# THE OXIDATION OF ETHYLENE ON A SUPPORTED SILVER CATALYST IN A LIQUID PHASE

by

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## ABSTRACT

The kinetics of ethylene oxidation on a supported silver catalyst in dibutyl phthalate at 220°C have been investigated. The external mass transfer resistances and the intraparticle mass transfer resistance were found to be negligible. One constant ethylene partial pressure of 0.5 atm was used. The oxygen partial pressure was varied from 0.115 atm to 0.282 atm and was the primary variable investigated. To evaluate the effects of reaction products on the rates, the feed flow rate was varied and the dependence of rates on the sum of the product partial pressures was examined.

The data were expressed in term of relative reaction rates to allow for observed variations in catalytic activity. These relative rates were ratios of measured rates with rates of bracketing runs at a defined set of standard conditions being used as the point of reference. To determine the relationship between relative rates and oxygen partial pressure, the relative rates were all compared at the same average total product concentration.

The rate of formation of ethylene oxide was found to be first order with respect to oxygen partial pressures, and for carbon dioxide formation, the order was found to be 1.73 . Inhibition of the reaction by reaction products

was also observed .

Dibutyl phthalate, used as the inert solvent, was found to be unstable in the presence of ethylene oxidation reaction . The saponification of the diester gave phthalic anhydride and butanol .

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# I INTRODUCTION

The vast potentialities of ethylene oxide as an organic intermediate in the chemical industry have stimulated many investigations dealing with the preparation, properties and uses of this compound. Since Lefort 's original patent (40) in 1931, the partial oxidation of ethylene to ethylene oxide with concurrent formation of carbon dioxide and water have been extensively studied. In a recent review of the catalytic oxidation of olefins, covering literature up to 1965, Voge and Adams (66) cited nearly 90 references in their discussion on the ethylene oxidation to ethylene oxide, and it is still a growing subject.

In the available literature, there is still much that is conflicting and dubious. Uncertainties remain concerning the species adsorbed on the catalyst. There is also contradiction between adsorption studies of reacting gases without reaction and studies of kinetics. The role of various moderators is still not well understood. Finally, no unifying reaction mechanism has as yet been proposed which satisfactorily takes into account all the accumulated knowledge of the subject.

In 1961, Shingu (59) patented a process in which a slurry reactor was used. His work gives the necessary inspiration for this study. Although some of his claims are questionable, the partial oxidation of ethylene on silver

in a slurry reactor would be an interesting subject for research , since there is still no published technical paper on the process invented by Shingu.

The purpose of this work is therefore to provide a preliminary step to the study of the feasibility of this process. Various mass transfer processes in the reaction were investigated. It was shown that the reaction was kinetically controlled under the experimental conditions employed, so that a kinetic study was feasible. The rates of formation of ethylene oxide and carbon dioxide were measured over a wide range of reactant partial pressures. The effects of oxygen pressure and product pressure on reaction rates were also studied.

It is hoped that this study will provide a first step to a full kinetic study. Although many problems still have to be overcome, with the growing number of published works recently on three phase reaction systems, the subject can prove to be both important and interesting .

## II BACKGROUND AND REVIEW OF LITERATURE

### 2-1 General :

Catalytic partial oxidations of hydrocarbons to useful products are currently of great commercial interest, including the case of ethylene oxidation. Several reviews of catalytic oxidation have appeared recently. The most extensive reviews are those of Voge and Adams (66) and Klugherz (34) . Also noteworthy are reviews of hydrocarbon oxidation by Margolis (41) and Sampson and Shooter (65) . Although the gas phase ethylene oxidation has been extensively studied since the Lefort's patent issued in 1931, the reaction in a liquid phase is not a well treated subject. In 1961, Shingu (59) patented a process in which a slurry reactor was used . It was claimed that a very high selectivity was achieved for ethylene oxide formation in the partial oxidation of ethylene. Since then there is no published work on the subject.

The review of literature to follow has been divided into several sections. After a brief description of the chemistry of the reactions involved, previous works concerned with adsorption, kinetics of the reaction and the effect of moderators are presented . All works were in gas phase systems, but it is necessary for the understanding of the mechanism in a three phase reaction system. The final section will concern the Shingu patent . Also various aspects in a slurry reactor will be discussed .

## 2-2 Process Description :

There are three reactions involved in the formation of ethylene oxide, carbon dioxide and water from ethylene by oxidation on silver catalyst. Reaction (A) and (B) describe the formation of products by the direct oxidation of ethylene :

$$C_2H_4 + \frac{1}{2} O_2 \longrightarrow C_2H_4O \qquad (A)$$

$$C_2H_4 + 3 O_2 \longrightarrow 2CO_2 + 2 H_2O \qquad (B)$$

Reaction (C) indicates that by-products are also formed by further oxidation of ethylene oxide :

$$C_2H_4O + \frac{5}{2} O_2 \longrightarrow 2CO_2 + 2 H_2O \qquad (C)$$

All three reactions are exothermic and highly irreversible .The reaction is usually run at temperatures of 200° to 300°C and at pressures ranging from one to about twenty atmospheres. Oxygen is used either alone or diluted with an inert gas,as in air . Selectivity defined as the percent ethylene oxide formed, based on the amount of ethylene reacted, is of prime concern from an economic point of view. Selectivities for this reaction commonly range from 50 to 70 % .

