OXIDATION OF ISOBUTENE OVER SELENIUM DIOXIDE MODIFIED COPPER OXIDE CATALYSTS

by

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A thesis submitted in partial fulfillment
of the requirements for the degree of

Master of Science

in the
Department of Chemical Engineering
University of Ottawa
November 1966

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ACKNOWLEDGMENT

The author is grateful to his director Dr. R.S. Mann, for his guidance, patience and encouragement throughout the course of this work and his help in the preparation of this thesis.

He also wishes to acknowledge his sincere gratitude to Dr. B. C.-Y. Lu for providing the facilities for this research work; to Messrs. F. Giacobbi and G. Gasperetti for their technical assistance, to Miss N. Renaud for typing the manuscript and to Dr. K.C. Khulbe for proof reading the manuscript.

The author is much indebted to the members of the teaching staff of the Chemical Engineering Department for stimulating discussions and suggestions.

Finally, the author wishes to express his sincere thanks to the Selenium-Tellurium Development Corporation for financial aid.

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I. ABSTRACT

The effect of various amounts of SeO_2, a p-type impurity, in modifying the selectivity of the copper oxide catalysts for methacrolein production, in the catalytic oxidation of isobutylene was investigated, at different feed ratios and several temperatures up to 425°C, in an isothermal integral flow reactor. The reaction products were analyzed quantitatively by gas chromatography.

It has been found that there is an optimal amount of SeO_2 required at each operating condition to enhance the selectivity of the catalyst. The experimental results are explained with the electron theory of catalysis on semiconductors and a reaction mechanism proposed. It has been postulated that the rate determining step in the partial oxidation of isobutene to methacrolein is a p-type and its further oxidation to water and CO_2 is an n-type, under the operating conditions.

II. INTRODUCTION

The fundamental concepts with which we are concerned in catalysis are the concepts of the "activity" and "selectivity" of a catalyst. The former characterizes the reaction rate and the latter is related to the product distribution.

Every reaction consists as a rule of a number of intermediate stages which occur both in parallel and consecutively. However, it is understood that if a catalyst can accelerate the first step of a consecutive reaction it will also accelerate all the subsequent steps. Also if it can accelerate one of the parallel reactions it will accelerate the others as well (1). In other words a certain catalyst alone can not affect the selectivity under a certain operating condition. From industrial view point selectivity is always more appreciated than the reactivity itself, for instance in the oxidation of unsaturated hydrocarbons, one is more interested in the yield of an intermediate product such as the aldehydes and not the final products such as carbon dioxide and water.

The purpose of the present study was to investigate the means by which the activity and selectivity of the copper catalyst could be improved by adding some other components besides the primary active catalytic agent that may be present during the catalytic action. The additives defined as "catalyst modifiers" may include promotors, inhibitors, accelerators and poisons. When the amount of the additives is extremely small compared with the parent catalyst, it is called "doped catalyst". The catalyst used for the parent study belongs to this class. Here a general concept of "modifier" is used to replace the individual terms since a given modifier on a given catalyst may be a promotor for one reaction and a poison for another even in the same reaction, it may act as a promotor at one stage and then act as a poison at another stage.

The partial oxidation of isobutylene into methacrolein over copper oxide catalyst was studied to illustrate this phenomena using selenium dioxide as the modifier. Both catalyst and modifier, by their electrical properties belongs to the class of semiconductors.

The catalytic activity of semiconductors was discovered long before the concept of a semiconductor itself appeared. However, until recently the relationship between catalytic activity of the solid and its semiconductivity was unknown. Most of the researches carried out in this direction have been of a qualitative nature. The so-called electron or charge transfer theory of catalysis on semiconductors cannot be regarded at present as a theory which could explain the catalytic activity of semiconductors completely satisfactorily on a quantitative basis. It is being erected on the foundation of the modern theory of chemical bonding on the one hand and on the foundation of the modern theory of solids on the other hand.

In the present study, the importance of different amounts of impurity on the concentrations of free electron and positive hole on the surface which in turn determine the rates of adsorption and desorption of molecules, atoms and ions is illustrated.

An hypothesis "the chemisorption of both reactants on the surface of this catalyst are necessary steps in heterogeneous catalysis" is proposed in this work. In other words, the surface reaction can only occur between the charged species. It is proposed that the Rideal mechanism is only a special case of the Langmuir-Hinshelwood mechanism and that adsorption constant of one of the adsorbate is relatively and comparatively smaller than the other one. But since the adsorption constant of one of this reactant could be increased or decreased by changing the properties especially the work function of the catalyst, the conversion and yield of a reaction might be changed.

This hypothesis does not contraverse in any way the existing results obtained by different researchers. It is shown that it is possible to resolve and explain many conflicts in the experimental data concerning the reaction order and activation energy which are reported in the literature and which can not be explained by the old active center concept.

III LITERATURE SURVEY

A. LITERATURE RELATED TO OXIDATION OF ISOBUTYLENE

Bretton, Wan and Dodge (2) found that the vapor phase oxidation of four carbon hydrocarbons over a vanadium pentoxide catalyst can for the most part be explained by a scheme of atomic dehydrogenation and peroxidation, similar to that suggested by Waters (3) and by peroxide decomposition. The first step according to this scheme was the removal of a hydrogen atom from the hydrocarbon forming a free radical which then reacted with a molecule of oxygen to form a peroxide radical. This last product then became a peroxide by gaining a hydrogen atom.

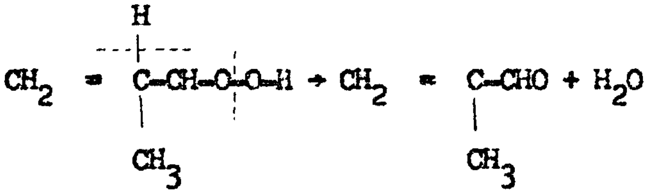
According to Water's mechanism, the peroxide radical abstracted a hydrogen atom from another hydrocarbon molecule and the reaction proceeded in a chain like fashion. The experimental results were explained by considering the catalyst as a hydrogen atom abstractor and donor. This role of the catalyst is represented by the following reaction:

$$RH + X \rightarrow HX + R- \qquad (1)$$

$$R- + O_2 \rightarrow R-O-O- \qquad (2)$$

$$R-O-O- + HX \rightarrow ROOH + X \qquad (3)$$

where X represents the catalyst. The decomposition of the peroxide occurs by scission at the O-O bond followed by scission of an adjacent C-H or the weakest adjacent C-C bond. The presence of methacrolein in the products of oxidation of isobutylene indicated that the initial point of oxidative attack on the mono-olefins might be at the α-methyl or methylenic carbon atom.



$$CH_2 = \underset{CH_3}{\overset{H}{C}}-CH-O-O-H \rightarrow CH_2 = \underset{CH_3}{C}-CHO + H_2O$$

Baldwin (4) described a method whereby isobutylene could be oxidized to methacrolein. He has given a list of possible metals, their organic compounds and common supports, which form useful catalysts for oxidation of hydrocarbons.

Dowden and Caldwell (5) studied the effect of reactant ratios, contact times and temperatures on the conversion and yield of isobutylene to methacrolein. They claim that by passing 100 liter/hour of a mixture of 85% air and 15% by volume of isobutylene 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.

Kitahara and Moriya (6) investigated the catalytic oxidation of isobutylene to methacrolein over various metal oxides and their mixtures.

They found that a V_2O_5 : MoO_3 : P_2O_5 catalyst supported on an aluminum-sponge was the most effective catalyst for oxidation. They also studied the effects of various types of supports, grain size of aluminum-sponge, space velocity, isobutylene/oxygen ratio in the feed, and the promotional effects of steam. Methacrolein and other liquid products (aldehydes, ketones, acids and ethers) were obtained by condensing the reaction products in the ice cooled traps and an absorption train containing methanol. The products which were collected in condensation and absorption trains contained 90% methacrolein.

Popava, Mil'man and Latysheva (7) studied the oxidation of isobutylene with oxygen over a 0.1-1.5% copper oxide (70% Cu_2O + 30% CuO) catalyst supported on silite, at 350°-370°C. They used an isobutylene oxygen ratio of 5.6 over a wide range of space velocities. 3.8% of the isobutylene was converted to carbonyl compounds; 82.5% of which was methacrolein, 7.2% propionaldehyde, 6.2% acetaldehyde and 4.1% acrolein.

Popova, Vermel and Mil'man (8) followed the oxidation of isobutylene in a flow reactor on 0.5% and 1.5% cupric oxide supported on silite with and without the addition of MoO_3 and WO_3. They found that the reaction was first order with respect to oxygen for the formation of aldehyde and carbon dioxide. The formation rate of the unsaturated aldehydes depended on the structure of the oxidized hydrocarbons and the reactivity of the aldehydes formed. Addition of MoO_3 and WO_3 did not change the activation energy of the dienals but increased activation energy of the carbon dioxide formation and the oxidation selectivity of the dienes, which was relatively lower than that of the monoolefins. Electronic considerations of these experimental data showed that the formation rate of unsaturated aldehydes on the copper catalyst was determined by the degree of polarization of hydrogen in the methyl groups conjugated with a double bond as well as by space difficulties while being oriented toward the catalyst surface.

Skirrow and Williams (9) examined the gas-phase oxidation of isobutylene by a static method between 252° and 320°C. They found that the reaction proceeded with an initial pressure decrease during which formaldehyde and acetone were produced in equivalent amounts. They suggested that the isobutyraldehyde detected at the lower temperatures was probably formed by the isomerization of isobutylene oxide. Much of the pressure decrease during the course of the reaction was attributed to the overall process,

$$(CH_3)_2-C = CH_2 + {}^1\!/_2O_2 \rightarrow (CH_3)_2CHCHO$$

rather than to peroxide formation, since under certain conditions, the yield of peroxide was much too small to provide a satisfactory explanation. The more important primary products could be accounted for in terms of a radical addition mechanism initiated by addition of a hydroxyl radical to the terminal CH_2 group and followed by peroxy radical formation and its subsequent decomposition. The formation of methyl allyl hydroperoxide and methacrolein showed that some abstraction of methyl hydrogen occured, although to be less important than the addition attack. The carbon oxides, water and propylene were formed by reactions of the primary products. It has been suggested that the branching occured by aldehyde oxidation.

Mann and Rouleau (10) studied the oxidation of isobutylene over a pumice supported copper catalyst by a static method between 360° and 400°C and found that the order of the reaction was first and zero order with respect to oxygen and isobutylene respectively. They also obtained an activation energy of 21.65 ± 0.05 kcal/mole.

They studied the same reaction between 350°-450°C for a reciprocal space velocity of 0.12 to 16.8 and an oxygen/isobutylene ratio of 0.25 to 4.0 in an isothermal integral flow reactor. They found that with an increase in the process variables of temperature reactant ratio, copper concentration and reciprocal of space velocity, the conversion of isobutylene increased and that the yield of methacrolein decreased. A rate equation based on Hougen-Watson type approach was also derived by them (11). A surface reaction between adsorped isobutylene and oxygen in the gas phase or between strongly adsorbed isobutylene and weakly adsorbed oxygen was found to be the rate determining step.

While the concentrations of oxygen and isobutylene were changed from 2 to 3 and 7 to 80% by volume respectively, the contact times were changed approximately 20 times. Shapovalova, Gorokhovastiskii and

Rubanik (12) found that in the partial oxidation of isobutylene, the rate of reaction was first order with respect to oxygen and zero order with respect to isobutylene. However, they found that in case of complete oxidation of isobutylene, the rate of reactions were 0.8 and zero order with respect to oxygen and isobutylene respectively.

B. LITERATURE RELATED TO CATALYST MODIFICATION

The phenomenon of catalyst promotion and poisoning by impurities has long been well-known and has been widely used in the chemical industries. Numerous experimental papers are devoted to this problem. An excellent literature survey concerning the catalyst promotion and poisoning by some other components besides the primary catalytic agent was carried out by Inns (13). Where Inns reviewed the literature from 1942 to 1952, the earlier literature has been reviewed by Berkman, Morrell and Egloff (14).

The very fact that the additives may affect the yield and reaction kinetics, make a study of the catalyst modification an interesting subject.

Parravano and Boudart (15) reported that the activation energy for the carbon monoxide oxidation in the temperature range 180-250°C is increased by doping NiO with trace amounts of Li_2O and decreased by doping NiO with 0.01 mol % WO_3. The activation energies for the Li^+ doped pure and W^{+++} doped NiO are 25, 13.7 and 6.5 kcal/mole respectively.

Schwab and Block (16) obtained results which were exactly opposite to those obtained by Parravano and Boudart. They studied the same reaction in the temperature range 300° to 450°C with Li^{+} and Ge^{+++} doped NiO and found that the addition of a trivalent ion lowered the conductivity and raised the enrgy of activation for the catalytic reaction. The addition of a monovalent ion increased the conductivity and lowered the energy of activation. The conflicting observations of Schwab and Parravano now have been resolved by the electron theory of catalysis on semiconductors.

Margolis and Krylov (17) investigated the oxidation of ethylene on MgO. Cr_2O_3 catalyst with Na_2SiO_3 impurity. They found that the activity of the catalyst was not a linear function of its impurity content.

Hauffe, Glang and Egnell (18) found out that though an addition of 0.1 mol % Li_2O to ZnO caused a distinct increase in the rate of nitrous oxide decomposition, an excess addition of Li_2O of about 3-5 mol % to ZnO slowed down this reaction very drastically.

Many authors have pointed out that the same impurity in the same catalyst in relation to the same reaction can assume the role of a promoter or poison at a given temperature depending on its concentration.

Zhahrova and Fokina (19) studied the decomposition of hydrogen peroxide on MgO catalyst with different amount of Sb_2O_3 impurity. Roginskiĭ (20) has investigated the complete oxidation of iso-octane on WO_3 crystal with added NaOH. Element (21) studied the same reaction on WO_3 crystal with added HNO_3 or B_2O_3. Both of the above mentioned reactions were found to be promoted at one concentration and inhibited at another concentration.

V.E. Ostrovkiĭ et al (22) studied the modifying effect of S, Se, Te and Cl on a silver catalyst for oxidation of ethylene using a radiochemical method. The additives concentration varied within the limits 10^{-5} to 10^{-1} atom %. In each case the optimum activity was found to lie in the modifier concentration range which corresponded to small coverages of the catalyst surface.

Data were obtained on the modifier distribution within the catalyst and on its surface and on their volatility to the gaseous phase.

The changes in the activity of the catalysts due to the added modifiers have been attributed to a change in the bond energy of adsorbed oxygen.

Krosjalov et al (23) studied the air oxidation of propylene into acrolein over $CuSeO_3$ on active alumina oxide, silica gel etc. as carriers. They explained the function of selenium as follows:

"Due to chemisorption it blocks the active centers essential for complete oxidation of propylene. In addition, during the formation of acrolein, selenium participates in the transfer of oxygen to the propylene molecules". They proposed that selenium assists the rupture of the chain reaction for the decomposition of the allyl hydroperoxide radical, or acts as a promoter on the active centers of the catalyst during the catalytic reaction.

Margolis et al (24) investigated the effects of many additives upon the catalytic activity and selectivity of metals and semiconductor catalysts (silver and copper oxide) for the oxidation of ethylene and propylene. They found that with the modifying additives with electronegative value greater than of the catalyst decreased the activity and increased the yield of electrons of the catalyst, at the same time, increased the work function and the selectivity of oxidation of ethylene and propylene.

Many patents concerning the partial oxidation of propylene and other olefins to acrolein and higher unsaturated aldehydes in presence of selenium have been granted between 1950 and 1960 to Hadley and coworkers at Distillers Company Limited. The process was carried out in vapor phase and the catalyst consisted of copper on various supports impregnated with elemental selenium (25). Alternatively, the selenium was introduced as vapor in the reactant stream (26). In many of these the method described was essentially the following: 25 liters of gas mixture per hour were passed over 8 to 10 grams of catalyst mass between 200° and 400°C, preferably about 300°C. The mixture consisted of 98% air and 2% olefin by volume. It also contained 0.0008 gram of selenium vapor per liter. They claimed that in either case, selenium lengthened the life of the copper catalyst and increased the yield of unsaturated aldehydes. However, they do not give any information regarding selectivity under different operating conditions.

A careful search of the literature has revealed that most of the literature which is devoted to the catalyst modification is concerned with the practical phases. The existing information does not appear to be of great importance in understanding the catalytic oxidation processes.

IV THEORY

In recent years a better understanding of heterogeneous catalysis has been obtained as a result of the recognition that a direct electron exchange takes place between the reactants or products and the catalyst. In developing this theme for the case of electron transfer on the surface of semiconductor, it is convenient to begin with some background information from the solid state physics.

I. BASIC CONSIDERATIONS

A. The band model

When the electronic processes in semiconductors are concerned, the band theory provides the most useful basis for discussion.

(1) Energy levels

The energy levels of the various electrons within a single atom can be measured from the spectral studies, each of these electron has an energy such that if the electron is removed from the structure energy changes giving rise to absorption spectra are observed. The subsequent capture of an electron and the accompanying energy changes give rise to the emission spectra.

These energy levels are discrete since the Pauli Principle states that only two electrons can have the same set of quantum numbers in an isolated atom.

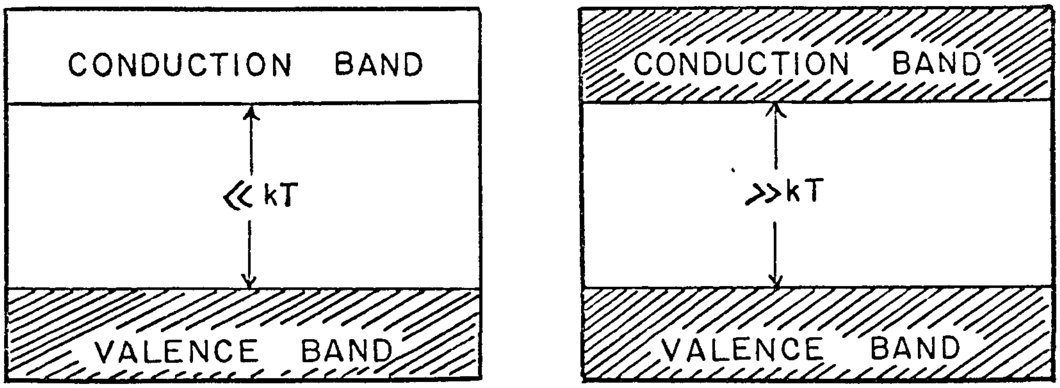
(ii) Energy bands

If atoms are brought together from large distances to form a solid, the electrons of the individual atoms will interact, this interaction does not change the number of electrons in a filled subshell but it makes it impossible to assign the individual electrons to the individual atoms, one has to consider the electrons to be more or less collectively shared by the individual atomic nuclei.

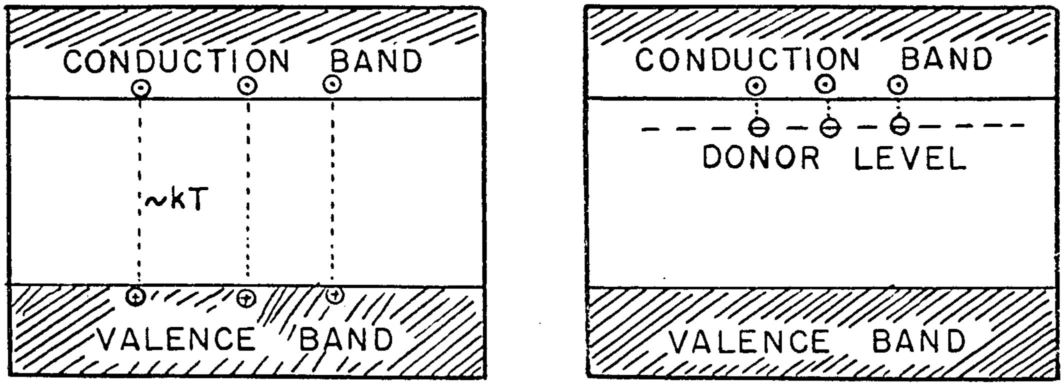
As a consequence of the interaction, the discrete binding energy of an electron in a single atom is changed into a bond of allowed binding energies in the crystal. The discrete energy levels of the electrons in a single atom thus correspond to bands of allowed energies in a solid. The energy gap between the two allowed bands is called the forbidden energy gap. If the allowed energy band is filled, we call it "Valence Band", if it is empty or partly filled we call it "Conduction Band".

B. Conductors, Insulators and Semiconductors

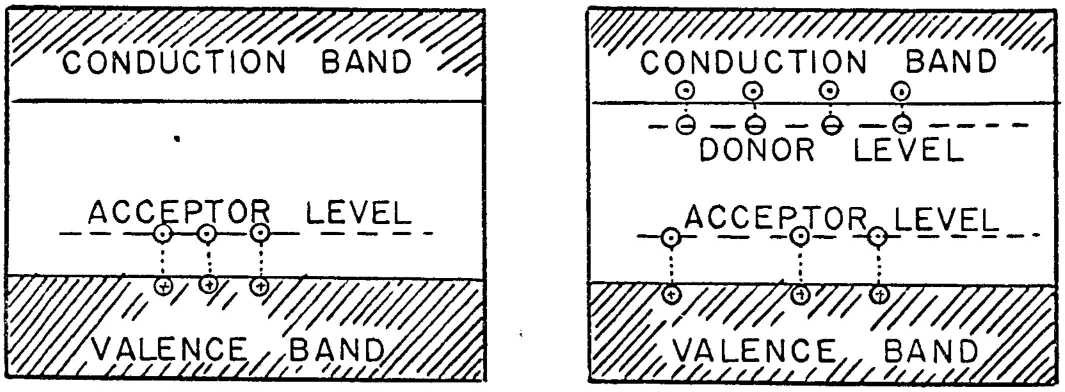
Their differences and definitions are better understood with the band model, for conductor (Figure 1a), the energy gap is much less than kT (here k is the Boltzmann constant and T is absolute temperature) and the conduction band is partially filled so that it is easy to excite electrons from valence band to conduction band. For



(a) Conductor (b) Insulater



(c) Intrinsic semiconductor (d) n-Type semiconductor



(e) p-Type semiconductor (f) Mixed type semiconductor

Figure 1 Conductor, Insulator and Semiconductor insulator (Figure 1b), the energy gap is much larger than kT and the conduction band is empty, the electrons transfer between these two bands is very difficult. For semiconductor (Figure 1f), the energy gap has a value near kT and the conduction band also is empty. At the absolute zero temperature the application of an electric field to semiconductor could not cause conduction since none of the electrons are free to move under the incluence of the external field, it is therefore an insulator at very low temperatures. However, its electrical conductivity is very sensitive to temperatures and increases rapidly with increasing temperatures. Since the width of the energy gap is different for different semiconductors, so when the energy gap increases, the temperature required to produce a significant amount of semiconduction also increases.

C. Classification of Semiconductors

There are in principle two types of semiconductors, intrinsic and extrinsic.

(1) Intrinsic semiconductor (Figure 1c)

The name "intrinsic" implies that the semiconductivity property of the material is its own characteristic property and they are essentially insulators at low temperature. However, as the temperature is increased their conductivity is increased, contrary to the behaviour of metallic conductors.

The conduction process in case of intrinsic semiconductors is carried by two types of carriers. The one type is of course the free electrons in the conduction band. For every electron appearing in the conduction band there must be an electron missing from the valence band. Such a vacant spot in the valence band is called a free hole, it acts in many respects as a positive charge and is mobile in the opposite direction to the free electrons and thus takes part in the conduction process.

(ii) Extrinsic semiconductors

In intrinsic semiconductors, the current is carried by two types of carriers, electrons and holes but in many respects, it would be much more convenient to have semiconductivity with only one type of the carriers either electron or hole, so we therefore have two kinds of extrinsic semiconductors.

a) n-type (negative type Figure 1d)

Semiconductor, in which the current is carried predominately by electrons, is called "n-type semiconductor". In between the filled valence band and the empty conduction band there is another discrete occupied energy level, slightly below the conduction band. One has only to increase the temperature slightly in order to raise the bounded electrons in this level to the conduction band. It is for this reason, that the energy level is caller "donor level". One typical n-type semiconductor is ZnO. Due to a structure defect of Zn atom excess in Zn, a free electron is wandering through the crystal:

$$Zn^{+} \rightleftharpoons Zn^{++} + e$$

b) p-type (positive type Figure 1e)

p-type semiconductor is a kind of semiconductor in which the current is carried predominately by positive holes. Sometimes between the filled valence band and the empty conduction band, there is another discrete unoccupied energy level which is slightly above the valence band. One can raise the electrons from the valence band to these unoccupied energy levels to leave free holes behind in the valence band. Such energy levels are called acceptor levels. One typical example of a p-type semiconductor is Cu_2O. Due to a structure defect of excess oxygen in Cu_2O a free hole is wandering through the lattice:

$$Cu^{++} \rightleftharpoons Cu^{+} + \oplus$$

c) mixed-type semiconductor

In mixed type semiconductors both acceptors and donors are present in the material. Due to the compensation effect the difference between donor and acceptor concentration will determine the carrier type and concentration.

Besides, the semiconductors which show conductivity due to structure defect or non-stoichoimetry, the n-type or p-type semiconductor can also be made by introducing some kinds of altervalent ions as impurities, for example doped Li^{+} can increase the hole concentration of Cu_2O and doped Cr^{+++} can decrease it. Thus the rigid classification of a catalyst as "p-type" or "n-type" is probably a less important criteria than the so-called "degree of p-typeness" or "degree of n-typeness" (27) which a catalyst can maintain during the conditions of a given catalytic reaction.

d) Fermi-Dirac Distribution and Fermi Level

Fermi level or Fermi energy is a parameter characteristic of the semiconductors. It plays an extremely important part in the electron theory of catalysis on semiconductors.

Each electron in the crystal is characterized by a particular energy E_i and the number of available states at this energy by Z_i. At equilibrium out of a total of N electrons, n_i will be situated at this energy E_i. The total energy of the assembly of electrons is E Thus

$$N = \sum n_i \quad (1)$$

$$E = \sum n_i E_i \quad (2)$$

and

$$Z_{total} = \Sigma Z_i = Z_1 + Z_2 \cdots + Z_E \qquad (3)$$

Since we have a total energy of E no levels greater than E would be occupied.

Assuming that a given electron has no preference for any state, the probability of it being in any state, P would be

$$P = \frac{1}{Z_{total}} \qquad (4)$$

At a given energy E_i, there would be Z_i levels. According to the Pauli exclusion principle since no two electrons would have the same quantum number, each energy state would be occupied by only one electron at most.

A given electron has a probability P of being in a particular state. Thus the probability that n_i levels are simultaneously filled with n_i electrons for the particular complexion is P^{n_i}. There are, however, many ways in which these Z_i states may be occupied by n_i electrons besides the particular one chosen, then, the number of complexion is given as

$$W = \frac{Z_i\,!}{n_i!\,(Z_i - n_i)!} \qquad (5)$$

Since the electrons are indistinguishable and if the states are also indistinguishable, the probability $p(n_i)$ of finding n_i electrons at energy E_i would be

$$p(n_i) = p^{n_i} w_i = p^{n_i} \frac{Z_i}{n_i\,!\,(Z_i-n_i)\,!} \qquad (6)$$

Similarly, for a different energy E_j

$$p(n_j) = p^{n_i} w_j = p^{n_j} \frac{Z_i}{n_j\,!\,(Z_j-n_j)\,!}$$

Therefore, the probability of finding N electrons with n_i electrons at the level E_i, n_j electrons at E_j etc. is $p(n_i) \cdot p(n_j)$

Thus

$$p(n_i) \cdot p(n_j) --- = p^{n_i} \cdot p^{n_j} --- w_i \cdot w_j --- = p^n \Pi w_i = p^n W \qquad (7)$$

N, Z_{total} are constants then p is fixed, thus p^n is a constant.

At equilibrium, W in equation (7) should be a maximum and

$$W = \Pi w_i \qquad (8)$$

$$\ln W = \Sigma \ln w_i \qquad (9)$$

using Stirling's approximation for w_i in equation (5) we have 1

$$\ln W = \Sigma \left[Z_i \ln Z_i - n_i \ln n_i - (Z_i-n_i) \ln (Z_i-n_i)\right] \qquad (10)$$

differentiating equation (10)

$$d \ln W = \sum [-\ln n_i + \ln (Z_i - n_i)] \, d n_i = 0 \qquad (11)$$

Equations (1) and (2) can be written as:

$$dn = \sum d n_i = 0 \qquad (12)$$

$$dE = \sum E_i \, d n_i = 0 \qquad (13)$$

Since the maximum in ln W is dependently upon many variables (n_i, n_j ----), $W_{max.}$ is a constrained maximum. Using the Langrandrian multiplier to equations (11), (12) and (13), we have

$$\frac{\partial \ln w_i}{n_i} - \lambda_1 - \lambda_2 E_i = 0 \qquad (14)$$

and

$$\frac{\partial \ln w_j}{n_j} - \lambda_1 - \lambda_2 E_j = 0 \qquad (15)$$

or

$$\ln \frac{Z_i - n_i}{n_i} - \lambda_1 - \lambda_2 E_i = 0 \qquad (16)$$

and

$$\ln \frac{Z_j - n_j}{n_j} - \lambda_1 - \lambda_2 E_j = 0 \qquad (17)$$

where λ_1 and λ_2 are the Lagrangian multipliers solving equations (16) and (17) we have

$$n_i = \frac{Z_i}{1 + \exp(\lambda_1)\exp(\lambda_2 E_i)} \qquad (18)$$

Further consideration shows that

$$\lambda_1 = -\frac{E_f}{kT} \qquad (19)$$

$$\lambda_2 = \frac{1}{kT} \qquad (20)$$

where k is Boltzmann constant T is absolute temperature and E_f is known as Fermi level.

Thus $f(E_i)$, the probability or the fraction of sites occupied with a given energy E_i is:

$$f(E_i) = \frac{n_i}{Z_i} = \frac{1}{1 + \exp[(E_i - E_f)/kT]} \qquad (21)$$

This is known as the Fermi-Dirac distribution. If $E_i - E_f \gg kT$, (usually when $E_i - E_f > 4kT$ then

$$f(E_i) \simeq \frac{n_i}{Z_i} \simeq \exp[-\frac{E_i - E_f}{kT}] \qquad (22)$$

is known as the Maxwell-Boltzmann distribution.

