%) was obtained. The increase in the yield was more than 33 mole % compared with the one when the additive was continuously fed to the reactor with the reactants. However, no mention is made regarding the optimum amount of the additives which could be used to enhance the methacrolein yield.

Ishikawa and Kamio[42] studied the oxidation of propene over silica gel supported copper catalyst prepared from different chemical compounds, such as cupric oxide, copper nitrate and copper halide. They found that the activity varied depending on the nature of the copper compound used as the starting material; copper halides being

superior to copper oxide or copper nitrate. With copper halide catalyst, the high yield of acrolein was only obtained after about five hours of reaction. No mention was made regarding the stability of the copper halide catalyst. The findings of Ishikawa and Kamio suggest that halogens in larger amounts in copper catalyst would inhibit the oxidation.

Due to lack of experimental information regarding the nature of elementary steps in the catalytic oxidation of olefins, it is difficult to establish the true mechanism of heterogeneous catalytic reactions. Recently, some mechanisms have been proposed by several investigators regarding the oxidation of olefins, particularly propene.

Adams and co-workers[2, 4] and Sachtler and de Boer[78] used radioactivity tracer techniques to illustrate successfully that olefin is chemisorbed on the catalyst surface by abstraction of an allylic hydrogen to form a symmetric π-allyl intermediate. This is followed by further reaction at either end of the adsorbed allylic intermediate, and the inclusion of a hetero atom (o) occurs after abstraction of the second hydrogen atom. However, they did not mention either the role played by oxygen in the activation of the catalyst or the importance of electronic factor governing the rates of reaction at the surface.

Margolis et al.[62] have studied the effect of several additives on the copper oxide catalyst for propene oxidation. The character of the electron transitions in adsorption and desorption was considered. They suggest that allyloxy or allyperoxy species are the intermediates for the charged adsorbed reactants. They also made a correlation between the change in work function, as induced by additives and the

activation energies for acrolein and carbon dioxide formation and the selectivity of the reaction. However, they did not consider the effect of quantity of modifiers on the variation in the product distribution and the selectivity of the catalyst.

The data collected in the laboratory has been applied in conjunction with the Electronic Theory of Catalysis to obtain a satisfactory reaction mechanism. The following assumptions have been made in arriving at a satisfactory mechanism for the oxidation reaction.

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

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

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

It is to be noted that these assumptions do not exclude the possible presence of adsorbed species in a neutral form, such as radicals and the homogeneous oxidation of aldehyde, especially when its concentration in the product stream is high.

The formation of acrolein or methacrolein by the partial oxidation of propene or 2-methylpropene over copper oxide catalyst is visualized to be taking place according to the following scheme.

Reaction I Partial Oxidation

$$RH(g) \rightleftarrows RH(s) \overset{\dot{P}L}{\rightleftarrows} R - H^+(s) \tag{6-1}$$

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

$$R - H^+(s) + O^-(s) \rightleftarrows \text{activated complex} \rightleftarrows R'CHO^+(s) + H_2O(s) \tag{6-3}$$

$$R'CHO^+(s) \overset{\dot{e}L}{\rightleftarrows} R'CHO(s) \rightleftarrows R'CHO(g) \tag{6-4}$$

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

Overall reaction $$C_4H_8 + O_2 \rightleftharpoons C_4H_6O + H_2O \tag{6-6}$$

or $$C_3H_6 + O_2 \rightleftharpoons C_3H_4O + H_2O \tag{6-7}$$

Reaction II Further Oxidation

$$R'CHO^+(s) + O^-(s) \rightleftarrows \text{activated complex} \rightleftarrows CO_2(s) + H_2O^+(s) \tag{6-8}$$

$$CO_2(s) \rightleftarrows CO_2(g) \tag{6-9}$$

$$H_2O^+(s) \overset{\dot{e}L}{\rightleftarrows} H_2O(s) \rightleftarrows H_2O(g) \tag{6-10}$$

Overall reaction $$C_4H_6O + 5O_2 \rightleftharpoons 4CO_2 + 3H_2O \tag{6-11}$$

or $$C_3H_4O + 7/2\,O_2 \rightleftharpoons 3CO_2 + 2H_2O \tag{6-12}$$

Reaction III Direct Oxidation

$$R\text{-}H^{+}(s) + O^{-}(s) \rightleftarrows \text{activated complex} \rightleftarrows CO_2(s) + H_2O^{+}(s) \quad (6\text{-}13)$$

$$CO_2(s) \rightleftarrows CO_2(g) \quad (6\text{-}14)$$

$$H_2O^{+}(s) \overset{\dot{e}L}{\rightleftarrows} H_2O(s) \rightleftarrows H_2O(g) \quad (6\text{-}15)$$

Overall reaction

$$C_4H_8 + 6O_2 \rightleftharpoons 4CO_2 + 4H_2O \quad (6\text{-}16)$$

$$C_3H_6 + 9/2\,O_2 \rightleftharpoons 3CO_2 + 3H_2O \quad (6\text{-}17)$$

Where $\dot{e}L$ and $\dot{p}L$ represent free electrons and positive holes on the catalyst surface respectively. (s) and (g) indicate surface or gaseous species. The sign of the electrical charge on each adsorbed species is determined from work function measurements[62, 28] assuming that all charged species are bound to the surface. Olefin is adsorbed on the catalyst surface through a π-allyl species and the hydrogen atom to be removed is positively charged.

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

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

$$r_1 = k_1 C_{H\cdot C\cdot}{}^{+\,m_1} \cdot C_{O^-}{}^{n_1} - k_1' C_{A^+}{}^{m_1'} \cdot C_{H_2O^+}{}^{n_1'} \qquad (6\text{-}18)$$

$$r_2 = k_2 C_{A^+}{}^{m_2} \cdot C_{O^-}{}^{n_2} - k_2' C_{CO_2}{}^{m_2'} \cdot C_{H_2O^+}{}^{n_2'} \qquad (6\text{-}19)$$

$$r_3 = k_3 C_{H\cdot C\cdot}{}^{+\,m_3} \cdot C_{O^-}{}^{n_3} - k_3' C_{CO_2}{}^{m_3'} \cdot C_{H_2O^+}{}^{n_3'} \qquad (6\text{-}20)$$

Where $C_{H\cdot C\cdot}{}^{+}$, C_{O^-}, C_{A^+} 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 reactions can be neglected and the reaction rates r_1, r_2 and r_3 would be $k_{1_{n_3}} C_{H\cdot C}{}^{+\,m_1} \cdot C_{O^-}{}^{n_1}$; $k_2 C_{A^+}{}^{m_2} \cdot C_{O^-}{}^{n_2}$ and $k_3 C_{H\cdot C\cdot}{}^{+\,m_3} \cdot C_{O^-}$ respectively.

Though quantitive determinations of these surface concentrations are difficult, some satisfactory qualitative explanation concerning reaction orders, activity and selectivity of the catalyst could be obtained.

The proposed mechanism could explain (i) Different reaction orders with respect to oxygen and olefin over the two different type of catalysts - cuprous oxide and bismuth molybdate, (ii) The increase and decrease in conversion and yield in presence of modifiers.

(A) Reaction Orders

When oxygen is adsorbed on cuprous oxide catalyst (p-type),

due to the electronegative nature of oxygen, electrons flow from the catalyst to oxygen, and are removed from the valence band creating positive holes. Since the supply of these electrons from the valence band is very great, charged adsorption of oxygen on the surface is fast. The existing oxygen ions on the catalyst surface do not hinder the further charged adsorption of oxygen. Since less energy is required for the charged adsorption, the surface coverage of oxygen ions is extensive. Therefore, at any time, the surface concentration of adsorbed oxygen ion, C_{O^-} is strongly dependent on the number of molecules in the gas phase, P_O. Hence, the reaction being nearly first order with respect to oxygen, as suggested by Equation (6-18) is quite understandable.

On the other hand, when olefin is adsorbed on cuprous oxide, electrons flow from the olefin to the catalyst and pass through the acceptor level as the hydrogen atom to be removed from the olefin is electropositive with respect to the catalyst. The ability of accepting these electrons in the acceptor level of the catalyst is limited since the charged adsorption of olefin is hindered by the existing olefin ions, and require much more energy. It is for these reasons that the surface covered by the adsorbed charged olefin is always low, and far from equilibrium. Therefore, at any time, the surface concentration of adsorbed olefin ion, $C_{H \cdot C \cdot}^{+}$ is strongly dependent on the surface defect and is relatively immaterial to the number of molecules of olefin in the gas phase. Hence the reaction rate being zero order with respect to olefin is understandable.

Using similar arguments, the first and zero order of reaction with respect to olefin and oxygen respectively on the bismuth molybdate catalyst (n-type) could be explained.

(B) Catalyst Modification

Voge, et al.[40] and Isaev et al.[90] and the experimental results of the present investigations have shown that the final oxidation product, carbon dioxide is due to further oxidation of aldehydes in which case $r_2 >> r_3$. The conversion of olefin would depend on the reaction rate r_1 and the yield for aldehyde would be determined by r_1 and r_2.

In the absence of a modifier, the activity and the selectivity of the copper oxide catalyst depend on the concentration of charged adsorbed olefin, oxygen and aldehyde ions which are dependent on the operating conditions and intrinsic properties of the catalyst. The addition of a modifier, having electronegativity higher than that of catalyst particularly such as bromine and chlorine, which are well-known for being good electron acceptors, (86) in small amounts increases the surface concentration of charged olefin and aldehyde ($C_{H.C.}^{+}$, C_A^{+}) and decreases the surface concentration of oxygen ions (C_O^{-}) so that

$$\frac{d\, C_{H.C.}^{+}}{dZ} > 0, \quad \frac{d\, C_A^{+}}{dZ} > 0 \text{ and } \frac{d\, C_O^{-}}{dZ} < 0 \qquad (6\text{-}21)$$

Where Z represents the amount of modifier in the feed. The rates r_1 for the partial oxidation of olefin to aldehyde and r_2 for further oxidation of aldehyde depend on $C_{H.C}^{+}$, C_A^{+} and C_O^{-}. According to Equations (6-18) and (6-19), and noting that in the initial stage of catalyst modification $C_{H.C}^{+} << C_O^{-}$; the increase in $C_{H.C.}^{+}$ would dominate rate r_1 and the decrease in C_O^{-} would dominate rate r_2,

so that

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

Hence, both the conversion of olefin and the yield of aldehyde increased in the presence of small amounts of the modifiers.

However, in the presence of larger amounts of the modifiers (more than the optimum) the decrease in C_O - would cause both r_1 and r_2 to decrease, so that

$$\frac{dr_1}{dZ} < 0 \quad \text{and} \quad \frac{dr_2}{dZ} < 0 \tag{6-23}$$

Also at this stage, the significance of the homogeneous oxidation of aldehyde can not be completely ignored[72]. Hence, both the conversion of olefin and yield of aldehyde declined with an excess supply of modifiers.

There are two main reasons for assuming the existence of two types of active sites on the catalyst surface, the first being that it would be difficult to explain the function of a promoter if all active sites are identical, the other reason is that the recent adsorption-desorption measurements carried out using many different techniques - notably, field emission, ion field microscopy[24] indicate that there are more than one set of adsorption enthalpy.

In the present proposed mechanism, if the assumptions of (i) irreversible electron transfer and (ii) surface reaction to be at equilibrium conditions are made, the same rate expressions as by using the redox mechanism can also be obtained. Redox mechanism

was proposed by Mars and Krevelen[64] and has been successfully applied to the oxidation of aromatic hydrocarbons by Mars and Krevelen and Graydon et al.[82] and to the oxidation of methanol to formaldehyde by Jiru et al.[44] and Mann and Hahn[56].

The catalytic oxidation of olefin can also be considered to be taking place by a redox cycle of copper oxide catalyst

$$CuO,\ Cu_2O \xrightarrow[\text{in air}]{\text{activated}} CuO \qquad (6\text{-}24)$$

$$CuO \xrightarrow{\text{olefin}} Cu_2O \text{ (stoichiometric)} \qquad (6\text{-}25)$$

$$Cu_2O \text{ (stoichiometric)} \xrightarrow[\text{amounts of oxygen}]{\text{diffusion of small}} Cu_2O \text{ (non-stoichiometric)} \qquad (6\text{-}26)$$

$$Cu_2O \text{ (non-stoichiometric)} \xrightarrow[\text{oxygen}]{\text{excess}} CuO \qquad (6\text{-}27)$$

The probability and stability of these valency state and stoichiometry in copper would determine the surface concentration of the charged adsorbed olefin and oxygen ions which in turn would determine the conversion and product distribution of the oxidation process.

Popova and Vermel[76] studied the variations of the chemical composition of the copper oxide catalyst during the oxidation of propene. They found that while a catalyst with low content of copper oxide (1.5% on SiC) was converted to a mixture of cuprous oxide (70%) and cupric oxide (30%) independent of the initial phase composition, the composition of the catalyst with higher content of copper oxide (3-5% on SiC) was changed to the system cupric oxide - cuprous oxide - copper. The appearance of metallic copper sharply reduced the

yield of acrolein and rapidly deactivated the catalyst. A slow reduction of cupric oxide to cuprous oxide led to an increase in the yield of acrolein.

While Isaev et al. [40] found cuprous oxide to be the active catalyst for acrolein formation, Kominami et al. [49] observed cupric oxide to be an excellent catalyst for complete oxidation.

Recently, Wood, Wise and Yolles [96] studied the oxidation of propene to acrolein on the surface of a copper oxide crystal. Simultaneous measurements were carried out to determine the catalytic activity, the electrical conductivity, and the optical properties of the catalyst in situ. They found that while the most active solid phase for acrolein formation was stoichiometric or copper -rich cuprous oxide, oxygen rich cuprous and cupric oxide favored the complete oxidation of propene to carbon dioxide.