Silver, most often supported on a low surface area support such as $\alpha$-alumina, is used as the catalyst. There are many references to catalyst preparation in the literature, particularly patents concerned with promoters to improve the selectivity of the reaction (66) .

It is interesting to note that ethylene is the only olefin which is converted to an epoxide by reaction on silver. All other olefins are oxidized essentially to carbon dioxide. Silver is also the only heterogeneous catalyst for ethylene oxidation to ethylene oxide .

Several studies have been concerned with the importance of reaction (C), production of $CO_2$ by further oxidation of ethylene oxide, as compared with step (B) , formation of $CO_2$ by a parallel route. However, most studies of the kinetics of ethylene oxidation agree on the predominance of the parallel oxidation to ethylene oxide and carbon dioxide (66, 42, 53 ). It is likely that the few studies which show consecutive oxidation of ethylene oxide to be important , such as those of Twigg (64, 65) and Andrianova and Todes (3 ) , are not at all typical of normal flow system oxidation over silver .

2-3 Adsorption :

For silver catalyst, the formation of $Ag_2O$ or other silver oxides is impossible under usual operating conditions. Data reviewed by Dushman (71) show that the equilibrium oxygen pressure over $Ag_2O$ equals that of atmospheric air (159 mm) at 149°C and is at 3.3atm at 227°C. Thus, under conditions commonly used for fundamental studies of ethylene oxidation, the oxide phase cannot exist. Most adsorption studies have therefore been concerned with the interaction

of various gases with silver, prepared as a metallic film, precipitated as powder, or deposited on a support. Although silver oxide does not exist as a separate phase at reaction conditions, studies on oxygen covered surfaces , where the oxide could be considered to exist as a surface phase, have recently become important.

2-3-1 Oxygen Adsorption :

Oxygen adsorption on silver has been studied most extensively. Both kinetic and equilibrium measurements have been made, and oxygen is known to be fairly strongly chemisorbed on silver at temperatures used in oxidation ( 4 , 7 , 8 ,19 ,61 ). An exellent review is by Voge and Adams (66 ). On the basis of studies of adsorption kinetics, Smeltzer , Tollefson and Cambon (61) and Czanderna (19) postulated that more than one type of oxygen complex is present on the surface .

Smeltzer et al (61) observed a transition in the rate of adsorption at about 50 % coverage of the surface. They concluded that at low coverages, each oxygen atom was associated with two silver atoms, but at high coverages, two oxygen atoms were associated with each pair of silver atoms. In other words, oxygen atoms and oxygen molecules were both present on the surface. Since two kinds of oxygen were present, they recommended that caution should be observed in the development of rate equations for the kinetics

of reactions on silver catalysts.

Smeltzer et al. (61), Meisenheimer et al. (45), and Czanderna (19) all showed that the rate of adsorption on silver was very fast up to about 50 % coverage and then decreased to a much lower value. This contrasted with the behavior expected for Langmuir kinetics , in which the rate of adsorption decreased linearly with increasing coverage. Over limited ranges of surface coverage, particularly above 50 %, Smeltzer et al. and Meisenheimer et al. found that their adsorption kinetics could be fitted to the semi-impirical Elovich equation :

$$\frac{dq}{dt} = ae^{-bq}$$

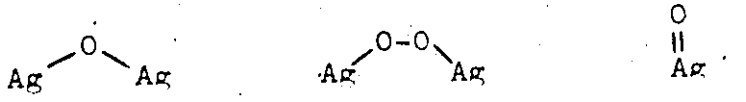
where q is the amount adsorbed, t is the time and a and b are constants.

A significant fraction of oxygen on silver was irreversibly adsorbed. Meisenheimer et al. (45) reported that more than 50 % of the adsorbed oxygen could not be removed by evacuation for several hours at 200°C. According to Benton and Drake ( 8 ) the oxygen could not all be desorbed even by evacuation at 300°C . Treatment with hydrogen was necessary to remove this tightly bound oxygen. Czanderna (19 ) reported that by outgassing a sample at 350°C most of the oxygen could be desorbed from silver. However, chemical treatment with CO for example, was required to remove the oxygen completely.

Finally, it is interesting to note that the rate of oxygen adsorption has been found to be over a hundred times

slower at a fractional surface coverage of 0.7 than the rate of oxygen consumption during oxidation at 200°C over the same catalyst (45). This suggests that the reaction probably proceeds at a lower oxygen coverage than that corresponding to the equilibrium of the surface with oxygen in the gas phase.

Many studies have revealed a strong dependence of the heat of adsorption of oxygen on the degree of coverage of the silver surface. Ostrovskii and Temkin (48) determined the heat of chemical adsorption both directly from adsorption experiments using a calorimeter, and indirectly from the heat of reaction of hydrogen with a surface layer of chemisorbed oxygen. The heat of adsorption was found to decrease almost linearly from 130 Kcal/mole at zero coverage to 80Kcal/mole at a surface coverage corresponding to a ratio of about one atom of oxygen for every two atoms of silver. At higher oxygen coverage, the heat of chemisorption fell more rapidly, until at a surface coverage approaching a monolayer, the heat of adsorption levelled off at about 10 Kcal/mole. Ostrovskii and Temkin interpreted their results in terms of a transition from a structure of type (I) at a low coverage, to one of type(II) (a peroxide) or type (III) at high coverage:




(I) (II) (III)

These types of structure have also been proposed by other authors, such as Smeltzer et al(61), to represent atomic oxygen

adsorption (structure I) and molecular oxygen adsorption (II).