(ii) Comparison of Fermi level with chemical potential. In order to obtain the chemical potential of an electron of the crystal, consider the entropy change of a crystal resulting from the introduction of one electron of zero energy into the crystal where it has an energy E_i

$$\frac{ds}{dn_i} = k\left(\frac{d \ln w_i}{d\, n_i}\right) \qquad (23)$$

Since from equation (11), we have

$$\frac{d \ln w_i}{dn_i} = [-\ln n_i + \ln(Z_i - n_i)] = \ln\left(\frac{Z_i - n_i}{n_i}\right) \qquad (24)$$

Letting $dn_i = 1$ electron and substituting equation (24) in (23) we have

$$ds = k \ln\left(\frac{Z_i - n_i}{n_i}\right) \qquad (25)$$

substituting $f(E_i)$ from equation (21) for $\frac{n_i}{Z_i}$ into equation (25), we have

$$ds = k \ln\left[\frac{f(E_i) - 1}{f(E_i)}\right] = \frac{-E_f}{T} + \frac{E_i}{T} \qquad (26)$$

Let S be a function of the number of electrons N, choosing E and V in addition to N and specifying that V is a constant, we have the relationship

$$ds = \left(\frac{\partial s}{\partial N}\right)_{E,V} dN + \left(\frac{\partial s}{\partial E}\right)_{N,V} dE \qquad (27)$$

Since

$$dN = 1, \qquad dE = E_1.$$

Thus,

$$dS = \left(\frac{\partial S}{\partial N}\right)_{E,V} + \left(\frac{\partial S}{\partial E}\right)_{N,V} E_1 \tag{28}$$

Equating equation (26) to equation (28) yields

$$\left(\frac{\partial S}{\partial N}\right)_{E,V} = \frac{-E_f}{T}$$

and

$$\left(\frac{\partial S}{\partial E}\right)_{N,V} = +\frac{1}{T}$$

The chemical potential per electron is

$$\mu_e = \left(\frac{\partial G}{\partial N}\right)_{P,T}$$

and from classical thermodynamics we find that

$$\mu_e = \left(\frac{\partial G}{\partial N}\right)_{P,T} = -T\left(\frac{\partial S}{\partial N}\right)_{E,V}$$

Therefore

$$\mu_e = E_f \tag{29}$$

It would thus be seen that the Fermi level in the semiconductor is just the same as the chemical potential per electron. Though the importance of the chemical potential in the thermodynamics is well known yet the important role the Fermi level can play in the field of heterogeneous catalysis is still very obscure.

B THE MODEL OF ELECTRON TRANSFER HETEROGENOUS CATALYSIS

The model of a chemical reaction proceeding on semiconductor catalyst is postulated as Figure 2.

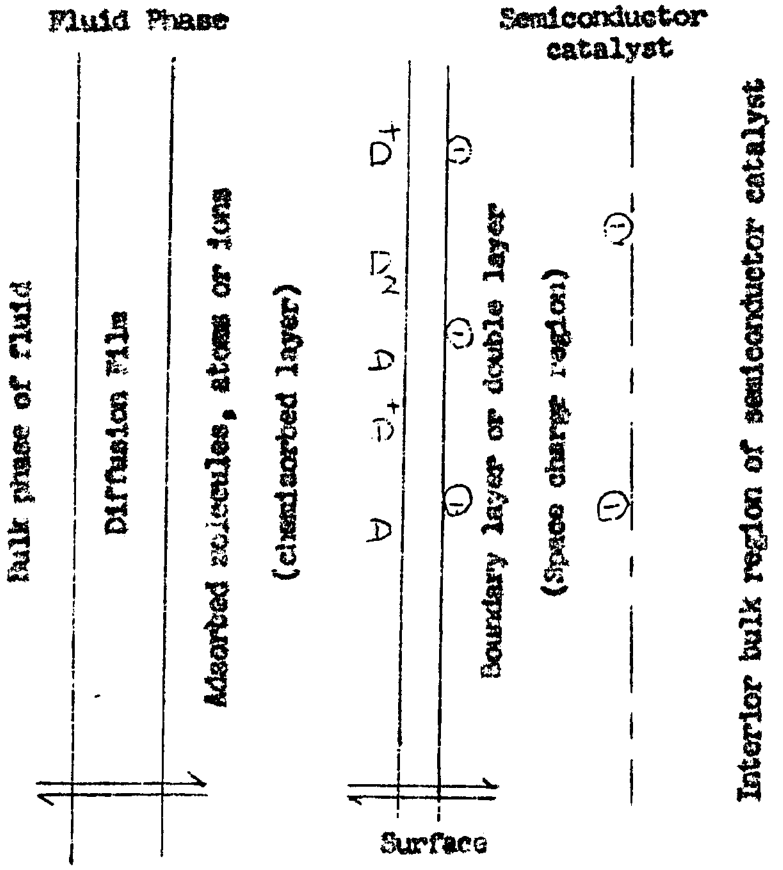


Figure 2 Simplified Model of Donors at a Fluid-Catalyst Interface

The sequence of reaction mechanisms according to the classical chemical point of view is modified as follows:

Step 1 Diffusion of reactants across the gas film towards the catalyst.
Step 2 Adsorption of neutral gas molecules onto the semiconductor catalyst surface.
Step 3 The formation of charged particles (adions) by electron transfer between neutral particles and the catalyst.
Step 4 Reaction between adions and/or neutral particles on the surface by radom migration to create new adions and/or neutral particles.
Step 5 Formation of new neutral particles (products) by recombination of new adions formed in step 4 with charged carriers from the catalyst.
Step 6 Desorption of products formed in step 5.
Step 7 Diffusion of products across the gas film into the gas phase.

The diffusion of reactants and products across the gas film in Steps 1 and 7 above is not important in this study (11).

III CHEMISORPTION ON SEMICONDUCTORS: (28) (29)

The mechanism of a heterogeneous catalytic process cannot be completely understood until the mechanism of the intermediate stages of the process-adsorption and desorption has been elucidated. Therefore the theory of heterogeneous catalysis inescapably starts from the theory of adsorption.

A. Physical adsorption and chemisorption

There are two kinds of adsorption, physical adsorption and chemisorption. The difference between them is the origin of the force which retain the adsorbed molecule on the surface of the solid. As physical adsorption is concerned the forces are of electrostatic origin (van der Waals' forces) or forces due to electrostatic polarization. For chemisorption, the forces responsible for adsorption are of a chemical nature (forces of the exchange type). In this case, the adsorption constitutes a chemical combination of the gas molecule with the solid with the formation of a chemical bond. The forces producing the bond may be covalent or ionic and in many cases, both of them.

In treating physical adsorption, a system of adsorbed particles is often considered as a two-dimensional gas which covers the surface of the adsorbent. However, in the case of chemisorption this approach becomes unacceptable. It is convenient to treat the chemisorbed particles as "Impurities" which have penetrated into the surface of the cyrstal (30) in other words, as a kind of structure defects which destroy the strictly periodic structure of the surface. The chemisorbed particles and the lattice of the adsorbent emerge as a single quantum mechanic system. The chemisorbed particles are therefore automatically included in the electronic system of the lattice, which by no means denotes that the adsorbed particles are rigidly localized. They still retain some degree of ability to move over the surface.

Thus a chemisorbed particle regarded as a sort of structure defect on the surface may be considered as a center of localization for the free electrons of the lattice, serving as a trap for them and thus playing the part of an acceptor. It may also serve as a center of localization for a positive hole, thus playing the part of a doner. This role depends not only on the adsorbent but also on the nature of the adsorbate. In the general case, the same chemisorbed particle on the same adsorbent may simultaneously be both acceptor and doner, possessing a definite affinity for both a free electron and a hole as mentioned in the section of extrinsic semiconductor.

It is highly essential that the localization of a free electron or positive hole on a chemisorbed particle not only cause a change in the character but also in the strength of its bond with the surface.

B. Types of chemisorption on semiconductors

There are in principle two types of chemisorption

(i) Weak chemisorption

In case of weak chemisorption, the chemisorbed particles (considered together with its adsorption center) remain electrically neutral and electrons or positive holes of the lattice do not contribute to the bond between the lattice and the particle.

(ii) Strong chemisorption

In the case of strong chemisorption, the chemisorbed particle captures a free electron or a free hole of the lattice. Such a free electron or free hole may participate directly in the chemisorption bond. Due to the different characters of the particles and semiconductors, four different situations may in fact arise as follows (31).

(a) Anionic chemisorption on an n-type semiconductor

During the adosprtion process, electrons flow from the surface to the adsorbed particles, which becomes anionic in character and a strong n-bond or acceptor bond is formed.

An example of this phenomena is the adsorption of oxygen on ZnO. Here owing to the strong electronegative nature of the oxygen, electrons will flow from the semiconductors. Since the supply of these electrons is limited, this type of chemisorption is generally called "depletive type".

(b) Cation adsorption on a p-type semiconductor

In this case, the electron flow is from the adsorbed particle to the solid, or the positive holes of solid be localized, which thus the adsorbed particle becomes cationic in character and a strong p-bond or donor bond is formed. An example of this is the adsorption of hydrogen on Cu_2O. Here owing to the electropositive nature of the hydrogen, the tendency is for the electrons to flow from the hydrogen to the surface. These electrons will pass into the acceptor level. Since the supply of these is also limited, so it is also a kind of depletive chemisorption.

(c) Anionic adsorption on a p-type semiconductor

In this case, electrons pass from solid to adsorbed particles.

Thus a strong p-bond or donor bond is formed. An example of this is the adsorption of oxygen on Cu_2O. Since the electrons in the acceptor level are bounded, the electrons are drawn from the valence band to the adsorped species. As the supply of electrons in the valence band is very great, the concentration of free holes in the valence band is increased. This kind of chemisorption is known as accumulative chemisorption.

(d) Cationic adsorption on a n-type semiconductor

In this case just like (b), the positive holes of solid are localized and also a p-bond is formed. An example of this type is the adsorption of hydrogen on ZnO. Where electrons pass from the hydrogen to the solid. But since in this case, the donor levels are filled, the electrons must pass into the conduction band. As the conduction band is capable of holding a large number of electrons so just like (c) it is a kind of accumulative chemisorption.

IV. THE ELECTRON THEORY OF CATALYSIS ON SEMICONDUCTORS

A. The concept of free valencies in a catalyst and its relation to the reactivities of chemisorbed particles.

As mentioned in the section of extrinsic semiconductors, there is a positive free hole Wandering through the Cu^+ ions of the Cu_2O lattice. From the view point of valence bond theory Cu^+ ion possesses a closed electron shell and its valence is zero. The Cu atom is characterized by one electron in excess of the closed shell, so the valence is +1. Since Cu^{++} ion lacks one electron in its closed shell, its valence is -1. Hence, in this case, a free hole is equivalent to an unsaturated negative valence. Following an indentical argument it can be seen that a free electron is equivalent to an unsaturated positive valence.

The free electrons or holes may be treated as free valencies capable of breaking the valence bond in the chemisorbed particles and themselves becoming saturated by those bonds. The weak bond is equivalent to the valence saturated from chemisorption, electric neutral on the surface. The strong n-bond and p-bond are equivalent to the positive or negative valence unsaturated (radical or ion radical) chemisorption respectively and are positively or negatively charged on the surface.

The treatment of free electrons and holes as free valencies is very convenient in describing chemical processes on the surface of a semiconductor. It has the following properties (30).

(i) Every free valence has a mean lifetime, that is, the valencies can appear and disappear. A crystal continually produces and absorbs free valencies.

(ii) The free valencies are not localized in the lattice but migrate through the crystal. In other words, as long as we are dealing with an ideal crystal, there is an equal probability of finding a free valence at any point of the crystal.

(iii) The equilibrium concentration of free valencies in the bulk and surface of the crystal depends not only on the nature of the crystal but also on external conditions; it increases with a rise in temperature and may be artificially increased or decreased under the influence of external agents such as illumination, impurities etc.

(iv) There is a continuous interchange of valencies between the bulk and the surface of the crystal. Valencies pass from the surface into the bulk and vice versa, so that the bulk of the crystal is just like a reservoir, absorbing the free valencies of the surface and supplying them back to the surface.

(v) The free valencies of a crystal can form pairs, each such pair wandering through the crystal as an entity until it breaks up.

The participation of a free valence of the surface in chemisorption leads to the transformation of a valence-saturated particle into an ion-radical or radical and vice versa, to the transfomration of a radical into a valence-saturated electrically charged formation. Naturally, in radical forms of chemisorption, the chemisorbed particles possess enhanced reactivity, i.e., enhanced ability to form chemical compounds with ether chemisorbed particles or with the particles arriving from the gaseous phase. Thus the various forms of chemisorption differ not only in the character and strength of the bond, but also in the reactivity of the chemisorbed particles.

The free valencies do not necessarily have to pre-exist on the surface. They may be formed by an act of chemisorption.

B. The role of Fermi level in the equilibrium between different forms of chemisorption

Using the idea of free valencies, it is easily realized that one form of chemisorption may change into another. It may pass from a state with one type of bonding to a state with another type of bonding. Such transitions denote that a free electron or hole is localized or delocalized on the adsorbed particle.

It is convenient to describe such transitions in terms of the energy band scheme of a semiconductor depicted in Figure 3

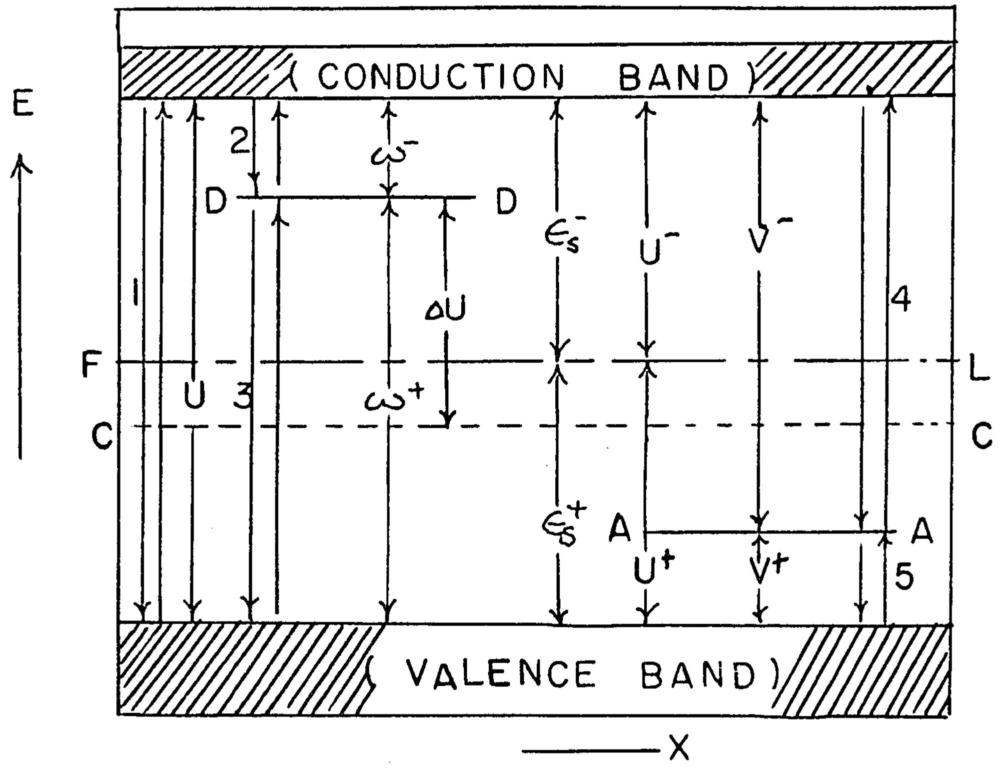


Figure 3 Electronic Equilibrium on the Semiconductor Surface

when a foreign particle is weakly chemisorbed on the surface it is reflected by an energy c—c in the energy spectrum. A particle which has an affinity for a free electron is represented by a local acceptor level, A; a particle having an affinity for a free hole corresponds to a local donor level D. Electronic transitions, on semiconductors are possible between the valence and conduction bands (transition I) and also between the energy bands and the local levels shown in Figure 3 (transitions 2, 3, 4 and 5). The transitions may be written down as follows:

$$eL + pL \rightleftharpoons L \qquad 1$$

$$CpL + eL \rightleftharpoons CL \qquad 2$$

$$CL + pL \rightleftharpoons CpL \qquad 3$$

$$CL + eL \rightleftharpoons CeL \qquad 4$$

$$CeL + pL \rightleftharpoons CL \qquad 5$$

where eL, pL denotes the free electron and hole in the crystal respectively, L represents the uncharged lattice, CL represents the weak bond, CpL and CeL represent the strong p-bond and strong n-bond respectively.

The occurrence of an electron on the local level A indicates the transition of the chemisorbed particle C from a state of "weak" bonding to a state of strong acceptor bonding (n-bonding) with the surface. The removal of an electron (or the occurrence of a free hole) from the level D indicates the transition of the chemisorbed particle C from a state of "weak" to a state of "strong" donor bonding.

When the electronic equilibrium is established on the surface, then a certain fraction of the total number of acceptor levels A will be occupied by electrons and a certain fraction of the total number of donor levels D will be free from electrons. In other words, out of the total number of chemisorbed particles N, there will be N^o, N^-, N^+ particles in the state of "weak", "strong" acceptor and "strong donor" bonding with the surface respectively. Using the notations shown in Figure 3 where E is the energy of the system.

The X-axis is parallel to the adsorbing surface of the semiconductor which is considered planar.

$$n^o = \frac{N^o}{N}, \qquad n^- = \frac{N^-}{N}, \qquad n^+ = \frac{N^+}{N} \tag{30}$$

since

$$N = N^o + N^- + N^+ \tag{31}$$

Also,

$$n^o + n^- + n^+ = 1 \tag{32}$$

From the Fermi-Dirac distribution equation (21).

Thus,

$$\frac{N^-}{N^-+N^o} = \frac{1}{1+\exp\left(\frac{\varepsilon_s^- - v^-}{kT}\right)} \tag{33}$$

$$\frac{N^+}{N^++N^o} = \frac{1}{1+\exp\left(\frac{\varepsilon_s^+ - \omega^+}{kT}\right)} \tag{34}$$

Substituting equations (33) and (34) in (30) by using equation (31), the following relations can be obtained,

$$n^o = \frac{1}{1+\exp\left(-\frac{\varepsilon_s^- - v^-}{kT}\right)+\exp\left(-\frac{\varepsilon_s^+ - \omega^+}{kT}\right)}$$

$$= \frac{1}{1+2\exp\left(-\frac{\Delta u}{kT}\right)\cosh\left(-\frac{t_s^+ - u^+}{kT}\right)} \tag{35}$$

$$n^{-} = \frac{\exp(-\frac{\varepsilon_s^{-}-v^{-}}{KT})}{1+\exp(-\frac{\varepsilon_s^{-}-v^{-}}{KT})+\exp(-\frac{\varepsilon_s^{+}-\omega^{+}}{KT})}$$

$$= \frac{\exp(-\frac{\Delta u-\varepsilon_s^{+}+u^{+}}{KT})}{1+2\exp(-\frac{\Delta u}{KT})\cosh(\frac{\varepsilon_s^{+}-u^{+}}{KT})} \qquad (36)$$

$${}^{+} = \frac{\exp(-\frac{\varepsilon_s^{+}-\omega^{+}}{KT})}{1+\exp(-\frac{\varepsilon_s^{-}-v^{-}}{KT})+\exp(-\frac{\varepsilon_s^{+}-\omega^{+}}{KT})}$$

$$= \frac{\exp(-\frac{\Delta u+\varepsilon_s^{+}-u^{+}}{KT})}{1+2\exp(-\frac{\Delta u}{KT})\cosh(\frac{\varepsilon_s^{+}-u^{+}}{KT})} \qquad (37)$$

In case of $\varepsilon_s^{+} - u^{+} \gg KT$ or $N^{-} \gg N^{+}$ equation (35) can be simplified to

$$n^{o} \simeq \frac{N^{o}}{N^{o}+N^{-}} = \frac{1}{1+\exp(-\frac{\varepsilon_s^{-}-v^{-}}{KT})} \qquad (38)$$

and

$$\eta^- \simeq \frac{N^-}{N^0+N^-} = \frac{1}{1+\exp\left(\frac{\varepsilon_s^- - v^-}{kT}\right)} \qquad (39)$$

In case of $N^+ \gg N^-$ or $\varepsilon_s^- - u^- \gg kT$ similarly equations (35) and (37) can be simplified to

$$\eta^0 \simeq \frac{N^0}{N^0+N^+} = \frac{1}{1+\exp\left(-\frac{\varepsilon_s^+ - \omega^+}{kT}\right)} \qquad (40)$$

and

$$\eta^+ \simeq \frac{N^+}{N^0+N^+} = \frac{1}{1+\exp\left(\frac{\varepsilon_s^+ - \omega^+}{kT}\right)} \qquad (41)$$

The quantities η^0, η^-, η^+ characterize the relative contents of the various forms of chemisorption at equilibrium, or the average relative lifetime of the chemisorbed particle in the corresponding states. Since these quantities also depend on the Fermi level, ε_s^+, therefore, the reactivities can be unambiguously determined by the position of the Fermi level.

In addition to the electronic equilibrium established on the surface, an adsorption equilibrium between the surface and the gaseous phase can be represented as shown in Figure 4

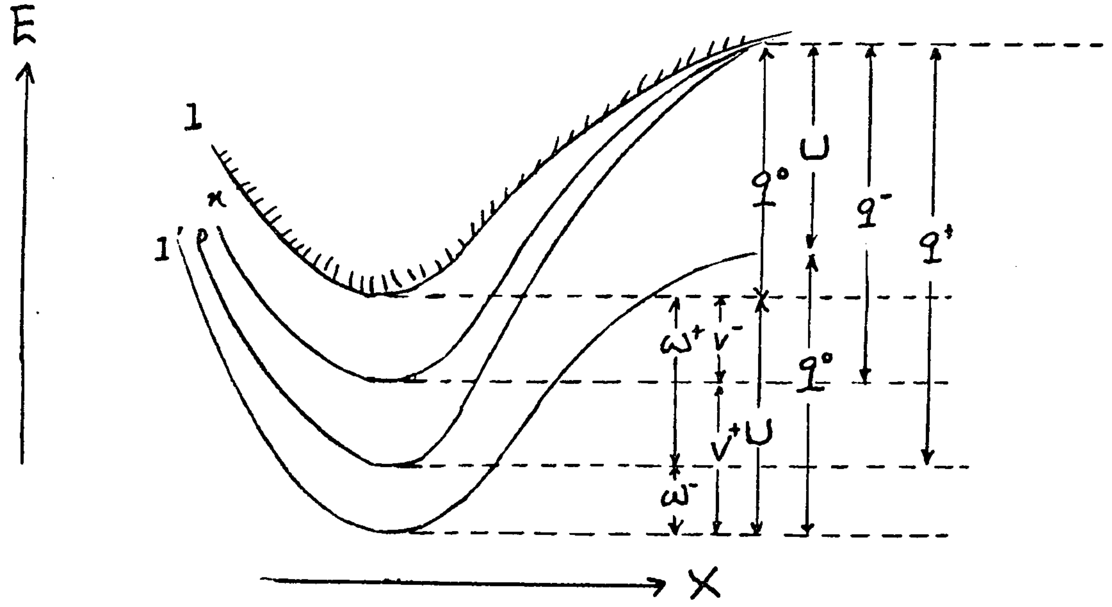


Figure 4. Adsorption Equilibrium Between Gases and the Surface

where E = the energy of the system

x = distance between the particle and surface

1 = adsorption curve on the clean surface

1' = adsorption curve on the adsorbed surface

n and p = adsorption curves for strong acceptor and strong donor chemisorption respectively.

The adsorption equilibrium can be expressed by the equation

$$\alpha p(1-sN) = \alpha^{o}N^{o}\exp(-q^{o}/kT) + \nu^{-}N^{-}\exp(-\frac{q^{-}}{kT}) + \nu^{+}N^{+}\exp(-\frac{q^{+}}{kT}) \qquad (42)$$

where p = the gaseous pressure

$\alpha = (2\pi MKT)^{1/2}$

s = the effective area of the chemisorbed particle

v^0, v^-, v^+ are constants

Using the relationship

$$q^+ = q^0 + \omega^+$$

$$q^- = q^0 - v^-$$

Equation (42) can be reduced to

$$\alpha p(1-sN) = [1+ \frac{v^-}{v^0} \frac{n^-}{n^0} \exp(-\frac{v}{KT}) + \frac{v^+}{v^0} \frac{n^+}{n^0} \exp(-\omega^+/KT]$$

$$v^0 n^0 N \exp(-\frac{q^0}{KT})]$$

in accordance with equations (35-37) we obtain

$$\alpha p(1-sN) = 1+ \frac{v^-}{v^0} \exp(-\frac{\varepsilon_s^-}{KT}) + \frac{v^+}{v^0} \exp(-\frac{\varepsilon_s^+}{KT}) v^0 n^0 N \exp(-\frac{q^0}{KT}) \qquad (43)$$

The adsorption capacity of a surface in relation to a given type of molecules, N, is dependent on the position of the Fermi level at a fixed temperature and pressure.

C. The interactions of the surface properties with the bulk properties of the semiconductor

The catalytic action occur on the surface of the semiconductor. It has already been visualized in the forgoing paragraph that the fundamental chemisorption and catalytic properties of a surface is determined by the position of the Fermi level at the surface. The relation between surface properties, (free electrons concentration, Fermi level in the surface, etc.) and the bulk properties (determinable from Hall-effect measurement, etc.) is an extreme important topic in relating the catalytic properties (surface) and the semiconductivities (bulk) of the materials.

The boundary layer of a chemisorption system is quite similar to the boundary layer of crystal rectifiers in which an electron equilibrium between a metal and a semiconductor exists.

Aigrain and Dugas (32), Hauffe and Engell (33) and Weisz (34) have done some theoretical explorations concerning the rate processes in chemisorption and catalysis from the Schotty-Mott (35) theory.

(1) Boundary layer theory

It has been shown that when a particle is chemisorbed by a free electron or free hole from the crystal lattice, a strong bond is formed between them. Consequently as the surface get charged resulting in the appearance of a space charge in the layer adjacent to the surface of the semiconductor which is opposite in sign to the surface charge and compensates for it. This produces bending of the energy bands near the surface of the semiconductor and thus a boundary layer is formed.

According to Hauffe, there are two kinds of boundary layers, one is "exhaustion boundary layer" which is formed by the chemisorption of anions (cations) on n-type (p-type) semiconductors. This would subsequently reduce the conc. of free electrons in the boundary layer. The other boundary layer known as "inundation boundary layer", is formed by chemisorption of anions (cations) on p-type (n-type) semiconductors. The concentration of free holes in this boundary layer will be increased.

The bending of the bands is shown in Figure 5.
Figure a corresponds to an electrically neutral surface.
Figure b to a positive one (isobutylene gas) and
Figure c to a negative one (oxygen gas).

When electronic equilibrium is established, the surface and the bulk of the semiconductor have a common Fermi level.

In order to evaluate the variation of $\varepsilon - \varepsilon_V$ or the diffusion potential as functions of distance beneath the semiconductor surface. Poisson's equation can be integrated by assuming that the diffusion potential tends to zero in the bulk. In one-dimensional form, the equation for positive charge is:

$$\frac{d^2V(x)}{dx^2} = \frac{d^2(\varepsilon^+ - \varepsilon_V^+)}{dx^2} = \frac{d^2\varepsilon^+}{dx^2} = -\frac{4\pi e}{K} \rho(x, \varepsilon_V^+) \qquad (44)$$

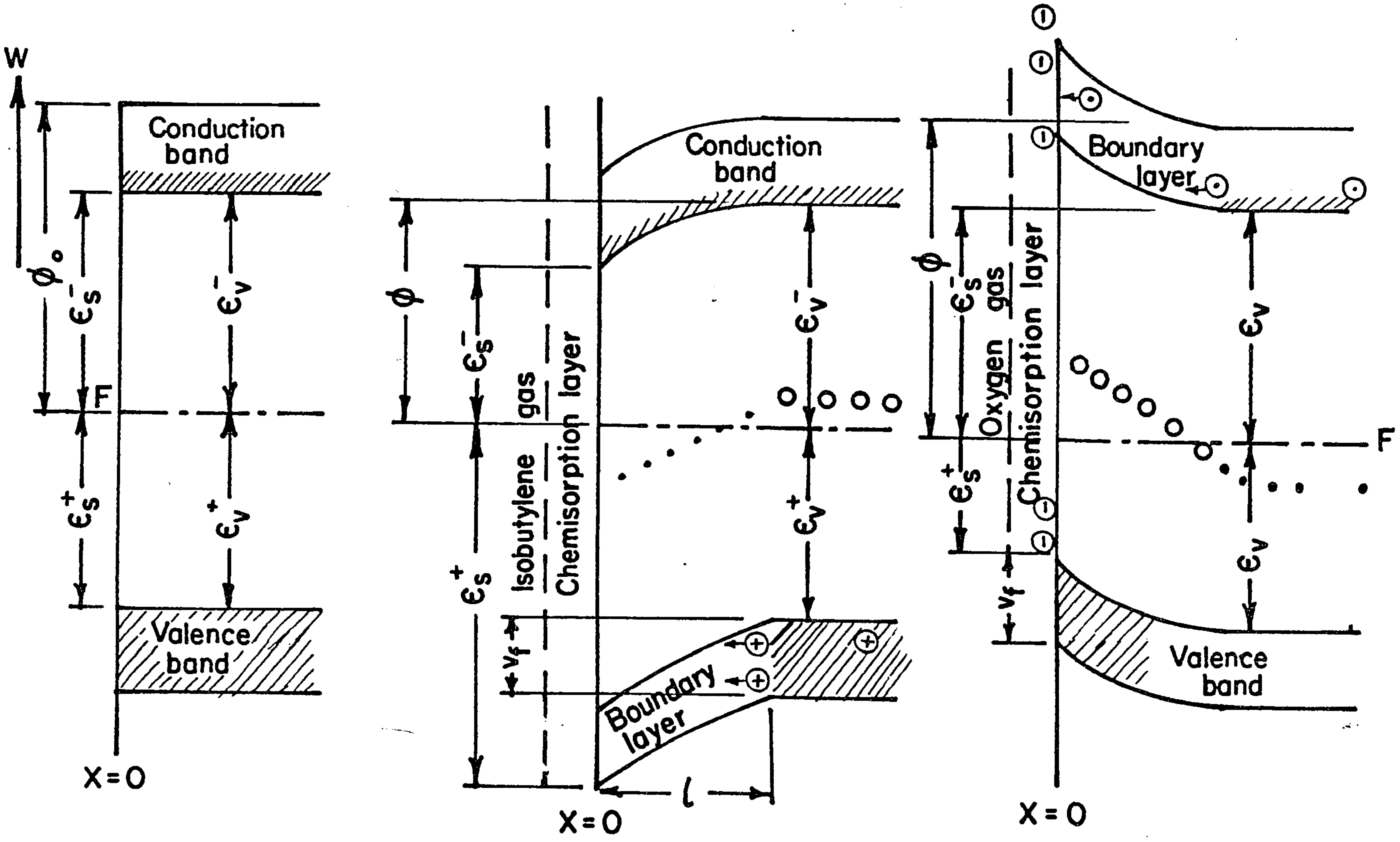


Figure a

Figure b

Figure c

Figure 5 Chemisorption of Gases on Cu_2O

Where $V(x)$ = the potential barrier in the boundary layer statvolts

x = the distance into the bulk from the surface, cm.

k = dielectric constant, dimensionless

$e\rho(x, \varepsilon_v^{+})$ = space charge density, $1/cm^3$.

e = absolute unit charge 4.80×10^{-10} e.s.u.