The X-Ray diffraction patterns of the different catalysts used for the oxidation of 2-methylpropene (Figures 17 - 18 and Table 3) confirms the earlier findings of Popova [74], Isaev [40], Kominami [49] and Wood [96]. While the unmodified copper oxide, a mixture of cupric and cuprous oxide gave a moderate selectivity for methacrolein production from 2-methylpropene oxidation, very high selectivities were obtained over copper oxide catalyst modified with proper amounts of chlorine in the feed. In the presence of an optimum amount of chlorine, the catalyst was virtually all cuprous oxide and no cupric oxide. When chlorine more than the optimum amount was used as a modifier, selectivity for methacrolein decreased, and the catalyst was found to be a mixture of cupric and cuprous oxide and some other unidentified component.

It is believed that without a modifier, a high proportion of the active phase of the catalyst (cuprous oxide) for the selective oxidation is difficult to maintain, especially under rigorous operating conditions; while an optimum amount of acceptor type modifier as used in the present study effectively prevents the oxidation of cuprous oxide to cupric oxide and make the catalyst very selective. Overdoped modifiers further reduce the cuprous oxide to metallic copper or form other copper compound and thereby deactivates the catalyst.

VII CONCLUSIONS AND RECOMMENDATIONS

The catalytic oxidation of propene and 2-methylpropene was investigated over various modified copper oxide catalysts in an isothermal integral flow reactor between 200 and 450°C with feed ratios (O_2/olefin) 0.5 - 2.5 and reciprocal of space velocity up to 10.5 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.

An experimental setup used in this study enabled a precise adding of trace amount of modifiers to the catalyst continuously. An accurate analysis of the products was made feasible by the use of gas chromatographic techniques.

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

1) All of the modifiers enhancing the activity and selectivity of copper oxide catalyst for olefin oxidation, namely, selenium, sulfur, bromine, chlorine, and iodine are acceptor type which have higher electronegativities than that of the skeleton catalyst.

2) A continuous supply of a constant amount of modifier to the catalyst is essential for high selectivity for aldehydes.

3) The weight ratio of modifier to olefin in the feed is the most important factor in selective oxidation. A smaller amount of modifier improves both the conversion of olefin and selectivity for aldehyde but larger amount tends to decrease it. The optimum value of the weight ratio of modifier to olefin is in the range of 0.0005 to 0.0015 for oxidation of 2-methylpropene.

4) These modified oxidation processes proved more suitable for oxidation taking place under rigorous conditions (i.e., increase in feed ratios, contact time or reaction temperature) since the high selectivity (around 76%) for methacrolein formation can be maintained even with a high conversion.

5) Electronic factors governing the rates 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.

6) The active component of copper oxide catalyst for selective oxidation is confirmed to be cuprous oxide.

7) The Hougen-Watson approach based on the modified Langmuir-Hinshelwood Mechanism was used for the kinetic analysis of data. The most satisfactory rate equation correlating the data is

$$r = \frac{K_S K_H P_H}{1 + K_H P_H + K_M P_M} \cdot \frac{0.6 P_O}{1 + 0.6 P_O}$$

Where K_H, K_M and K_S are temperature dependent constants. The values of constant K_S increased but K_H and K_M decreased respectively as the temperature increased from 350° to 425°C.

It is recommended that

1) Further work on the oxidation of olefin over other p-type and n-type oxides (such as nickel oxide and bismuth molybdate) 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. APPENDIX

Appendix A

Thermodynamic Aspects of Oxidation of Olefins

Thermodynamic Aspects

The values of the change in Gibb's free energy, $\Delta F°$, and the equilibrium constant, K, of the gaseous oxidation of 2-methyl-propene to methacrolein are given in the following table:

TABLE

The Values of $\Delta F°$ and K for Gaseous Methacrolein Formation at 1 atm and Different Temperatures

Temperature °C	$-\Delta F°$ 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}

The values were calculated as functions of temperature, necessary data being either collected from the literature or calculated by the group contribution method[48] (for methacrolein). Since the values of K are very large, the process can be considered highly irreversible.