2-3-2 Ethylene Adsorption :

The question of whether ethylene is adsorbed on the catalyst during the reaction has not yet been answered satisfactorily. It has often been reported by Twigg (64,65) Trapnel (63,29) and others (21,22,23) that ethylene is not adsorbed on silver. However, a number of studies have appeared recently in which adsorption of ethylene on a oxygen covered surface has been discussed. Of course,at sufficiently high temperatures, the ethylene reacts with oxygen(64,65).However, studies of ethylene adsorption can be made at sufficiently low temperatures, using either silver covered with a film of adsorbed oxygen or silver oxide as a separate phase.

Trapnell (29,63) and Margolis (43) have both reported that ethylene is adsorbed on an oxygen covered silver surface. Margolis pointed out that the behaviour was quite similar to that observed for adsorption on metal oxides.Ethylene was adsorbed on metallic silver too, although the coverage was low. The same was found to be true by Allen and Scafe (1 ) by their study of adsorption of silver on silver oxide.

A most interesting study has been published by Belousov and Rubanik (6 ). They used a"competing reaction" technique in which they determined the effect of various hydrocarbons present in the gas mixture on the extent of ethylene oxidation. Thus it was found, for example, that

when propylene was removed from a gas mixture containing ethylene and oxygen and replaced with nitrogen, the conversion of ethylene was increased from about 6% to 64%. It was concluded that this effect would be impossible if ethylene oxidation proceeded by an "impact" mechanism, i.e. reaction between adsorbed oxygen and gaseous ethylene. Reaction must involve an adsorbed ethylene species as well as adsorbed oxygen .

2-3-3 Adsorption of other gases :

The adsorption of the products of ethylene oxidation on silver has also been studied. Twigg (64,65) found that ethylene oxide was adsorbed with decomposition . Others such as McCarty (72) have reported the same result. Allen and Sciafe ( 2) reported that ethylene oxide was adsorbed on silver oxide at temperatures greater than 250°K. Reaction with the surface was observed above 323°K .

Drake and Benton (20) and Czanderna (19) reported that $CO_2$ was adsorbed on oxygen covered silver, although $CO_2$ was not chemisorbed on the reduced metal surface .

2-4Kinetics and Mechanism:

The reaction kinetics of ethylene oxidation on silver catalysts prepared by a variety of techniques has been extensively studied. However, there is no general agreement on a mechanism based on the kinetic data obtained. Many

workers have sought to relate these data to what is known regarding adsorption on the catalyst. Here, too, there has not yet been agreement. For example, as discussed in the previous section, chemisorption measurements show that ethylene is adsorbed only weakly on silver, if at all. On the other hand, the observed kinetics indicate fairly strong adsorption during reaction. Furthermore, questions have arisen as to whether atomic or molecular adsorbed oxygen is the species that reacts with ethylene.

The review articles by Voge and Adams (66), Klugherz (34) and Margolis (41) contain exellent tabulations of work on ethylene oxidation kinetics. In the following section, only some of the significant papers will be discussed.

It is generally acknowledged that Twigg (64, 65) was the first to present a study of the fundamental phenomena involved in ethylene oxidation. Many of his results are recognized as invalid, however, since much of his work was done in a static system. If a reaction is relatively rapid, as it is here, it is likely that steady state conditions on the surface are never achieved, since concentrations are changing continuously.

Orzechowskii and MacCormack (51) were the first to show that, following a change in operating conditions, conversions and selectivities continued to change slowly after reaching new values. These "slow processes" were attributed to slow establishment of equilibrium with respect to

" fixation" of adsorbed oxygen and reaction products on the surface. Catalyst pretreatment conditions and previous history were found to have a considerable effect on the activity. Orzechowskii and McCormack felt that it was necessary to base all data on the same reference state if meaningful information on reaction kinetics was desired.

They measured the kinetics of ethylene oxidation at 234°C and 270°C at partial pressures ranging from about 0.1 to 0.8 atm for oxygen and 0.02 to 0.1 atm for ethylene. They extrapolated their conversion data back to zero contact time in order to obtain initial reaction rates useful for testing the rate equation they had developed. The data were found to fit satisfactorily a rate expression based on the assumption of interaction between gaseous ethylene molecules and irreversibly adsorbed oxygen atoms. The equation they presented was of the form :

$$r_{C_2H_4O} = \frac{k}{1 + \frac{a}{P_E} + \frac{b}{P_O}} \qquad (2\text{-}1)$$

where k, a and b are constant. Nault, Bolme and Johanson[47] have shown, however, that the rate equations based on other mechanisms can also fit Orzechowskii and MacCormack data .

Temkin with coworkers have published several studies on the kinetics of the catalytic oxidation of ethylene (37, 38, 49). Experiments were carried out in a recirculating reactor, and part of the work was concerned with the effects of products on the reaction rates. It was found that removal

of any of reaction products ( $C_2H_4O$, $CO_2$ and $H_2O$ )from the gas mixture by the use of traps caused an increase in rate.