The total charge density inside the semiconductor (algebraic sum of all fixed charge and all mobile charge) arises from holes and electrons. The net concentration of positively charged space then is:

$$\rho(x, \varepsilon_v^{+}) = (N_{d^+} - N_{a^-}) + p(x) - n(x)$$

where N_{a^-} = concentration of acceptors centers in the bulk acceptors/cm^3

N_{d^+} = concentration of donors centers in the bulk donors/cm^3

$p(x)$ = hole concentration at x holes/cm^3

$n(x)$ = electron concentration at x electrons/cm^3

on the surface the net surface charge is

$$e\sigma = e(\ d\,D^{d+} - \ \ aA^{a-}) \qquad (45)$$

where $e\sigma$ = the net positive surface charge esu/cm^2

D^{d+} = the ionized donors with valence d^+

A^{a-} = the ionized acceptors with valence a^-

By the principle of conservation of charge (electron neutrality) the following condition must be obeyed

$$e\sigma + \int_0^\infty e\rho\ (x)\ dx\ =\ 0$$

or

$$\sigma\ =\ -\int_0^\infty \rho\ (x)\ dx\ =\ (\ \Sigma\ dD^{d^+}\ -\ \Sigma\ aA^{a^-})$$

$$=\ \sigma(p,\ T,\ \varepsilon_s^{\ +}) \qquad (46)$$

now integrating Poisson's equation:

$$\frac{d^2\varepsilon^+}{dx^2}\ =\ -\frac{4\pi e}{k}\ \rho\ (\varepsilon^+,\ x)$$

With the following boundary conditions

$$\varepsilon^+\ =\ \varepsilon_s^{\ +}\quad \text{at}\quad x\ =\ 0$$

$$\varepsilon^+\ =\ \varepsilon_v^{\ +}\quad \text{at}\quad x\ =\ \infty$$

$$\int_0^\infty \rho(x)\ dx\ =\ -\frac{k}{4\pi e}\int_0^\infty \frac{d^2\varepsilon^+}{dx^2}\ dx$$

$$=\ -\frac{k}{4\pi e}\int_0^\infty \frac{d}{dx}\ (\frac{d\varepsilon^+}{dx})\ dx$$

$$=\ \frac{k}{4\pi e}\ (\frac{d\varepsilon^+}{dx})_{x=0} \qquad (47)$$

and

$$\int_{\varepsilon_s^+}^{\varepsilon_v^+} \rho(\varepsilon^+)\, d\varepsilon^+ = -\frac{k}{4\pi e}\int_{\varepsilon_s^+}^{\varepsilon_v^+} \frac{d^2\varepsilon^+}{dx^2}\, d\varepsilon^+$$

$$= -\frac{k}{8\pi e}\int_{0}^{\infty} \frac{d}{dx}\left(\frac{d\varepsilon^+}{dx}\right)^2 dx$$

$$= \frac{k}{8\pi e}\left(\frac{d\varepsilon^+}{dx}\right)^2_{x=0} \qquad (48)$$

combination of equation (47) and (48) yields:

$$\int_{0}^{\infty} \rho(x)\, dx = \left[\frac{k}{2\pi e}\int_{\varepsilon_s^+}^{\varepsilon_v^+} \rho\,(\varepsilon_v^+)\, d\varepsilon^+\right]^{1/2}$$

$$= f(T, \varepsilon_s, \varepsilon_v) \qquad (49)$$

Substituting equation (41) into equation (44), we obtain

$$\sigma(p, T, \varepsilon_s^+) = -f\,(T, \varepsilon_s^+, \varepsilon_v^+) \qquad (50)$$

In order to investigate all possible interrelationships between the charge on the surface and the electrical nature of the semiconductor, it is necessary to consider the different chemisorped particles on different type of semiconductors. This increases the mathematical complexity of solving equation (50).

Several special and limiting cases have been discussed in literature.

In this thesis, a treatment somewhat similar to that of Hauffe has been used to elucide some of the current theories of heterogeneous catalysis.

(ii) The relationship between work function, electrical conductivity and semiconductivity

The appearance of chemisorbed particles on the surface of a semiconductor leads to a change in the magnitude (and sometimes in the sign) of the surface charge. If σ and σ_o be the surface charge in the presence and absence of chemisorbed particles respectively, then

$$\Delta\sigma = \sigma - \sigma_o \tag{51}$$

where $\Delta\sigma$ is the contribution made by the chemisorbed particles.

Due to the change in the surface charge, the bending of the bands are produced, which in turn produces two different effects. The first effect is a change in the work function of the semiconductor. If ϕ_o and ϕ be the work function in the absence and presence of chemisorbed particles respectively, then

$$\Delta\phi = \phi_o - \phi \tag{52}$$

where $\Delta\phi$ is the work function change due to chemisorption. From Figures b and c, it is obvious that if the chemisorbed particles make a positive contribution to the surface charge, i.e. if $\Delta\sigma > o$, then $\Delta\phi < o$, if $\Delta\sigma < o$ then $\Delta\phi > o$.

The other effect due to the bending of the bands is the change in the electrical conductivity of the semiconductor.

Since the electrical conductivity is determined by the concentration of free electrons and free holes in the conduction and valence band respectively, which is in turn determined by the position of Fermi level in the forbidden gap, the bridge between semiconductivity and chemisorptivity is built by the Fermi level.

If I_o and I be the conductivity of the specimen in the absence and presence of chemisorbed particles respectively, then

$$\Delta I = I_o - I \qquad (53)$$

while a positive charge on the surface ($\Delta\sigma > o$) will produce enrichment of the layer adjacent to the surface by electrons and depletion of its holes, a negative charge on the surface ($\Delta\sigma < o$) acts in the opposite way.

It can be concluded therefore that in the case of an n-type semiconductor

$$\Delta I > 0, \quad \Delta\phi < 0 \quad \text{if} \quad \Delta\sigma > 0$$
$$\Delta I < 0, \quad \Delta\phi > 0 \quad \text{if} \quad \Delta\sigma < 0 \qquad (54)$$

and

$$\Delta I > 0, \quad \Delta\phi > 0 \quad \text{if} \quad \Delta\sigma < 0$$
$$\Delta I < 0, \quad \Delta\phi < 0 \quad \text{if} \quad \Delta\sigma > 0 \qquad (55)$$

in the case of a p-type semiconductor.

V. MODIFICATIONS OF CATALYSTS

From the above discussions, it would be seen that the position of the Fermi level at the surface is the key which regulates the concentration of free electrons and free holes on the surface. This concentration in turn regulates the chemisorptivity and activity of a catalyst.

Therefore, any change in the Fermi level at the surface would change the reactivity of a simple reaction and consequently the selectivity of a complex reaction.

The method of preparation, illumination (photocatalysis), heat treatment, application of an external electric field and also the introduction of an impurity could change the Fermi level. In this study, we limit ourselves to the investigation of modification of catalyst by introducing a certain kind of impurity.

The concept of impurity has a broader meaning. Any local disturbance in the strictly periodic structure of the lattice such as vacant sites, foreign atoms replacing the proper lattice atoms, or nature atoms ejected into the interstics or onto the surface of the crystal may be included. The chemisorbed particles whether they participate in the reaction or not can be considered as an impurity in the catalyst.

Using this broad concept of impurities, the two types of impurities can be classified as: acceptor and donor impurities. These impurities play the part of traps, i.e., localization centers for the free electrons or free holes of the lattice respectively.

Impurities play the role of acceptors or donors depending not only on their nature but also on the manner of their inclusion in the lattice; i.e., whether they form an interstitial solution or a substitutional one with the semiconductor. Even in the case of substitutional solution the same impurity may behave as an acceptor or donor impurity depending on the type of the lattice they are dissolved in. While a certain impurity may act as an acceptor at one stage of a reaction with a certain amount of catalyst it may act as a donor at another stage of the reaction with another amount. This concept of impurities is illustrated in more detail in the section, "Discussions of Results".

The introduction of an impurity, whether it is introduced into the interior or its surface leads generally speaking to a displacement of Fermi level at the surface ε_s^+. Surface impurities act directly on ε_v^+ unchanged, bulk impurities change ε_v^+ and thereby produce changes in ε_s^+, provided the particle are not smaller than the screen length (approximate the length of the boundary layer 10^{-4} cm.).

Introduction of acceptor impurities always increase the hole concentration in the valence band, displacing the Fermi level downwards. Donor impurities increase the free electron concentration in the conduction band displacing the Fermi level upwards. For a given surface coverage, we have

$$\varepsilon_s^+ = \varepsilon_s^+ (T, Z)$$

where Z is the concentration of surface or bulk impurity centers.

In the case of an acceptor impurity we have

$$\frac{\partial \varepsilon_s^+}{\partial Z} \leq 0, \qquad \frac{\partial \varepsilon_s^+}{\partial T} \geq 0 \qquad (56)$$

and

$$\frac{\partial \varepsilon_s^+}{\partial Z} \geq 0, \qquad \frac{\partial \varepsilon_s^+}{\partial T} \leq 0 \qquad (57)$$

for the case of a donor impurity.

Extending the meaning of the reaction to the adsorption and desorption process one can classify the reactions into two types:

1) Acceptor or n-type reaction. This is accelerated by the presence of free electrons or by raising the Fermi level.

2) Donor or p-type reaction. This is accelerated by the presence of free holes or by lowering the Fermi level on the surface.

The rate of a given reaction occurring on the surface, g, depends on P, T and $_s^+$ as shown previously

$$g = g(T, \varepsilon_s^+) \tag{58}$$

Hence, from the definition of types of reactions and equation (48) for acceptor or n-type reaction:

$$\frac{\partial g}{\partial \varepsilon_s^+} > o \tag{59}$$

for donor or p-type reaction:

$$\frac{\partial g}{\partial \varepsilon_s^+} < o \tag{60}$$

combining equations (56) and (57) with equations (59) and (60) we can define the impurity as a promotor or poison if

$$\frac{\partial g}{\partial Z} = \frac{\partial \varepsilon_s^+}{\partial Z} \cdot \frac{\partial g}{\partial \varepsilon_s^+}$$

is > or < than o. Consequently a conclusion can be drawn that acceptor reaction are accelerated by a donor impurity and are slowed down by an acceptor impurity. Similarly it would be concluded that the donor reactions would be accelerated by a donor impurity.

IV. SOME SUGGESTIONS

A final quantitative treatment of chemisorption on semiconductor similar with Hauffe's approach (36) for the oxidation of isobutylene is given below, the detailed derivation is given in the appendix.

Since Cu_2O is a kind of p-type semiconductor and oxygen is an acceptor type gas, isobutylene and methacrolein are donor type gases. Thus,

$$C_4H_8\ (g) + \oplus^{(R)} \underset{k_d}{\overset{k_a}{\rightleftharpoons}} C_4H_8^{+}\ (ads.)$$

$$\frac{1}{2}O_2\ (g) \underset{k_{d'}}{\overset{k_{a'}}{\rightleftharpoons}} 2O^{-}\ (ads.) + \oplus^{(R)}$$

At equilibrium

$$C_{C_4H_8^+} = \frac{k_a}{k_d} P_{C_4H_8} \cdot n_{(+)}^{(R)}$$

$$= K_{C_4H_8} P_{C_4H_8} \cdot \exp(-e V_D/kT) \cdot n_{(+)}^{(R)}$$

$$= K_{C_4H_8} P_{C_4H_8} \cdot \left\{\exp\left[-\frac{2\pi e^2}{\kappa\, kT} \frac{(C_{C_4H_8^+})^2}{n_{(+)}^{(H)}}\right] n_{(+)}^{(H)}\right\} \qquad (61)$$

$$C_{O^-} = K_{O_2} P_{O_2}^{1/2} \frac{1}{n_{(+)}^{(H)}} \cdot \exp(- e V_D'/kT)$$

$$= K_{O_2} P_{O_2}^{1/2} \frac{1}{n_{(+)}^{(H)}} \cdot \exp\left\{2 \sinh^{-1} \left[\left(\frac{2\pi e^2}{\epsilon\, kT\, n_{(+)}^{(H)}}\right)^{1/2} \frac{C_{O^-}}{2}\right]\right\} \tag{62}$$

where $C_{C_4H_8^+}$ = the concentration of adsorbed isobutylene.

C_{O^-} = the concentration of adsorbed oxygen.

K_{O_2} . $K_{C_4H_8}$ = the adsorption constants of isobutylene and oxygen, respectively.

$n_{(+)}^{(H)}$ = concentration of free holes in the bulk.

$n_{(+)}^{(R)}$ = concentration of free holes in the boundary layer.

V_D = Fermi level difference between the surface and the bulk.

Equations (51) and (52) show that $C_{C_4H_8^+}$, C_{O^-} are not directly proportional to $P_{C_4H_8}$ and $P_{O_2}^{1/2}$ respectively.

The heterogeneous catalytic reaction

$$A + B \rightleftharpoons C + D$$

is viewed traditionally to occur through the following steps:

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

(ii) Adsorption and desorption of reactants and products.

(iii) Surface reaction.

We modify these steps from the view of theory of electron transfer. Besides diffusion, other steps concerned are as follows:

(i) Adsorption and desorption of reactants and products. (Physical adsorption and weak chemisorption).

(ii) Surface reaction includes

a) Electron transfer to or from the reactants (Strong chemical bond formation).

b) Homogeneous reaction (Formation of activated complex and rearrangement of the charged particles on the surface).

c) Electron transfer to or from the products.

We propose the following two hypothesis: firstly, to treat the free electrons or holes as one of the reactants and the electron transfer step is also considered as a chemical reaction. Therefore, the active center on the surface is not limited to one kind and the total number is not necessarily constant. In reality, there are two kinds of active centers, free electrons and free holes respectively. The concentration of free electrons and free holes would affect the reactivity and selectivity of a reaction and the concentration of these carriers do not only depend on the presence of different amount of impurities but also on the operating conditions such as temperature, feed composition, space velocity or contact time etc.

Secondly, it is proposed that the surface reaction can only occur between the charged particles and that Rideal mechanism is only a special and limiting case of Langumuir-Hinshelwood mechanism. In such reactions one of the reactants (i.e. A) is very rapidly charged, or K_A' (the adsorption constant of A in Hougen-Watson type approaches) is negligibly small as compared with the other terms in the overall rate expression. The oxygen adsorption in many oxidation reactions and hydrogen adsorption in various hydrogenation processes are but few examples of the surface reactions.

The electron transfer step could be accelerated or deaccelerated by modifying the catalyst surface through the introduction of a certain amount of impurity and change of the operating conditions.

With these two hypothesis the following conflicts could be solved.

Firstly different reaction orders and activation energies observed by different researchers is due to the fact that usually the power law

$$v' = k' P_A^{m'} P_B^{n'} \tag{63}$$

is used instead of the real one

$$v = k C_{A^+}^{m} C_B^{n} \tag{64}$$

From equations (61) and (62) we have known C_{A^+} is linearly proportional to P_A, ... only under the special and limiting case in general $C_A = C$ (T, Z, K_A and other operating conditions).

Therefore the existing conflicts is obviously appeared.

Secondly the different reaction mechanisms of the same reaction but at different operating conditions are reported in the literature. This is due to the fact that in the traditional approach, the importances of the properties of the catalyst surface (i.e. free electron and hole concentration) to the individual steps of the reaction have been completely ignored. Some experimental evidence to support this point of view will be given in the section "Discussions of Results".

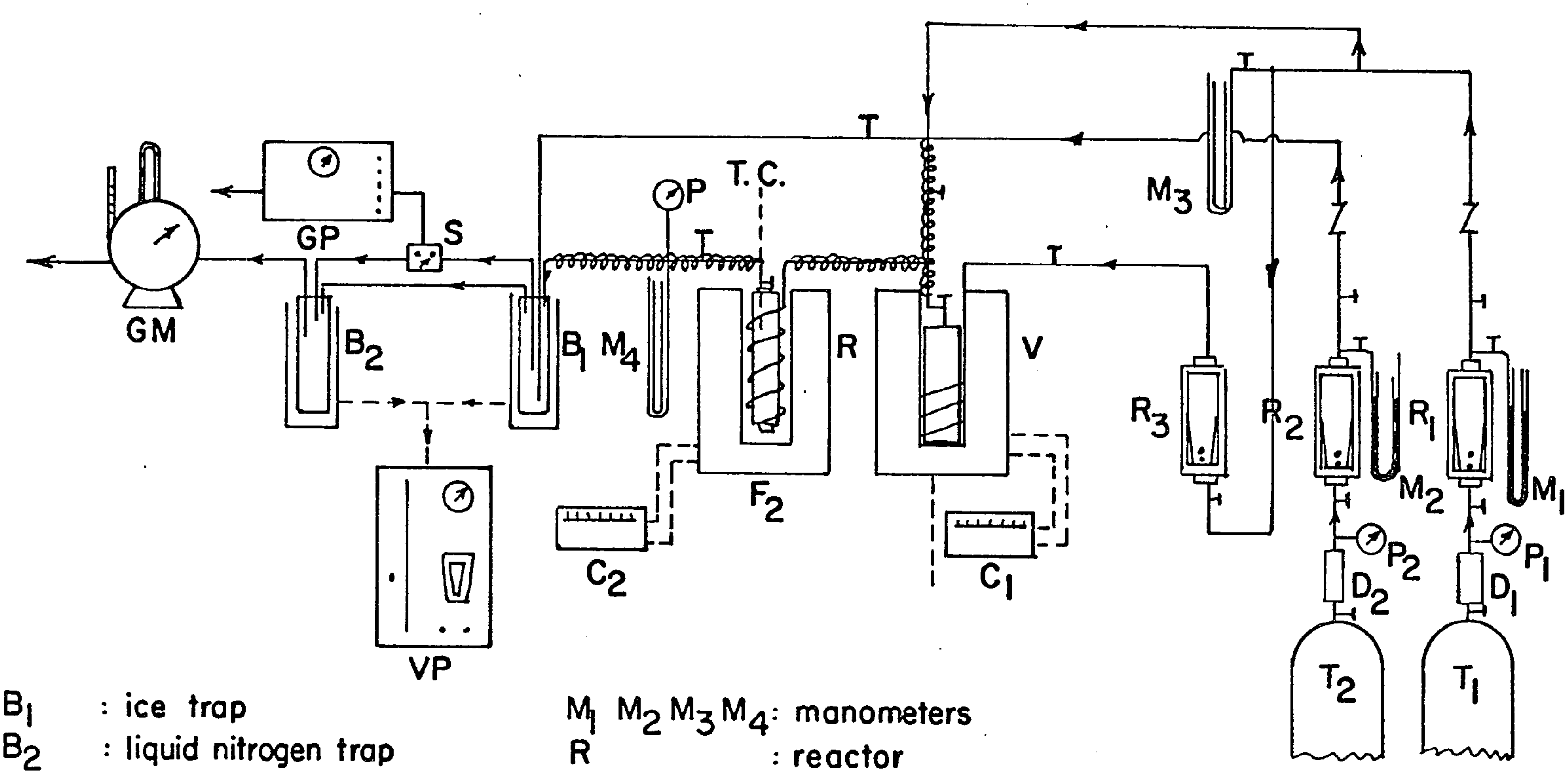
V EXPERIMENTAL

I. APPARATUS

The partial oxidation of isobutylene to methacrolein in the constant and continuous supply of selenium dioxide was investigated in a flow system. The apparatus used is shown in Figure 6.

The reactants dry air and c.p. grade isobutylene with minimum purity of 99% were obtained from high pressure cylinders, through a series of high pressure diaphram type regulators, whereby the pressure of air and isobutylene were reduced to 20 psig. The compressed gases were passed through tubes containing indicating drierite to remove any possible trace amount of moisture. The gas lines, made out of $\frac{1}{8}$ in. O.D. 316 stainless steel tubing, were immersed in a constant temperature bath prior to their passing through the rotameters. The various pressure fittings used in the equipment were made of 316 stainless steel and were capable to withstand pressures of 5000 psia. The flow rates were measured by Matheson rotameters.

Each rotameter was connected with a mercury manometer so that the pressure and temperature effect on the gas flow rates could be corrected. Two streams of air were used; one stream was passing through the selenium dioxide vaporizer to carry the selenium dioxide vapor and the other stream was bypassed. These three gas streams were mixed before they entered the preheating section.



B_1 : ice trap
B_2 : liquid nitrogen trap
C_1 C_2 : temperature controllers
D_1 D_2 : drying tubes
F_1 F_2 : furnaces
V P : Vapour fractiometer
GP : gas partitioner
GM : wet gas meter

M_1 M_2 M_3 M_4: manometers
R : reactor
R_1 R_2 R_3 : rotameters
P_1 P_2 P_3 : pressure gauges
S : sampling valve
T_1 : air tank
T_2 : isobutylene tank
V : selenium vaporizer

Figure 6 Schematic Diagram of Apparatus

The selenium dioxide vaporizer was made of 6 in. long, 1 in. O.D. 304 stainless steel tubing with a Swagelok connection on the top. A 1 in. long glass tube was put in the vaporizer. About 10 grams of selenium dioxide was placed inside the tube. Details of the vaporizer are shown in Figure 7. The vaporizer was heated by an electric furnace. The temperature of the furnace was controlled to within ± 1°C by a Honeywell Pyr-o-vane temperature controller. Two Chromel constantan thermocouples touched the bottom of the vaporizer for control and measurement of temperature. Between the vaporizer and the preheating section, the line was heated by a heating tape. The temperature of the preheated section was maintained a little higher than the vaporizer in order to prevent the possibility of selenium dioxide vapor condensing in the lines. The preheating section, which was immersed in a constant temperature liquid metal bath, consisted of a 6 ft. long, $\frac{1}{8}$ in. O.D. 316 stainless steel tubing wound around the reactor which was made of a 6 in. long, $\frac{1}{2}$ in. O.D. 304 stainless steel tubing. Details of the preheater and reactor are shown in Figure 8. The gases entered the reactor at the bottom through a porous stainless steel plate which served as a support for the catalyst. The catalyst granules of 20-40 mesh size were kept in space by plugging loosely some glass wool at the top. The liquid metal bath consisted of a mixture of 50% bismuth and 50% lead by weight. The metal mixture was heated by an electrical furnace. The temperature of the furnace was controlled to within ± 1°C by another Honeywell temperature controller.

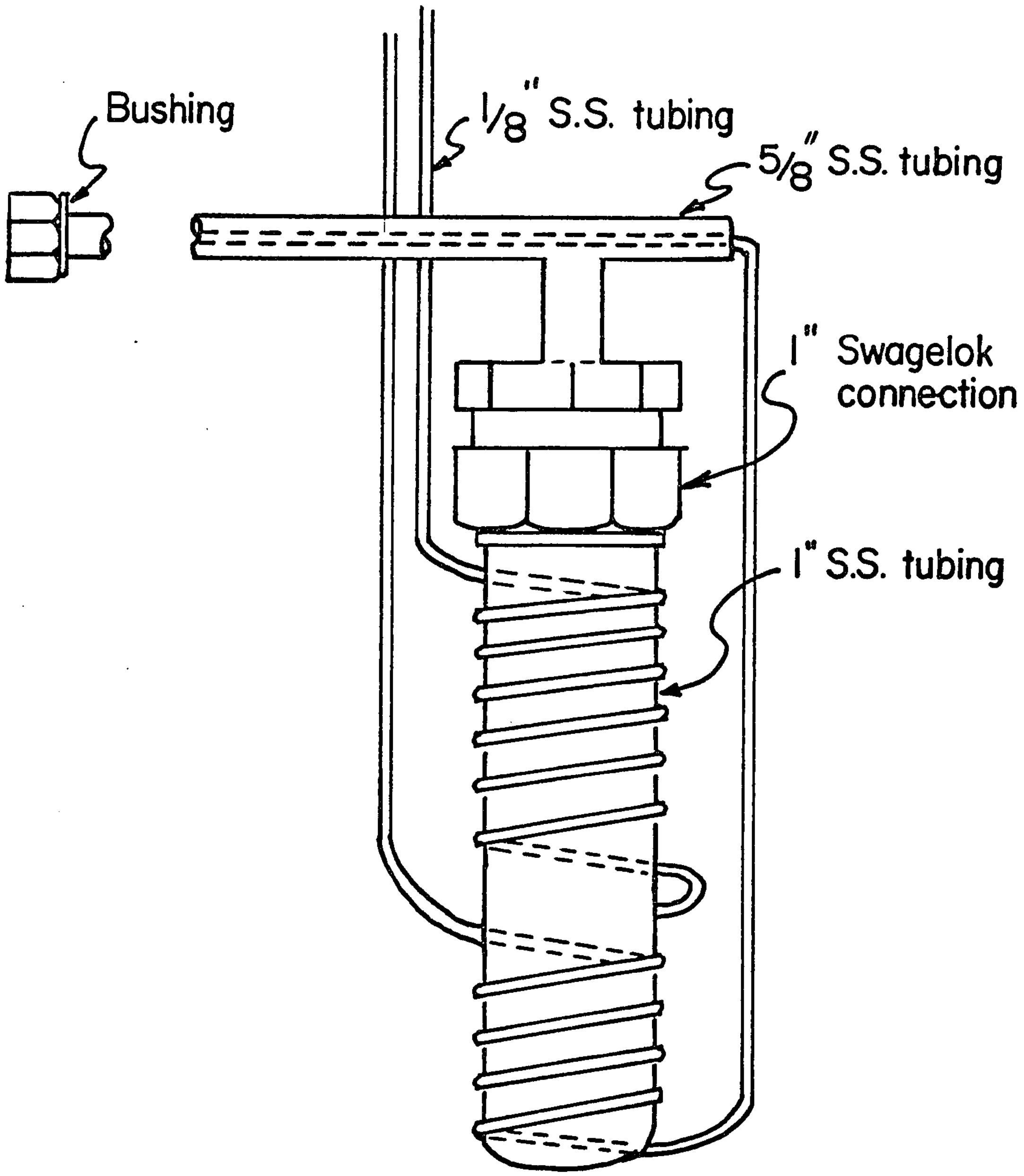


Figure 7. Selenium Dioxide Vaporizer

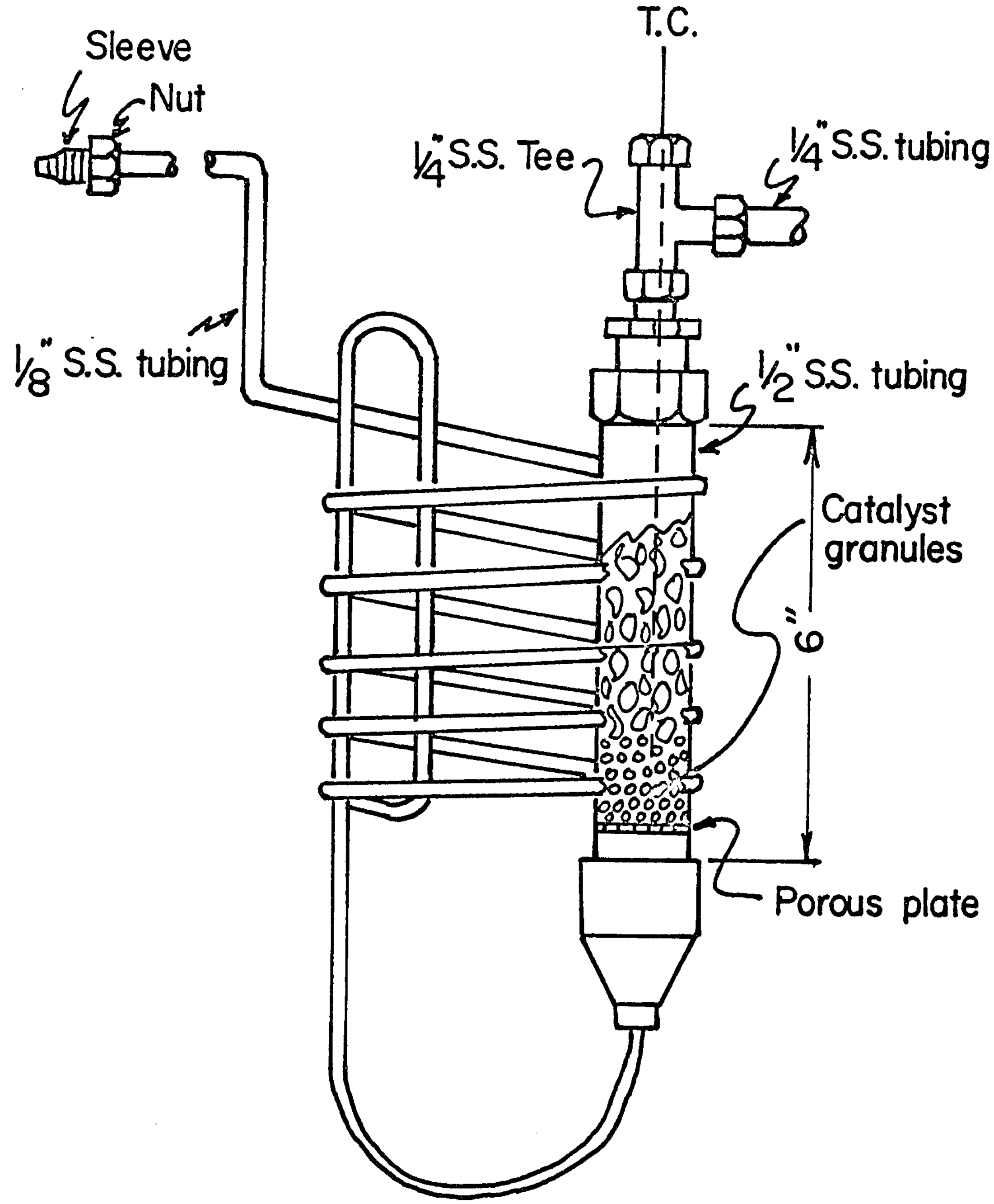


Figure 8 Preheater and Reactor

The design of the reactor was such that the reaction took place more or less under isothermal conditions. Blank runs were made with an iron-constantan thermocouple inserted inside the reactor. At high flow rates of gases, no temperature difference was observed between the metal bath and the inside of the reactor which indicated that the preheating section was long enough to heat the gases entering the reactor to the desired reaction temperature. Comparisons were also made with the reactor filled with the catalyst and under a high conversion. The highest temperature difference obtained in this case was about 4°C. Although the oxidation of isobutylene to methacrolein is a highly exothermic reaction, the rate of heat transfer through the metal wall of the reactor was high enough to maintain the reaction near isothermal conditions.