Appendix B

Calibration of Equipment

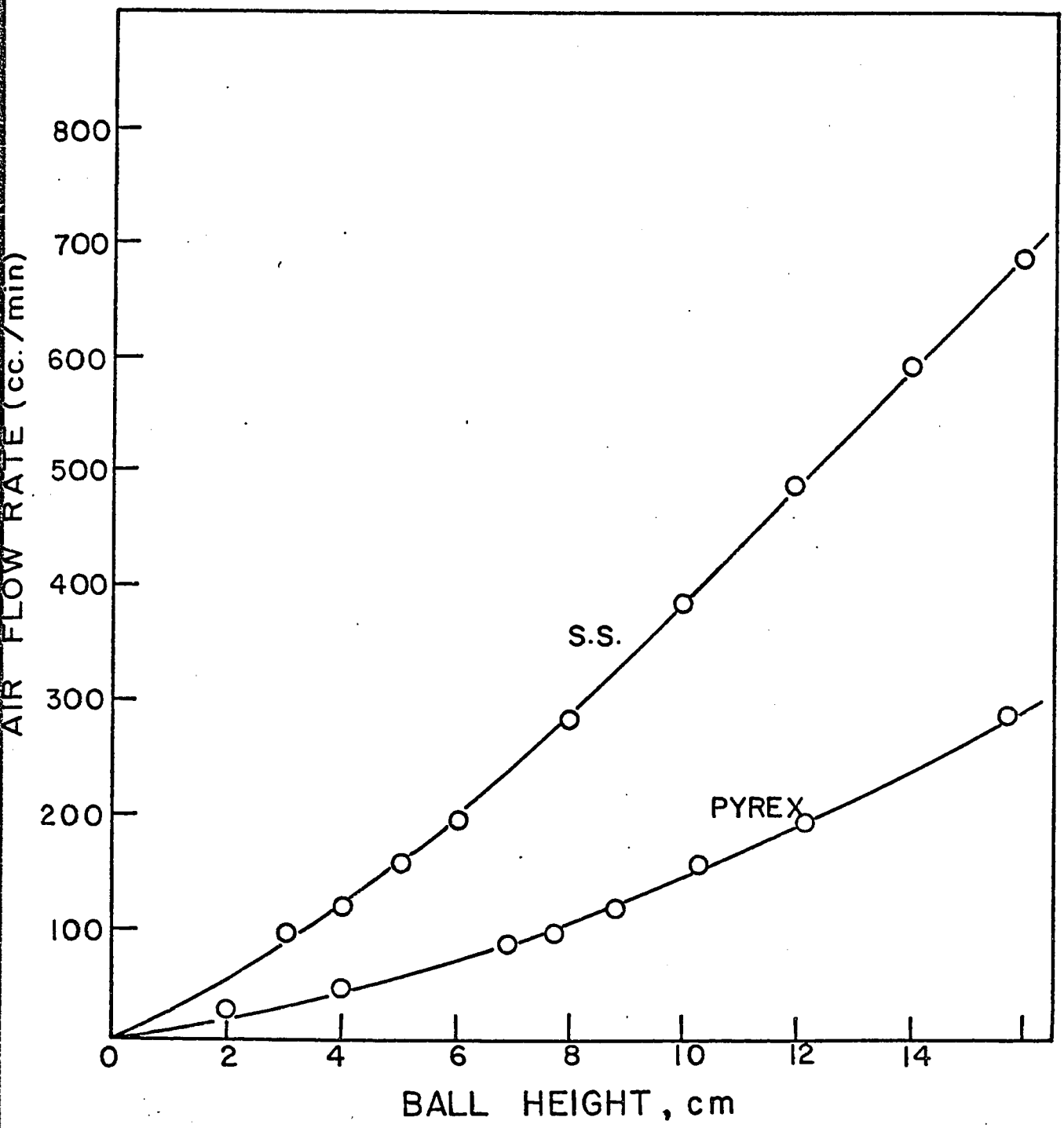


Figure 36- Rotameter Calibration for Air

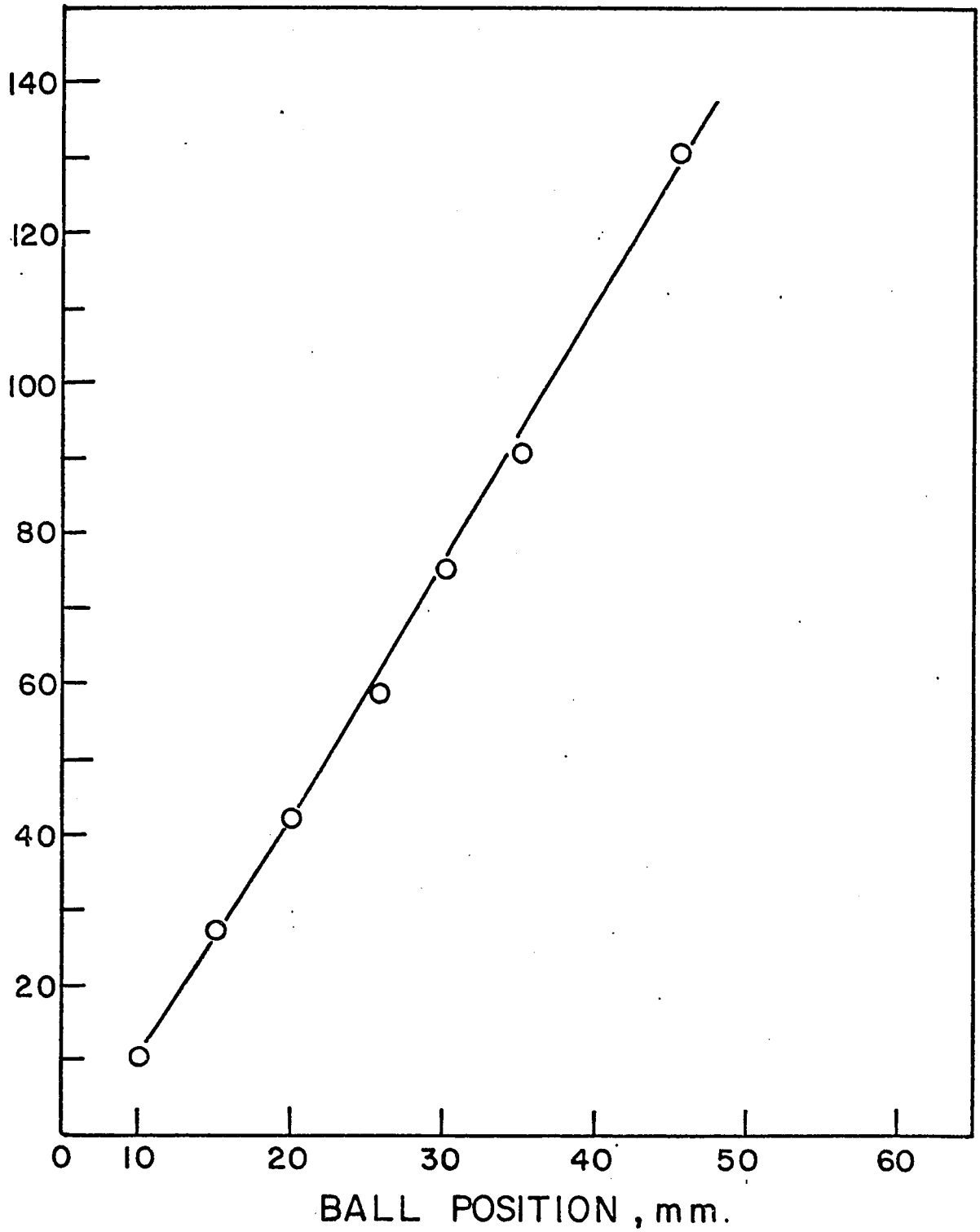


Figure 37 - Rotameter Calibration for 2-methylpropene

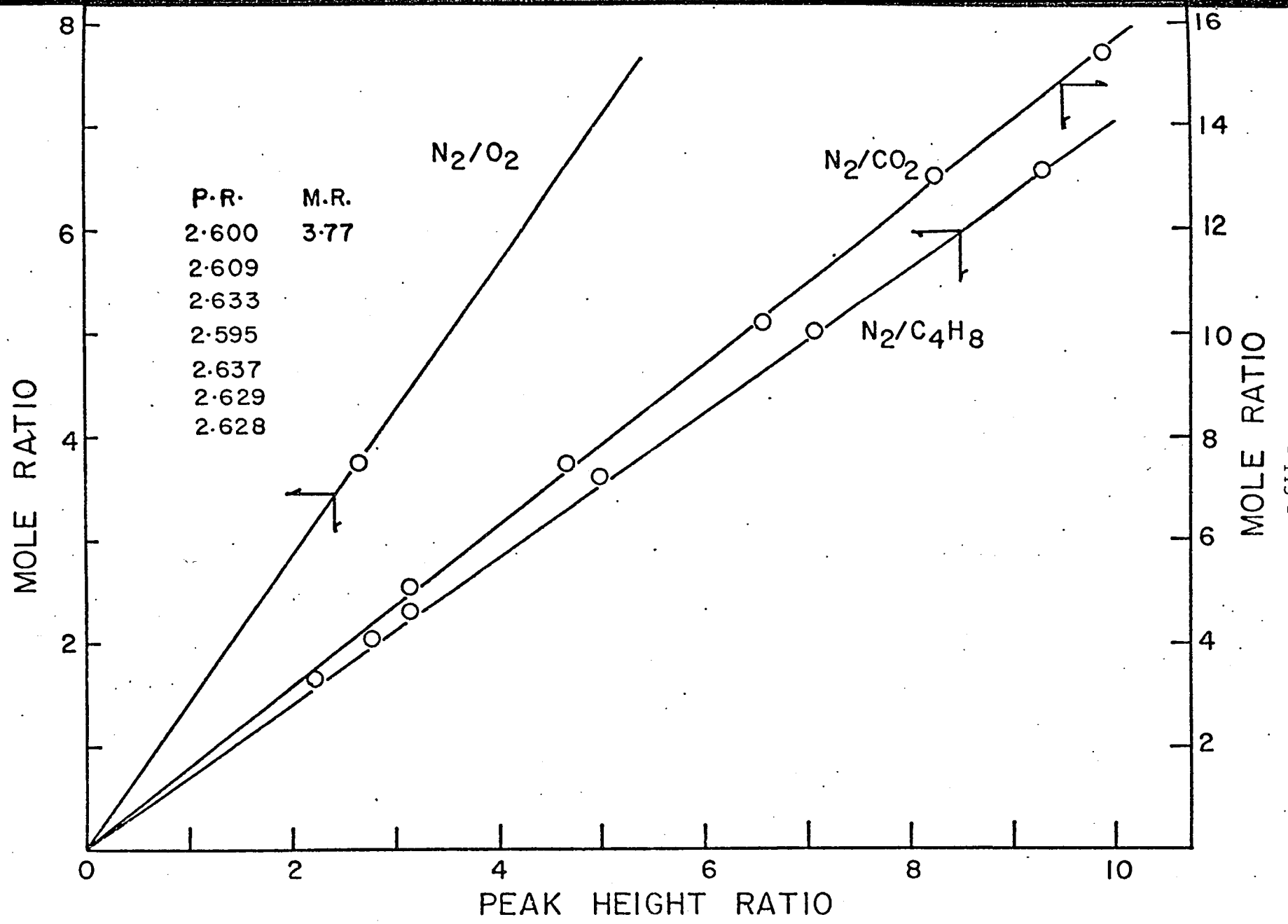


Figure 38- Calibration of Fisher Gas Partitioner

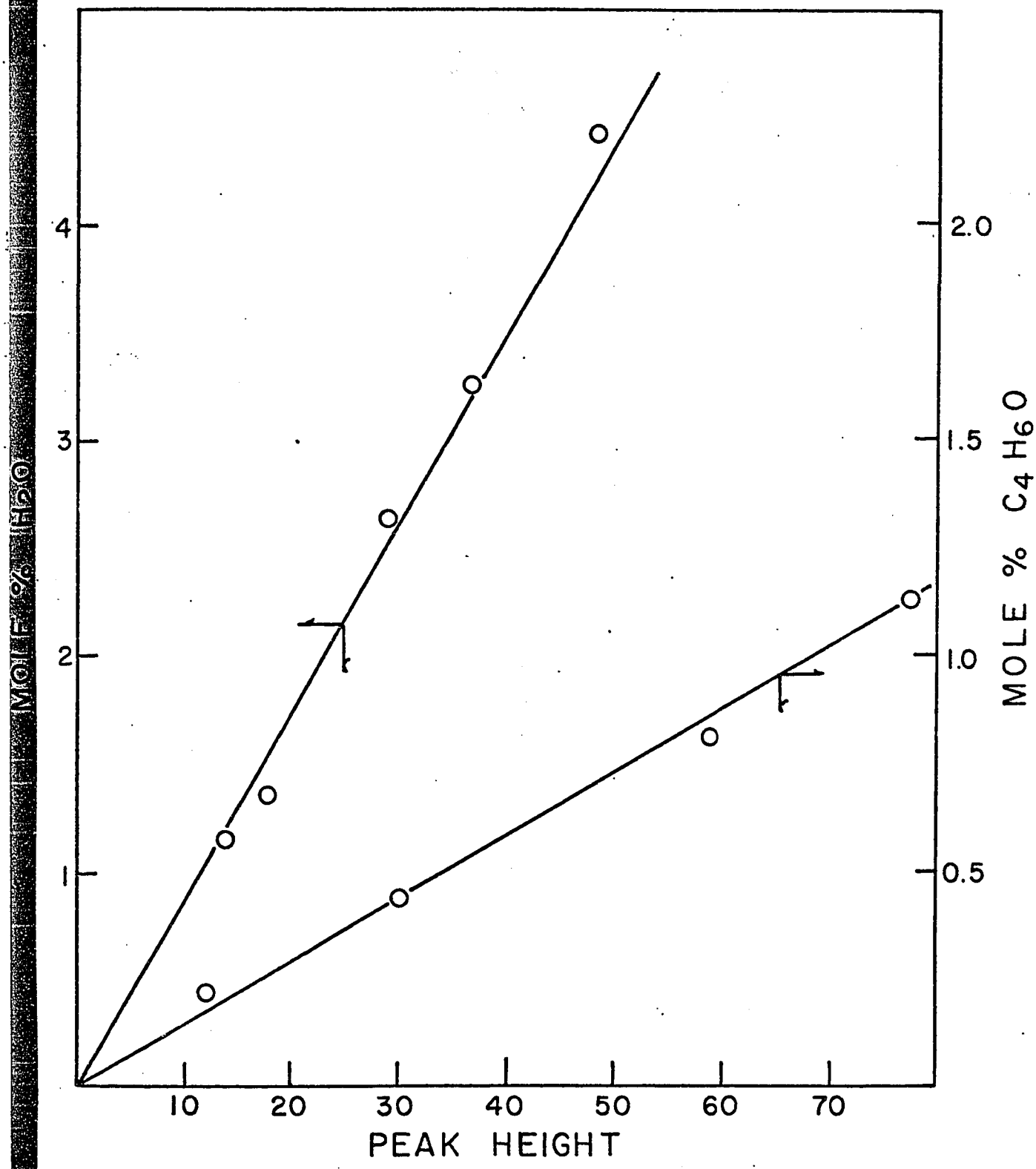


Figure 39 - Calibration of Perkin-Elmer Vapor Fractometer

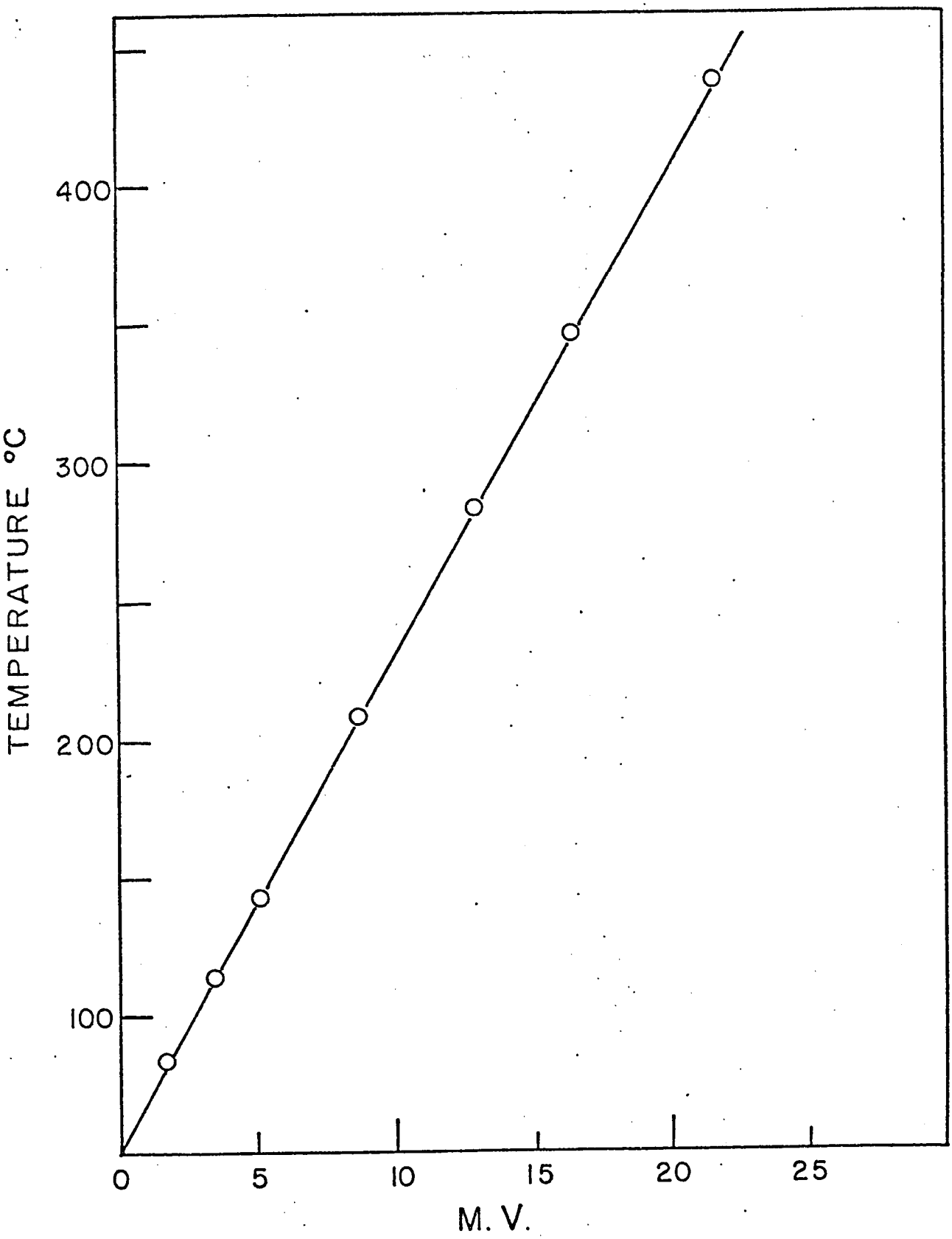


Figure 40 - Calibration of Thermocouples

Calibration of Syringe Pump

Syringe : 1 ml Hamilton gas tight syringe

pump setting position	flow rate ml/hr			
6	1.2587			
	1.2721			
	1.2700	avg.	1.2669	ml/hr
7	0.6304			
	0.6266			
	0.6298	avg.	0.6289	ml/hr
8	0.3141			
	0.3152			
	0.3142	avg.	0.3145	ml/hr
9	0.1285			
	0.1305			
	0.1285	avg.	0.1292	ml/hr
10	0.0653			
	0.0649	avg.	0.0651	ml/hr
11	0.0260			
	0.0268	avg.	0.0269	ml/hr

Appendix C

Density Determination of Methacrolein

Temperature 20°C

Weight of Pychometer (dry)	=	27.6310	gms.
Weight of Pychometer with Water	=	52.2220	gms.
Weight of Water at 20°C	=	24.5910	gms.
Density of Water at 20°C	=	0.9982	gm/c. c.
Volume of Pychometer $= \frac{24.5910}{0.9982}$	=	24.6353	c. c.
Weight of Pychometer with methacrolein	=	49.2570	gms.
Weight of methacrolein	=	21.6260	gms.
Density of methacrolein at 20°C $= \frac{21.6260}{24.6353}$	=	0.8778	gm/c. c.

Appendix D

Tabulated Experimental Data

TABLE A-D-1

Experimental Data for Oxidation of 2-Methylpropene Over Selenium Modified Copper Oxide Catalyst

Temp. = 400° C, $\bar{R}$ = 0.9910, W/F = 1.68

Run No.	Weight Ratio of $^{Se}/_{C_4H_8}$ $Z \times 10^4$	Feed moles/hr			% Conversion	Yield	
		C_4H_8	O_2	N_2	$X_{C_4H_8}$	$Y_{C_4H_6O}$	Y_{CO_2}
121	0	0.3898	0.3863	1.4566	21.54	0.0615	0.4327
122	2.0	0.3898	0.3863	1.4566	35.42	0.1457	0.3550
123	6.0	0.3898	0.3863	1.4566	34.25	0.1554	0.2308
124	12.6	0.3898	0.3863	1.4566	27.82	0.1126	0.2367

Run No.	Products moles/hr						% Selectivity
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2	$S_{C_4H_6O}$
121	0.3058	0.0772	1.4566	0.0240	0.1706	0.1687	28.57
122	0.2517	0.0539	1.4566	0.0568	0.1820	0.1384	41.12
123	0.2563	0.1312	1.4566	0.0606	0.1666	0.0900	48.67
124	0.2813	0.1099	1.4566	0.0439	0.1433	0.0923	40.46

* M. Sc. Work

TABLE A-D-2

Experimental Data for Oxidation of 2-Methylpropene Over

Sulfur Modified Copper Oxide Catalyst

Temp. = 400°C, W/F = 1.68

Run No.	Weight Ratio of S/C_4H_8	Feed moles/hr			% Conversion	Yield	
	$Z \times 10^3$	C_4H_8	O_2	N_2	$X_{C_4H_8}$	$Y_{C_4H_6O}$	Y_{CO_2}
201	0	0.3854	0.2131	0.8040	13.70	0.0526	0.3666
202	0.69	0.3854	0.2131	0.8040	15.95	0.0768	0.3196
203	1.26	0.3854	0.2131	0.8040	13.41	0.0557	0.3204
209	0	0.3854	0.3151	1.1892	21.04	0.0814	0.4994
210	0.69	0.3854	0.3151	1.1892	23.37	0.1053	0.4654
211	1.26	0.3854	0.3151	1.1892	19.97	0.0845	0.4400

Run No.	Products moles/hr						% Selectivity
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2	$S_{C_4H_6O}$
201	0.3326	-	0.8040	0.0203	0.1180	0.1413	38.44
202	0.3239	0.0216	0.8040	0.0296	0.1315	0.1232	48.13
203	0.3337	0.0163	0.8040	0.0215	0.1252	0.1235	41.58
209	0.3043	-	1.1892	0.0314	0.2183	0.1925	38.71
210	0.2953	0.0091	1.1892	0.0406	0.2279	0.1794	45.06
211	0.3084	0.0349	1.1892	0.0326	0.1963	0.1696	42.33

TABLE A-D-2 (Continued)

Temp. = 400°C, $\bar{R}$ = 0.6883, W/F = 1.68

Run No.	Weight Ratio of S/C_4H_8 $Z \times 10^3$	Feed moles/hr			% Conversion	Yield	
		C_4H_8	O_2	N_2	$X_{C_4H_8}$	$Y_{C_3H_4O}$	Y_{CO_2}
204	0	0.3854	0.2653	1.0051	16.86	0.0656	0.4377
205	0.48	0.3854	0.2653	1.0051	19.61	0.0923	0.4038
206	0.69	0.3854	0.2653	1.0051	20.10	0.0952	0.3894
207	1.26	0.3854	0.2653	1.0051	16.13	0.0697	0.3907
208	2.94	0.3854	0.2653	1.0051	16.18	0.0695	0.3898

Run No.	Products moles/hr						% Selectivity
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2	$S_{C_4H_6O}$
204	0.3204	-	1.0051	0.0253	0.1621	0.1687	38.92
205	0.3098	0.0028	1.0051	0.0356	0.1812	0.1564	47.08
206	0.3079	0.0118	1.0051	0.0367	0.1821	0.1501	47.35
207	0.3232	0.0190	1.0051	0.0269	0.1587	0.1506	43.24
208	0.3230	0.0196	1.0051	0.0268	0.1595	0.1502	43.01