Data were taken over a wide range of concentrations up to about 70% of ethylene and nearly 100% for oxygen (at 1 atm total pressure ). Rate equations were developed based in part on the mechanism presented by Orzechowskii and MacCormack (51 ). Irreversible oxygen adsorption was assumed and reaction was postulated to occur between adsorbed oxygen and gaseous ethylene. All products were assumed to be adsorbed on oxidized silver. Ethylene oxide adsorption on bare silver was also considered. The rate equations were derived by applying a steady state approach. The resulting expression for ethylene oxide formation, presented first by Kurilenko et al. (37 ) and later modified by Ostrovskii et al. (49 ) is:

$$r_{C_2H_4O} = \frac{k_1 P_E}{\left[1+\left(\frac{k_1+6k_2}{2k_4}\right)\left(\frac{P_E}{P_O}\right)(1+K_3 P_{C_2H_4O})+\left(\frac{k_1}{k_3}\right)P_E + K_5 P_{C_2H_4O} + K_6 P_{H_2O} + K_7 P_{CO_2}\right]} \qquad (2\text{-}2)$$

where k's are rate constants for different steps in the mechanism, and K's are adsorption equilibrium constants. The equation for $CO_2$ is identical except for the replacement of $k_1$ by $k_2$ in the numerator. At zero product concentrations the above equation reduces to one identical with that developed by Orzechowskii and MacCormack (51 ) .

Murray (46) reported that the presence of either water or $CO_2$ in the reactor feed stream led to a reduction in the degree of conversion to products. Selectivity appeared to be slightly higher when water was present in the feed gas stream. The rates of reaction were found to increase with increasing concentrations of both ethylene and oxygen, but no rate equations were presented. McKim and Cambron (44) used the results of experiments with excess air to determine the order of reactions with respect to ethylene . They concluded that the rate of the reaction was proportional to the square root of ethylene pressure. When ethylene was present in excess the rate was approximately proportional to the oxygen concentration.

Other studies concerned with the effect of reaction products on the rate should be mentioned here. Gorokhovatski et al. (25) found that an increase in the flow rate in their reactor resulted in an increase of reaction rate. The effect was ascribed to the inhibition by reaction products. In other experiments , when the products were removed from the circulating flow reactor, the reaction rates increased. Only the removal of $CO_2$ was found to have an effect on the selectivity and it was concluded that $CO_2$ had more of an inhibiting effect on the complete oxidation to $CO_2$ than it did on the partial oxidation to ethylene oxide .

Hayes (28), on the other hand, obtained quite different results in his work. Added $CO_2$ was found to affect

only the rate of ethylene oxide production, while the addition of $H_2O$ had no effect on either reaction. It was observed that, beyond a certain point, the rate of $C_2H_4O$ formation was not affected by a further increase in the partial pressure of $CO_2$. To explain this, Hayes postulated that adsorption of $CO_2$ requires both a bare silver surface site and an adsorbed $O^-$ ion. Reaction was thought to involve adsorption of ethylene on a oxygen covered surface, the oxygen species being $O^-$ in the case of $C_2H_4O$ formation and $O_2^-$ in the path to $CO_2$. Aside from the proposal that two different adsorbed oxygen species participate in the reaction, the mechanism is similar to that proposed by Orzechowskii and MacCormack (51).

Nault et al. (47) studied the reaction kinetics at partial pressures up to 0.1 atm for ethylene and 0.2 atm for oxygen. It was found that there was no correlation between adsorption as deduced from kinetics and chemisorption on silver or silver oxide. It was concluded that, on the basis of kinetic data, ethylene and $CO_2$ were adsorbed strongly at the catalytic site while oxygen was only slightly adsorbed, if at all.

These results are similar to those reported for chemisorption on silver oxide but quite different from those reported for metallic silver. Particularly since $CO_2$ strongly inhibits the formation of both ethylene oxide and $CO_2$, these authors were convinced that the catalytic site was not simply

metallic silver. They proposed that the catalytic sites might be located at the silver-silver oxide interface.

The two rate equations, both corresponding to dual-site mechanism were found to fit best Bolme's data for ethylene oxide formation.

$$r_{C_2H_4O} = \frac{4980\ P_E^2\ P_O}{(\ 1 + 164\ P_E + 269\ P_{CO_2}\ )^2} \qquad (2\text{-}3)$$

$$r_{C_2H_4O} = \frac{14.7\ P_E\ P_O}{(1 + 15.3\ P_E + 1.62 P_O + 35\ P_{CO_2})^2} \qquad (2\text{-}4)$$

Equation (2-3) corresponds to reaction of two adjacently adsorbed ethylene molecules with gaseous oxygen, Equation (2-4) corresponds to reaction between adsorbed ethylene and adsorbed oxygen molecules on competitive sites. Nault et al. also tested these equations using Orzechowski and MacCormack's (51) results. Indeed only equation (2-4) can be fitted. Thus the reaction between competitively adsorbed ethylene and oxygen remains as the only mechanism which agrees with the data of both Nault et al. and Orzechowski and MacCormack .