The exit gases from the reactor were first led to an air condenser where selenium dioxide was removed and then through an ice cooled trap where acids, water and a small portion of the aldehydes condensed. The non-condensed gases were passed through a gas sampling valve leading to a Fisher gas partitioner which could analyze carbon dioxide, oxygen, nitrogen, methane, isobutylene and carbon monoxide. The off gases from the sampling valve were passed through a liquid nitrogen trap, where the remainder of the aldehydes, which did not condense at ice temperature were condensed.

II. REAGENTS

A. Isobutylene

A Matheson c.p. grade isobutylene gas with a minimum purity of 99% was used. The gas was received in cylinders containing 40 lbs. of liquid isobutylene at a pressure of 23 psig (70°F). It was found from the analysis of isobutylene on the gas chromatograph that the main impurities in the isobutylene were isobutane, n-butane and a cis and trans--butylenes. These impurities were in such minor quantities, that they did not interfere with the experimental accuracy.

B. Air

The air used was supplied by the Linde Company in compressed cylinders at a pressure of 2500 psig. The gas chromatograms of air showed that it contained 20.95% oxygen, 79.00% nitrogen and trace amount of carbon dioxide.

C. Selenium dioxide

The reagent grade selenium dioxide was obtained from Matheson Coleman and Bell Company.

D. Diethyl ether

A spectrograde diethyl ether was obtained from Eastman and Kodak Company.

E. Cupric nitrate $Cu(NO_3)_2 3H_2O$

A reagent grade cupric nitrate meeting the A.C.S. specification was obtained from Baker Chemical Company.

III. CATALYST

The pumice supported copper oxide catalyst with 16% by weight of copper was prepared by impregnating 20-40 mesh crushed pumice stone, supplied by Fisher Scientific Company with copper nitrate solution, the pumice stones were cleaned by boiling with concentrated hydrochloric acid for half an hour and washed with warm distilled water until the addition of a 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 in an oven at 105°C for at least 10 hours at 550°-600°C 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.

The activity of the catalyst was verified periodically by passing a specified mixture of isobutylene and air over the catalyst and determining the percentage conversion of isobutylene. In each case, the conversion of isobutylene never varied by more than 5%.

IV. OPERATING PROCEDURES

A. Leakage test

The system was tested for any leaks in the following way:

(i) There was no indication of pressure drop in the system within a few hours when the inlet and outlet valves were closed.

(ii) No indication of gas flow through the rotameter as the downstream valve was closed.

(iii) Every connection part was tested by soap solution.

B. Calibrations

(i) Rotameters

Rotameters were calibrated against an American Gas Company's Wet test meter and re-checked with the water displacement method to obtain a relationship between the floats position and the volumetric flow rate of the gases. The pressure and temperature effects on the flow rate were measured by the attached manometers and the temperature of the bath respectively. These measurements were consequently corrected to standard temperature and pressure conditions. The calibration curves are shown in appendix D .

(ii) Rate of selenium dioxide

The flow rate of the incoming air was fixed. Different amounts of selenium dioxide were carried in the air stream by changing the temperature of the vaporizer. After steady-state was reached, the selenium dioxide vapor was condensed in a weighing bottle filled with glass wool which was immersed in a dry ice trap. After certain time, the weighing bottle was removed and dried in the desicator and the weight of condensed selenium dioxide was obtained by the chemical balance. A calibration curve is shown in appendix D. At low concentrations of selenium dioxide, direct measurement became difficult and then the extrapolated values were used.

C. Experimental runs

Before starting runs with a catalyst a series of blank runs without catalyst were performed. It was found that in the temperature rang 350°-450°C and in the absence of catalyst, no methacrolein was formed and no isobutylene reacted. For the start of a run, air was slowly passed through the reactor while the catalyst and the selenium dioxide vaporizer was brought to the required temperature. When the required temperature was attained, isobutylene was added to the feed and the flow rates of isobutylene and air were adjusted so as to give the desired total flow rate and molar ratios of oxygen/isobutylene in the feed. The gases were maintained at their specified flow rates during the runs. After the steady state conditions had been reached, the first trap was immersed in a freezing mixture of ice and water and the second in liquid nitrogen.

The steady states run was continued for one hour during which time the isobutylene and air flow rates were constantly kept at their specified values. During the course of reaction, the exit gases from the reactor were periodically injected into the Fisher gas partitioner. In this way the composition of the gaseous products were determined from time to time. As average value of the compositions were used for calculation of rates. At the end of one hour, the isobutylene feed was shut off. The sample from the two traps were collected, weighed and analyzed. The air was kept flowing through the catalyst bed for one hour to purge the catalyst before the start of the second run.

V. ANALYSIS OF THE PRODUCTS

A. Acids

The total acid content was obtained by titration of the condensate from the ice cooled trap with 0.05 N KOH solution, phenolphthalein was used as indicator. The total acid content was very low and too insignificant to affect the material balance. Therefore, it is not included in the analysis of the products from the gas chromatogram. The condensate was found to contain minor quantities of aldehydes and acids.

B. Gases

The inlet feed gas and the gaseous products were analyzed for carbon dioxide, oxygen, nitrogen, isobutylene and carbon monoxide by periodic injection of approximately 3 ml. sample into the Fisher gas partitioner containing a 6 ft. hexamethyl phosphoramide column and a 13 ft. 13 X molecular sieve column connected in series. A typical analysis of the products from the gas partitioner is given in appendix D. The composition of various gases from the reactor was determined by comparing the peak heights with those calibrated gas chromatogram which was made by blending a known composition gases mixtures. The various calibration curves for the percent compositions of carbon dioxide, carbon monoxide, oxygen and isobutylene is shown in appendix D. Nitrogen was obtained by difference since it was an inert gas in this reaction. Peak heights were used for determining the quantity of the gases instead of the peak area. This procedure was adopted as the peaks for all gases were very sharp and narrow. The error involved was around ± 2%.

C. Aldehydes

Since the sample from the liquid air trap was volatile, volume of the liquid sample could not be measured accurately. In order to overcome this difficulty, the sample from the liquid air trap was diluted with approximately 12 ml. diethyl ether and placed in a constant temperature vessel which was kept at approximately 5°C. After 3 hours temperature equilibrium was reached. Around 3 µl. of the mixture was injected into a 154 D Perkin-Elmer gas fractometer containing two 4 meter columns of carbowax 1500 on Teflon. The column used could separate several saturated and unsaturated aldehydes and water. However, methacrolein was the only product observed in the liquid sample except for traces of acrolein. A typical analysis of methacrolein from the Perkin-Elmer gas chromatograph is shown in appendix D. The molal ratio of ether to methacrolein was obtained by comparing with the calibration curve in which the molar ratio has been plotted against peak height ratio. By following this procedure, the inaccuracy due to sample volume was avoided. A calibration curve is shown in the appendix D. The error was within ± 3%.

VI. SAMPLE CALCULATION

Feed rates were calculated on the basis of the rotameter readings and the effects of pressure and temperature were corrected. The effluent rates were computed on the basis of the nitrogen fed and on the percentage composition of the reaction products. Since the moles of nitrogen in the feed and in the effluent stream were the same, the percent composition of nitrogen in the product gas was used as a constant denominator in calculating the molal effluent rate of the gases. All the experiments were carried out at atmospheric pressures.

A sample calculation is given in appendix E.

VI RESULTS AND DISCUSSIONS

The effect of different weight percentage of selenium dioxide in the supported copper oxide catalyst, oxygen (in the air/isobutylene ratio in the feed, operating temperatures on the conversion of isobutylene and the rates of formation of various product i.e., carbon dioxide, water and methacrolein was investigated between 350°C to 425°C.

While conversion is referred as the ratio of moles of isobutylene reacted per hour to the moles of isobutylene fed per hour, the rate of formation is referred as the moles of various products formed per hour per gram weight of catalyst.

The weight of the catalyst and the isobutylene charged into the feed were maintained constant during the runs. A different feed composition ratio was obtained by adjusting the air flow rate.

The effects of weight percentage of selenium dioxide in the catalyst on the conversion and rates of formation for a W/F = 1.6800 at 425°C, 400°C, 375°C and 350°C are shown in Figures 9-12, 13-16, 17-20 and 21-23 respectively. The data for this is given in appendix F. The feed ratio was varied between 0.7168 and 1.6644.

The conversion of isobutylene increased rapidly with the increase of selenium dioxide up to 0.15% by weight of catalyst and then slightly decreased with increase of selenium dioxide.

The rate of carbon dioxide formation decreased slowly in the beginning and then decreased rapidly with the increase amount of selenium dioxide up to 0.45% by weight of catalyst.

The rate of water formation increased slowly with the increased concentrations of selenium dioxide up to the range 0-0.15% by weight of catalyst and then decreased.

On the other hand the rate of methacrolein formation increased steadily until a 0.45% selenium dioxide content was reached, after that it slightly decreased.

The selectivity for methacrolein which is defined as the percentage of moles of methacrolein produced per hour to the total moles of products formed per hour is calculated and tabulated in appendix F. In Figures (9) - (23) are shown the effect of different amounts of selenium dioxide on the selectivity of the catalyst for methacrolein formation.

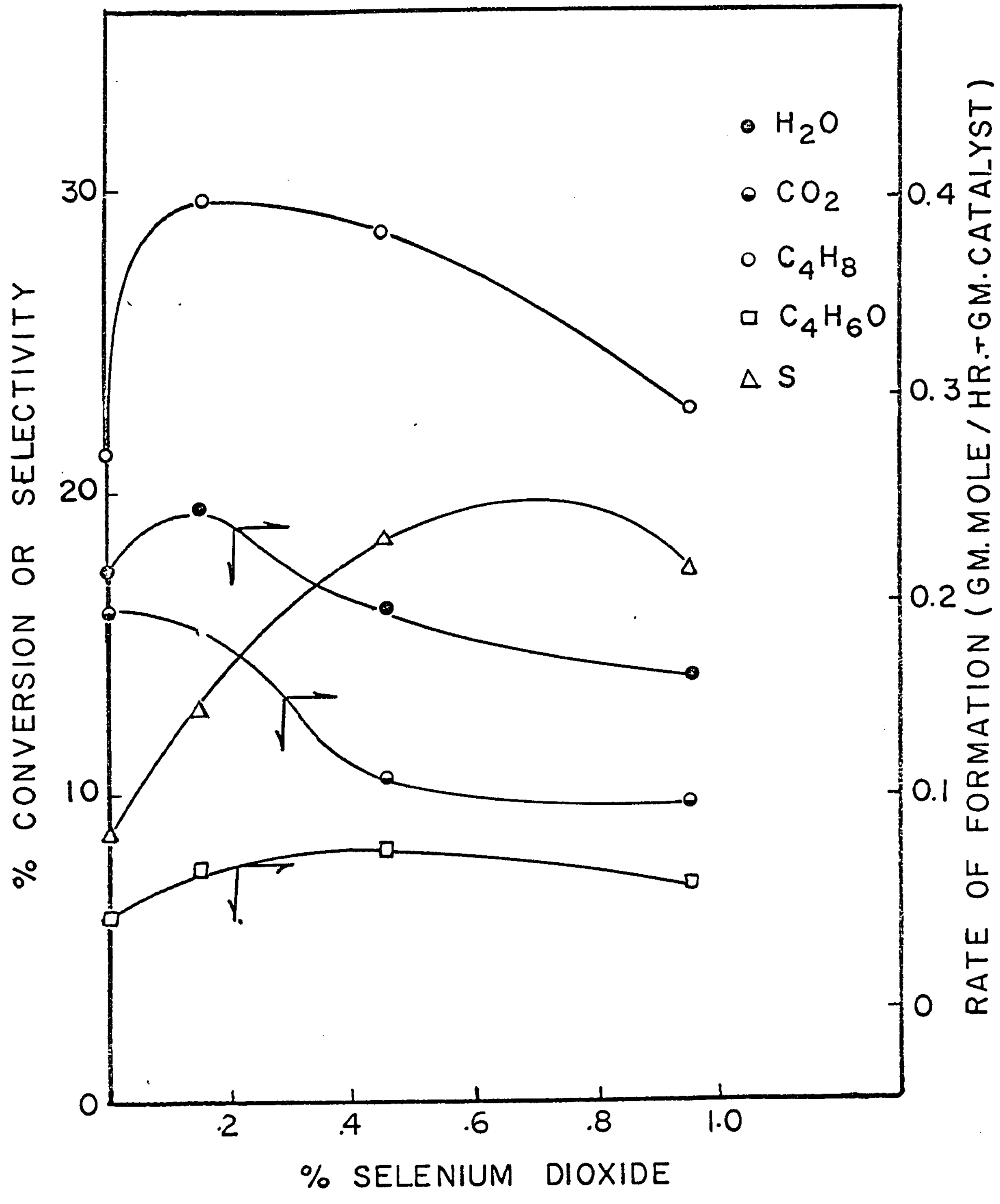


Figure 9 Effect of Selenium Dioxide on Conversion, Rate of Formation and Selectivity at 425°C for R = 0.7168

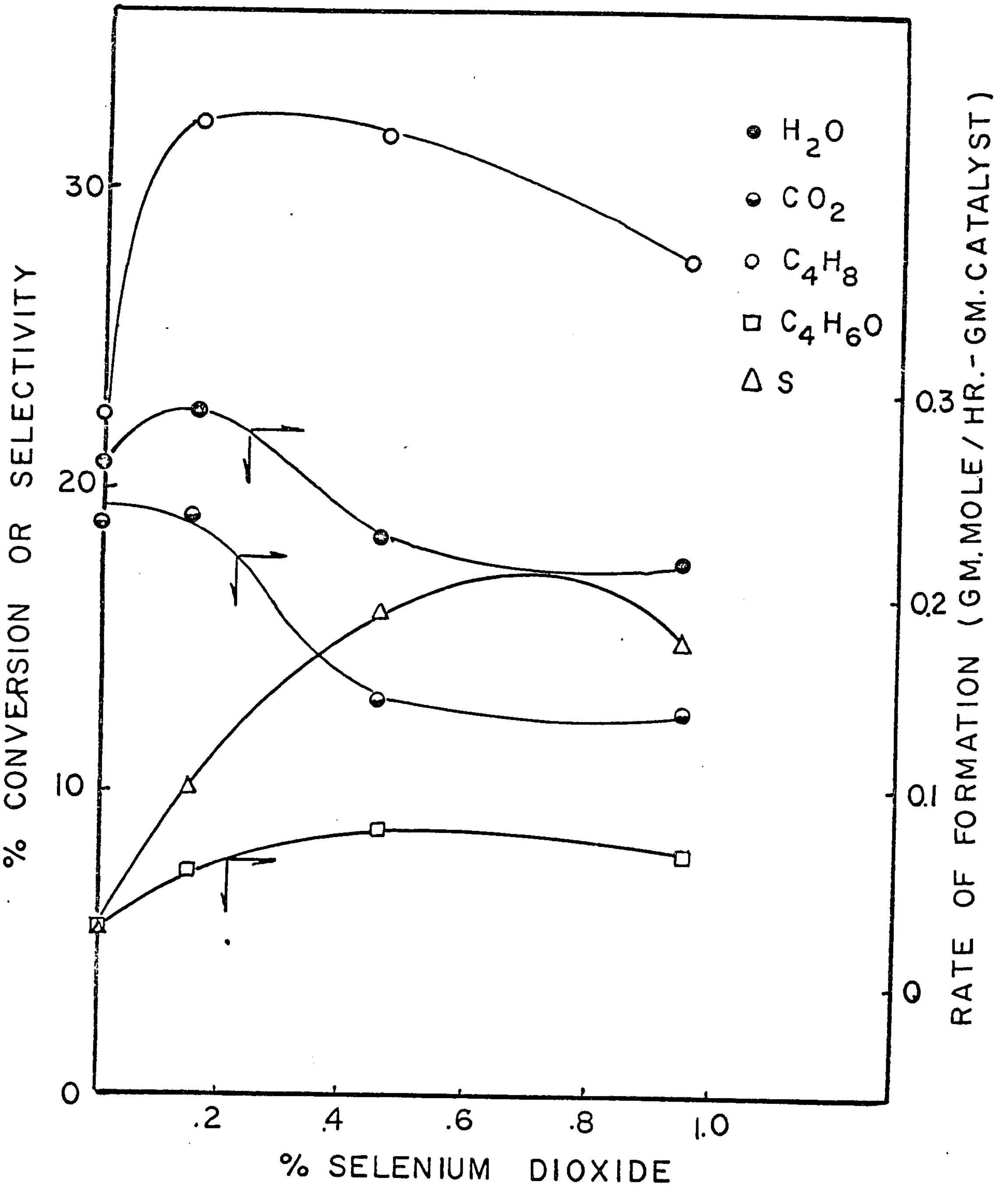


Figure 10 Effect of Selenium Dioxide on Conversion, Rate of Formation and Selectivity at 425°C for R = 0.9910

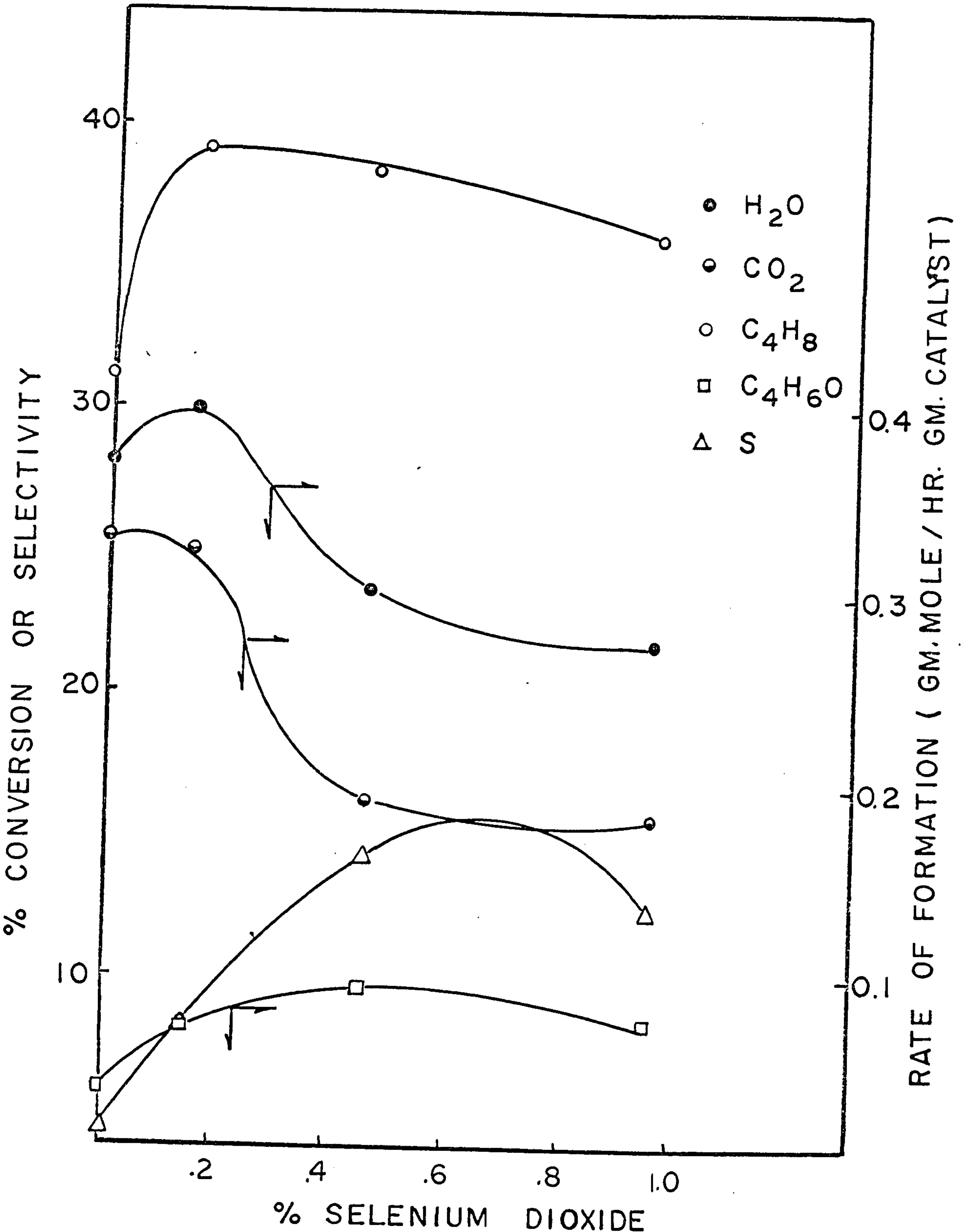


Figure 11 Effect of Selenium Dioxide on Conversion Rate of Formation and Selectivity at 425°C for R = 1.3746

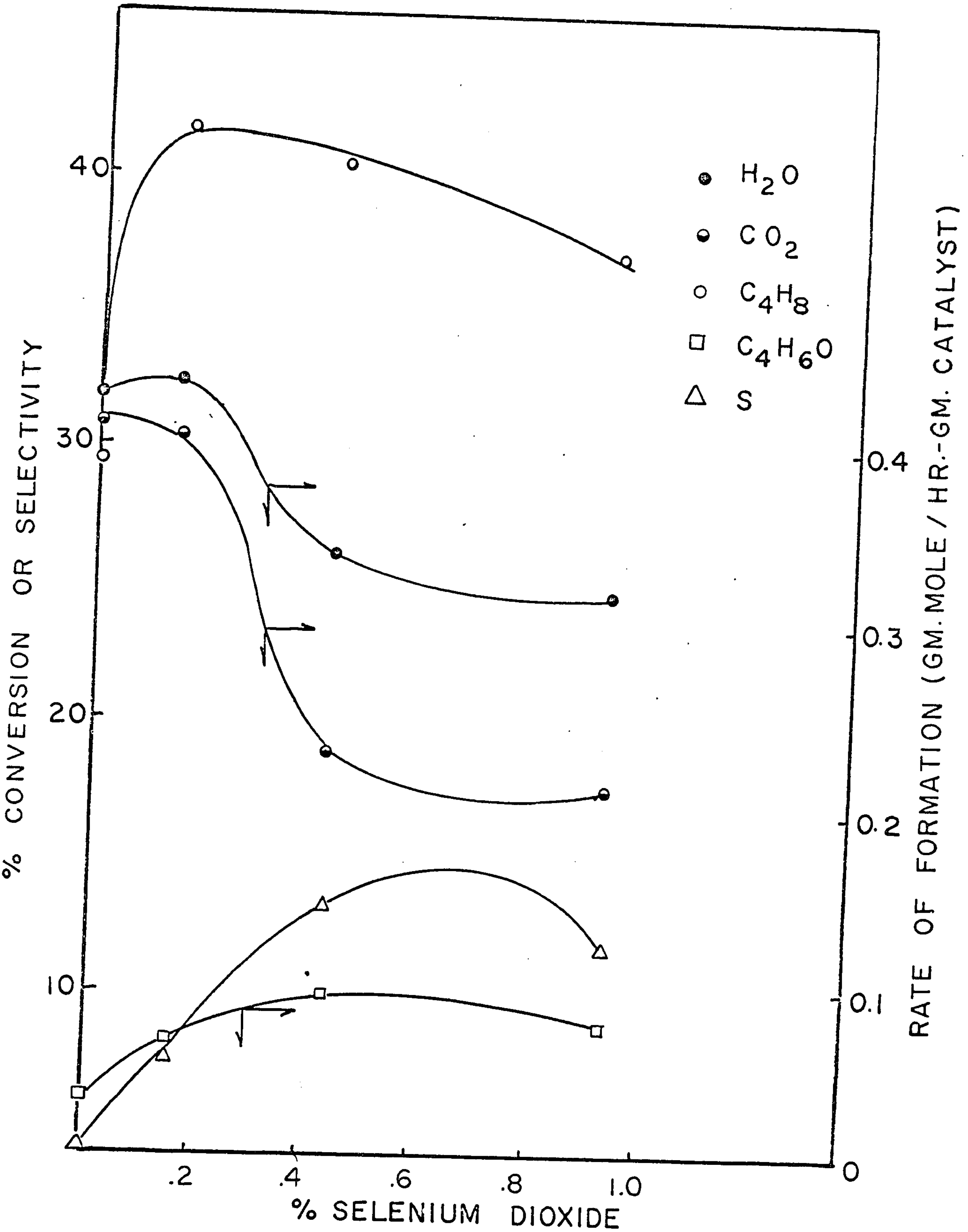


Figure 12 Effect of Selenium Dioxide on Conversion, Rate of Formation and Selectivity at 425°C for R = 1.6644

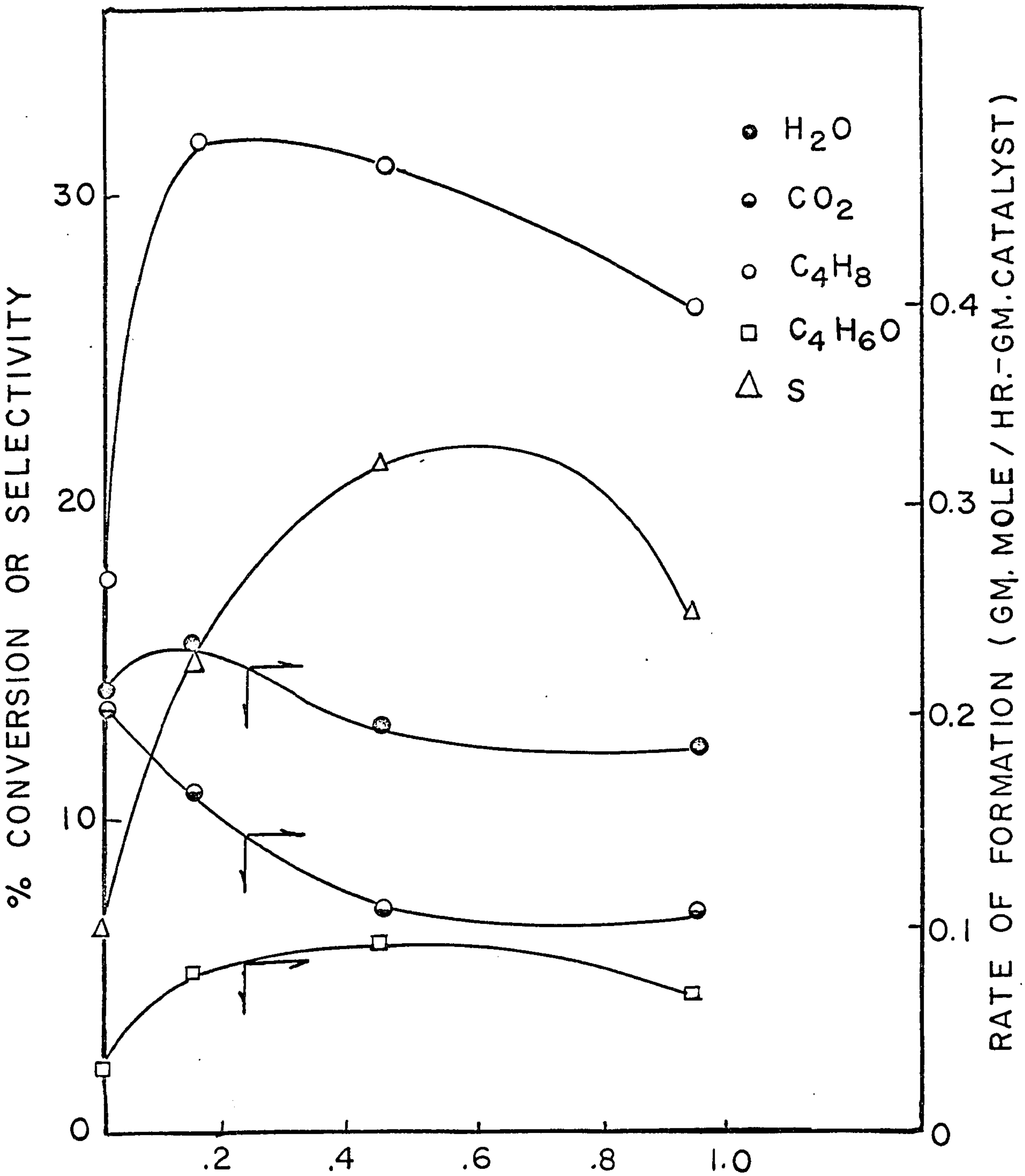


Figure 13 Effect of Selenium Dioxide on Conversion Rate of Formation and Selectivity at 400°C for R = 0.7168