TABLE A-D-2 (Continued)

Temp. = 400°C, W/F = 1.68

Run No.	Weight Ratio of S/C_4H_8	Feed moles/hr			% Conversion	Yield	
	$Z \times 10^3$	C_4H_8	O_2	N_2	$X_{C_4H_8}$	$Y_{C_4H_6O}$	Y_{CO_2}
212	0	0.3854	0.3561	1.3436	25.01	0.0892	0.5630
213	0.69	0.3854	0.3561	1.3436	27.42	0.1229	0.5202
214	1.26	0.3854	0.3561	1.3436	23.68	0.1030	0.5129
215	0	0.3854	0.4290	1.6187	29.08	0.0983	0.6696
216	0.69	0.3854	0.4290	1.6187	31.73	0.1382	0.6271

Run No.	Products moles/hr						% Selectivity
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2	$S_{C_4H_6O}$
212	0.2890	-	1.3436	0.0344	0.2670	0.2170	36.68
213	0.2797	0.0059	1.3436	0.0474	0.2769	0.2005	44.84
214	0.2941	0.0229	1.3436	0.0397	0.2388	0.1977	43.48
215	0.2733	0.0034	1.3436	0.0379	0.3270	0.2581	33.80
216	0.2631	0.0102	1.3436	0.0533	0.3270	0.2417	43.58

TABLE A-D-2 (Continued)

Temp. = 375°C, W/F = 1.68

Run No.	Weight Ratio of S/C_4H_8	Feed moles/hr			% Conversion	Yield	
	$Z \times 10^3$	C_4H_8	O_2	N_2	$X_{C_4H_8}$	$Y_{C_4H_6O}$	Y_{CO_2}
217	0	0.3854	0.2131	0.8040	8.27	0.0352	0.3528
218	0.69	0.3854	0.2131	0.8040	10.76	0.0576	0.2965
219	1.26	0.3854	0.2131	0.8040	11.13	0.0511	0.2970
220	0	0.3854	0.2653	1.0051	13.33	0.0555	0.4265
221	0.69	0.3854	0.2653	1.0051	17.28	0.0858	0.3723
222	1.26	0.3854	0.2653	1.0051	18.42	0.0970	0.3334

Run No.	Products moles/hr						% Selectivity
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2	$S_{C_4H_6O}$
217	0.3326	0.0040	0.8040	0.0136	0.0856	0.1360	42.63
218	0.3239	0.0098	0.8040	0.0222	0.1248	0.1143	53.49
219	0.3337	0.0261	0.8040	0.0197	0.1094	0.1145	45.92
220	0.3043	0.0055	1.0051	0.0214	0.1367	0.1644	41.63
221	0.2953	0.0085	1.0051	0.0331	0.1843	0.1435	49.69
222	0.3984	0.0107	1.0051	0.0374	0.2139	0.1285	52.67

TABLE A-D-2 (Continued)

Temp. = 375°C, W/F = 1.68

Run No.	Weight Ratio of S/C_4H_8	Feed moles/hr			% Conversion	Yield	
	$Z \times 10^3$	C_4H_8	O_2	N_2	$X_{C_4H_8}$	$Y_{C_4H_6O}$	Y_{CO_2}
223	0	0.3854	0.3151	1.1892	18.37	0.0755	0.4813
224	0.69	0.3854	0.3151	1.1892	20.83	0.1019	0.4429
225	1.26	0.3854	0.3151	1.1892	21.53	0.0998	0.4231
226	0	0.3854	0.3561	1.3436	20.78	0.0809	0.5456
227	0.69	0.3854	0.3561	1.3436	24.36	0.1167	0.4935
228	1.26	0.3854	0.3561	1.3436	24.28	0.1149	0.4348

Run No.	Products moles/hr						% Selectivity
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2	$S_{C_4H_6O}$
223	0.3146	0.0068	1.1892	0.0291	0.2017	0.1855	41.11
224	0.3053	0.0060	1.1892	0.0393	0.2286	0.1707	48.94
225	0.3024	0.0187	1.1892	0.0385	0.2367	0.1631	46.38
226	0.3053	0.0109	1.3436	0.0312	0.2275	0.2103	38.95
227	0.2915	0.0056	1.3436	0.0450	0.2753	0.1902	47.92
228	0.2918	0.0308	1.3436	0.0443	0.2877	0.1676	47.32

Experimental Data for Oxidation of 2-Methylpropene Over

Bromine Modified Modified Copper Oxide Catalyst

Temp. = 400°C , R = 0.5819 , W/F = 1.61

Run No.	Weight Ratio of Br/C_4H_8 $Z \times 10^4$	Feed moles/hr			% Conversion	Yield	
		C_4H_8	O_2	N_2	$X_{C_4H_8}$	$Y_{C_4H_6O}$	Y_{CO_2}
501	0	0.3626	0.2110	0.7963	14.83	0.0590	0.3359
502	0.9	0.3626	0.2110	0.7963	18.03	0.0777	0.3052
503	2.3	0.3626	0.2110	0.7963	16.82	0.0874	0.2399
504	7.0	0.3626	0.2110	0.7963	15.63	0.1232	0.0965

Run No.	Products moles/hr						% Selectivity
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2	$S_{C_4H_6O}$
501	0.3088	0.0173	0.7963	0.0214	0.1307	0.1218	40.28
502	0.2972	0.0267	0.7963	0.0282	0.1509	0.1107	43.11
503	0.3016	0.0570	0.7963	0.0317	0.1277	0.0870	51.96
504	0.3059	0.1230	0.7963	0.0447	0.0735	0.0350	78.83

TABLE A-D-3 (Continued)

Temp. = 400°C , $\bar{R}$ = 0.6591 , W/F = 1.61

Run No.	Weight Ratio of Br/C_4H_8	Feed moles/hr			% Conversion	Yield	
	$Z \times 10^4$	C_4H_8	O_2	N_2	$X_{C_4H_8}$	$Y_{C_4H_6O}$	Y_{CO_2}
505	0	0.3626	0.2390	0.9021	18.91	0.0703	0.3673
506	0.9	0.3626	0.2390	0.9021	20.51	0.0827	0.3391
507	2.3	0.3626	0.2390	0.9021	18.36	0.0959	0.2675
508	7.0	0.3626	0.2390	0.9021	17.04	0.1323	0.0984

Run No.	Products moles/hr						% Selectivity
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2	$S_{C_4H_6O}$
505	0.2940	0.0261	0.9021	0.0255	0.1671	0.1332	39.21
506	0.2882	0.0467	0.9021	0.0300	0.1666	0.1230	40.32
507	0.2960	0.0645	0.9021	0.0348	0.1450	0.0970	52.25
508	0.3008	0.1481	0.9021	0.0480	0.0800	0.0357	77.66

TABLE A-D-3 (Continued)

Temp. = 400°C, $\bar{R}$ = 0.8185, W/F = 1.61

Run No.	Weight Ratio of Br/C_4H_8	Feed moles/hr			% Conversion	Yield	
	$Z \times 10^4$	C_4H_8	O_2	N_2	$X_{C_4H_8}$	$Y_{C_4H_6O}$	Y_{CO_2}
509	0	0.3626	0.2968	1.1200	23.44	0.0882	0.4299
510	0.9	0.3626	0.2968	1.1200	23.82	0.1020	0.3747
511	2.3	0.3626	0.2968	1.1200	22.33	0.1155	0.3229
512	4.2	0.3626	0.2968	1.1200	22.09	0.1431	0.2418
513	7.0	0.3626	0.2968	1.1200	20.04	0.1547	0.0832

Run No.	Products moles/hr						% Selectivity
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2	$S_{C_4H_6O}$
509	0.2776	0.0396	1.1200	0.0320	0.2161	0.1559	37.64
510	0.2762	0.0669	1.1200	0.0370	0.2014	0.1359	42.82
511	0.2816	0.0766	1.1200	0.0419	0.1942	0.1171	51.72
512	0.2825	0.1123	1.1200	0.0519	0.1610	0.0877	64.79
513	0.2899	0.2000	1.1200	0.0561	0.0975	0.0338	77.16

TABLE A-D-3 (Continued)

Temp. = 400°C, $\bar{R}$ = 0.9299 , W/F = 1.61

Run No	Weight Ratio of Br/C_4H_8 Z	Feed moles/hr			% Conversion	Yield	
		C_4H_8	O_2	N_2	$X_{C_4H_8}$	$Y_{C_4H_6O}$	Y_{CO_2}
514	0	0.3626	0.3372	1.2724	26.58	0.0990	0.4597
515	0.9	0.3626	0.3372	1.2724	25.70	0.1144	0.4007
516	2.3	0.3626	0.3372	1.2724	26.19	0.1348	0.3488
517	7.0	0.3626	0.3372	1.2724	22.11	0.1778	0.0951

Run No	Products moles/hr						% Selectivity
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2	$S_{C_4H_6}$
514	0.2662	0.0679	1.2724	0.0359	0.2316	0.1667	37.24
515	0.2694	0.0852	1.2724	0.0415	0.2214	0.1453	44.52
516	0.2676	0.0875	1.2724	0.0489	0.2401	0.1265	51.47
517	0.2824	0.2266	1.2724	0.0645	0.1109	0.0345	80.42

TABLE A-D-4

Experimental Data for Oxidation of 2-Methylpropene Over Chlorine Modified Copper Oxide Catalyst

Temp. = 400°C, $\bar{R}$ = 0.9543, W/F = 5.26

Run No.	Weight Ratio of Cl/C_4H_8 $Z \times 10^3$	Feed moles/hr			% Conversion	Yield	
		C_4H_8	O_2	N_2	$X_{C_4H_8}$	$Y_{C_4H_6O}$	Y_{CO_2}
431	0	0.1138	0.1086	0.4100	20.12	0.0500	0.5878
432	0.5	0.1138	0.1086	0.4100	34.09	0.2293	0.4639
433	1.0	0.1138	0.1086	0.4100	37.69	0.2785	0.4349
434	2.5	0.1138	0.1086	0.4100	37.87	0.3040	0.3418
435	5.0	0.1138	0.1086	0.4100	34.18	0.2732	0.2838
436	10.2	0.1138	0.1086	0.4100	28.38	0.2170	0.2513

Run No.	Products moles/hr						% Selectivity
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2	$S_{C_4H_6O}$
431	0.0909	-	0.4100	0.0057	0.0696	0.0669	24.89
432	0.0750	-	0.4100	0.0261	0.0742	0.0528	67.36
433	0.0709	0.0051	0.4100	0.0317	0.0732	0.0495	73.89
434	0.0707	0.0163	0.4100	0.0346	0.0685	0.0389	80.27
435	0.0749	0.0299	0.4100	0.0311	0.0611	0.0323	79.94
436	0.0815	0.0418	0.4100	0.0247	0.0533	0.0286	76.47

TABLE A-D-5

Experimental Data for Oxidation of 2-Methylpropene Over

Iodine Modified Copper Oxide Catalyst

Temp. = 400°C, $\bar{R}$ = 0.9543, W/F = 5.26

Run No.	Weight Ratio of I/C_4H_8 $Z \times 10^3$	Feed moles/hr			% Conversion	Yield	
		C_4H_8	O_2	N_2	$X_{C_4H_8}$	$Y_{C_4H_6O}$	Y_{CO_2}
431	0	0.1138	0.1086	0.4100	20.12	0.0500	0.5878
601	0.3	0.1138	0.1086	0.4100	34.44	0.2434	0.4657
602	0.5	0.1138	0.1086	0.4100	41.65	0.3189	0.4103
603	0.7	0.1138	0.1086	0.4100	37.35	0.2882	0.4332
604	1.4	0.1138	0.1086	0.4100	27.94	0.1344	0.5738
605	3.0	0.1138	0.1086	0.4100	21.35	0.0307	0.6423

Run No.	Products moles/hr						% Selectivity
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2	$S_{C_4H_6O}$
431	0.0909	-	0.4100	0.0057	0.0696	0.0669	24.89
601	0.0746	0.0050	0.4100	0.0277	0.0689	0.0530	70.66
602	0.0664	0.0072	0.4100	0.0363	0.0725	0.0467	76.58
603	0.0713	0.0053	0.4100	0.0328	0.0678	0.0493	77.17
604	0.0820	0.0069	0.4100	0.0153	0.0606	0.0653	48.11
605	0.0895	0.0079	0.4100	0.0035	0.0623	0.0731	14.40

TABLE A-D-6

Experimental Data for Oxidation of Methacrolein

Over Chlorine Modified Copper Oxide Catalyst

Temp. = 327°C, $\bar{R}$ = 7.6976, W/F = 7.0

Run No.	Weight Ratio of Cl/C_4H_6O $Z \times 10^3$	Feed moles/hr			% Conversion	Yield
		C_4H_6O	O_2	N_2	$X_{C_4H_6O}$	Y_{CO_2}
436	0	0.0086	0.0663	0.2500	72.09	2.8837
437	1.2	0.0086	0.0663	0.2500	54.65	2.2441
438	2.7	0.0086	0.0663	0.2500	39.53	1.8139
439	5.4	0.0086	0.0663	0.2500	31.39	1.3837
440	10.8	0.0086	0.0663	0.2500	29.06	1.2790

Run No.	Yield	Products moles/hr				
	Y_{H_2O}	O_2	N_2	C_4H_6O	H_2O	CO_2
436	1.7209	0.0374	0.2500	0.0024	0.0148	0.0248
437	1.4883	0.0428	0.2500	0.0039	0.0128	0.0193
438	1.4069	0.0454	0.2500	0.0052	0.0121	0.0156
439	1.2906	0.0496	0.2500	0.0059	0.0111	0.0119
440	1.2325	0.0507	0.2500	0.0061	0.0106	0.0110