The kinetics of ethylene oxidation on silver was also the subject study by Buntin (13). Reaction rates were measured at ethylene partial pressures from 25 to 100 mmHg and oxygen pressures from 100 to 400 mmHg. Activities for ethylene oxide and carbon dioxide formation were found to vary independently when the catalyst was subjected to different

pretreatments. Buntin concluded that different catalytic sites were involved in the two parallel reactions. In the kinetic study, data taken frequently at a set of standard conditions were used to correct for the variations in catalytic activity. The correction was applied by calculating rate ratios. The initial reaction rates were obtained by correcting all runs to zero product concentration. In agreement with most other works, he showed that all the reaction products inhibited both reactions. The rate of surface reaction was assumed to be the rate controlling step. The following equations were found to represent the data satisfactorily:

$$R_{C_2H_4O} = \frac{0.00125\ P_E\ P_O^{\frac{1}{2}}}{1 + 0.0323\ P_E} \qquad (2\text{-}5)$$

$$R_{CO_2} = \frac{0.00234\ P_E\ P_O^{\frac{1}{2}}}{(1 + 0.0323 P_E)(1 + 0.0623\ P_O^{\frac{1}{2}})} \qquad (2\text{-}6)$$

The mechanism Buntin proposed to account for both of these rate expressions involved reaction of an adsorbed oxygen atom with an ethylene molecule adsorbed on a non - competitive site. The adsorption equilibrium constant for oxygen was approximately zero in the equation for ethylene oxide formation. On the other hand, the rate expression for $CO_2$ formation did contain a term for oxygen adsorption . Thus , it was concluded that two types of oxygen were involved in the two different reactions. A weakly adsorbed oxygen atom reacted with adsorbed ethylene to form ethylene

oxide, while $CO_2$ was formed by reaction of the adsorbed ethylene with a fairly strongly adsorbed atomic oxygen species.

Buntin pointed out that the activities of the catalyst for ethylene oxide formation and for $CO_2$ formation varied independently, which supported the idea of two different types of oxygen adsorption. He also suggested a mechanism for ethylene oxide formation which would lead to the same rate expression. Reaction would occur between adsorbed ethylene and adsorbed oxygen molecules. In order to account for the observed kinetics, it must be assumed that only a small fraction of the total adsorbed oxygen was present as molecules. Most of it remained dissociated.

Finally the work of Klugherz (34) should be mentioned. Kinetics of ethylene oxidation at 220°C was studied over a wide range of ethylene and oxygen pressures. High partial pressures of each gas, up to 1.32 atm, were used. The data were expressed in terms of relative reaction rates to allow for observed variation in catalytic activity, and all the ratios of rates were corrected to 0.01 atm of the product partial pressure. Klugherz reported that the rates of formation of ethylene oxide passed through maxima with increasing ethylene pressure . He concluded that the reaction took place between adsorbed ethylene and adsorbed oxygen species on active sites. The active site was formed by the dissociative adsorption of a lower layer of oxygen on

metallic silver. Ethylene and oxygen as well as reaction products, competed for adsorption sites on the catalytic surface, which was considered to be similar to silver oxide. Therefore the concentration of active sites depended on the oxygen partial pressure. Such a mechanism could explain the maxima with respect to ethylene pressure and the orders in oxygen greater than unity. In contrast to previous works , this mechanism takes into account the known adsorption behavior.

The rate expressions were derived by assuming that the adsorption of oxygen to form the active sites and the adsorption of ethylene and oxygen on these sites follow the Langmuir isotherm :

$$r = \frac{k\, P_E\, P_O^2}{(1 + K_E P_E + K_O P_O + K_p P_p)^2 (1 + K_s P_O)^2} \qquad (2\text{-}7)$$

and :

$$r = \frac{k\, P_E\, P_O^{3/2}}{(1 + K_E P_E + K_O P_O + K_p P_p)^2 (1 + K_s P_O)^2} \qquad (2\text{-}8)$$

where K's are adsorption constants and k is the reaction rate constant. It was found that the ethylene oxide kinetic data could be fitted to equations derived for reaction of adsorbed ethylene with either molecular (Eq.2-7) or atomic oxygen adsorbed (Eq.2-8) on the oxide surface. The carbon dioxide data could only be reasonably fitted to equation (2-7) developed for reaction of ethylene with molecular oxygen. In all cases, ethylene was more strongly adsorbed than oxygen on the"silver oxide"surface. The two reactions

probably took place on different sites, involving different binding energy for oxygen adsorption. He also suggested that the lower layer of oxygen, formed by dissociative chemisorption of oxygen is desorbed only slowly from the surface and is not in equilibrium with oxygen in the gas phase.Oxygen adsorbed on this layer might be removed by reactions.

Before going to the next section, it is interesting to note that several recent developments related to the molecular adsorption of oxygen and the formation of ethylene oxide have been reported by various authors. Voge and Adams (66 ) observed a striking characteristic of ethylene oxidation, that is an upper limit in the selectivity of about 70% ( with moderated silver ) over a wide range of conversions and temperatures. Voge (67 ) discussed the idea of a coupled reaction system, which he attributed to Worbs (70 ). Reaction between adsorbed ethylene and peroxidic adsorbed oxygen molecules is postulated to form ethylene oxide and adsorbed oxygen atoms. These oxygen atoms then react with more ethylene to produce , eventually $CO_2$ . One possible sequence of steps is :

$$M + O_2 \longrightarrow M.O_{2ads.}$$

$$M.O_{2ads.} + C_2H_{4ads.} \longrightarrow C_2H_4O + M.O_{ads.}$$

$$4M.O_{ads.} + C_2H_{4ads.} \longrightarrow 2\ CO + 2H_2O + 4M$$

$$2CO + M.O_{2ads.} \longrightarrow 2\ CO_2 + M$$

In these equations, M represents the catalytic

site, consisting of either a single Ag atom or a group of two or more. The above sequence predicts a selectivity of 4/5= 80% . Other coupled system can be imagined in which the ethylene oxide formation step is the same but further reactions to form $CO_2$ are different, resulting in various values for the limiting selectivity. A mechanism of this type would also account for the frequent observation that selectivity remains relatively constant when the temperature is varied.