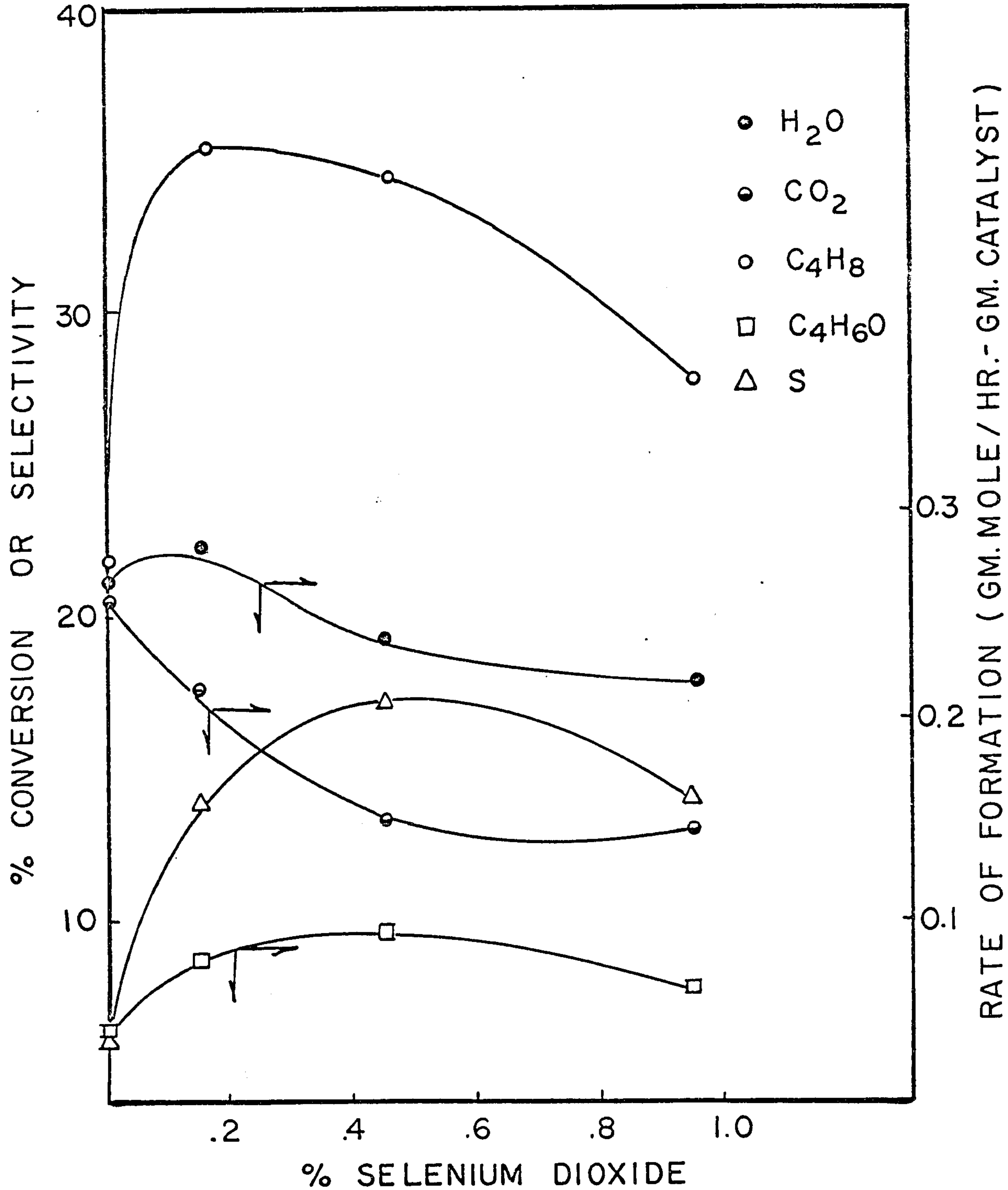


Figure 14 Effect of Selenium Dioxide on Conversion Rate of Formation and Selectivity at 400° C for R = 0.9910

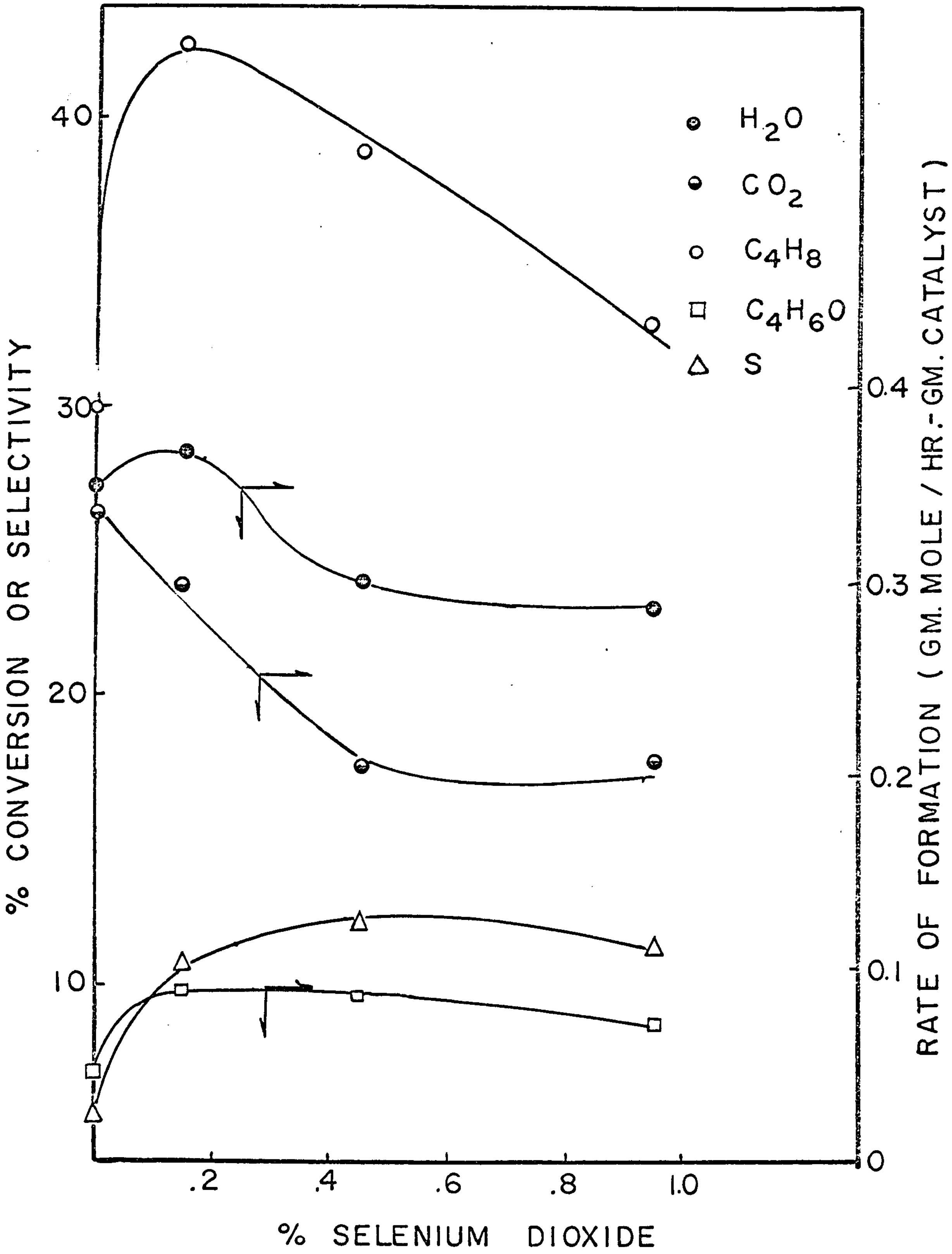


Figure 15 Effect of Selenium Dioxide on Conversion Rate of Formation and Selectivity at 400° C for R = 1.3746

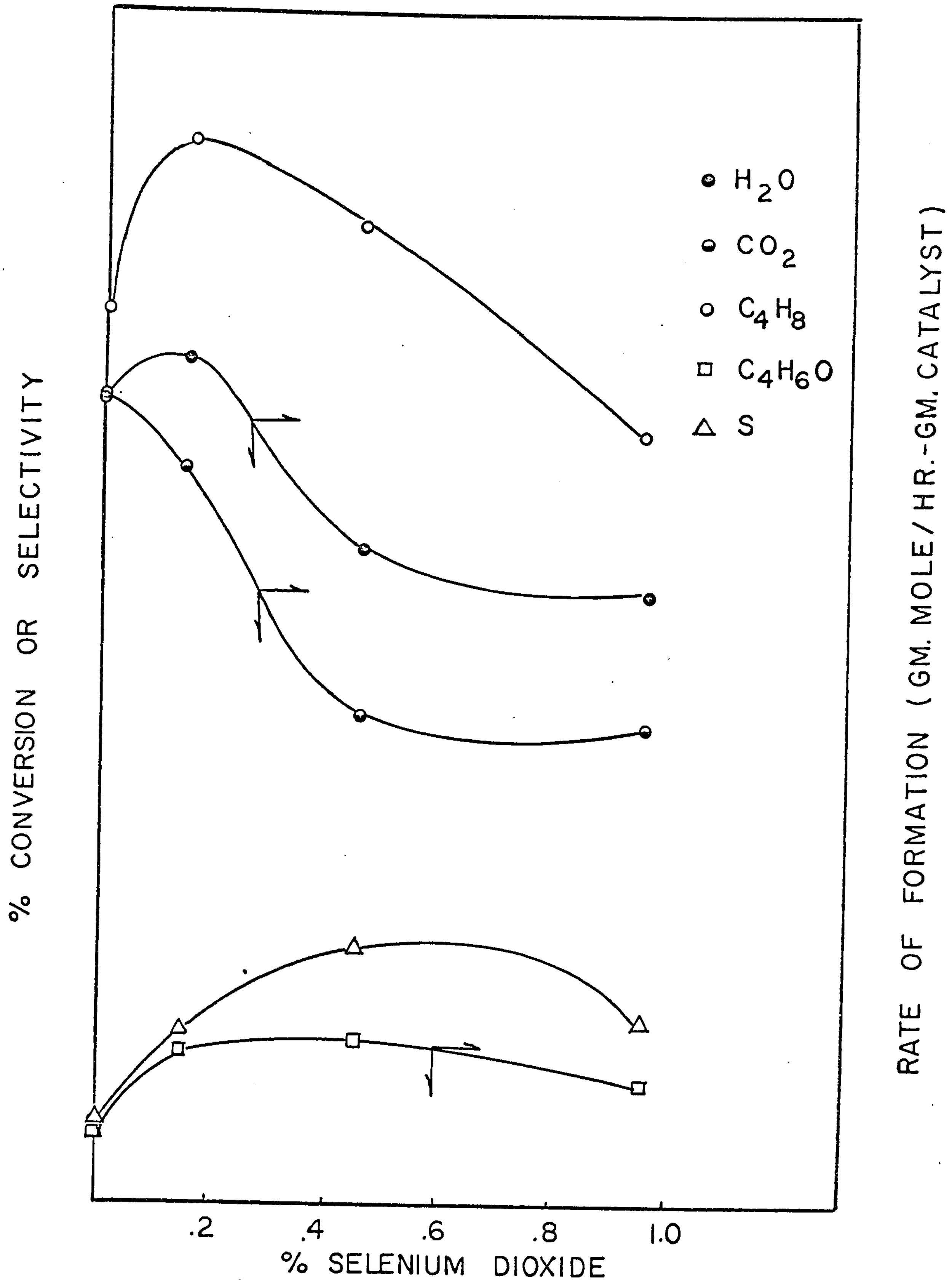


Figure 16 Effect of Selenium Dioxide on Conversion Rate of Formation and Selectivity at 400° C for R = 1.6644

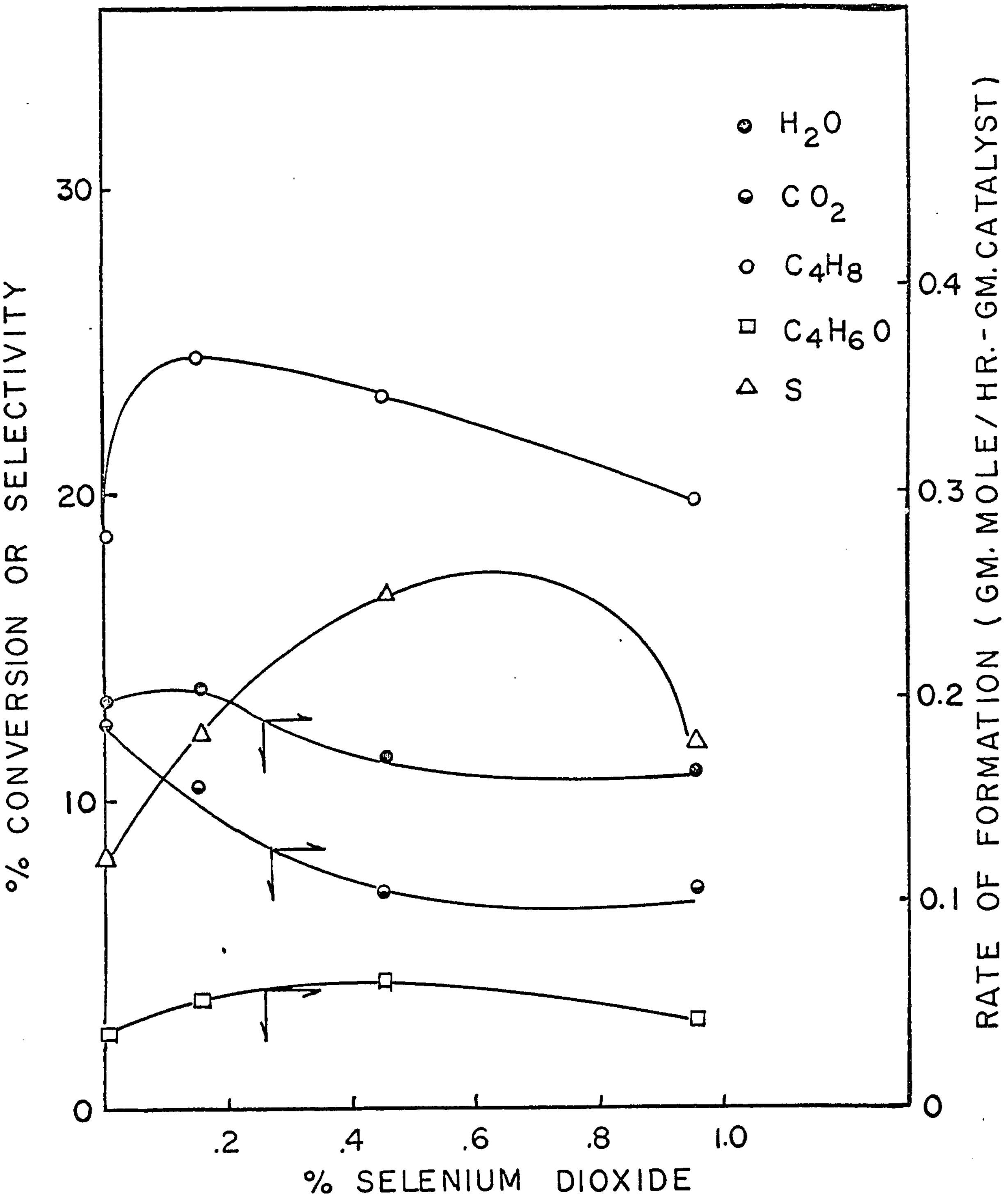


Figure 17 Effect of Selenium Dioxide on Conversion Rate of Formation and Selectivity at 375° C for R = 0.7168

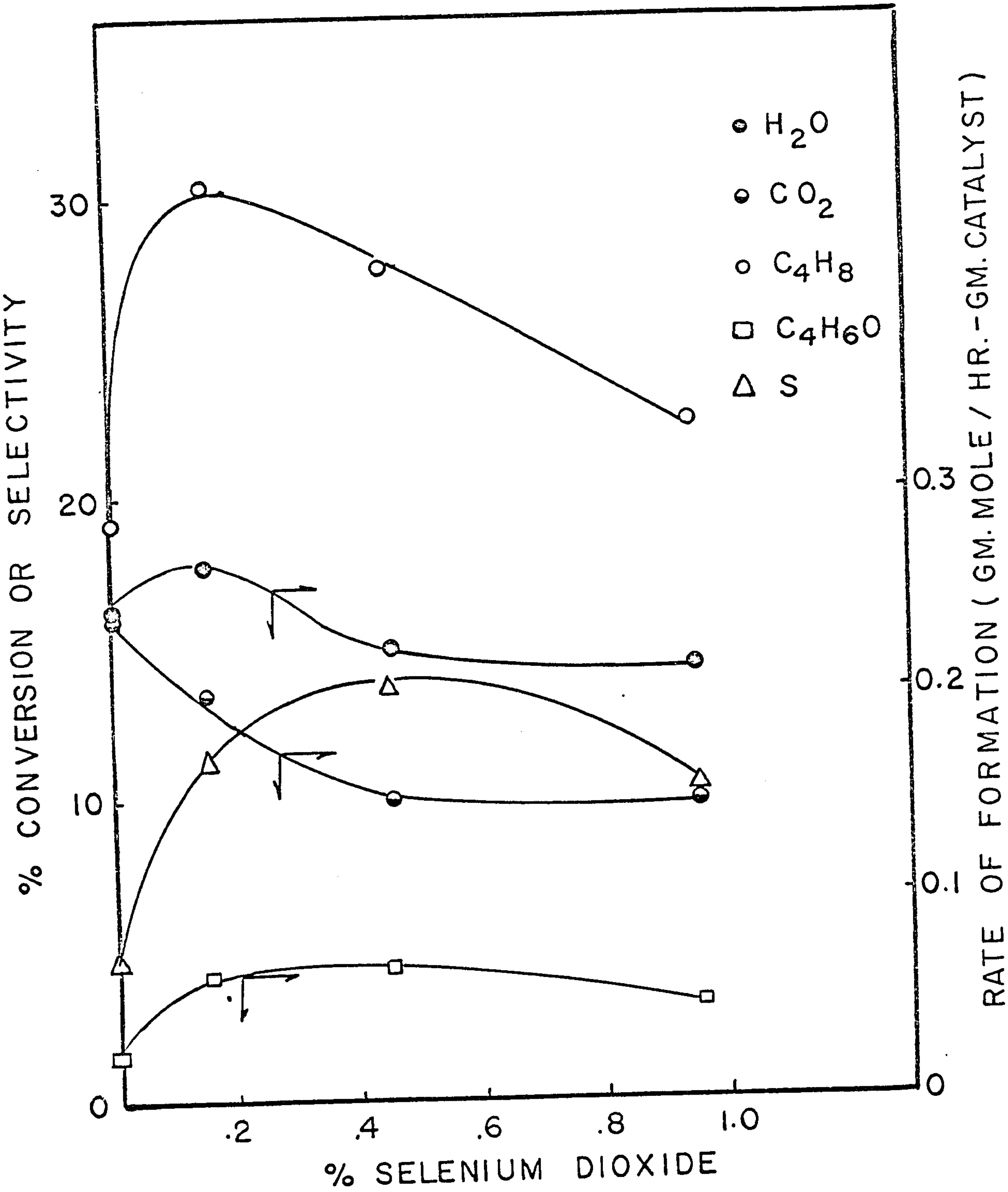


Figure 18 Effect of Selenium Dioxide on Conversion Rate of Formation and Selectivity at 375°C for R = 0.9910

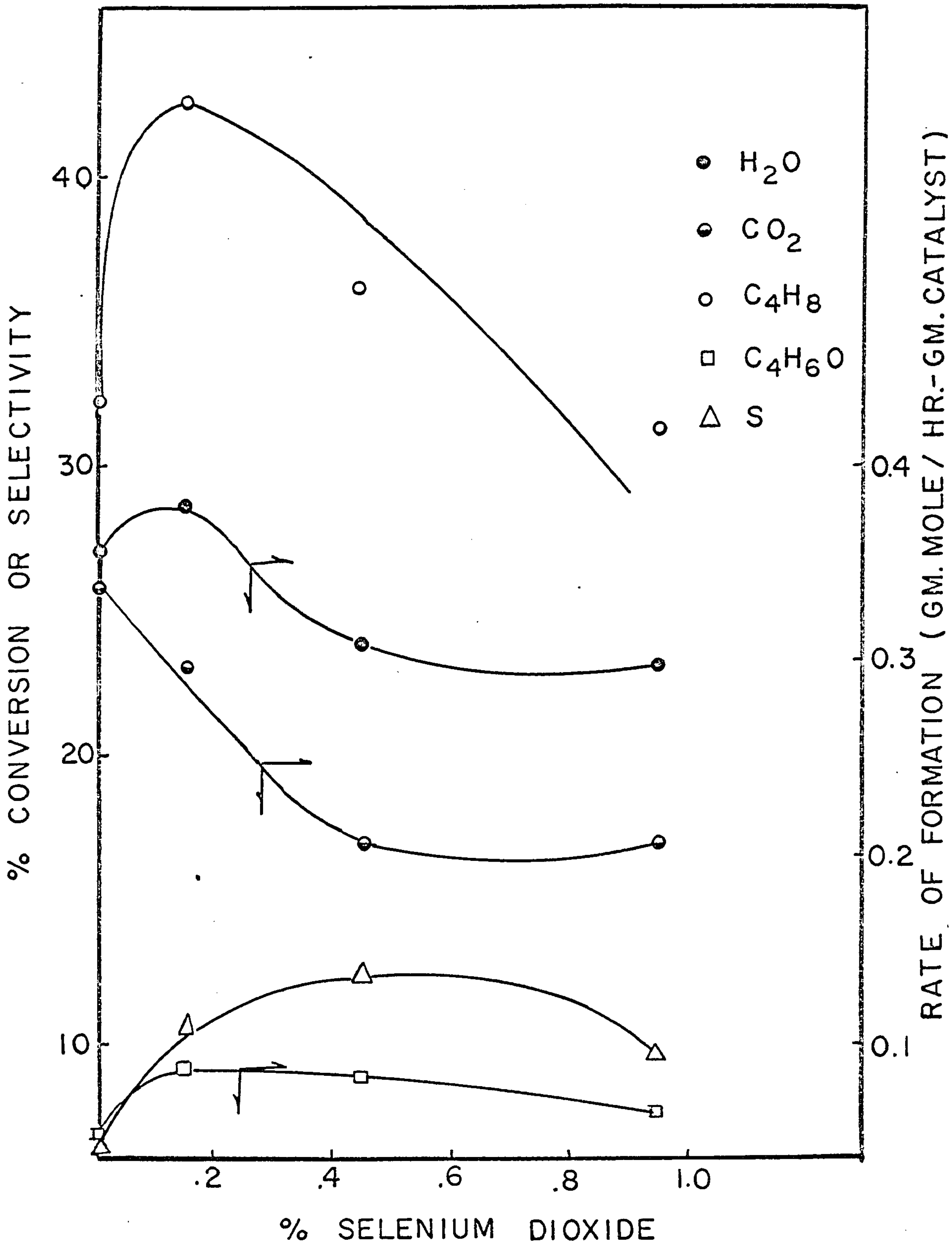


Figure 19 Effect of Selenium Dioxide on Conversion Rate of Formation and Selectivity at 375° C for R = 1.3746

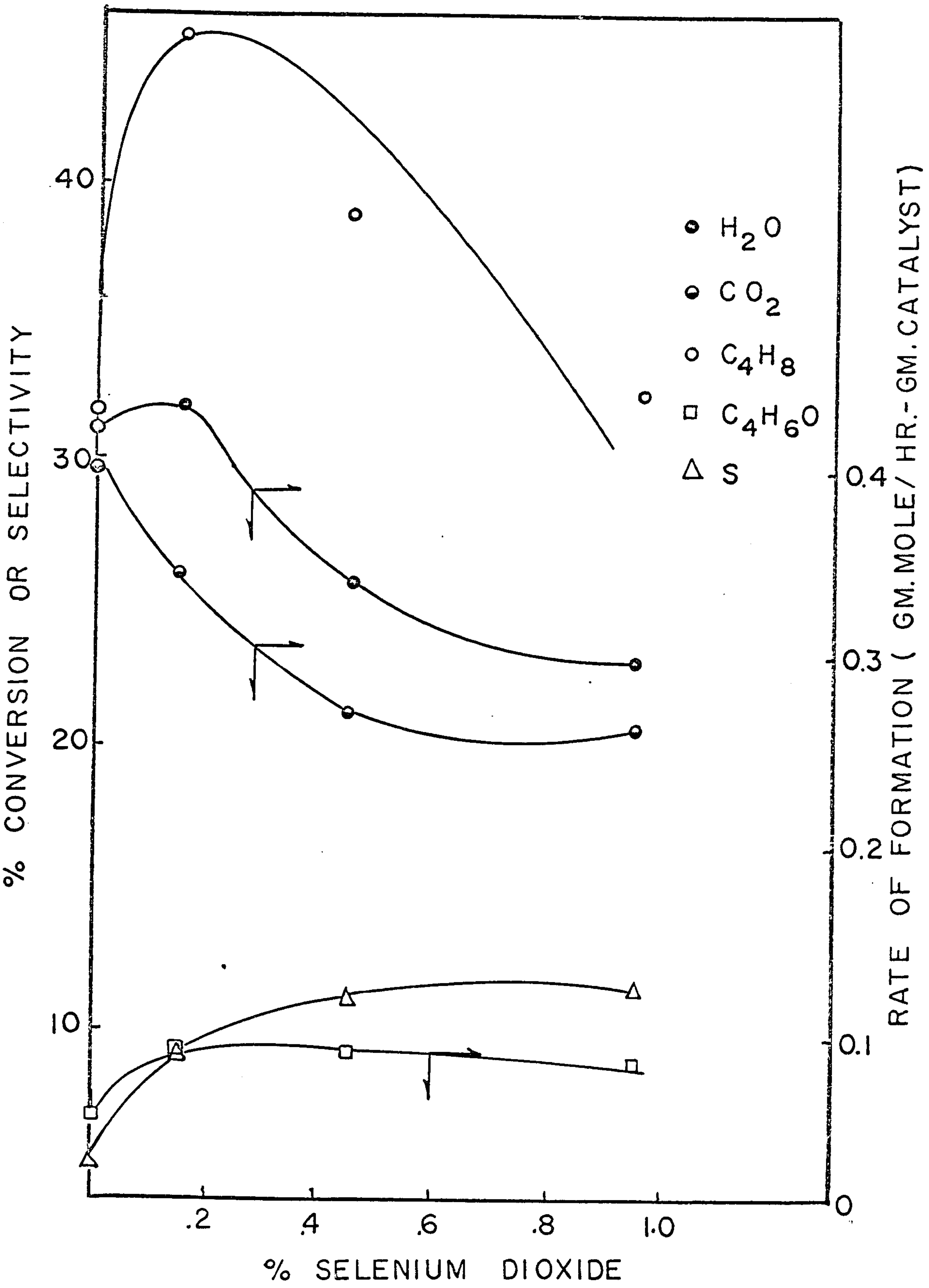


Figure 20 Effect of Selenium Dioxide on Conversion Rate of Formation and Selectivity at 375°C for R = 1.6644

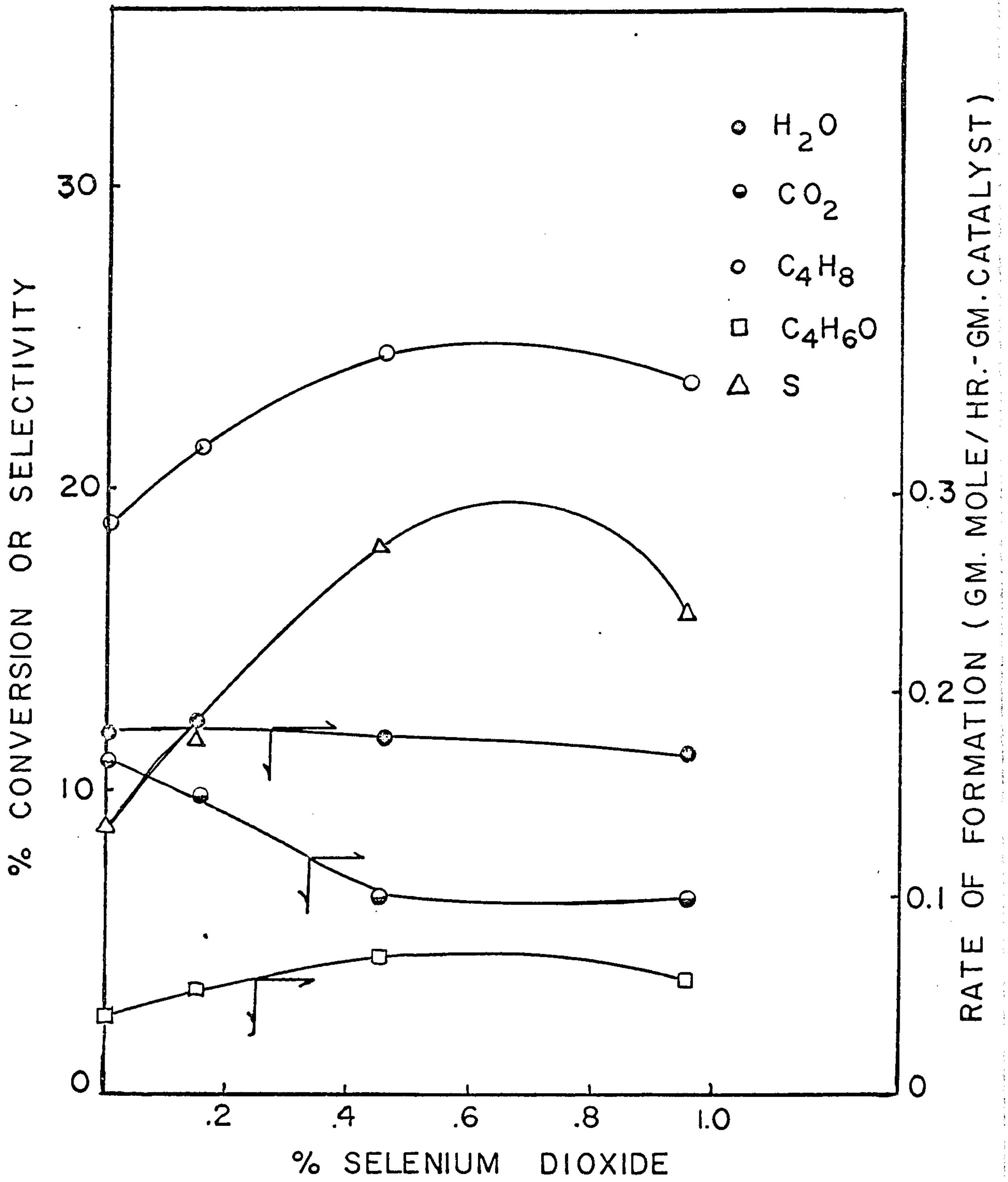


Figure 21 Effect of Selenium Dioxide on Conversion Rate of Formation and Selectivity at 350°C for R = 0.7168