TABLE A-D-7

Experimental Data for Oxidation of Propene Over

Chlorine Modified Copper Oxide Catalyst

Temp. = 375°, R = 0.6332 , W/F = 6.38

Run No.	Weight Ratio of Cl/C_3H_6	Feed moles/hr			% Conversion	Yield	
	$Z \times 10^3$	C_3H_6	O_2	N_2	$X_{C_3H_6}$	$Y_{C_3H_4O}$	Y_{H_2O}
441	0	0.1047	0.0663	0.2500	21.01	0.0735	0.4116
442	0.30	0.1047	0.0663	0.2500	28.36	0.1766	0.3228
443	0.75	0.1047	0.0663	0.2500	29.70	0.2043	0.2788
444	1.50	0.1047	0.0663	0.2500	29.41	0.2082	0.2578
445	3.00	0.1047	0.0663	0.2500	25.78	0.1776	0.2406
446	7.30	0.1047	0.0663	0.2500	20.15	0.1088	0.2798
447	14.80	0.1047	0.0663	0.2500	16.33	0.0171	0.4403

Run No.	Products moles/hr						% Selectivity
	C_3H_6	O_2	N_2	C_3H_4O	H_2O	CO_2	$S_{C_3H_4O}$
441	0.0827	-	0.2500	0.0077	0.0506	0.0431	35.00
442	0.0751	-	0.2500	0.0185	0.0521	0.0338	62.28
443	0.0736	0.0011	0.2500	0.0214	0.0505	0.0292	68.81
444	0.0739	0.0040	0.2500	0.0218	0.0488	0.0270	70.77
445	0.0777	0.0098	0.2500	0.0186	0.0438	0.0252	68.88
446	0.0836	0.0110	0.2500	0.0114	0.0405	0.0293	54.02
447	0.0876	-	0.2500	0.0018	0.0044	0.0461	10.52

TABLE A-D-8

Experimental Data of Effect of Temperature On Oxidation

of 2-Methylpropene Over Bromine Modified Copper Oxide

$\bar{R} = 0.8185$, $W/_F = 1.61$, $Z = 0.00042$

Run No.	Temp. °C T	Feed moles/hr			% Conversion	Yield	
		C_4H_8	O_2	N_2	$X_{C_4H_8}$	$Y_{C_4H_6O}$	Y_{CO_2}
518	315	0.3626	0.2968	1.1200	7.52	0.0676	0.0985
519	345	0.3626	0.2968	1.1200	11.94	0.0938	0.1900
512	400	0.3626	0.2968	1.1200	22.09	0.1429	0.2418
520	465	0.3626	0.2968	1.1200	30.25	0.1660	0.3624
521	488	0.3626	0.2968	1.1200	29.56	0.1608	0.3789

Run No.	Products moles/hr						% Selectivity
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2	$S_{C_4H_6O}$
518	0.3353	0.2596	1.1200	0.0245	0.0357	0.0081	89.74
519	0.3193	0.2327	1.1200	0.0340	0.0689	0.0194	78.52
512	0.2825	0.1122	1.1200	0.0519	0.1610	0.0877	64.79
520	0.2529	0.0318	1.1200	0.0602	0.2282	0.1314	54.87
521	0.2554	0.0254	1.1200	0.0583	0.2239	0.1374	54.38

TABLE A-D-9

Effect of W/F on Conversion, Yields and Selectivity for Oxidation of 2-Methylpropene Over Modified Copper Oxide Catalyst With an Optimum Amount of Chlorine

Temp. = 350°C, $\bar{R}$ = 0.5913, Z = 0.0015

Run No.	W/F	Feeds moles/hr			% Conversion	Yields mole/hr/mole/hr	
		C_4H_8	O_2	N_2	$X_{C_4H_8}$	$Y_{C_4H_6O}$	Y_{CO_2}
301	0.75	0.1138	0.0673	0.2539	7.02	0.0562	0.0492
302	1.50	0.1138	0.0673	0.2539	11.52	0.0869	0.0878
303	2.25	0.1138	0.0673	0.2539	14.13	0.1054	0.1230
304	4.50	0.1138	0.0673	0.2539	19.02	0.1449	0.1616
305	6.00	0.1138	0.0673	0.2539	21.50	0.1687	0.1862
306	10.50	0.1138	0.0673	0.2539	22.03	0.1625	0.1933

Run No.	Products moles/hr						% Selectivity
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2	$S_{C_4H_6O}$
301	0.1059	0.0503	0.2539	0.0064	0.0160	0.0056	81.01
302	0.1007	0.0398	0.2539	0.0099	0.0261	0.0100	75.57
303	0.0978	0.0327	0.2539	0.0120	0.0299	0.0140	75.00
304	0.0922	0.0215	0.2539	0.0165	0.0388	0.0184	76.38
305	0.0894	0.0135	0.2539	0.0192	0.0446	0.0212	78.68
306	0.0887	0.0127	0.2539	0.0185	0.0488	0.0220	73.70

TABLE A-D-9 (Continued)

Temp. = 350°C, $\bar{R}$ = 0.9710, Z = 0.0015

Run No.	W/F	Feed mole/hr			% Conversion	Yield	
		C_4H_8	O_2	N_2	$X_{C_4H_8}$	$Y_{C_4H_6O}$	Y_{CO_2}
307	0.75	0.1138	0.1105	0.4168	7.50	0.0623	0.0562
308	1.50	0.1138	0.1105	0.4168	12.61	0.0949	0.1124
309	2.25	0.1138	0.1105	0.4168	16.44	0.1256	0.1441
310	4.50	0.1138	0.1105	0.4168	24.45	0.1889	0.2179
311	6.00	0.1138	0.1105	0.4168	26.85	0.2100	0.2565
312	10.50	0.1138	0.1105	0.4168	27.34	0.2021	0.2460

Run No.	Products moles/hr						% Selectivity
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2	$S_{C_4H_6O}$
307	0.1053	0.0925	0.4168	0.0071	0.0149	0.0064	83.52
308	0.0995	0.0790	0.4168	0.0108	0.0268	0.0128	75.52
309	0.0951	0.0705	0.4168	0.0143	0.0335	0.0164	76.47
310	0.0860	0.0506	0.4168	0.0215	0.0485	0.0248	77.33
311	0.0833	0.0403	0.4168	0.0239	0.0551	0.0292	78.36
312	0.0827	0.0424	0.4168	0.0230	0.0602	0.0280	73.95

TABLE A-D-9 (Continued)

Temp. = 350°C, $\bar{R}$ = 1.3998, Z = 0.0015

Run No.	W/F	Feed mole/hr			% Conversion	Yield	
		C_4H_8	O_2	N_2	$X_{C_4H_8}$	$Y_{C_4H_6O}$	Y_{CO_2}
313	0.75	0.1138	0.1593	0.6010	7.65	0.0606	0.0702
314	1.50	0.1138	0.1593	0.6010	13.50	0.1028	0.1335
315	2.25	0.1138	0.1593	0.6010	18.02	0.1405	0.1581
316	4.50	0.1138	0.1593	0.6010	26.88	0.2214	0.2530
317	6.00	0.1138	0.1593	0.6010	29.85	0.2275	0.3057
318	10.50	0.1138	0.1593	0.6010	31.10	0.2346	0.2882

Run No.	Products moles/hr						% Selectivity
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2	$S_{C_4H_6O}$
313	0.1051	0.1394	0.6010	0.0069	0.0158	0.0080	79.31
314	0.0985	0.1228	0.6010	0.0117	0.0292	0.0152	76.47
315	0.0933	0.1139	0.6010	0.0160	0.0376	0.0180	78.04
316	0.0833	0.0866	0.6010	0.0252	0.0553	0.0288	82.62
317	0.0799	0.0798	0.6010	0.0259	0.0604	0.0348	76.40
318	0.0784	0.0800	0.6010	0.0267	0.0670	0.0328	75.42

TABLE A-D-9 (Continued)

Temp. = 350°C, $\bar{R}$ = 1.7240, Z = 0.0015

Run No.	W/F	Feed mole/hr			% Conversion	Yield	
		C_4H_8	O_2	N_2	$X_{C_4H_6O}$	$Y_{C_4H_6O}$	Y_{CO_2}
319	0.75	0.1138	0.1962	0.7403	8.23	0.0623	0.0843
320	1.50	0.1138	0.1962	0.7403	14.65	0.1063	0.1335
321	2.25	0.1138	0.1962	0.7403	19.67	0.1537	0.1757
322	4.50	0.1138	0.1962	0.7403	28.35	0.2258	0.2811
323	6.00	0.1138	0.1962	0.7403	33.17	0.2601	0.3128
324	10.50	0.1138	0.1962	0.7403	33.65	0.2688	0.3198

Run No.	Products moles/hr						% Selectivity
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2	$S_{C_4H_6O}$
319	0.1045	0.1739	0.7403	0.0071	0.0173	0.0096	76.34
320	0.0972	0.1600	0.7403	0.0121	0.0315	0.0152	72.89
321	0.0915	0.1461	0.7403	0.0175	0.0410	0.0200	78.47
322	0.0816	0.1206	0.7403	0.0257	0.0563	0.0320	79.81
323	0.0761	0.1087	0.7403	0.0296	0.0709	0.0356	78.51
324	0.0755	0.1015	0.7403	0.0308	0.0786	0.0364	80.41

TABLE A-D-9 (Continued)

Temp. = 350°C, $\bar{R}$ = 2.2337, Z = 0.0015

Run No.	W/F	Feed mole/hr			% Conversion	Yield	
		C_4H_8	O_2	N_2	$X_{C_4H_8}$	$Y_{C_4H_6O}$	Y_{CO_2}
325	0.75	0.1138	0.2542	0.9592	9.31	0.0764	0.0949
326	1.50	0.1138	0.2542	0.9592	16.01	0.1142	0.1476
327	2.25	0.1138	0.2542	0.9592	22.34	0.1836	0.2038
328	4.50	0.1138	0.2542	0.9592	32.82	0.2601	0.2952
329	6.00	0.1138	0.2542	0.9592	35.54	0.2970	0.3374
330	10.50	0.1138	0.2542	0.9592	37.42	0.3022	0.4042

Run No.	Products moles/hr						% Selectivity
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2	$S_{C_4H_6O}$
325	0.1033	0.2258	0.9592	0.0087	0.0226	0.0108	82.85
326	0.0956	0.2133	0.9592	0.0130	0.0373	0.0168	71.42
327	0.0884	0.1954	0.9592	0.0209	0.0507	0.0232	82.28
328	0.0765	0.1713	0.9592	0.0296	0.0657	0.0336	79.35
329	0.0734	0.1497	0.9592	0.0338	0.0855	0.0384	83.66
330	0.0712	0.1418	0.9592	0.0344	0.0859	0.0460	80.75

TABLE A-D-9 (Continued)

Temp. = 375°C, $\bar{R}$ = 0.5913, Z = 0.0015

Run No.	W/F	Feed mole/hr			% Conversion	Yield	
		C_4H_8	O_2	N_2	$X_{C_4H_8}$	$Y_{C_4H_6O}$	Y_{CO_2}
331	0.75	0.1138	0.0673	0.2539	10.86	0.0782	0.0738
332	1.50	0.1138	0.0673	0.2539	17.13	0.1274	0.1616
333	2.25	0.1138	0.0673	0.2539	21.36	0.1608	0.1757
334	4.50	0.1138	0.0673	0.2539	24.32	0.1845	0.2214
335	6.00	0.1138	0.0673	0.2539	26.08	0.1968	0.2179
336	10.50	0.1138	0.0673	0.2539	27.23	0.2021	0.2495

Run No.	Products moles/hr						% Selectivity
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2	$S_{C_4H_6O}$
331	0.1015	0.0432	0.2539	0.0089	0.0255	0.0084	72.35
332	0.0944	0.0235	0.2539	0.0145	0.0365	0.0184	74.74
333	0.0895	0.0165	0.2539	0.0183	0.0453	0.0200	75.30
334	0.0862	0.0044	0.2539	0.0210	0.0543	0.0252	76.08
335	0.0842	0.0051	0.2539	0.0224	0.0544	0.0248	75.67
336	0.0828	-	0.2539	0.0230	0.0570	0.0284	74.19

TABLE A-D-9 (Continued)

Temp. = 375°C, $\bar{R}$ = 0.7710, Z = 0.0015

Run No.	W/F	Feed mole/hr			% Conversion	Yield	
		C_4H_8	O_2	N_2	$X_{C_4H_8}$	$Y_{C_4H_6O}$	Y_{CO_2}
337	0.75	0.1138	0.1105	0.4168	12.51	0.0931	0.1089
338	1.50	0.1138	0.1105	0.4168	18.86	0.1405	0.1757
339	2.25	0.1138	0.1105	0.4168	24.00	0.1854	0.2214
340	4.50	0.1138	0.1105	0.4168	30.56	0.2293	0.2530
341	6.00	0.1138	0.1105	0.4168	33.88	0.2486	0.3057
342	10.50	0.1138	0.1105	0.4168	35.36	0.2855	0.3057

Run No.	Products mole/hr						% Selectivity
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2	$S_{C_4H_6O}$
337	0.0996	0.0798	0.4168	0.0106	0.0267	0.0124	74.64
338	0.0924	0.0633	0.4168	0.0160	0.0387	0.0200	74.76
339	0.0865	0.0496	0.4168	0.0211	0.0490	0.0252	77.28
340	0.0791	0.0381	0.4168	0.0261	0.0646	0.0288	75.21
341	0.0753	0.0267	0.4168	0.0283	0.0736	0.0348	73.50
342	0.0713	0.0232	0.4168	0.0325	0.0759	0.0348	76.47

TABLE A-D-9 (Continued)

Temp. = 375°C, $\bar{R}$ = 1.3998, Z = 0.0015

Run No.	W/F	Feed mole/hr			% Conversion	Yield	
		C_4H_8	O_2	N_2	$X_{C_4H_8}$	$Y_{C_4H_6O}$	Y_{CO_2}
343	0.75	0.1138	0.1593	0.6010	13.35	0.1036	0.1230
344	1.50	0.1138	0.1593	0.6010	21.34	0.1801	0.1933
345	2.25	0.1138	0.1593	0.6010	26.07	0.1933	0.2319
346	4.50	0.1138	0.1593	0.6010	36.56	0.2741	0.2987
347	6.00	0.1138	0.1593	0.6010	39.83	0.2908	0.4112
348	10.50	0.1138	0.1593	0.6010	42.27	0.3277	0.3690