This mechanism has recently been supported by Sachtler and coworkers (54,33). Sachtler et al. studied the oxygen adsorption on supported silver catalysts and identified the occurence of three chemisorption processes, (I) an almost non-activated dissociative adsorption, (II) activated (33 KJ/mole) non-dissociative adsorption, and (III) activated (60 KJ/mole) dissociative adsorption, respectively. Using infra red spectroscopy and isotopic oxygen, they proved the presence of diatomic oxygen species on Ag, and showed that this species readily reacted with ethylene to give ethylene oxide. In another study where chlorine was first adsorbed, they showed that the effect of chlorine was to inhibit dissociative adsorption of oxygen. Since its effect on the oxidation of ethylene over silver catalyst was to increase the selectivity, they concluded that the diatomic oxygen species on silver was responsible for the selective oxidation of ethylene to ethylene oxide.

2-5 Catalyst and Moderators:

Voge and Adams (66) gave a good account of various types of silver catalyst. It appears from this literature and from earlier data, the following points are valid:

- The carrier should be inert .
- Too large a surface for carrier is undesirable.
- A fairly large silver area is desirable, say 0.05 to 0.5 $m^2$/g.silver.
- Diffusion effects in the catalyst particle are to be avoided.
- Promoters such as Ca and Ba probably act mainly to stabilize the silver from sintering.

Harriott (27) recently published a study on various alumina and silica supports for silver. He suggested that the very low selectivity for silver on some supports was not caused by heat or mass transfer effects or by oxidation of ethylene oxide on the support. The low selectivity might have been caused by a greater dispersion of the silver, with the smallest particles having high activity for further oxidation of ethylene oxide. The particle size of silver was determined by the nature of supports and conditions used in preparing the catalyst. Strong adsorption of the impregnating salt on a porous support tended to give very small particles, but crystal growth during drying and reduction gave some large particles and a broad distribution. This technique

was suggested to be used to prepare similar catalysts with different grain sizes of silver to check the effect of sizes on the activity and the selectivity .

Moderators for silver play an important role in controlling both the activity and the selectivity. Evidence is now very good that pure silver surface used with excess air has a characteristic activity and selectivity ( about 45% ) for ethylene oxidation. Electronegative moderators are necessary in proper amount for maximum selectivity; too much moderator, however, destroys activity. It was once thought that different crystal faces or unusual surface sites of silver were responsible for the differences in the performance of catalysts prepared in different ways. Kummer (36) studying the oxidation of ethylene on single crystals of silver found that reaction rates and selectivity were the same on different crystallographic surfaces. Wilson and coworkers (69) also reported that films having different crystal orientations all possessed about the same catalytic activity. More significant, though, was their observation that the films recrystallized when used as catalyst for ethylene oxidation even though no changes took place when heated in air. Thus, even if a particular crystal face was unusually active or selective, it would not persist when the catalyst was exposed to the reaction.

To show that the properties of pure silver catalyst are independent of the method of preparation, Balaya and

and Rubanik ( 5) prepared silver by fifteen different methods, and observed activities per unit surface area, as well as selectivities. Initially there were variations in specific activity by a factor of ten, but after cleaning by soaking in concentrated $NH_4OH$ solution., the variations were within a factor of 1.6. Furthermore, larger amount of chloride was found in the washings from the catalysts of lower initial specific activity and high selectivity. The clean catalysts all had selectivities in the range 41 to 48% . It can be concluded that clean silver surface has a characteristically high activity, and gives a selectivity under conditions (3% $C_2H_4$ in air, 1 atm pressure, 200°C) of about 45%.

Moderators which appear to improve the selectivity of silver are Cl, Br, I, S, Se, Te, P, Bi, and perhaps a few others. The exact state of combination of these elements on a silver surface under operating conditions is not known. Sufficient moderation to cause selectivity improvement always lowered activity relative to that of unmoderated silver. The behavior seems strange, but may be possibly explained by too strong oxygen bonding on an unmoderated silver (50).

2-6 The Shingu Patent :

There is necessary an indication of time in discussing the Shingu patent (59) which was granted in 1961. Thus, this section begins with a brief description of the process. Then some comparisions with various recent reviews

will be presented.

It is interesting to know that since the patent was granted, no published work has appeared concerning this study. It might be that the patent was not mentioned in any review until Satterfield published his book in 1970 (56). It is also possible that nobody has been able to reproduce his claims.

Shingu reported in his patent that he was able to produce various olefin oxides in a slurry reactor. In the case of ethylene oxide, with a flow rate of 20 cc/min of ethylene gas mixture containing 12% of oxygen, a conversion of 8 to 35% and selectivity from 80 to 96% were achieved. For other oxides, with appropriate range of reacting temperature , selectivities from 70 to 90's per cent were achieved. The catalysts employed in his invention were those containing silver, copper or both, preferably in the oxide form, which was finely divided or deposited on a support. The solvent liquids used for example were dibutyl phthalate and nitro benzol. It was suggested that several other organic liquids might be used which are stable to heat and oxidation, chemically indifferent and high boiling :dialkyl phthalates, trialkyl and triary phosphates, aromatic nitro compounds, high boiling carboxylic acids and esters.

In view of several recent publications on the subject of catalytic oxidation of olefins,several points of the Shingu patent should be put forward for discussion :

- Several reviews (66,34,41) were in agreement that no other metal or metallic oxide could act as catalyst for ethylene oxide formation. Voge and Adams (66) in 1967 suggested that silver was an unique catalyst for oxidation of ethylene to ethylene oxide. The sole product of ethylene oxidation on copper was carbon dioxide.