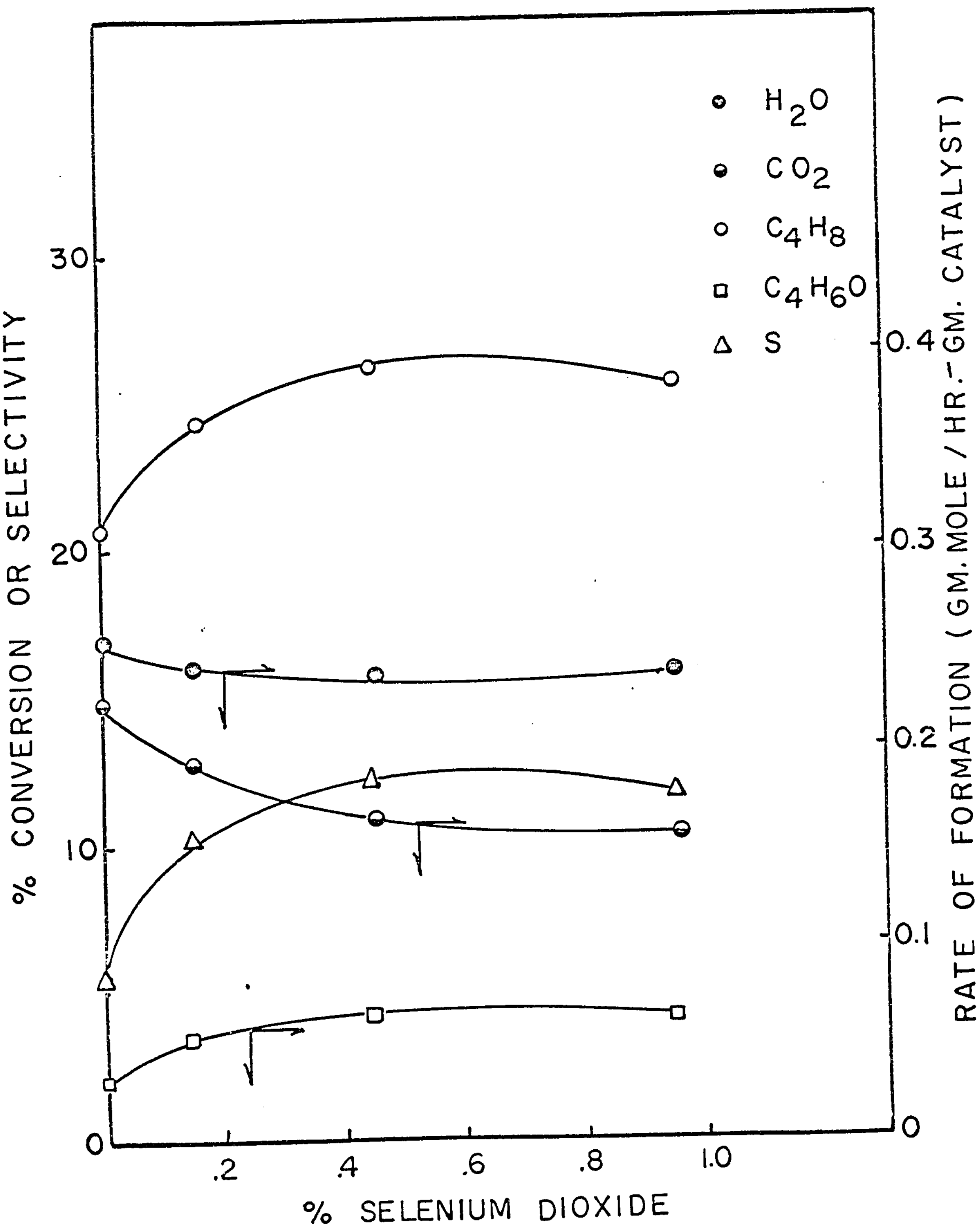


Figure 22 Effect of Selenium Dioxide on Conversion Rate of Formation and Selectivity at 350° C for R = 0.9910

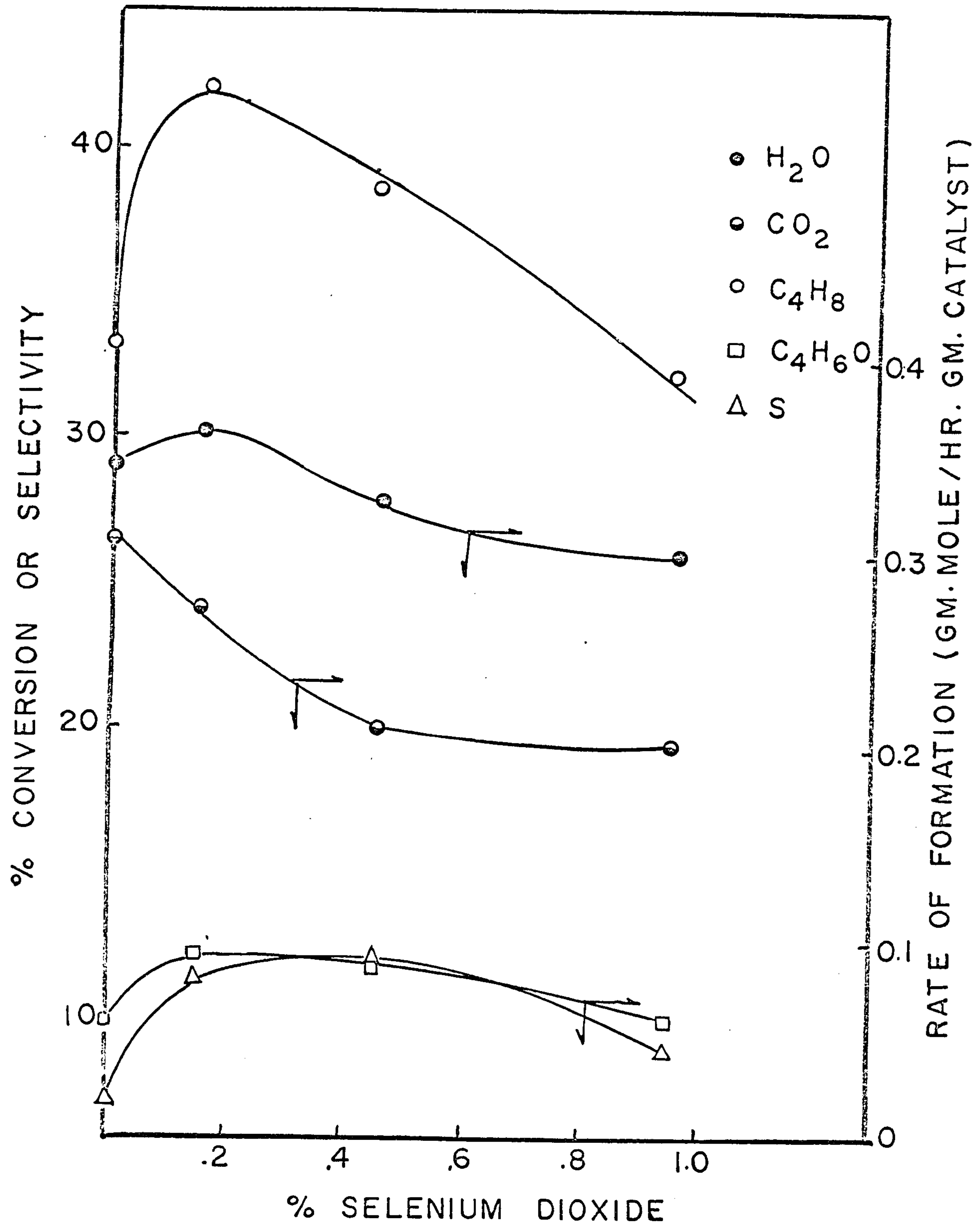
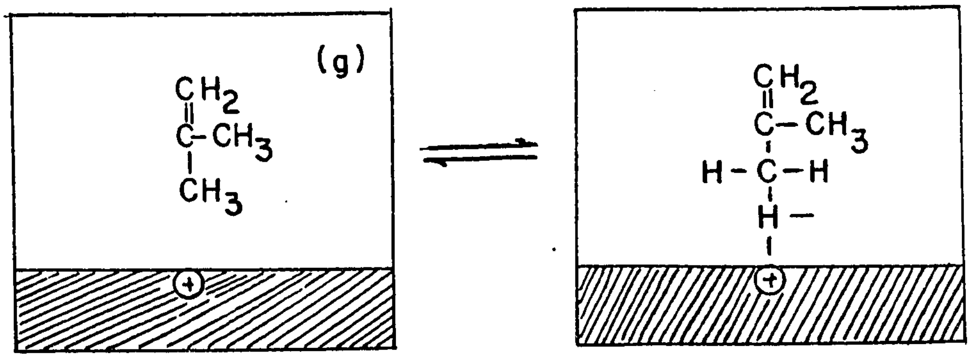


Figure 23 Effect of Selenium Dioxide on Conversion Rate of Formation and Selectivity at 350°C for R = 1.3746

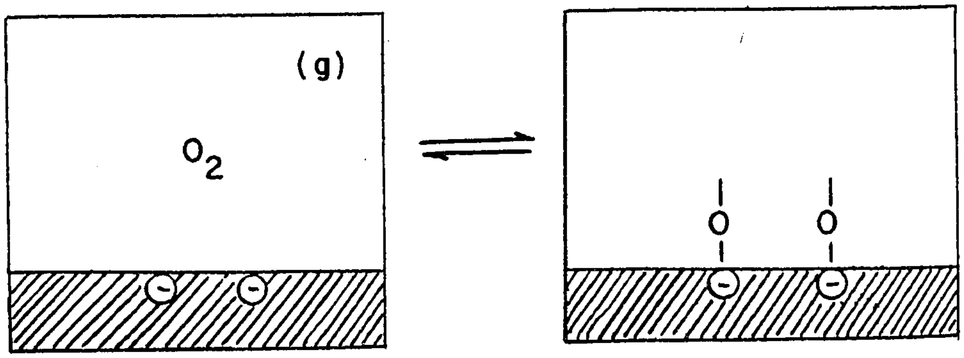
The formation of methacrolein from the partial oxidation of isobutylene over copper oxide catalyst are proposed by the following main mechanisms:

Reaction I (partial oxidation)

(A) C_4H_8 (g) + $\dot{p}L \rightleftharpoons C_4H_8^+$(ads.) (p-type)

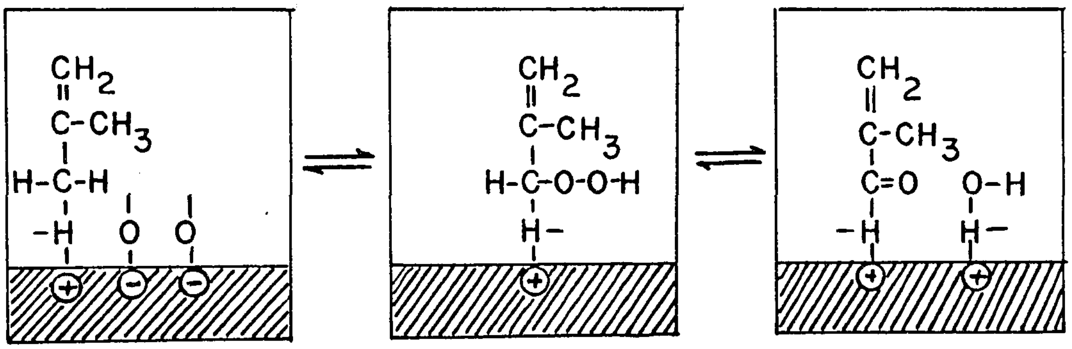


(B) O_2 (g) + $\dot{e}L \rightleftharpoons 2\ O^-$ (ads) (n-type)
or O_2 (g) $\rightleftharpoons 2\ O^-$ (ads.)+$\dot{p}L$ (n-type)

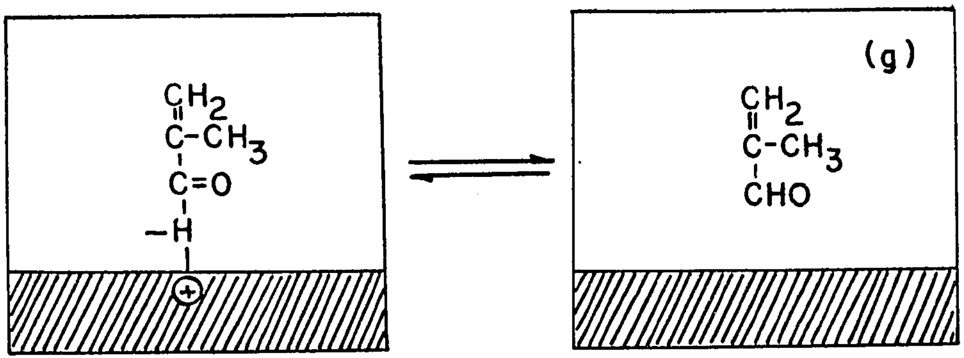


(C) $C_4H_8^+$ (ads.) + 2 O^- (ads.) $\rightleftharpoons$ Actived Complex

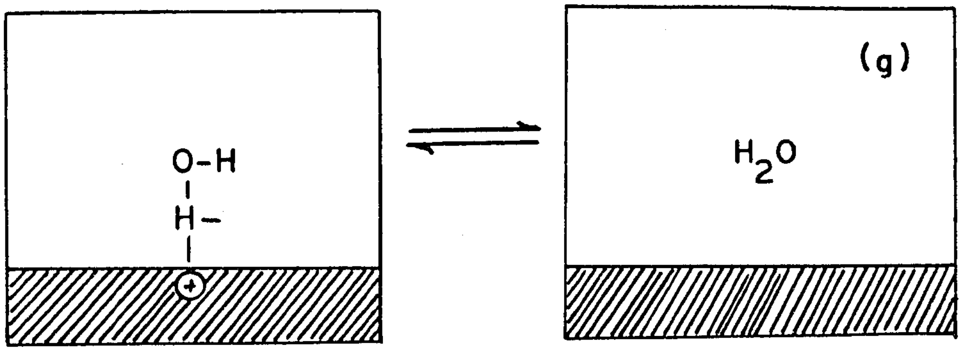
$\rightleftharpoons$ $C_4H_6O^+$ (ads,) + H_2O^+ (ads.)



(D) $C_4H_6O^+$ (ads.) + eL $\rightleftharpoons$ C_4H_6O (g) (n-type)



(E) H_2O^+ (ads.) + eL $\rightleftharpoons$ H_2O (g) (n-type)



Overall $C_4H_8 + O_2 \rightleftharpoons C_4H_6O + H_2O$

Using the same argument

Reaction II (further oxidation)

(A) $C_4H_6O^+$ (ads.) + 10 O^- (ads.) $\rightleftharpoons$ activated complex $\rightleftharpoons$
CO_2^+ (ads.) + H_2O^+ (ads.)

(B) CO_2^+ (ads.) + eL $\rightleftharpoons$ CO_2 (g) (n-type)

(C) H_2O^+ (ads.) + eL $\rightleftharpoons$ H_2O (g) (n-type)

overall $C_4H_6O + 5O_2 \rightleftharpoons 4CO_2 + 3H_2O$

Reaction III (complete oxidation)

(A) $C_4H_8^+$ (ads.) + 12 O^- (ads.) $\rightleftharpoons$ activated complex $\rightleftharpoons$
$4CO_2^+$ (ads.) + $4H_2O^+$ (ads.)

(B) CO_2^+ (ads.) + eL $\rightleftharpoons$ CO_2 (g) (n-type)

(C) H_2O^+ (ads.) + eL $\rightleftharpoons$ H_2O (g) (n-type)

overall $C_4H_8 + 6O_2 \rightleftharpoons 4CO_2 + 4H_2O$

each step in the above reactions may contribute a certain resistance. The overall rate is always determined by the so-called rate controlling step.

The sign of electrical charge in each adsorbed particles is determined from the work function change measurement (37), (38), (39). The steps involving the electron transfer can be accelerated or deaccelerated in the presence of impurities. These steps depend on the nature of impurities and the type of the reactions as mentioned previously. Using the definitions, step 1-A is p-type and the others are n-type.

Selenium dioxide may be considered as an acceptor impurity to cuporous oxide (42), a p-type semiconductor. The evaluation of surface concentration of charged isobutylene and oxygen particles are important for investigating the effect of selenium dioxide amounts of the conversion of isobutylene (reaction I, II), yield of carbon dioxide (reaction II, III) and yield of water and methacrolein (reaction I, II).

From equation (61) and (62)

$$C_{C_4H_8^+} = K_{C_4H_8} N_{(+)}^{(H)} \exp\left[- \frac{2\,e^2}{kT} \frac{C_{C_4H_8^+}}{N_{(+)}^{(H)}}\right] P_{C_4H_8} \qquad (61)$$

and

$$C_{O^-} = K_{O_2} \frac{1}{N_{(+)}^{(H)}} \exp\left[2 \sinh^{-1} \left(\frac{2\,e^2}{kT\, N_{(+)}^{(H)}}\right)^{1/2} \frac{C_{O^-}}{2}\right] P_{O_2}^{1/2} \qquad (62)$$

it would be seen that $C_{C_4H_8^+}$ and C_{O^-} are not only a function of $P_{C_4H_8}$ and P_{O_2} but aoso depend on the free hole concentration in the catalyst bulk, $N_{(+)}^{(H)}$ respectively.

While $C_{C_4H_8^+}$ is increased by increasing $N_{(+)}^{(H)}$ and $P_{C_4H_8}$; C_{O^-} is decreased by increasing $N_{(+)}^{(H)}$ and by decreasing $P_{O_2}^{1/2}$ are obviously.

Since the presence of selenium dioxide on cuporous oxide increases the hole concentration or decreases the free electron concentration in the valence or conduction band of the catalyst, the surface concentration of oxygen ion C_{O^-} therefore would be decreased and the others increased.

Reaction I, II and III can be expressed in terms of power rate law as follows:

$$r_1 = k_1 C_{C_4H_8^+}^{m_1} C_{O^-}^{n_1} - k_1' C_{C_4H_6O^+}^{m_1'} C_{H_2O^+}^{n_1'}$$

$$r_2 = k_2 C_{C_4H_6O^+}^{m_2} C_{O^-}^{n_2} - k_2' C_{CO_2^+}^{m_2'} C_{H_2O^+}^{n_2'}$$

$$r_3 = k_3 C_{C_4H_8^+}^{m_3} C_{O^-}^{n_3} - k_3' C_{CO_2^+}^{m_3'} C_{H_2O^+}^{n_3'}$$

Although the quantitative treatments of these rate equations are difficult, yet some satisfactory explanations still could be obtained in a qualitative level.

The oxidation of isobutylene to methacrolein over copper oxide catalyst in the absence of selenium dioxide was studied by Mann and Rouleau (40). This is comparable to the one in which the amount of selenium dioxide is very low in the feed. They found that oxidation of isobutylene is a surface reaction controlling between strongly adsorbed isobutylene and weakly adsorbed oxygen. Now, considering that the adsorption of isobutylene is the next slow step to surface reaction. This is easily realized from the fact that when isobutylene (a donor type gas) is adsorbed on cuporous oxide (a p-type semiconductor) a depletive or exhausion boundary layer is formed. This implies that chemisorption should cease at very low coverages. Since adsorption of oxygen and desorption of products are both comparatively fast, therefore any increase in the adsorption rate of isobutylene will definitely increase the overall reactionI. At this moment, the decrease in the free electron concentration on the surface (or increase in the free holes concentration in the boundary layer) is still comparatively negligible to the increase in the concentration of free holes. In other words, the decrease of oxygen adsorption rate and the decrease of methacrolein desorption rate are still insignificant. Therefore while isobutylene conversion (reaction I) increased rapidly at the beginning of the introduction of selenium dioxide (< 0.15%), carbon dioxide is only slightly influenced. This is in agreement with Vogue, Wagner and Stevenson (41) and Margolis (42) who found that at temperatures in excess of 350°C, carbon dioxide is mainly produced from reaction II but not from reaction III.

When more selenium dioxide is added (0.45% < selenium dioxide < 0.15%) a certain amount of selenium will compete with oxygen for the free electrons on the surface. Selenium has a higher tendency to combine with free electrons. This results in the rate of adsorption of oxygen slowing down. In such a case, adsorption of oxygen becomes the rate determining step for reaction II (from the power rate law it is also easy to find out that C_{O^-} has a predominating influence on reaction II). Therefore, reaction II is slowed down rapidly and reaction I is only slightly influenced after a compensation effect of C_{O^-} and $C_{C_4H_8^+}$ and $C_{C_4H_6O^+}$.

For selenium dioxide concentration exceeding 0.45% by weight of catalyst, the surface concentration of adsorbed oxygen ions become lesser and lesser, but in the mean time, the increase of surface concentration of adsorbed methacrolein ions becomes significant, also it may be due to the fact that when selenium dioxide concentration exceeding 0.45% by weight of catalyst, the modifier enters the catalyst lattice substitutionally instead of interstitially. Hence, either the conversion or carbon dioxide formation would be slightly decreased. This is in agreement with Parravano and Boudart (15) who found the same result when litium ions are introduced into the nickel oxide catalyst.

Water is the product from reaction I and II. The formation of water will therefore increase with increased conversions of isobutylene and with increased amounts of carbon dioxide. Therefore, due to the compensation effect, the yield of water increases first and then decreases as selenium dioxide amount reaches 0.2% by weight of catalyst.

Methacrolein, on the other hand is the product from reaction I and is a reactant in reaction II. The yield of methacrolein will therefore depend on the extent of reaction I and II.

Selectivity of methacrolein is calculated from the percentage of methacrolein yield to the total yield. An optium amount of selenium dioxide which gives best selectivity for methacrolein under different operating conditions is about 0.7% by weight of the catalyst.

If we assume that the adsorption of one of the charged reactants, say oxygen, is not necessary step (we have in mind that at least one of the reactants which is adsorbed on the surface is charged), then it would be difficult to explain the increased conversion of isobutylene with lesser amounts of selenium dioxide and a decrease in conversion for more than 0.15% selenium dioxide by weight of catalyst. If we apply the rate law (either power or exponential)

$$r_1 = k_1 \, C_{C_4H_8^+}^{\;m_1} \, P_{O_2}^{\;n_1} - k_1' \, C_{C_4H_6O^+}^{\;m_1'} \, C_{H_2O^+}^{\;n_1'} \tag{66}$$

the conversion should always increase due to there being no interaction of oxygen gas with the semiconductor. On the other hand, the formation of carbon dioxide should not decrease if rate law

$$r_2 = k_2 \, C_{C_4H_6O^+}^{\;m_2} \, P_{O_2}^{\;n_2} - k_2' \, C_{H_2O^+}^{\;m_2'} \, C_{CO_2^+}^{\;n_2'} \tag{67}$$

is applied.

However, if it is assumed that in case of a heterogeneous reaction, it is essential to have a surface reaction between the adsorbed charged reactants, it can be easily seen that the isobutylene conversion and carbon dioxide yield will depend on the amounts of selenium dioxide. These dependencies are due to the fact that the carriers concentration are involved. Hence it is proposed that for heterogeneous reactions, a surface reaction between the charged reactant particles is a necessary step.

This proposal is also in agreement with a paper written by Mann and Rouleau (47) in which they pointed out that at low feed composition ratio, the conversion of isobutylene rapidly increased with increased feed composition ratios, gradually decreased when the feed composition ratio was larger than 2. This can be explained on the basis of the hypothesis that oxygen adsorption will promote the isobutylene adsorption (due to the increase of free holes on the surface) but in the meantime adsorption of oxygen itself becomes difficult in high coverage of oxygen. Since conversion of isobutylene resulted in these two opposite effects, there is an inversion point on the conversion curve.

Hougen-Watson type approach is based on the Langumuir isotherm which is considered to be an ideal case in the sense that the surface effect is ignored.

For the sake of explanation, take an example

$$A + B \rightleftharpoons C$$

in which both of reactants and products are adsorbed. Then

$$K_A' = \frac{\theta_A}{P_A\ (1-\theta_A-\theta_B-\theta_C)} = \frac{C_A}{P_A C_V} \qquad (68)$$

$$\frac{C_A}{C_T} = \frac{K_A' P_A}{1 + K_A' P_A + K_B' P_B + K_C' P_C} \qquad (69)$$

and

$$\frac{C_V}{C_T} = \frac{1}{1 + K_A{}'P_A + K_B{}'P_B + K_C{}'P_C} \qquad (70)$$

where $K_A{}'$ is the adsorption constant of reactant A, C_A, C_V, C_T are the molar concentration of active sites occupied by A, vacant and in total respectively.

Now if the surface effect is considered, for example

$$A \rightleftharpoons A^- + (+)^R$$

$$K_A = \frac{N_{(+)}^{(R)}\ N_{A^-}}{P_A} \qquad (71)$$

where $N_{(+)}^{(R)}$ is the molar concentration of positive holes in the boundary layer N_{A^-} is the molar concentration of charged A on the surface. Then, from equations (68) and (71), $K_A{}' = K_A$ only under the condition

$$\frac{C_A}{P_A C_V} = \frac{N_{(+)}^{R}\ N_{A^-}}{P_A} \qquad (72)$$

or

$$\frac{C_A}{C_V} = N_{(+)}^{R}\ N_{A^-} \qquad (73)$$

and since $N_{A^-} \propto C_A = m\, C_A$ (m is a constant).

so if $K_A' = K_A$

$$N_{(+)}^{R} = \frac{1}{m\,C_V} \tag{74}$$

must be satisfied.

Therefore, the Hougen-Watson type approach is only limited to a certain case in which the free charge concentration on the surface is to be considered as constant. Now, if one increases $N_{(+)}^{(H)}$, then $N_{(+)}^{(R)}$ is increased and from equation (74) C_V must be decreased but

$$\frac{C_V}{C_T} = \frac{1}{1 + K_A'P_A + K_B'P_B + K_C'P_C} \tag{75}$$

C_T is to be considered as a constant in Hougen-Watson type approach. Therefore if one increases $N_{(+)}^{(H)}$, then K_A' term in the Hougen-Watson type rate equation must be increased. In other words, K_A' is directly dependent on $N_{(+)}^{(R)}$ and will increase with increased value of $N_{(+)}^{(H)}$.

Therefore, we can conclude that K_A' in the Hougen-Watson type rate equation is not only a temperature-dependent constant but also depends on the surface charge concentrations, which in turn is determined by the operating variables and the presence of impurities.

In the absence of selenium dioxide or at low feed composition ratios, since $N_{(+)}^{H}$ is small, K_{O_2}' will therefore be negligibly small compared with $K'_{C_4H_8}$. But, when selenium dioxide, a p-type impurity is introduced $N_{(+)}^{(H)}$ increases. Hence K'_{O_2} also increases and $K'_{C_4H_8}$ decreases

It would be thus seen that the importance of oxygen adsorption cannot be neglected for the oxidation of isobutylene in the presence of selenium dioxide or at very high feed composition ratio. Thus the reaction mechanism or the rate-determining step could be changed by different operating conditions and in the presence of different kind and different amounts of impurities. It is for this reason that different reaction mechanism have been reported in the literature for the same system but under different operating conditions.

VII CONCLUSION AND RECOMMENDATION

The modification of supported copper oxide catalyst with selenium dioxide was studied by impregnation of selenium dioxide solution and by continuous introduction of its vapor into the reactant stream. The former method was discarded because the activity of the catalyst could not be maintained constant due to the volatility of selenium dioxide at the reaction temperature.

From the experimental results, the following conclusions can be drawn.

(1) There are two kinds of active sites on the surface of the catalyst. Both oxygen and isobutylene molecules are chargedly chemisorbed, but the concentration of these charged particles on the surface is different at different operating conditions and in the presence of different amount of impurities.

The adsorption constant of the reactants are influenced quite differently by the concentration of the charged adsorbents on the surface. The adsorption constants vary with not only temperature, but with many other factors, which can affect the properties of the surface, such as illumination, introduction of impurities and the presence of other reactants.

(2) Selenium dioxide is a promoter for reaction I, the partial oxidation of isobutylene (isobutylene conversion) for SeO_2 concentration is less than 0.15% by weight of catalyst and the reaction I is p-type. But SeO_2 is also

a poison for the same reaction when its concentration exceeds 0.15% by weight of catalyst and the same reaction I turns to n-type.

(3) Selenium dioxide is a poison to reaction II, the further oxidation of the reaction at all concentrations and reaction II is an n-type reaction.

(4) An optium amount of selenium dioxide giving the highest selectivity of methacrolein was found to be about 0.7% by weight of catalyst.

(5) Surface effects of free charges are important in heterogeneous catalytic reaction, and the free charges must be considered as reactants. It is proposed that the charged adsorption of both reactants on the surface of the catalyst is an essential step in heterogeneous catalytic reactions. It is also believed that during a complex heterogeneous catalytic reaction the rate-determining step (slowest step) is not always fixed, but on the contrary, it could change with the change in the electronic properties of the catalyst surface. It is due to this reason that the diverse reports concerning reaction order, activation energy and rate equation originate.