Run No.	Products moles/hr						% Selectivity
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2	$S_{C_4H_6O}$
343	0.0987	0.1241	0.6010	0.0118	0.0293	0.0140	78.14
344	0.0896	0.0982	0.6010	0.0205	0.0498	0.0220	84.71
345	0.0842	0.0942	0.6010	0.0220	0.0572	0.0264	74.32
346	0.0722	0.0744	0.6010	0.0312	0.0758	0.0340	75.00
347	0.0685	0.0533	0.6010	0.0331	0.0861	0.0468	73.06
348	0.0657	0.0559	0.6010	0.0373	0.0853	0.0420	77.54

TABLE A-D-9 (Continued)

Temp. = 375°C, $\bar{R}$ = 1.3998, Z = 0.0015

Run No.	W/F	Feed mole/hr			% Conversion	Yield	
		C_4H_8	O_2	N_2	$X_{C_4H_8}$	$Y_{C_4H_6O}$	Y_{CO_2}
349	0.75	0.1138	0.1962	0.7403	14.20	0.1098	0.1300
350	1.50	0.1138	0.1962	0.7403	22.55	0.1783	0.1968
351	2.25	0.1138	0.1962	0.7403	28.11	0.2170	0.2636
352	4.50	0.1138	0.1962	0.7403	41.02	0.3216	0.3550
353	6.00	0.1138	0.1962	0.7403	45.50	0.3365	0.4253
354	10.50	0.1138	0.1962	0.7403	46.53	0.3646	0.4288

Run No.	Products moles/hr						% Selectivity
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2	$S_{C_4H_6O}$
349	0.0977	0.1583	0.7403	0.0125	0.0324	0.0148	77.63
350	0.0882	0.1375	0.7403	0.0203	0.0501	0.0224	79.29
351	0.0819	0.1218	0.7403	0.0247	0.0619	0.0300	77.42
352	0.0672	0.0910	0.7403	0.0366	0.0904	0.0404	78.54
353	0.0621	0.0821	0.7403	0.0383	0.0959	0.0484	74.08
354	0.0608	0.0764	0.7403	0.0415	0.0965	0.0488	78.30

TABLE A-D-9 (Continued)

Temp. = 375°C, $\bar{R}$ = 2.2337, Z = 0.0015

Run No.	W/F	Feed mole/hr			% Conversion	Yield	
		C_4H_8	O_2	N_2	$X_{C_4H_8}$	$Y_{C_4H_6O}$	Y_{CO_2}
355	0.75	0.1138	0.2542	0.9592	16.12	0.1221	0.1405
356	1.50	0.1138	0.2542	0.9592	24.64	0.1994	0.2108
357	2.25	0.1138	0.2542	0.9592	31.55	0.2486	0.2847
358	4.50	0.1138	0.2542	0.9592	45.66	0.3857	0.4147
359	6.00	0.1138	0.2542	0.9592	47.75	0.3506	0.4604
360	10.50	0.1138	0.2542	0.9592	49.10	0.3093	0.5061

Run No.	Products moles/hr						% Selectivity
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2	$S_{C_4H_6O}$
355	0.0955	0.2127	0.9592	0.0139	0.0372	0.0160	75.95
356	0.0858	0.1884	0.9592	0.0227	0.0565	0.0240	81.07
357	0.0779	0.1684	0.9592	0.0283	0.0745	0.0324	78.83
358	0.0619	0.1225	0.9592	0.0439	0.1093	0.0472	84.58
359	0.0595	0.1305	0.9592	0.0399	0.1051	0.0524	73.48
360	0.0579	0.1132	0.9592	0.0352	0.1462	0.0576	62.96

TABLE A-D-9 (Continued)

Temp. = 400°C, $\bar{R}$ = 0.5913, Z = 0.0015

Run No.	W/F	Feed mole/hr			% Conversion	Yield	
		C_4H_8	O_2	N_2	$X_{C_4H_8}$	$Y_{C_4H_6O}$	Y_{CO_2}
361	0.50	0.1138	0.0673	0.2539	11.52	0.0826	0.1300
362	0.75	0.1138	0.0673	0.2539	14.72	0.1098	0.1300
363	1.50	0.1138	0.0673	0.2539	21.12	0.1608	0.1757
364	2.25	0.1138	0.0673	0.2539	23.29	0.1687	0.1933
365	4.50	0.1138	0.0673	0.2539	26.03	0.1871	0.2495
366	6.00	0.1138	0.0673	0.2539	28.12	0.2021	0.2478

Run No.	Products moles/hr						% Selectivity
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2	$S_{C_4H_6O}$
361	0.1007	0.0341	0.2539	0.0094	0.0271	0.0148	71.75
362	0.0971	0.0309	0.2539	0.0125	0.0317	0.0148	74.85
363	0.0898	0.0172	0.2539	0.0183	0.0436	0.0200	76.25
364	0.0873	0.0124	0.2539	0.0192	0.0512	0.0220	72.45
365	0.0842	0.0012	0.2539	0.0213	0.0571	0.0284	71.95
366	0.0818	-	0.2539	0.0230	0.0611	0.0280	71.87

TABLE A-D-9 (Continued)

Temp. = 400°C, $\bar{R}$ = 0.9710, Z = 0.0015

Run No.	W/F	Feed mole/hr			% Conversion	Yield	
		C_4H_8	O_2	N_2	$X_{C_4H_8}$	$Y_{C_4H_6O}$	Y_{CO_2}
367	0.50	0.1138	0.1105	0.4168	12.14	0.0949	0.1441
368	0.75	0.1138	0.1105	0.4168	17.40	0.1441	0.1581
369	1.50	0.1138	0.1105	0.4168	25.65	0.2056	0.2284
370	2.25	0.1138	0.1105	0.4168	29.34	0.2355	0.2741
371	4.50	0.1138	0.1105	0.4168	36.51	0.2636	0.3655
372	6.00	0.1138	0.1105	0.4168	37.37	0.2732	0.3635

Run No.	Products moles/hr						% Selectivity
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2	$S_{C_4H_6O}$
367	0.1000	0.0723	0.4168	0.0108	0.0286	0.0164	78.26
368	0.0940	0.0627	0.4168	0.0164	0.0387	0.0180	82.82
369	0.0847	0.0442	0.4168	0.0234	0.0534	0.0260	80.41
370	0.0804	0.0336	0.4168	0.0268	0.0601	0.0312	81.34
371	0.0723	0.0149	0.4168	0.0300	0.0802	0.0416	72.28
372	0.0713	0.0137	0.4168	0.0311	0.0811	0.0416	73.17

TABLE A-D-9 (Continued)

Temp. = 400°C, $\bar{R}$ = 1.3998, Z = 0.0015

Run No.	W/F	Feed mole/hr			% Conversion	Yield	
		C_4H_8	O_2	N_2	$X_{C_4H_8}$	$Y_{C_4H_6O}$	Y_{CO_2}
373	0.50	0.1138	0.1593	0.6010	13.27	0.1151	0.1511
374	0.75	0.1138	0.1593	0.6010	18.02	0.1502	0.1827
375	1.50	0.1138	0.1593	0.6010	28.25	0.2398	0.2636
376	2.25	0.1138	0.1593	0.6010	33.14	0.2539	0.3163
377	4.50	0.1138	0.1593	0.6010	42.52	0.3233	0.3796
378	6.00	0.1138	0.1593	0.6010	53.11	0.3418	0.4288

Run No.	Products moles/hr						% Selectivity
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2	$S_{C_4H_6O}$
373	0.0987	0.1141	0.6010	0.0131	0.0339	0.0172	86.75
374	0.0936	0.1058	0.6010	0.0171	0.0401	0.0208	84.65
375	0.0817	0.0808	0.6010	0.0273	0.0596	0.0300	85.04
376	0.0761	0.0677	0.6010	0.0289	0.0795	0.0360	76.65
377	0.0655	0.0491	0.6010	0.0368	0.0974	0.0432	76.19
378	0.0620	0.0395	0.6010	0.0389	0.1035	0.0488	74.83

TABLE A-D-9 (Continued)

Temp. = 400°C, $\bar{R}$ = 1.7240, Z = 0.0015

Run No.	W/F	Feed mole/hr			% Conversion	Yield	
		C_4H_8	O_2	N_2	$X_{C_4H_8}$	$Y_{C_4H_6O}$	Y_{CO_2}
379	0.50	0.1138	0.1962	0.7403	15.02	0.1335	0.1546
380	0.75	0.1138	0.1962	0.7403	19.85	0.1748	0.2073
381	1.50	0.1138	0.1962	0.7403	31.10	0.2636	0.2952
382	2.25	0.1138	0.1962	0.7403	38.86	0.2873	0.4358
383	4.50	0.1138	0.1962	0.7403	50.10	0.3725	0.5210
384	6.00	0.1138	0.1962	0.7403	53.11	0.3971	0.6678

Run No.	Products moles/hr						% Selectivity
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2	$S_{C_4H_6O}$
379	0.0968	0.1463	0.7403	0.0152	0.0396	0.0176	89.41
380	0.0913	0.1323	0.7403	0.0199	0.0482	0.0236	88.44
381	0.0785	0.1090	0.7403	0.0300	0.0658	0.0336	84.98
382	0.0696	0.0805	0.7403	0.0327	0.0941	0.0496	73.98
383	0.0568	0.0573	0.7403	0.0424	0.1146	0.0592	74.38
384	0.0534	0.0488	0.7403	0.0452	0:1265	0.0604	74.83

TABLE A-D-9 (Continued)

Temp. = 400°C, $\bar{R}$ = 2.2337, Z = 0.0015

Run No.	W/F	Feed mole/hr			% Conversion	Yield	
		C_4H_8	O_2	N_2	$X_{C_4H_8}$	$Y_{C_4H_6O}$	Y_{CO_2}
385	0.50	0.1138	0.2542	0.9592	16.12	0.1362	0.1616
386	0.75	0.1138	0.2542	0.9592	21.06	0.1915	0.2108
387	1.50	0.1138	0.2542	0.9592	32.25	0.3101	0.3268
388	2.25	0.1138	0.2542	0.9592	40.36	0.3550	0.4604
390	4.50	0.1138	0.2542	0.9592	55.88	0.4323	0.5413
390	6.00	0.1138	0.2542	0.9592	57.40	0.4200	0.6678

Run No.	Products moles/hr						% Selectivity
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2	$S_{C_4H_6O}$
385	0.0955	0.2029	0.9592	0.0155	0.0427	0.0184	84.69
386	0.0899	0.1805	0.9592	0.0218	0.0618	0.0240	91.21
387	0.0771	0.1470	0.9592	0.0353	0.0759	0.0372	96.18
388	0.0679	0.1192	0.9592	0.0404	0.0971	0.0524	88.01
389	0.0503	0.0932	0.9592	0.0492	0.1413	0.0616	77.48
390	0.0485	0.0807	0.9592	0.0478	0.1398	0.0760	73.20

TABLE A-D-9 (Continued)

Temp. = 425°C, $\bar{R}$ = 0.5913, Z = 0.0015

Run No.	W/F	Feed mole/hr			% Conversion	Yield	
		C_4H_8	O_2	N_2	$X_{C_4H_8}$	$Y_{C_4H_6O}$	Y_{CO_2}
391	0.50	0.1138	0.0673	0.2539	17.22	0.1247	0.1757
392	0.75	0.1138	0.0673	0.2539	20.64	0.1344	0.2108
393	1.00	0.1138	0.0673	0.2539	23.27	0.1678	0.2179
394	1.50	0.1138	0.0673	0.2539	25.18	0.1801	0.2434
395	2.25	0.1138	0.0673	0.2539	26.01	0.2100	0.2372
396	4.50	0.1138	0.0673	0.2539	26.34	0.1924	0.2469

Run No.	Products moles/hr						% Selectivity
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2	$S_{C_4H_6O}$
391	0.0943	0.0217	0.2539	0.0142	0.0374	0.0200	72.82
392	0.0904	0.0133	0.2539	0.0153	0.0501	0.0240	75.38
393	0.0874	0.0076	0.2539	0.0191	0.0529	0.0248	72.34
394	0.0852	0.0021	0.2539	0.0205	0.0571	0.0277	71.67
395	0.0843	-	0.2539	0.0239	0.0520	0.0270	81.01
396	0.0838	-	0.2539	0.0219	0.0587	0.0281	73.00

TABLE A-D-9 (Continued

Temp. = 425°C, $\bar{R}$ = 0.9710, Z = 0.0015

Run No.	W/F	Feed mole/hr			% Conversion	Yield	
		C_4H_8	O_2	N_2	$X_{C_4H_8}$	$Y_{C_4H_6O}$	Y_{CO_2}
397	0.50	0.1138	0.1105	0.4168	17.83	0.1441	0.1977
398	0.75	0.1138	0.1105	0.4168	23.12	0.1757	0.2434
399	1.00	0.1138	0.1105	0.4168	28.86	0.2144	0.3057
400	1.50	0.1138	0.1105	0.4168	32.23	0.2398	0.3207
401	2.25	0.1138	0.1105	0.4168	38.55	0.2961	0.3813
402	4.50	0.1138	0.1105	0.4168	40.37	0.2803	0.4007

Run No.	Products moles/hr						% Selectivity
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2	$S_{C_4H_6O}$
397	0.0936	0.0548	0.4168	0.0164	0.0429	0.0225	81.18
398	0.0875	0.0438	0.4168	0.0200	0.0544	0.0277	76.04
399	0.0810	0.0291	0.4168	0.0244	0.0664	0.0348	74.39
400	0.0760	0.0241	0.4168	0.0273	0.0751	0.0365	72.22
401	0.0700	0.0106	0.4168	0.0337	0.0761	0.0434	76.94
402	0.0679	0.0103	0.4168	0.0319	0.0853	0.0456	69.49

TABLE A-D-9 (Continued)