- It is interesting to know that ethylene is the only olefin which is converted to an epoxide by reaction on silver (66). All other olefins are oxidized essentially just to $CO_2$. The selective oxidation of propylene to propylene oxide is currently of great commercial interest. So far, no heterogeneous catalyst has been found for this reaction, although traces of oxide have been reported in the oxidation of propylene on silver (39). Therefore , claims by Shingu that he was able to produce propylene oxide, butylene oxide,etc. of very high selectivity should be challenged.

- A striking characteristic of ethylene oxidation is the nearly constant selectivity of 70% (with moderated silver) over a wide range of conversions and temperatures. Voge and Adams (66) suggested that the relative insensitivity of the selectivity to temperature meant that the oxidation to ethylene oxide and to $CO_2$ cannot differ in activation energy by more than 2 Kcal/mole. Therefore even though the temperature can be lowered in the case of a slurry reactor, improvement of the selectivity to 96% claimed by Shingu is questionable.

- Shingu reported that the solvent was stable

during oxidation. However the problem of reaction products reacting with the solvent was never mentioned.

2-7 Introduction to Slurry Reactor :

Catalytic reaction may be carried out in a liquid in which gas reactants are dissolved, the solid catalyst being suspended in granular or powdered form. The use of slurries is common in chemical industry, particularly for hydrogenation.

The use of slurries for continuous operation would appear to offer many advantages over fixed-bed. A stirred slurry can be kept at uniform temperature through out , eliminating the "hot spots" that detract seriously from the selectivity of catalysts in many vapour phase fixed bed operations. Heat recovery is practical, since the liquid phase heat transfer coefficient is large. Pelleting cost may be avoided and catalyst that are difficult to pelletize may be used. However, the slurry reactor also has its own disadvantages, particularly in oxidation. It is difficult to select a liquid solvent in which reactants are soluble and which is stable at elevated temperatures in contact with reactants and products. The behavior of a catalyst in contact with a liquid may also be possibly different than when in contact with a gas containing reactants at the same partial pressures and temperatures.

In constrast to fixed and fluidized bed reactors

several physical processes must occur in series before a reactant gas can reach a catalyst surface. Some of these are likely to affect the global rate appreciably, and others are not. The process can be visualized as occurring in the following sequence :

(1)- Mass transfer from the bulk concentration in the gas buble to the bubble liquid interface.

(2)- Mass transfer from the bubble liquid interface to the bulk liquid phase .

(3)- Mixing and diffusion in the bulk liquid.

(4)- Mass transfer to the external surface of the catalyst particles

(5)- Intra-particle mass transfer resistance.

(6)- Reaction at the catalyst surface.

(7-11)- The reverse of steps 1-5 for products of the reaction.

The rise of bubble through the liquid along with mechanical agitation, is normally sufficient to achieve uniform conditions in the bulk liquid. Hence the resistance of step (3) can be neglected.

The global rate can be expressed in terms of the known bulk concentrations for each of the remaining steps. The rates of all steps will be the same at steady state, and this equality permits elimination of the unknown interfacial concentrations. With the assumption of a first order irreversible catalytic reaction, and that the intra-

particle mass transfer resistance is negligible, the rate per unit volume of the bubble free slurry may be written:

$$r_v = k_o . a_p . C_g \qquad (2\text{-}9)$$

and

$$\frac{1}{k_o} = \frac{a_p}{a_g} . \frac{1}{k_g} + \frac{a_p}{a_g} \frac{H}{k_l} + H \left(\frac{1}{k_p} + \frac{1}{k}\right) \qquad (2\text{-}10)$$

where H is the Henry's law constant.

Equation(2-10) shows that the global rate is a function of the three mass transfer coefficients, the specific reaction rate k, and the area ratio $a_p/a_g$ .

Not all resistances indicated in the equation (2-10) are significant in every instance. The resistance to diffusion from the bulk gas (in the buble) to the bubble liquid interface is negligible in comparision with other resistances. Hence, the equation (2-10) becomes:

$$\frac{1}{k_o H} = \frac{a_p}{a_g} \frac{1}{k_l} + \left(\frac{1}{k_p} + \frac{1}{k}\right) \qquad (2\text{-}11)$$

and if $a_p$ is expressed as $a_p = C_{cat}/A$ , where A is a constant and $C_{cat}$ is the concentration of the catalyst in the slurry, equation (2-11) can be rewritten :

$$\frac{C_g}{r_v} = \frac{1}{k_o a_p} = \frac{H}{k_l a_g} + \frac{A.H}{C_{cat}} \left(\frac{1}{k_p} + \frac{1}{k}\right) \qquad (2\text{-}12)$$

From this equation, the ratio of $a_p/a_g$ can provide two approaches to the study of a slurry reactor:

- Using a large concentration of catalyst, $C_{cat}$ is large, so that only the first term of the equation is important, and equation (2-12) becomes :

$$\frac{C_g}{r_v} = \frac{H}{k_l a_g} \qquad (2\text{-}13)$$

and this provides a study of mass transfer resistance from the bubble liquid interface to the bulk liquid.