One difficulty in maintaining the catalytic activity constant is that it is not possible to keep the rate of trace amounts of selenium dioxide vapor in the reactants constant. Since the amount of selenium dioxide introduced in the feed is very sensitive to temperature, the experimental range is therefore limited by the temperature control on the selenium dioxide vaporizer.

A proposed method to overcome this difficulty is by using a heat-diffusion method to prepare the volatile doped catalyst. This can be done by first evacuating the vessel containing the catalysts and the required amount of modifier and then sealing the vessel. The vessel is substantially heated and annealed. The modifier is then placed into the crystal bulk. In this way the activity of the catalyst could be maintained.

It is recommended that the type of modifiers used to investigate the influence of impurities on the selectivity of a catalyst be extended. If the proposed mechanisms are correct, then the addition of any acceptor gas which has a higher electronegativity than copper oxide should give the same results. It is also recommended that for fundamental research some simple reaction should be studied instead of the complex one. Measurement of the work function change gives direct information on the position of the Fermi level at the surface of the crystal. From changes in activity one can unambiguously judge the acceptor or donor mechanism of the reaction, therefore it would be of interest to investigate the relationship between the work function of a semiconductor and its catalytic activity and adsorptivity, No such experimental data exist in the literature so far up to the present no comprehensive study has been made on the influence of other factors besides impurity, on the selectivity of the catalytic reactions.

A widening of the experimental basis is essential for the construction of a theory of selectivity which would be of a great practical significance.

VII APPENDICES

A. NOMENCLATURE

A^{a^-}	ionized acceptors with valence a^-.
C	molar concentration of adsorbed species on the surface.
c—c	
CL	weak bond
CpL	strong p-bond
CeL	strong n-bond
D^{d^+}	ionized donors with valence d^+
E	total energy
E_i	a particular energy for an electron in the crystal.
E_F	Fermi level
e	absolute unit charge
eL	free electrons
$e\rho$	space charge density
$e\sigma$	surface charge density
g	reaction rate
I	conductivity
K	equilibrium constant
K'	equilibrium constant in Hougen-Waston type approach
k	Boltzmann constant
k_a	rate constant of chemisorption
k_d	rate constant of desorption

L	crystal lattice
M	molecular weight
N	total number of electrons
N^o, N^-, N^+	number of particles in the state of "weak", "strong p" and "strong n" bonding with the surface
N_{a^-}	concentration of acceptors centers in the bulk
N_{d^+}	concentration of donors centers in the bulk
n_1	number of electrons at energy E_1
$n_{(+)}^{(H)}$	molar concentration of free holes in the bulk
$n_{(+)}^{(R)}$	molar concentration of free holes in the boundary layer
$n_{(x)}$	electron concentration at x in the conductivity band
P	pressure
P	probability of a given electron in any state
pL	free holes
p(x)	hole concentration in the valence band at x
R	feed ratio (moles of oxygen/moles of isobutylene)
r	reaction rate in terms of surface concentration
r'	reaction rate in terms of partial pressure
S	entropy
T	absolute temperature
U	energy gap of a semiconductor
U^+	distance between valence band and level c–c
U^-	distance between conduction band and level c–c

V	volume
V	potential barrier in the boundary layer
V_D	Fermi level difference between the surface and the bulk
V^+	distance between valence band and acceptor level
V^-	distance between conduction band and acceptor level
W	the number of complexion
x	distance into the bulk from the surface
Z_i	member of available states at energy E_i
Z	concentration of impurity
α	$(2\pi MkT)$
$\bar{V}^-$	distance between conduction band and Fermi level in the bulk
$\bar{V}^+$	distance between valence band and Fermi level in the bulk
ε_{s^-}	distance between conduction band and Fermi level on the surface
ε_{s^+}	distance between valence band and Fermi level on the surface
κ	dielectric constant
n^o, n^-, n^+	defined by eq. (30)
ΔU	distance between donor level and level c-c or distance between acceptor level and level c-c
μ_e	chemical potential per electron
ν^o, ν^-, ν^+	constants
ϕ	work function
ω^+	distance between valence band and donor level
ω^-	distance between conduction band and donor level
λ_1, λ_2	Lagrangian multipliers

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C. Evaluation of Surface Concentrations of Chargedly Adsorbed Isobutylene and Oxygen Cases

A. $C_{C_4H_8^+}$

$$C_4H_8(g) + (R) \underset{k_d}{\overset{k_a}{\rightleftharpoons}} C_4H_8^+ \text{ (ads.)} \tag{1}$$

$$r_a = k_a P_{C_4H_8} n_{(+)}^{(R)} \tag{2}$$

$$r_d = k_d C_{C_4H_8^+} \tag{3}$$

At equilibrium,

$$k_a P_{C_4H_8} \cdot n_{(+)}^{(R)} = k_d C_{C_4H_8^+}$$

or

$$C_{C_4H_8^+} = \frac{k_a}{k_d} P_{C_4H_8} n_{(+)}^{(R)}$$

$$= K_{C_4H_8} P_{C_4H_8} n_{(+)}^{(R)} \tag{4}$$

Apply the Boltzmann equation to obtain the distribution of holes

$$n_{(+)}^{(R)} = n_{(+)}^{(H)} \exp [+eV_D/kT] \tag{5}$$

substitute (5) into equation (4)

$$C_{C_4H_8^+} = K_{C_4H_8} \, P_{C_4H_8} \, n_{(+)}^{(H)} \exp\left[+eV_D/kT\right] \tag{6}$$

Assume every isobutylene molecule captures one positive hole, the number of surface charges equal the total number of ionized defects in the boundary layer having a density equal to $n_{(+)}^{(H)}$, the surface concentration of chemisorbed isobutylene molecules

$$C_{C_4H_8^+} = n_{(+)}^{(H)} \cdot l \tag{7}$$

and since $e\rho = en_{(+)}^{(H)}$ for $0 < \zeta < l$ (8)

$$\rho = 0 \qquad \text{for} \qquad \zeta > l \tag{9}$$

where ρ is the space charge density and l is the screen length.

Introducing equations (7) and (8) into the integrated Poisson equation

$$\frac{d^2V(x)}{dx^2} = \frac{d^2\varepsilon^+}{dx^2} = -\frac{4\pi e}{\kappa}\rho \tag{10}$$

the diffusion potential V_D after integration between $\chi = 0$ and $\chi = l$ is obtained

$$V_D = \frac{2\pi e}{\kappa} \; \frac{(C_{C_4H_8^+})^2}{n_{(+)}^{(H)}} \tag{11}$$

Substitute equation (11) into equation (6)

$$\therefore \; C_{C_4H_8^+} = K_{C_4H_8} \, P_{C_4H_8} \cdot n_{(+)}^{(H)} \cdot \exp\left[- \frac{2\pi e^2}{\kappa kT} \cdot \frac{C_{C_4H_8^+}{}^2}{n_{(+)}^{(H)}}\right] \tag{12}$$

B. $\underline{O^-}$

$$\frac{1}{2} O_2(g) \quad \overset{k_{a'}}{\underset{k_{d'}}{\qquad}} \quad O^- \text{ (ads.)} + \quad {}^{(R)} \tag{13}$$

$$r_a' = k_a' \, P_{O_2}{}^{1/2} \tag{14}$$

$$r_d' = k_d' \, C_{O^-} \cdot n_{(+)}^{(R)} \tag{15}$$

At equilibrium

$$k_a' \, P_{O_2}{}^{1/2} = k_d' \, C_{O^-} \cdot n_{(+)}^{(R)}$$

or

$$C_{O^-} = \frac{k_a'}{k_d'} \cdot \frac{P_{O_2}{}^{1/2}}{n_{(+)}^{(R)}}$$

$$= K_{O_2} \cdot P_{O_2}{}^{1/2} \cdot \frac{1}{n_{(+)}^{(R)}} \tag{16}$$

$$= K_{O_2} \cdot P_{O_2}^{1/2} \cdot \frac{1}{n_{(+)}^{(H)}} \cdot \exp(-eV_D'/kT) \qquad (17)$$

In the case of an inundation boundary layer, V_D' can be evaluated as follows. Let

$$eV_D'/kT = U$$

For a p-type semiconductor it can be assumed that the donor concentration in the bulk region is negligible in comparison with the acceptor concentration

$$\rho(x) = Na^{-} - n_{(+)}^{(R)} + n_{(-)}^{(R)} \qquad (18)$$

$$n_{(+)}^{(R)} = n_{(+)}^{(H)} \exp(U) \qquad (19)$$

$$n_{(-)}^{(R)} = n_{(-)}^{(H)} \exp(-U) \qquad (20)$$

now define

$$\exp(U_B) = \left(\frac{n_{(+)}^{(R)}}{n_{(-)}^{(R)}}\right)^{1/2} \qquad (21)$$

and since

$$(n_{(+)}^{(H)} \cdot n_{(-)}^{(H)})^{1/2} = Pi \qquad (22)$$

where Pi is the intrinsic concentration of holes. Substitute equations (19), (20), (21) and (22) into equation (18)

$$\rho(x) = Na^- - Pi \exp(U_B) \exp(U) + Pi \exp(-U_B) \exp(-U)$$

$$= Na^- - 2Pi \sinh(U_B + U) \tag{23}$$

In the bulk region of the semiconductor where $\rho(x) = 0$ then it follows that

$$\sinh U_B = \frac{Na^-}{aPi} \tag{24}$$

Poisson's equation can be written in an alternate expression

$$\frac{d^2U}{dx^2} = -\frac{4\,e^2}{\kappa kT}\,\rho(x)$$

$$= -2L_m\,\rho(x) \tag{25}$$

In the bulk of semiconductor the following boundary conditions can be established

$$U = 0 \text{ at } x = \infty \tag{26}$$

$$\frac{dU}{dx} = 0 \text{ at } x = \infty \tag{27}$$

The boundary condition at $x = 0$ can be defined as

$$U = U_S \text{ at } x = 0 \tag{28}$$

Integrating equation (25) with the boundary conditions

$$\frac{dU}{dx}\Bigg|_{x=0}^{x=\infty} = -2L_m \int_{0}^{\infty} \rho(x)\,dx \tag{29}$$

when this result is combined with

$$\Sigma \,\square + \int_{0}^{\infty} \rho(x)\,dx = 0 \tag{30}$$

it follows directly that

$$-\left(\frac{dU}{dx}\right)_{x=0} = 2L_m\,(\Sigma\,\square) = 2L_m \cdot C_{o}{-} \tag{31}$$

where Σ is the surface charge concentration and since

$$\frac{d^2U}{dx^2} = \frac{d}{dx}\left(\frac{dU}{dx}\right) = \frac{dU}{dx} \cdot \frac{d}{dU}\left(\frac{dU}{dx}\right)$$

$$= \frac{1}{2}\,\frac{d}{dU}\left[\left(\frac{dU}{dx}\right)^2\right] \tag{32}$$

equating equations (25) and (32)

$$\frac{1}{2}\,\frac{d}{dU}\left[\left(\frac{dU}{dx}\right)^2\right] = -2L_m\,\rho(U) \tag{33}$$

for an intrinsic semiconductor

$$\rho(x) = n_{(-)}^{(R)} - n_{(+)}^{(R)} \tag{34}$$

Substitute equations (19) and (20) into equation (34) and then in turn into equation (33)

$$\frac{1}{2}\ \frac{d}{dU}\left[\left(\frac{dU}{dx}\right)^2\right] = 4L_m\ Pi\ \sinh U \tag{35}$$

now equation (23) is substituted into equation (35) the resulting equation can be integrated using the boundary conditions defined in equations (26) and (27) at $x = \infty$. The result is

$$\left(\frac{dU}{dx}\right)^2 = 4L_m \left\{ 2Pi\ \cosh\ (U_B+U) - 2Pi\ \cosh\ U_B - (Na^-)U \right\} \tag{36}$$

$$= 4L_m \left\{ 4Pi\ \exp\ (U_B)\ [\sinh\ (U/2)]^2 \right.$$

$$\left. + 2Pi\ [1-\exp\ (-U)]\ \sinh\ U_B - (Na^-)U \right\} \tag{37}$$

at $x = 0$, $U = U_S$

When U_S is small, then $[1-\exp\ (-U_S)] \simeq U_S$ and the second term is R.H.S. concels from equation (24) when U_S is large then the exponentials in the $[\sinh]^2$ factor dominate the expression. Therefore by neglecting the second term, the result is

$$\left(\frac{dU}{dx}\right)_{x=0} = 4\ L_m\ n_{(+)}^{(H)}\ \sinh\ \left(\frac{U_s}{2}\right) \tag{38}$$

By combining equation (31) with equation (38) the result is

$$-\sinh\left(\frac{U_S}{2}\right) = \left(\frac{L_m}{n_{(+)}^{(H)}}\right)^{1/2} \frac{C_{o^=}}{2}$$

or

$$U_S = -2\sinh^{-1} \left[\frac{2\pi e^2}{\kappa kT \cdot n_{(+)}^{(H)}}\right]^{1/2} \cdot \frac{C_{o^=}}{2} \qquad (39)$$

$$\therefore C_{o^=} = K_{o_2} \cdot P_{o_2}^{1/2} \cdot \frac{1}{n_{(+)}^{(H)}} \exp\left[2\sinh^{-1} \left[\frac{2\pi e^2}{\kappa kT\, n_{(+)}^{(H)}}\right]^{1/2} \cdot \frac{C_{o^=}}{2}\right] \qquad (40)$$