Temp. = 425°C, $\bar{R}$ = 1.3998, Z = 0.0015

Run No.	W/F	Feed mole/hr			% Conversion	Yield	
		C_4H_8	O_2	N_2	$X_{C_4H_8}$	$Y_{C_4H_6O}$	Y_{CO_2}
403	0.50	0.1138	0.1593	0.6010	21.02	0.1748	0.2126
404	0.75	0.1138	0.1593	0.6010	26.58	0.2144	0.2530
405	1.00	0.1138	0.1593	0.6010	31.88	0.2565	0.3514
406	1.50	0.1138	0.1593	0.6010	38.38	0.2882	0.3954
407	2.25	0.1138	0.1593	0.6010	45.12	0.3514	0.4402
408	4.50	0.1138	0.1593	0.6010	46.48	0.3453	0.4736

Run No.	Products moles/hr						% Selectivity
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2	$S_{C_4H_6O}$
403	0.0899	0.0959	0.6010	0.0199	0.0499	0.0242	83.26
404	0.0836	0.0827	0.6010	0.0244	0.0645	0.0288	80.79
405	0.0776	0.0628	0.6010	0.0292	0.0726	0.0400	80.66
406	0.0702	0.0503	0.6010	0.0328	0.0912	0.0450	75.22
407	0.0625	0.0414	0.6010	0.0400	0.0907	0.0501	77.97
408	0.0609	0.0331	0.6010	0.0393	0.1040	0.0539	74.29

TABLE A-D-9 (Continued)

Temp. = 425°C, $\bar{R}$ = 1.7240, Z = 0.0015

Run No.	W/F	Feed mole/hr			% Conversion	Yield	
		C_4H_8	O_2	N_2	$X_{C_4H_8}$	$Y_{C_4H_6O}$	Y_{CO_2}
409	0.50	0.1138	0.1962	0.7403	22.19	0.2117	0.2346
410	0.75	0.1138	0.1962	0.7403	29.29	0.2574	0.2829
411	1.00	0.1138	0.1962	0.7403	33.26	0.2829	0.3576
412	1.50	0.1138	0.1962	0.7403	42.25	0.3312	0.4165
413	2.25	0.1138	0.1962	0.7403	50.52	0.3690	0.5448
414	4.50	0.1138	0.1962	0.7403	53.58	0.4121	0.6959

Run No.	Products moles/hr						% Selectivity
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2	$S_{C_4H_6O}$
409	0.0886	0.1159	0.7403	0.0241	0.0615	0.0267	95.63
410	0.0806	0.1020	0.7403	0.0293	0.0780	0.0322	87.98
411	0.0760	0.0876	0.7403	0.0322	0.0854	0.0407	85.18
412	0.0658	0.0736	0.7403	0.0377	0.1047	0.0474	78.54
413	0.0564	0.0477	0.7403	0.0420	0.1272	0.0620	73.17
414	0.0528	0.0407	0.7403	0.0469	0.1268	0.0640	76.88

TABLE A-D-9 (Continued)

Temp. = 425°C, $\bar{R}$ = 2.2337, Z = 0.0015

Run No.	W/F	Feed mole/hr			% Conversion	Yield	
		C_4H_8	O_2	N_2	$X_{C_4H_8}$	$Y_{C_4H_6O}$	Y_{CO_2}
415	0.50	0.1138	0.2542	0.9592	24.12	0.2073	0.2662
416	0.75	0.1138	0.2542	0.9592	31.37	0.2697	0.3233
417	1.00	0.1138	0.2542	0.9592	36.82	0.3286	0.3875
418	1.50	0.1138	0.2542	0.9592	43.15	0.3471	0.4595
419	2.25	0.1138	0.2542	0.9592	52.57	0.3989	0.6045
420	4.50	0.1138	0.2542	0.9592	59.64	0.4560	0.6959

Run No.	Products moles/hr						% Selectivity
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2	$S_{C_4H_6O}$
415	0.0864	0.1755	0.9592	0.0236	0.0589	0.0303	86.13
416	0.0782	0.1546	0.9592	0.0307	0.0779	0.0368	86.23
417	0.0719	0.1274	0.9592	0.0374	0.1022	0.0441	89.26
418	0.0647	0.1206	0.9592	0.0395	0.1083	0.0523	80.44
419	0.0540	0.0888	0.9592	0.0454	0.1346	0.0688	75.91
420	0.0459	0.0667	0.9592	0.0519	0.1490	0.0792	76.43

Stability of the Chlorine Modified Copper Oxide

Catalyst for Oxidation of 2-Methylpropene

Temp. = 400°C, $\bar{R}$ = 1.400, Z = 0.0015

Run No.	W/F	Feed moles/hr			% Conversion	Yield	
		C_4H_8	O_2	N_2	$X_{C_4H_8}$	$Y_{C_4H_6O}$	Y_{CO_2}
376	2.25	0.1138	0.1593	0.6010	33.14	0.2540	0.3163
376[a]	2.25	0.1138	0.1593	0.6010	31.65	0.2398	0.3119
376[b]	2.25	0.1138	0.1593	0.6010	32.70	0.2566	0.3198

Run No.	Products moles/hr						Time hrs
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2	
376	0.0761	0.0677	0.6010	0.0289	0.0795	0.0360	2
376[a]	0.0778	0.0684	0.6010	0.0279	0.0782	0.0355	24
376[b]	0.0766	0.0660	0.6010	0.0292	0.0788	0.0364	72

Appendix E

Sample Calculation and Material Balance

Sample Calculation:

This calculation is based on the experimental data of Run No. 375.

(1) Moles in:

moles C_4H_8/hr

$$= \frac{42.5 \text{cc/min} \times 60 \text{ min/hr}}{22,400 \text{ cc/g-mole}} = 0.1138 \text{ g-mole/hr}$$

moles O_2/hr

$$= \frac{284 \text{cc/min} \times 0.2095 \times 60 \text{ min/hr}}{22,400 \text{cc/g-mole}} = 0.1593 \text{ g-mole/hr}$$

moles N_2/hr

$$= \frac{284 \text{cc/min} \times 0.7905 \times 60 \text{ min/hr}}{22,400 \text{ cc/g-mole}} = 0.6010 \text{ g-mole/hr}$$

(2) Moles out:

Analysis

(A) From Gas Partitioner

Component	Peak height	Peak height ratio (N_2/Component)
CO_2	23.1	12.706
O_2	56.7	5.176
N_2	293.5	1.000
C_4H_8	28.4	10.334

(B) From Vapor Fractometer

Component	Peak height	Peak height ratio (C_4H_6O/H_2O)
C_4H_6O	60.9	2.743
H_2O	22.2	1.000

Since 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.

$$\text{moles } C_4H_8/\text{hr} = \frac{0.601}{0.712 \times 10.334} = 0.0817 \text{ g-moles/hr}$$

$$\text{moles } O_2/\text{hr} = \frac{0.601}{1.437 \times 5.716} = 0.0808 \text{ g-moles/hr}$$

$$\text{moles } CO_2/\text{hr} = \frac{0.601}{1.576 \times 12.706} = 0.0300 \text{ g-moles/hr}$$

$$\text{moles } N_2/\text{hr} = 0.601 \text{ g-moles/hr}$$

$$W_{C_4H_6O} + W_{H_2O} = 70 (N_{C_4H_6O}) + 18 (N_{H_2O})$$

$$= 32 ({}_oN_O) + 56 ({}_oN_H)$$

$$-32 (N_O) - 56 (N_H)$$

$$-44 (N_C)$$

$$= 32 \times 0.1593 + 56 \times 0.1138$$

$$-32 \times 0.0808 - 56 \times 0.0817$$

$$-44 \times 0.0300$$

$$= 2.9896 \text{ gms/hr} \qquad (1)$$

$$W_{C_4H_6O}/W_{H_2O} = 2.741 \times 0.167 \times \frac{70}{18} = 1.781 \qquad (2)$$

solving equation (1) and (2) gives

$$W_{C_4H_6O} = 1.9110 \text{ gm/hr}$$

$$W_{H_2O} = 1.5786 \text{ gm/hr}$$

and moles C_4H_6O/hr = 0.0273 moles/hr

moles H_2O/hr = 0.0596 moles/hr

Conversion $= \frac{0.1138 - 0.0817}{0.1138} = 28.25\%$

Yield of CO_2 $= \frac{0.0300}{0.1138} = 0.2636$

Yield of C_4H_6O $= \frac{0.0273}{0.1138} = 0.2398$

Yield of H_2O $= \frac{0.0596}{0.1138} = 0.5237$

Selectivity for C_4H_6O = 85.04%

Material Balance

Based on atomic oxygen

Component	in feed moles/hr	in product moles/hr
O_2	0.3186	0.1616
CO_2		0.0600
C_4H_6O		0.0273
H_2O		0.0596
Total	0.3186	0.3085

$$\% \text{ Deviation} = \frac{0.3186 - 0.3085}{0.3186}$$

$$= 3.17\%$$

Based on atomic hydrogen

Component	in feed moles/hr	in product moles/hr
O_2		
CO_2		
C_4H_8	0.9104	0.6536
C_4H_6O		0.1638
H_2O		0.1192
Total	0.9104	0.9366

$$\% \text{ Deviation} = \frac{0.9104 - 0.9366}{0.9104}$$

$$= -2.88\%$$

Based on atomic carbon

Component	in feed moles/hr	in products moles/hr
O_2		
CO_2		0.0300
C_4H_8	0.4552	0.3268
C_4H_6O		0.1092
H_2O		
Total	0.4552	0.4660

$$\% \text{ Deviation} = \frac{0.4552 - 0.4660}{0.4552}$$

$$= -2.38\%$$

Appendix F

Effect of Diffusion

(1) Internal Diffusion

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

The experimental results for molecular diffusion are given in Table A-F-2. The constancy of conversion indicates that molecular diffusion is not important in the catalytic oxidation of 2-methylpropene.

b) Knudsen Diffusion and Effectiveness Factor

The experimental results for Knudsen diffusion are given in Table A-F-1. An estimate of Knudsen diffusion and the effectiveness factor for the α-alumina supported copper oxide catalyst used in this study is calculated for Run 376, using a modified Thiele method and given as follows.

(i) Calculation of molecular weight of gas mixture

Component	Inlet mole fraction	Outlet mole fraction	Av. mole fraction
C_4H_8	0.1302	0.0866	0.1084
C_4H_6O	0	0.0409	0.0205
H_2O	0	0.0329	0.0165
O_2	0	0.0904	0.0452
N_2	0.1822	0.0770	0.1296
	0.6876	0.6836	0.6856

$$M_{av} = 32.2450$$

(ii) Calculation of Knudsen diffusion coefficient, $D_{K,eff}$

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

where $T = 400°C = 673°K$

β = porosity of catalyst = 0.40

τ = tortuosity = 5

S_g = catalyst surface = 8,400 cm^2/gm

ρ_p = particle density = 1.2743 gm/cm^3

M = molecular weight of gas mixture = 32.25

The tortuosity is an empirical factor related to pore geometry and its value must be estimated. The value of the tortuosity is conservatively estimated to about 5

$$D_{K,\,eff} = 19,400 \times \frac{(0.4)^2}{5 \times 8,400 \times 1.2473}\sqrt{\frac{673}{32.25}}$$

$$= 0.2698 \ cm^2/sec$$

(iii) Calculation of reaction (diffusion) rate

$$r = \frac{0.1472 \text{ gm-mole/hr-gm} \times 1.2743 \text{ gm/cm}^3}{3600 \text{ sec/hr}}$$

$$= 5.1 \times 10^{-5} \text{ gm-moles/sec-cm}^3 \text{ catalyst}$$

(iv) Calculation of reactant concentration, C

$$C = \frac{273}{673 \times 22,400} \text{ gm-moles/cm}^3$$

$$= 1.81 \times 10^{-5} \text{ gm-moles/cm}^3 \text{ catalyst}$$

(v) Calculation of dimensionless modulus, Φ

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

$$R = \text{particle radius} = 0.028 \text{ cm}$$

$$\Phi = \frac{(0.028)^2 \times 5.1 \times 10^{-5}}{0.2698 \times 1.81 \times 10^{-5}} \doteqdot 0.01$$

(vi) Calculation of effectiveness factor, E

$$E \doteqdot 1 \text{ from Figure 3-7 of reference (79)}$$

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

(2) External Diffusion (Drop in Partial Pressure)

The data for estimation of the external diffusion are obtained from Run 376. The conditions which apply to this evaluation are:

Temp. = 400°C

W/F = 6.0

$\bar{R}$ = 1.40

W = weight of catalyst = 0.6830 gm

composition:

	Inlet		Outlet	
	Flow g-mole/hr	Mole fraction	Flow g-mole/hr	Mole fraction
O_2	0.1593	0.1822	0.0395	0.0442
N_2	0.6010	0.6876	0.6010	0.6725
C_4H_8	0.1138	0.1302	0.0620	0.0694
CO_2	0	0	0.0488	0.0546
H_2O	0	0	0.1035	0.1158
C_4H_6O	0	0	0.0389	0.0435
	0.8741	1.0000	0.8937	1.0000

a) Calculations Based on the Method of Yoshida et al.

(i) Calculation of dimensionless term R_j

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

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

a_m = specific surface area = 8400 cm^2/gm

φ = shape factor

= 0.9 for irregular granules

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

$$= \frac{0.8741}{(\pi/4)\,(2.54 \times 0.430)^2}$$

= 0.9335 g-moles/hr-cm^2

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

y_j = mole fraction of component j at the interface $\doteqdot [(y_j)_{in} + (y_j)_{out}]/2$

The results are tabulated as follows, where Figure 2 of Yoshida's plots of $\Delta P_j/P_j$ versus R/y_j was referred.