D. Instrument Calibration and Analysis of Products

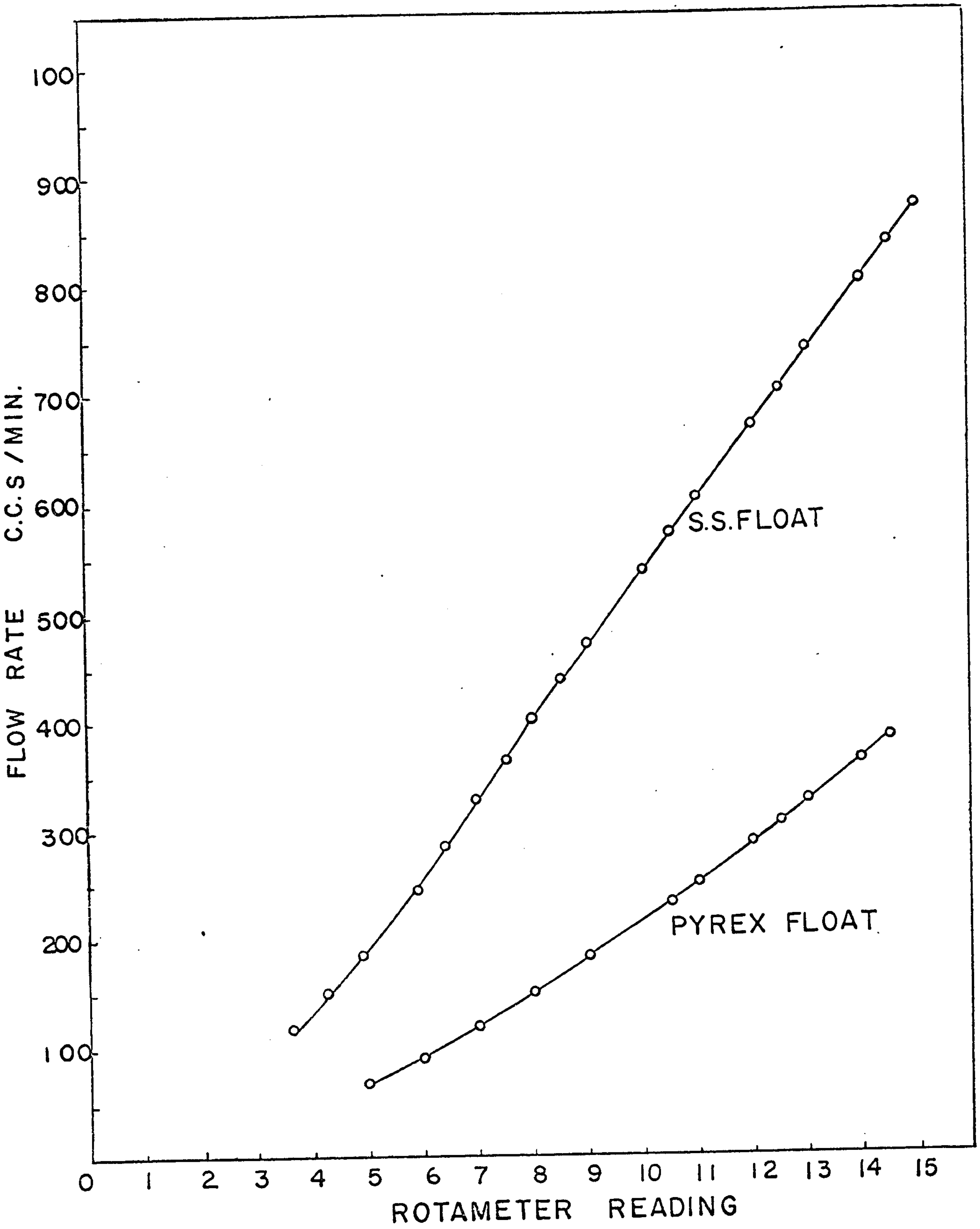

Figure 24 Air Calibration at 1 atm. and 0°C

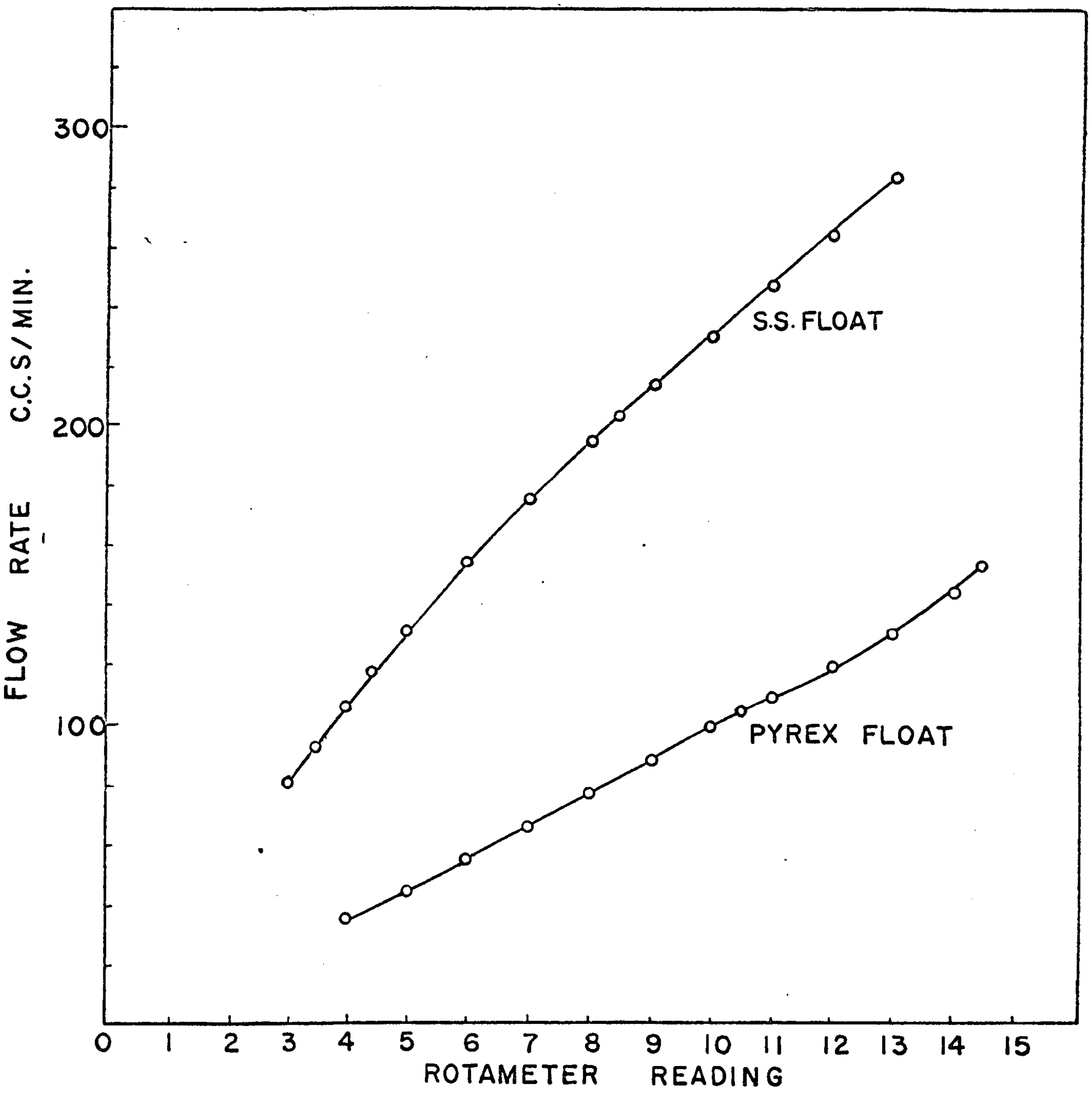

Figure 25 Isobutylene Calibration at 1 atm. and 0°C

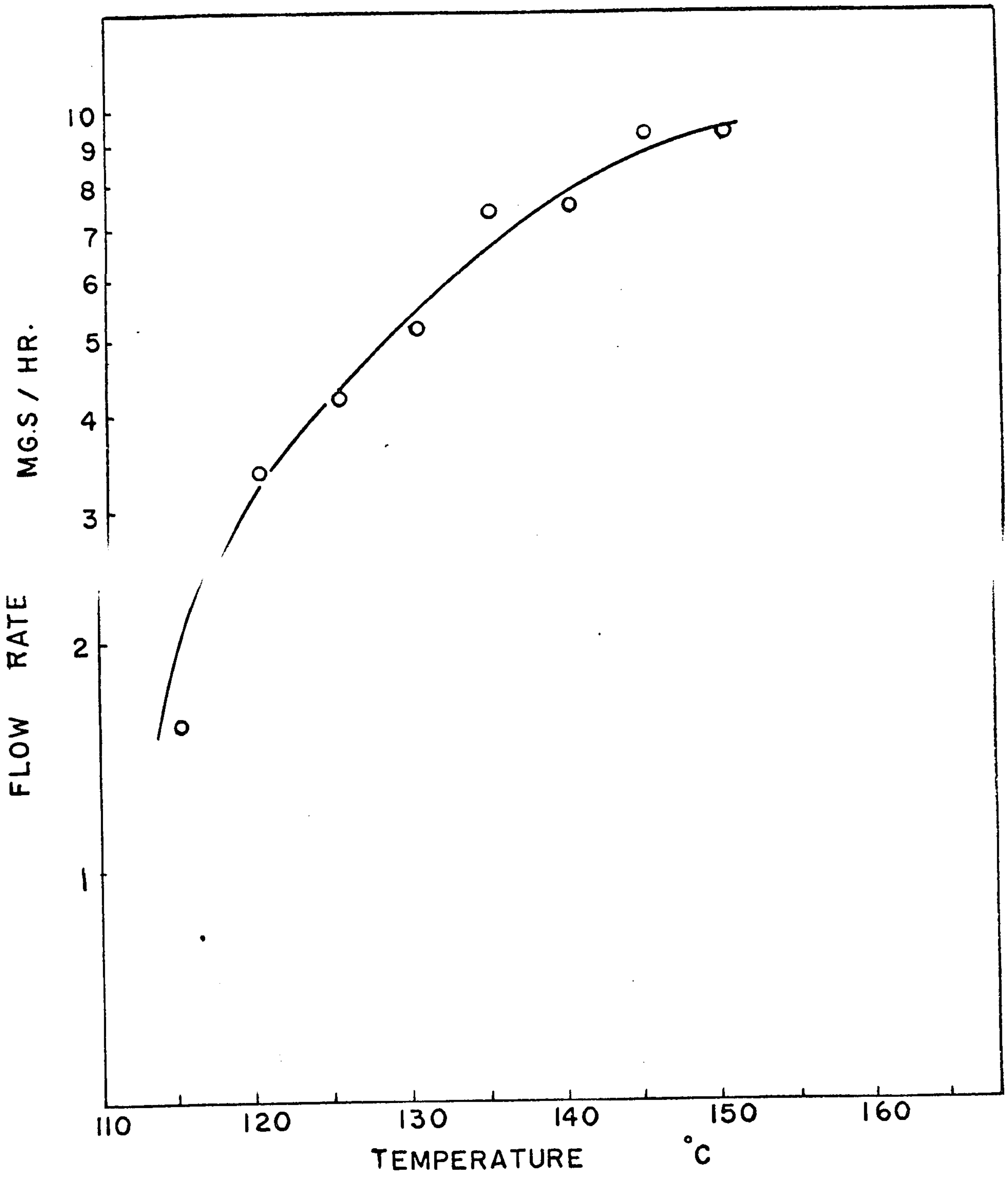

Figure 26 Selenium Dioxide Rate Calibration

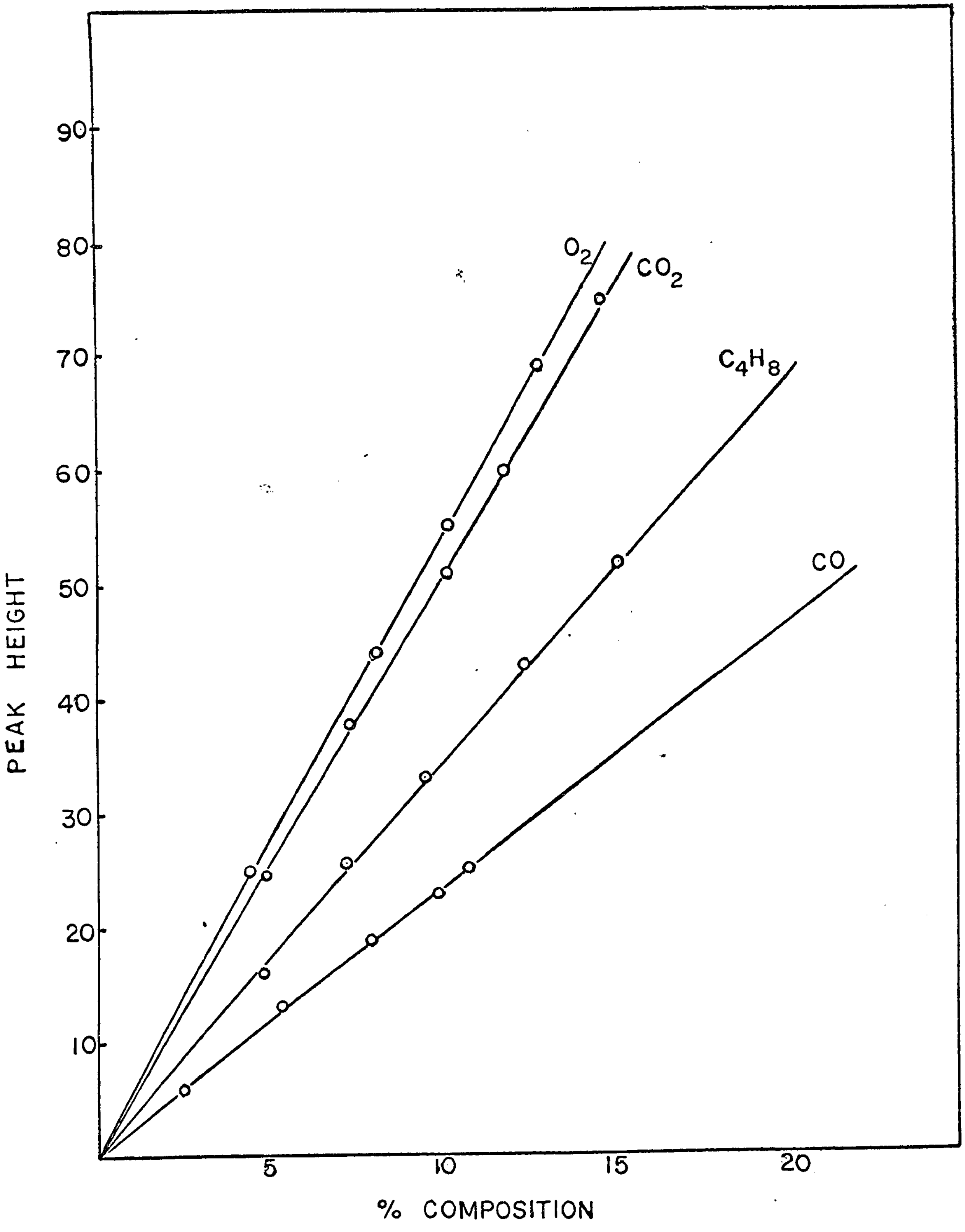

Figure 27 Calibration of Gases at 1 atm. and 25°C

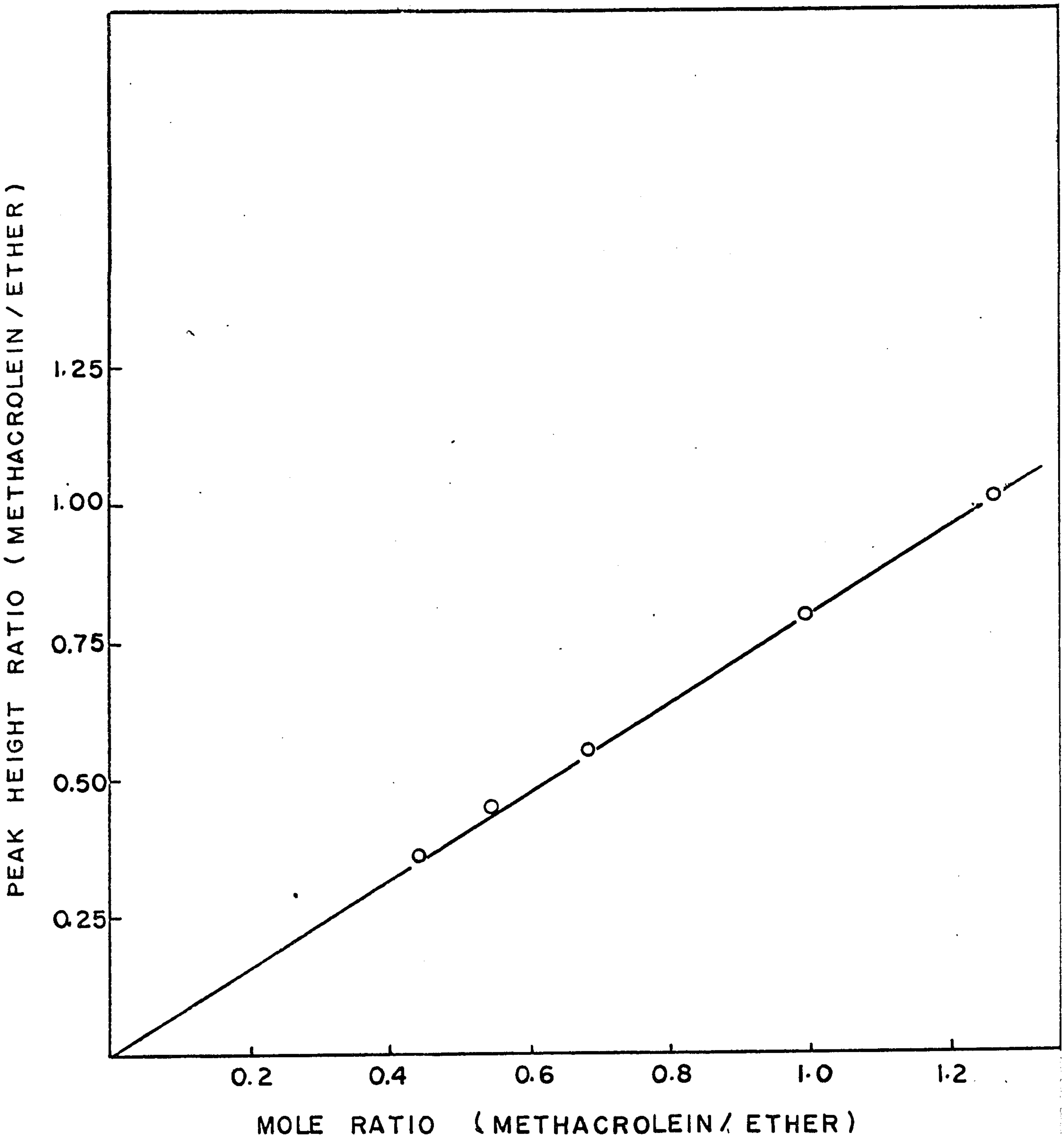

Figure 28 Calibration of Methacrolein

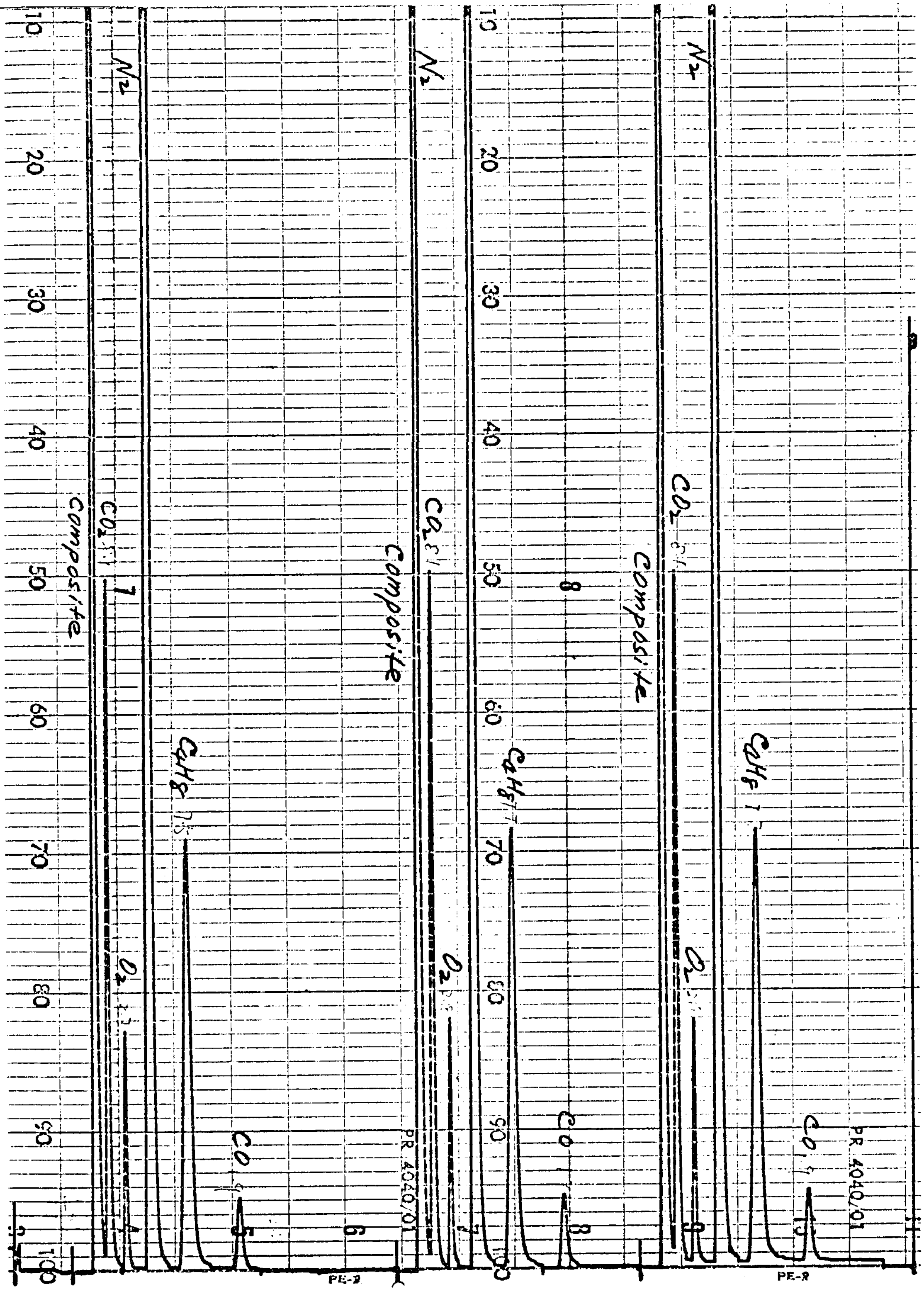

Figure 29 Typical Analysis of the Gaseous Products

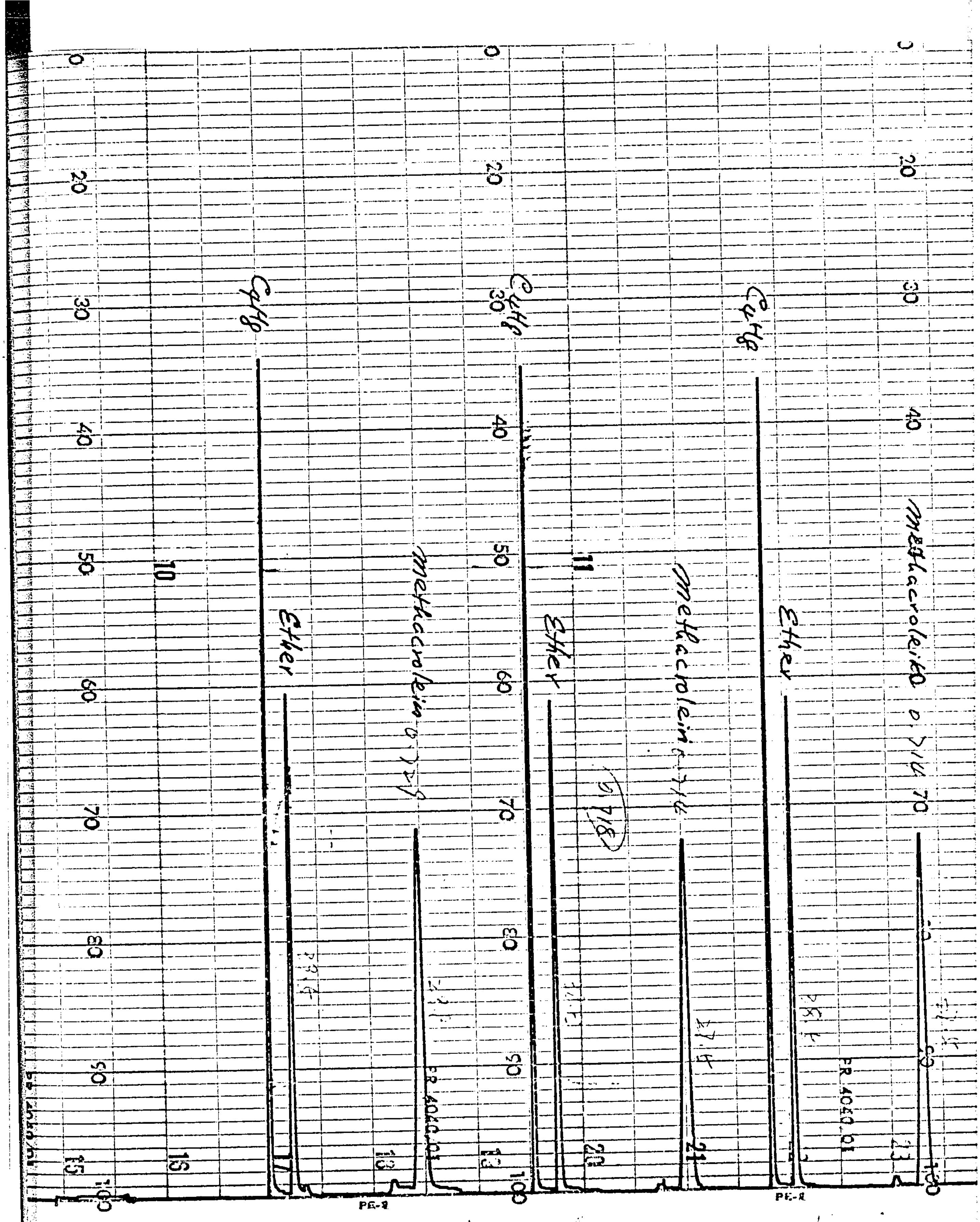

Figure 30   Typival Analysis of the Liquid Products

E. Sample Calculation

Weight of Catalyst	0.6547 gm.
Reaction Temperature	400°C
Weight Percentage of Selenium Dioxide	0.45

Moles In:

Moles C_4H_8/hr

$$= \frac{145.4 \text{ c.c./min.} \times 60 \text{ min./hr}}{22,414} = 0.3898 \text{ moles/hr}$$

Moles O_2/hr

$$= \frac{498 \text{ c.c./min.} \times 60 \text{ min./hr} \times 20.95\%}{22,414} = 0.2794 \text{ moles/hr}$$

Moles N_2/hr

$$= \frac{498 \text{ c.c./min.} \times 60 \text{ min./hr} \times 79.0\%}{22,414} = 1.0617 \text{ moles/hr}$$

Analysis

A. Gas	CO_2	4.5%
	O_2	6.5%
	N_2	69.7%

C_4H_8	17.7%
CO	1.6%

B.	Liquid	H_2O		2.3120 gm
		Peak Height Ratio	(Methacrolein/Ether)	0.476
		Moles Ratio	(Methacrolein/Ether)	0.604
		Ether		7.6203 gm

Moles Out:

$$\text{Moles } C_4H_8 = \frac{17.7}{69.7} \times 1.0617 = 0.2696 \text{ moles/hr}$$

$$\text{Moles } O_2\text{/hr} = \frac{6.5}{69.7} \times 1.0617 = 0.0990 \text{ moles/hr}$$

$$\text{Moles N/hr} = \frac{69.7}{69.7} \times 1.0617 = 1.0617 \text{ moles/hr}$$

$$\text{Moles } CO_2\text{/hr} = \frac{4.5}{69.7} \times 1.0617 = 0.0685 \text{ moles/hr}$$

$$\text{Moles CO/hr} = \frac{1.6}{69.7} \times 1.0617 = 0.0244 \text{ moles/hr}$$

$$\text{Moles } H_2O\text{/hr} = \frac{2.3120}{18.02} = 0.1283 \text{ moles/hr}$$

$$\text{Moles } C_4H_6O\text{/hr} = \frac{7.6203}{74.12} \times 0.604 = 0.0621 \text{ moles/hr}$$

Percent Conversion of Isobutylene

$$X = \frac{0.3898 - 0.2696}{0.3898} = \frac{0.1202}{0.3898} = 30.84\%$$

Rate of Formation

$$W_{CO_2} = \frac{0.0685}{0.6547} = 0.1046 \text{ mole/hr-gm}$$

$$W_{CO} = \frac{0.0244}{0.6547} = 0.0373 \text{ mole/hr-gm}$$

$$W_{H_2O} = \frac{0.1283}{0.6547} = 0.1960 \text{ mole/hr-gm}$$

$$W_{C_4H_6O} = \frac{0.0621}{0.6547} = 0.0921 \text{ mole/hr-gm}$$

Selectivity for Methacrolein Formation

$$S = \frac{W_{C_4H_6O}}{W_{CO_2} + W_{CO} + W_{H_2O} + W_{C_4H_6O}}$$

$$= \frac{0.0921}{0.1046 + 0.0373 + 0.1960 + 0.0921}$$

$$= \frac{0.0921}{0.4300} = 0.2142$$

F. Experimental Data

Temperature 425°C R = 0.7168

Run	Z	Feed moles/hr			Conversion	Selectivity
No.		C_4H_8	O_2	N_2	$X_{C_4H_8}$	S
301	0	0.3898	0.2794	1.0617	0.2109	0.0876
302	0.15%	0.3898	0.2794	1.0617	0.2968	0.1278
303	0.45%	0.3898	0.2794	1.0617	0.2898	0.1852
304	0.95%	0.3898	0.2794	1.0617	0.2260	0.1753

Run	Products moles/hr			Rates of Formation moles/hr-gms. catalyst.			
No.	C_4H_8	O_2	N_2	WCO_2	WCO	WH_2O	WC_4H_6O
301	0.3076	0.0328	1.0617	0.1955	0.0310	0.2157	0.0425
302	0.2741	0.0333	1.0617	0.1897	0.0322	0.2482	0.0689
303	0.2788	0.1011	1.0617	0.1100	0.0281	0.1958	0.0759
304	0.3017	0.1037	1.0617	0.0993	0.0237	0.1608	0.0603

Temperature 425°C   R = 0.9910

Run No.	Z	Feed moles/hr C_4H_8	Feed moles/hr O_2	Feed moles/hr N_2	Conversion $X_{C_4H_8}$	Selectivity S
305	0%	0.3898	0.3863	1.4566	0.2239	0.0539
306	0.15%	0.3898	0.3863	1.4566	0.3180	0.1007
307	0.45%	0.3898	0.3863	1.4566	0.3145	0.1606
308	0.95%	0.3898	0.3863	1.4566	0.2775	0.1478

Run No.	Products moles/hr C_4H_8	Products moles/hr O_2	Products moles/hr N_2	Rates of Formation moles/hr-gms. catalyst W_{CO_2}	Rates of Formation moles/hr-gms. catalyst W_{CO}	Rates of Formation moles/hr-gms. catalyst W_{H_2O}	Rates of Formation moles/hr-gms. catalyst $W_{C_4H_6O}$
305	0.3025	0.0876	1.4566	0.2364	0.0715	0.2656	0.0327
306	0.2658	0.0834	1.4566	0.2426	0.0455	0.2942	0.0652
307	0.2672	0.1362	1.4566	0.1477	0.0452	0.2311	0.0811
308	0.2816	0.1105	1.4566	0.1442	0.0490	0.2216	0.0719

Temperature 425°C R = 1.3746

Run No.	Z	Feed moles/hr C_4H_8	Feed moles/hr O_2	Feed moles/hr N_2	Conversion $X_{C_4H_8}$	Selectivity S
309	0%	0.3898	0.5358	2.0203	0.3098	0.0454
310	0.15%	0.3898	0.5358	2.0203	0.3916	0.0809
311	0.45%	0.3898	0.5358	2.0203	0.3824	0.1443
312	0.95%	0.3898	0.5358	2.0203	0.3612	0.1242

Run No.	Products moles/hr C_4H_8	Products moles/hr O_2	Products moles/hr N_2	Rates of Formation moles/hr-gms. catalyst W_{CO_2}	W_{CO}	W_{H_2O}	$W_{C_4H_6O}$
309	0.6295	0.1165	2.0203	0.3318	0.0891	0.3657	0.0374
310	0.2372	0.0829	2.0203	0.3284	0.0831	0.4025	0.0716
311	0.2407	0.1976	2.0203	0.1906	0.0635	0.3056	0.0944
312	0.2490	0.1639	2.0203	0.1877	0.0626	0.2794	0.0752

Temperature 425°C R = 1.6644

Run No.	Z	Feed moles/hr C_4H_8	O_2	N_2	Conversion $X_{C_4H_8}$	Selectivity S
313	0%	0.3898	0.6488	2.4704	0.2965	0.0434
314	0.15%	0.3898	0.6488	2.4704	0.4171	0.0725
315	0.45%	0.3898	0.6488	2.4704	0.4037	0.1325
316	0.95%	0.3898	0.6488	2.4704	0.3726	0.1189

Run	Products moles/hr			Rates of Formation moles/hr-gms. catalyst			
No.	C_4H_8	O_2	N_2	W_{CO_2}	W_{CO}	W_{H_2O}	$W_{C_4H_6O}$
313	0.2742	0.1534	2.4704	0.4108	0.0976	0.4220	0.0422
314	0.2272	0.1086	2.4704	0.4075	0.0900	0.4422	0.0735
315	0.2324	0.2540	2.4704	0.2346	0.0718	0.3453	0.0996
316	0.2446	0.2175	2.4704	0.2277	0.0759	0.3267	0.0851

Temperature 400°C   R = 0.7168

Run No.	Z	Feed moles/hr C_4H_8	O_2	N_2	Conversion $X_{C_4H_8}$	Selectivity S
317	0	0.3898	0.2794	1.0617	0.1737	0.0648
318	0.15%	0.3898	0.2794	1.0617	0.3163	0.1512
319	0.45%	0.3898	0.2794	1.0617	0.3084	0.2142
320	0.95%	0.3898	0.2794	1.0617	0.2617	0.1671

Run No.	Products moles/hr C_4H_8	O_2	N_2	Rates of Formation moles/hr-gm. cat. W_{CO_2}	W_{CO}	W_{H_2O}	$W_{C_4H_6O}$
317	0.3221	0.0492	1.0617	0.2036	0.0315	0.2083	0.0307
318	0.2665	0.0374	1.0617	0.1648	0.0367	0.2462	0.0797
319	0.2696	0.0990	1.0617	0.1046	0.0373	0.1960	0.0921
320	0.2878	0.0807	1.0617	0.1071	0.0350	0.1862	0.0658

Temperature 400°C   R = 0.9910

Run No.	Z	Feed moles/hr C_4H_8	Feed moles/hr O_2	Feed moles/hr N_2	Conversion $X_{C_4H_8}$	Selectivity S
321	0%	0.3898	0.3863	1.4566	0.2154	0.0603
322	0.15%	0.3898	0.3863	1.4566	0.3542	0.1387
323	0.45%	0.3898	0.3863	1.4566	0.3425	0.1731
324	0.95%	0.3898	0.3863	1.4566	0.2782	0.1405

Run No.	Products moles/hr C_4H_8	Products moles/hr O_2	Products moles/hr N_2	Rates of Formation moles/hr-gms. catalyst W_{CO_2}	Rates of Formation moles/hr-gms. catalyst W_{CO}	Rates of Formation moles/hr-gms. catalyst W_{H_2O}	Rates of Formation moles/hr-gms. catalyst $W_{C_4H_6O}$
321	0.3058	0.0772	1.4566	0.2577	0.0527	0.2606	0.0367
322	0.2517	0.0539	1.4566	0.2115	0.0500	0.2780	0.0869
323	0.2563	0.1312	1.4566	0.1376	0.0510	0.2545	0.0927
324	0.2813	0.1099	1.4566	0.1410	0.0510	0.2190	0.0672

Temperature 400°C R = 1.3746

Run No.	Z	Feed moles/hr C_4H_8	Feed moles/hr O_2	Feed moles/hr N_2	Conversion $X_{C_4H_8}$	Selectivity S
325	0%	0.3898	0.5358	2.0203	0.2997	0.0540
326	0.15%	0.3898	0.5358	2.0203	0.4265	0.1053
327	0.45%	0.3898	0.5358	2.0203	0.3874	0.1214
328	0.95%	0.3898	0.5358	2.0203	0.3299	0.1127

Run No.	Products moles/hr C_4H_8	Products moles/hr O_2	Products moles/hr N_2	Rates of Formation moles/hr-gms. catalyst W_{CO_2}	Rates of Formation moles/hr-gms. catalyst W_{CO}	Rates of Formation moles/hr-gms. catalyst W_{H_2O}	Rates of Formation moles/hr-gms. catalyst $W_{C_4H_6O}$
325	0.2730	0.1023	2.0203	0.3400	0.0810	0.3570	0.0445
326	0.2236	0.0735	2.0203	0.3101	0.0736	0.3728	0.0891
327	0.2388	0.1342	2.0203	0.2007	0.0629	0.3026	0.0782
328	0.2612	0.1649	2.0203	0.2099	0.0713	0.2911	0.0727

Temperature 400°C R = 1.6644

Run No.	Z	Feed moles/hr C_4H_8	Feed moles/hr O_2	Feed moles/hr N_2	Conversion $X_{C_4H_8}$	Selectivity S
329	0%	0.3898	0.6488	2.4704	0.2929	0.0369
330	0.15%	0.3898	0.6488	2.4704	0.3965	0.0813
331	0.45%	0.3898	0.6488	2.4704	0.3622	0.1099
332	0.95%	0.3898	0.6488	2.4704	0.2900	0.0832

Run No.	Products moles/hr C_4H_8	Products moles/hr O_2	Products moles/hr N_2	Rates of Formation moles/hr-gms. catalyst W_{CO_2}	Rates of Formation moles/hr-gms. catalyst W_{CO}	Rates of Formation moles/hr-gms. catalyst W_{H_2O}	Rates of Formation moles/hr-gms. catalyst $W_{C_4H_6O}$
329	0.2756	0.1429	2.4704	0.4316	0.0981	0.4298	0.0368
330	0.2352	0.1073	2.4704	0.3951	0.0904	0.4538	0.0831
331	0.2486	0.3172	2.4704	0.2587	0.0781	0.3510	0.0848
332	0.2768	0.2143	2.4704	0.2577	0.0924	0.3265	0.0616

Temperature 375°C   R = 0.7168

Run No.	Z	Feed moles/hr C_4H_8	Feed moles/hr O_2	Feed moles/hr N_2	Conversion $X_{C_4H_8}$	Selectivity S
333	0	0.3898	0.2794	1.0617	0.1860	0.0805
334	0.15%	0.3898	0.2794	1.0617	0.2440	0.1221
335	0.45%	0.3898	0.2794	1.0617	0.2306	0.1678
336	0.95%	0.3898	0.2794	1.0617	0.1955	0.1177

Run No.	Products moles/hr C_4H_8	Products moles/hr O_2	Products moles/hr N_2	Rates of Formation moles/hr-gms. catalyst W_{CO_2}	W_{CO}	W_{H_2O}	$W_{C_4H_6O}$
333	0.3134	0.0539	1.0617	0.1871	0.0313	0.2018	0.0368
334	0.2947	0.0586	1.0617	0.1579	0.0377	0.2039	0.0556
335	0.2999	0.1057	1.0617	0.1045	0.0284	0.1717	0.0614
336	0.3136	0.0894	1.0617	0.1101	0.0431	0.1662	0.0426

Temperature 375°C   R = 0.9910

Run	Z	Feed moles/hr			Conversion	Selectivity
No.		C_4H_8	O_2	N_2	$X_{C_4H_8}$	S
337	0%	0.3898	0.3863	1.4566	0.1901	0.0461
338	0.15%	0.3898	0.3863	1.4566	0.3105	0.1128
339	0.45%	0.3898	0.3863	1.4566	0.2724	0.1361
340	0.95%	0.3898	0.3863	1.4566	0.2250	0.1015

Run	Products moles/hr			Rates of Formation moles/hr-gms. catalyst			
No.	C_4H_8	O_2	N_2	W_{CO_2}	W_{CO}	W_{H_2O}	$W_{C_4H_6O}$
337	0.3157	0.0836	1.4566	0.2461	0.0530	0.2476	0.0264
338	0.2688	0.0784	1.4566	0.2036	0.0509	0.2719	0.0669
339	0.2836	0.1618	1.4566	0.1514	0.0495	0.2277	0.0675
340	0.3021	0.1273	1.4566	0.1543	0.0648	0.2178	0.0493

Temperature 375°C R = 1.3746

Run No.	Z	Feed moles/hr C_4H_8	O_2	N_2	Conversion $X_{C_4H_8}$	Selectivity S
341	0%	0.3898	0.5358	2.0203	0.3222	0.0624
342	0.15%	0.3898	0.5358	2.0203	1.4347	0.1047
343	0.45%	0.3898	0.5358	2.0203	0.3513	0.1232
344	0.95%	0.3898	0.5358	2.0203	0.3241	0.0958

Run No.	Products moles/hr C_4H_8	O_2	N_2	Rates of Formation moles/hr-gms. catalyst W_{CO_2}	W_{CO}	W_{H_2O}	$W_{C_4H_6O}$
341	0.2642	0.1023	2.0203	0.3328	0.0802	0.3631	0.0516
342	0.2204	0.0735	2.0203	0.2942	0.0852	0.3863	0.0895
343	0.2528	0.2342	2.0203	0.2073	0.0773	0.3111	0.0837
344	0.2635	0.1649	2.0203	0.2119	0.0959	0.3064	0.0651

Temperature 375°C R = 1.6644

Run	Z	Feed moles/hr			Conversion	Selectivity
No.		C_4H_8	O_2	N_2	$X_{C_4H_8}$	S
345	0%	0.3898	0.6488	2.4704	0.3196	0.0523
346	0.15%	0.3898	0.6488	2.4704	0.4512	0.0907
347	0.45%	0.3898	0.6488	2.4704	0.3443	0.1111
348	0.95%	0.3898	0.6488	2.4704	0.3250	0.1149

Run	Products moles/hr			Rates of Formation moles/hr-gms. catalyst			
No.	C_4H_8	O_2	N_2	W_{CO_2}	W_{CO}	W_{H_2O}	$W_{C_4H_6O}$
345	0.2652	0.1429	2.4704	0.4026	0.1019	0.4229	0.0512
346	0.2139	0.1073	2.4704	0.3511	0.1077	0.4356	0.0892
347	0.2556	0.3172	2.4704	0.2670	0.0791	0.3405	0.0858
348	0.2631	0.2143	2.4704	0.2598	0.1011	0.2991	0.0857

Temperature 350°C R = 0.7168

Run No.	Z	Feed moles/hr C_4H_8	O_2	N_2	Conversion $X_{C_4H_8}$	Selectivity S
349	0	0.3898	0.2794	1.0617	0.1916	0.0883
350	0.15%	0.3898	0.2794	1.0617	0.2122	0.1175
351	0.45%	0.3898	0.2794	1.0617	0.2455	0.1928
352	0.95%	0.3898	0.2794	1.0617	0.2370	0.1609

	Products moles/hr			Rates of Formation moles/hr-gms. catalyst			
Run No.	C_4H_8	O_2	N_2	W_{CO_2}	W_{CO}	W_{H_2O}	$W_{C_4H_6O}$
341	0.3151	0.0627	1.0617	0.1677	0.0287	0.182	0.0367
350	0.3071	0.0835	1.0617	0.1492	0.0385	0.1770	0.0486
351	0.2941	0.0919	1.0617	0.0959	0.0281	0.1784	0.0723
352	0.2974	0.0909	1.0617	0.0988	0.0353	0.1726	0.0588

Temperature 350°C   R = 0.9910

Run No.	Z	Feed moles/hr C_4H_8	Feed moles/hr O_2	Feed moles/hr N_2	Conversion $X_{C_4H_8}$	Selectivity S
353	0%	0.3898	0.3863	1.4566	0.2055	0.0544
354	0.15%	0.3898	0.3863	1.4566	0.2476	0.1023
355	0.45%	0.3898	0.3863	1.4566	0.2578	0.1205
356	0.95%	0.3898	0.3863	1.4566	0.2560	0.1180

Run No.	Products moles/hr C_4H_8	Products moles/hr O_2	Products moles/hr N_2	Rates of Formation moles/hr-gms. catalyst W_{CO_2}	W_{CO}	W_{H_2O}	$W_{C_4H_6O}$
353	0.3097	0.0953	1.4566	0.2232	0.0496	0.2528	0.0309
354	0.2933	0.1062	1.4566	0.1928	0.0490	0.2407	0.0550
355	0.2893	0.1465	1.4566	0.1647	0.0684	0.2516	0.0651
356	0.2790	0.1067	1.4566	0.1570	0.0755	0.2459	0.0640

Temperature 350°C R = 0.9910

Run	Z	Feed moles/hr			Conversion	Selectivity
No.		C_4H_8	O_2	N_2	$X_{C_4H_8}$	S
353	0%	0.3898	0.3863	1.4566	0.2055	0.0544
354	0.15%	0.3898	0.3863	1.4566	0.2476	0.1023
355	0.45%	0.3898	0.3863	1.4566	0.2578	0.1205
356	0.95%	0.3898	0.3863	1.4566	0.2560	0.1180

Run	Products moles/hr			Rates of Formation moles/hr-gms. catalyst			
No.	C_4H_8	O_2	N_2	W_{CO_2}	W_{CO}	W_{H_2O}	$W_{C_4H_6O}$
353	0.3097	0.0953	1.4566	0.2232	0.0496	0.2528	0.0309
354	0.2933	0.1062	1.4566	0.1928	0.0490	0.2407	0.0550
355	0.2893	0.1465	1.4566	0.1647	0.0684	0.2516	0.0651
356	0.2900	0.1067	1.4566	0.1570	0.0755	0.2459	0.0640