Component	R	y_j	R/Y_j	$(\Delta P_j/P_j)_{max.}$
O_2	2.5×10^{-5}	0.1132	2.2×10^{-4}	< 0.001
N_2	-	0.6800		
C_4H_8	1.1×10^{-5}	0.0998	1.1×10^{-4}	< 0.001
CO_2	1.1×10^{-5}	0.0273	3.7×10^{-4}	< 0.001
H_2O	2.2×10^{-5}	0.0579	3.8×10^{-4}	< 0.001
C_4H_6O	0.8×10^{-5}	0.0218	3.7×10^{-4}	< 0.001

b) Calculations of Pressure Drop for Oxygen from Equation (5-14)

$$\Delta y_o = \frac{\Delta P_o}{P_o} = R\,(j_D)^{-1}\, y_{f_A}\, (S_c)^{2/3} \qquad (5\text{-}14)$$

(i) Calculation of j_D

$$R_e = \frac{G_m}{a_v\, \varphi\, \mu}$$

where a_v = external surface area of catalyst particles per unit volume of catalyst bed

= 8,400/1.2743

= 6,590 cm^2/cm^3

μ = viscosity, which

Component	y_i, av	T_c (°K)	P_c (atm)	$\mu'_c \times 10^6$ (C.P.)	M (gm)
O_2	0.1132	154	49.7	250	32
N_2	0.6800	126	33.5	180	28
C_4H_8	0.0998	418	39.5	250	56
CO_2	0.0273	304	72.9	343	44
H_2O	0.0579	647	218.0	495	18
C_4H_6O	0.0218	563	57.6	150	70

$$M' = \Sigma M_i y_i = 32.0$$

$$T'_c = \Sigma T_{c,i} y_i = 202.9$$

$$P'_c = \Sigma P_{c,i} y_i = 48.22$$

$$\mu'_c = \Sigma \mu_{c,i} y_i = 217 \times 10^{-6}$$

$$T'_c = \frac{T}{T_c} = \frac{673}{2029} = 3.32$$

$$P'_r = \frac{P}{P_c} = \frac{1.092}{48.2} = 0.023$$

From the values of P'_r and T'_r and Figure 262A in Chemical Process Principles Chart by Hougen et al.

$$\mu'_r = 1.30$$

$$\mu = \mu'_r \cdot \mu_c = 1.30 \times 217 \times 10^{-6} = 2.82 \times 10^{-4} \text{ centipoise}$$

$$Re = \frac{G}{a_v \varphi \mu}$$

$$= \frac{0.9335}{6590 \times 0.9 \times 2.82 \times 10^{-4}} = 0.558$$

$$j_D = 0.84 (Re)^{-0.51} = 1.124$$

(ii) Calculation of Schmidt number, S_c

Diffusivity of oxygen in various gases is calculated from Gilliland equation

$$D_{AB} = 0.0043 \frac{T^{3/2}}{P (V_A^{1/3} + V_B^{1/3})^2} \left(\frac{1}{M_A} + \frac{1}{M_B}\right)^{1/2}$$

Component	V_i (cm^3/g-mole)	D_{o-i}
O_2	14.8	-
N_2	31.2	0.57
C_4H_8	118.8	0.53
CO_2	34.0	0.51
H_2O	18.9	0.77
C_4H_6O	88.9	0.31

$$\text{and } D_{o-M} = \frac{1 - y_o}{\Sigma y_i / D_{o-i}}$$

$$= \frac{1 - 0.1132}{1.193 + 0.188 + 0.054 + 0.075 + 0.070}$$

$$= 0.56 \text{ cm}^2/\text{sec}$$

where D_{o-i} = diffusivity of oxygen in component i

D_{o-M} = diffusivity of oxygen in mixtures

$$\rho = \frac{PM'}{RT}$$

$$= \frac{32.0 \times 1.092}{82.05 \times 673} = 0.00063 \text{ gm/cm}^3$$

$$(S_c)_{O_2} = \frac{\mu}{\rho D_{o-M}}$$

$$= \frac{2.82 \times 10^{-4}}{0.00063 \times 0.56} = 0.80$$

$$(S_c)_{O_2}^{2/3} = 0.86$$

$$R_{O_2} = 1.70 \times 10^{-5}$$

Let the overall reaction be represented by

$$2C_4H_8 + 7O_2 = 4CO_2 + C_4H_6O + 5H_2O$$

$$\text{Then } y_{f_o} = 1 + y_o \left(\frac{2 + 7 - 4 - 1 - 5}{7}\right)$$

$$= 1 - 0.43\, y_o$$

$$= 0.995$$

$$\left(\frac{\Delta P}{P}\right)_{O_2} = R\,(j_D)^{-1}\, y_{f_o}\, (S_c)^{2/3}_{O_2} \times \frac{1.092}{y_o}$$

$$= 1.70 \times 10^{-5} \times \frac{1}{1.124} \times 0.995 \times 0.86 \times \frac{1.092}{0.1132}$$

$$= 1.25 \times 10^{-4}$$

The results obtained from both a) and b) indicate the external diffusion effects can be neglected.

TABLE A-F-1

Experimental Data for Knudsen Diffusion with

Chlorine Modified Copper Oxide Catalyst

Temp. = 400°C, $\bar{R}$ = 1.400, Z = 0.0015

Run No.	W/F	Feed moles/hr			% Conversion	Yield	
		C_4H_8	O_2	N_2	$X_{C_4H_8}$	$Y_{C_4H_6O}$	Y_{CO_2}
375	1.50	0.1138	0.1593	0.6010	28.25	0.2400	0.2636
375[a]	1.50	0.1760	0.2483	0.9373	29.12	0.2306	0.1948
375[b]	1.50	0.2215	0.3110	1.1734	29.64	0.2595	0.1860

Run No.	Products moles/hr						Feed Velocity
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2	moles / hr
375	0.0817	0.0808	0.6010	0.0273	0.0596	0.0300	0.8741
375[a]	0.1248	0.1528	0.9373	0.0406	0.0871	0.0343	1.3617
375[b]	0.1559	0.1730	1.1734	0.0575	0.1248	0.0412	1.7059

TABLE A-F-2

Experimental Data for External Diffusion (Effect of Feed Velocity on Oxidation of 2-Methylpropene)

Temp. = 400°C, $\bar{R}$ = 1.400, Z = 0.0015

Run No.	W/F	Feed moles/hr			% Conversion	Yield	
		C_4H_8	O_2	N_2	$X_{C_4H_8}$	$Y_{C_4H_6O}$	Y_{CO_2}
376	2.25	0.1138	0.1593	0.6010	33.14	0.2540	0.3163
376[c]	2.25	0.1138	0.1593	0.6010	32.26	0.2592	0.3022

Run No.	Products moles/hr						Catalyst particle size mm
	C_4H_8	O_2	N_2	C_4H_6O	H_2O	CO_2	
376	0.0761	0.0677	0.6010	0.0289	0.0795	0.0360	0.56
376[c]	0.0771	0.0681	0.6010	0.0295	0.0774	0.0344	0.32

Appendix G
Temperature Drop from Catalyst Particle to Ambient Gas Stream

Temperature Drop From Catalyst Particle to Ambient Gas Stream

The data for estimation of temperature drop from catalyst particle to ambient gas stream are obtained from Run 376. The calculation is based on the method of Yoshida, Ramaswami and Hougen[98]. Figure 4 of their paper was used to determine ΔT versus Q

$$Q = \frac{V_{mA} \Delta H_A}{a_m \varphi C_p G_m}$$

where ΔH_A = molal heat of reaction of component A

C_p = molal heat capacity at constant pressure

Component	mole fraction		H_i, (at 400°C) K_{cal}/g-mole
	in	out	
O_2	0.1822	0.0442	4.00
N_2	0.6876	0.6725	4.73
C_4H_8	0.1302	0.0694	17.07
CO_2	0	0.0546	-87.85
H_2O	0	0.1158	-51.71
C_4H_6O	0	0.0435	-23.40

where H_i = heat content of component i

$\Delta H_{C_4H_8}$ = 260 K_{cal}/g-mole

Component	mole fraction av	C_{p_i} cal/gm-mole °C
O_2	0.1132	7.83
N_2	0.6800	7.32
C_4H_8	0.0998	37.80
CO_2	0.0273	11.70
H_2O	0.0579	8.85
C_4H_6O	0.0218	48.76

$C_p = 11.53$ cal/gm-mole, °C

$r_{m, C_4H_8} = \frac{0.0518}{0.683} = 0.0758$ gm-moles/gm-hr

$G_m = 0.9335$ gm-moles/hr-cm^2

$a_m = 8,400$ cm^2

$\varphi = 0.9$

$$Q = \frac{0.0758 \times 260,000}{8,400 \times 0.9 \times 11.53 \times 0.9335}$$

$$= 0.242$$

Since from Figure 4 of Yoshida et al., $\Delta T < 5$ °C, the catalyst surface temperature effect can therefore be neglected.

Appendix H

Correlation of Initial Rate Data

TABLE A-H-1

Correlation of Initial Rate Data

Temp. °C	$\bar{R}$	$_oP_H$, atm	r_o, g-moles/hr-gm
400°C	0.5913	0.2856	0.194
400°C	0.9710	0.1938	0.280
400°C	1.3998	0.1420	0.293
400°C	1.7240	0.1181	0.313
400°C	2.2337	0.0980	0.300

Appendix I
Effect of W/F

The effect of W/F on conversion (X) was studied in the experimental range 350 - 425°C for chlorine modified copper oxide catalyst. The running conditions used for the feed ratio of oxygen to 2-methylpropene ratio ($\bar{R}$) were

$\bar{R}_1 = 0.59$, $_oN_O = 0.0673$ moles/hr, $_oN_H = 0.1138$ moles/hr

$\bar{R}_2 = 0.97$, $_oN_O = 0.1105$ moles/hr, $_oN_H = 0.1138$ moles/hr

$\bar{R}_3 = 1.40$, $_oN_O = 0.1593$ moles/hr, $_oN_H = 0.1138$ moles/hr

$\bar{R}_4 = 1.72$, $_oN_O = 0.1962$ moles/hr, $_oN_H = 0.1138$ moles/hr

$\bar{R}_5 = 2.23$, $_oN_O = 0.2542$ moles/hr, $_oN_H = 0.1138$ moles/hr

The following is a sample tabulation of the deviation between the calculated (from the integrated rate equation, mechanism 11) and experimental W/F versus X relations. It is based on data obtained at 350°C with an oxygen to 2-methylpropene ratio ($\bar{R}$) of 0.5913 (Table A-D-9 Run no 301 - 306). The values for K_S, K_H and K_M were obtained from Table 7 abd a, b, d, e were obtained from equations (5 - 46), (5 - 47), (5 - 49) and (5 - 50) respectively.

$K_O = 0.6$ atm^{-1}, $a = 0.2856$ atm

$K_H = 66.8$ atm^{-1}, $b = 0.2171$ atm

$K_M = 355$ atm^{-1}, $d = 0.1689$ atm

$K_S = 1.27$ g-mole/gm-hr, $e = 0.8283$ atm

Substituting these values for the integrated equation of mechanism 11, the following comparison was obtained

X	$(W/F)_{exp.}$	$(W/F)_{cal}$	% Deviation
0.0702	0.75	0.83	-10.7
0.1152	1.50	1.68	-12.0
0.1413	2.25	2.36	- 4.9
0.1902	4.50	4.32	4.0
0.2150	6.00	6.03	- 0.5
0.2203	10.50	6.51	38%

Where % deviation $= \dfrac{(W/F)_{exp.} - (W/F)_{cal}}{(W/F)_{exp}}$

In general, all the divations determined were below 20% except for the last value of W/F.

IX. NOMENCLATURE

A	Component A
A_m	Specific surface area of catalyst, m^2/gm
a_m	External particle surface area per unit mass, m^2/gm
a_v	External particle surface area per unit volume, $m^2/c\ c$
a	$(oN_H)\ (P_t/N_t)$
B	Component B
b	$0.76\ (oN_H)\ (P_t/N_t)$
C_p	Specific heat of gas, cal/gm-mole-°C
C_{av}	Average specific heat of gas, cal/gm-mole-°C
C	Molal concentration of adsorbed reactants or products
c	$0.96\ (oN_H)\ (P_t/N_t)$
D_p	Diameter of particle, cm
$D_{K,eff}$	Effective Knudsen diffusion coefficient
D_{AM}	Average diffusivity of component A
d	$(oN_o)\ (P_T/N_T)$
E	Effectiveness factor of catalyst
e	$2.2\ (oN_H)\ (P_T/N_T)$
eL or ⊙	Free electrons
F	Flow rate of feed, gm-moles/hr
G	Molal velocity of gas flow based on the total cross-sectional area of the catalyst bed
ΔG	The change in Gibb's free change
ΔH_A	Heat of reaction per moles of A reacted
h_G	Heat transfer coefficient of the gas film

I	Component I
j_d	Chilton-Colburn mass-transfer factor
j_h	Chilton-Colburn heat-transfer factor
K	Thermodynamic equilibrium constant
K	Adsorption equilibrium constant (with subscript A, B, . . .)
k	Thermal conductivity of the gas
k_G	Mass transfer coefficient of the gas film
k_c	Thermal conductivity of the catalyst
k_s	Thermal conductivity of the support
k	Reaction rate constant (with subscript 1, 2)
L	Molal concentration of active sites per unit mass
M	Molecular weight
M_m	Mean molecular weight
P	Partial pressure
P_i	Partial pressure in the gas-solid interface
P_f	Film pressure factor
Pr	Prandtl number, $\frac{C_P \mu}{k}$
pL or □	Positive holes
Q	$\frac{r \quad \Delta H_A}{a_m \quad C_P G_M}$
q_m	Heat transfer rate per unit mass of catalyst
R	Component R
R	Oxygen to olefin mole ratio in the feed
R	$\frac{r_A}{a_m \quad G_M}$

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

Greek Symbols

β	Void fraction in catalyst particle
Δ	Finite increment or change of property
θ	Fractional coverage of catalyst surface by a certain component
μ	Viscosity
π	Total pressure
ρ	Density of gas
ρ_B	Bulk density of the catalyst
φ	Shape factor, ratio of actual external surface area available for mass and heat transfer to the total external surface area, assumed to be 0.90 for irregular granules

Φ Dimensionless modulus $= \dfrac{D_p^2 r}{D_{K,\,eff}} C$

τ Tortuosity of catalyst

Superscripts

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

Subscripts

A^+	Charged adsorbed aldehyde
C	Carbon dioxide
cal	Calculated
f	Properties at the average condition of the gas film
H	2-methylpropene
H. C.$^+$	Charged adsorbed olefin
I	Component I
i	Properties at the gas-solid surface interphase
in	Input
M	Methacrolein
O	Oxygen
o	Placed before a symbol means in the feed
O	Charged adsorbed oxygen
out	Output

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