- Using a low concentration of catalyst, and increasing the concentration of gas bubbles in the slurry, $a_g$ is large, and equation (2-12) becomes:

$$\frac{C_g}{r_v} = \frac{A.H}{C_{cat}} \left(\frac{1}{k_p} + \frac{1}{k}\right) \qquad (2\text{-}14)$$

this provides a study of reaction kinetics and mass transfer from bulk liquid to the catalytic surface. In the case where $k_p \gg k$ , the process is kinetically controlled; a slurry reactor can be used to measure the kinetics of the reaction directly.

## III EXPERIMENTAL APPARATUS AND MATERIALS

The system used in this study is shown in Fig.3-1 on page 32 . Besides the reactor, important components are the pressure measurement and temperature control system, the gas flow system and the analytical equipment. In the following sections , the major elements are described fully.

### 3-1 The Reactor :

The reactor is a magnedrive packless autoclave , standard model ABP-300, manufactured by Autoclave Engineers Inc. The vessel was fabricated with 316ss steel with a capacity of 300cc and was equipped with a cooling coil, a sampling tube and a thermowell.

The standard agitator is a turbine type, 6 blade impeller, which provides catalyst suspension. For the gas slurry system, the gaseous reactants were introduced through the sampling tube directly into the slurry phase prior to movement into the vapor phase for subsequent discharge. The unit was also equipped with a tachometer indicator which provides a measurement of the agitator shaft speed. The shaft for the impeller is a hollow tube with four orifices. Two are located at the blade position and the other two are 3/4 of an inch from the top cover of the reactor. Under agitation, the gas mixture was drawn from the gas space ,

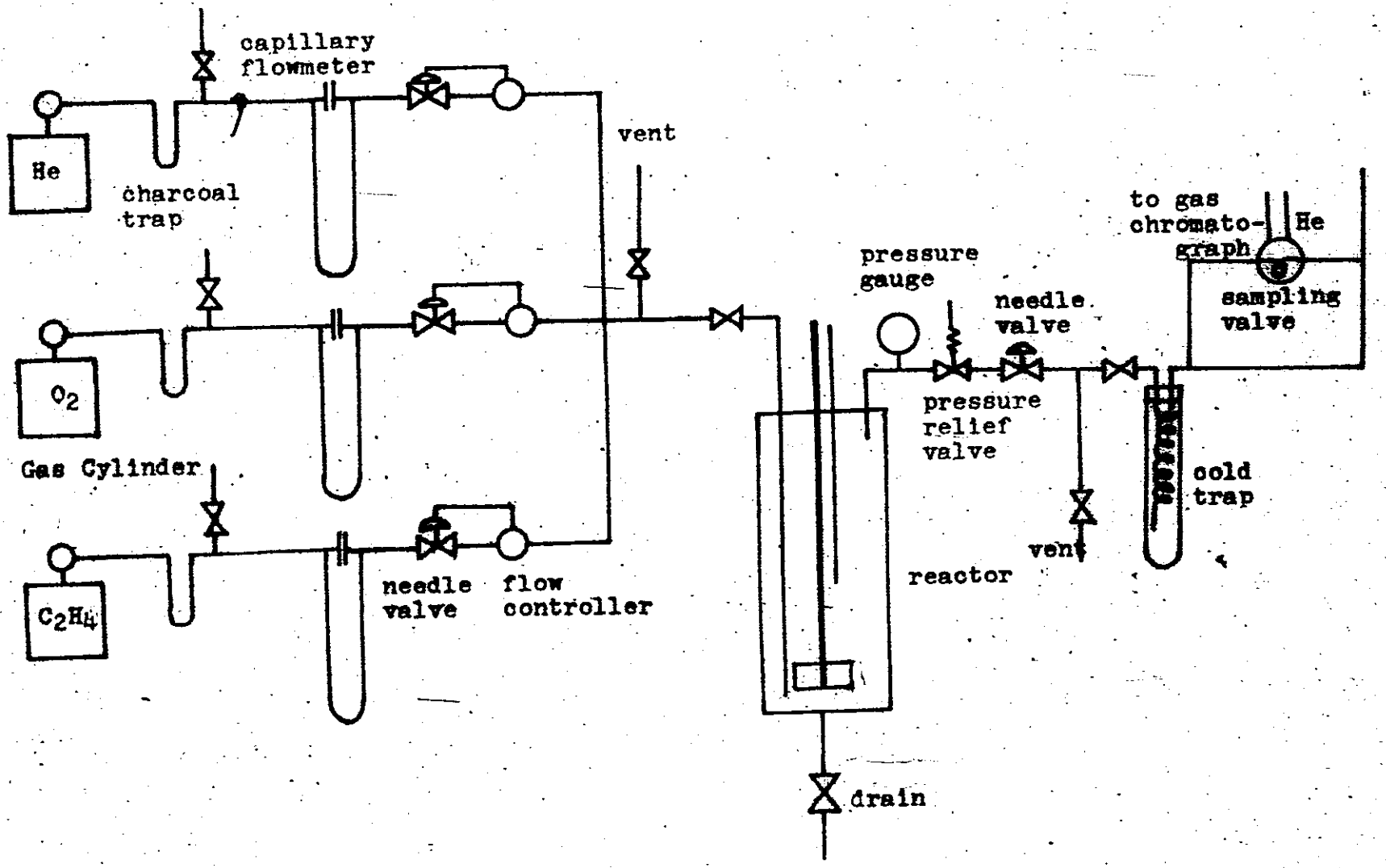



Fig. 3-1 : DIAGRAM OF EXPERIMENTAL APPARATUS

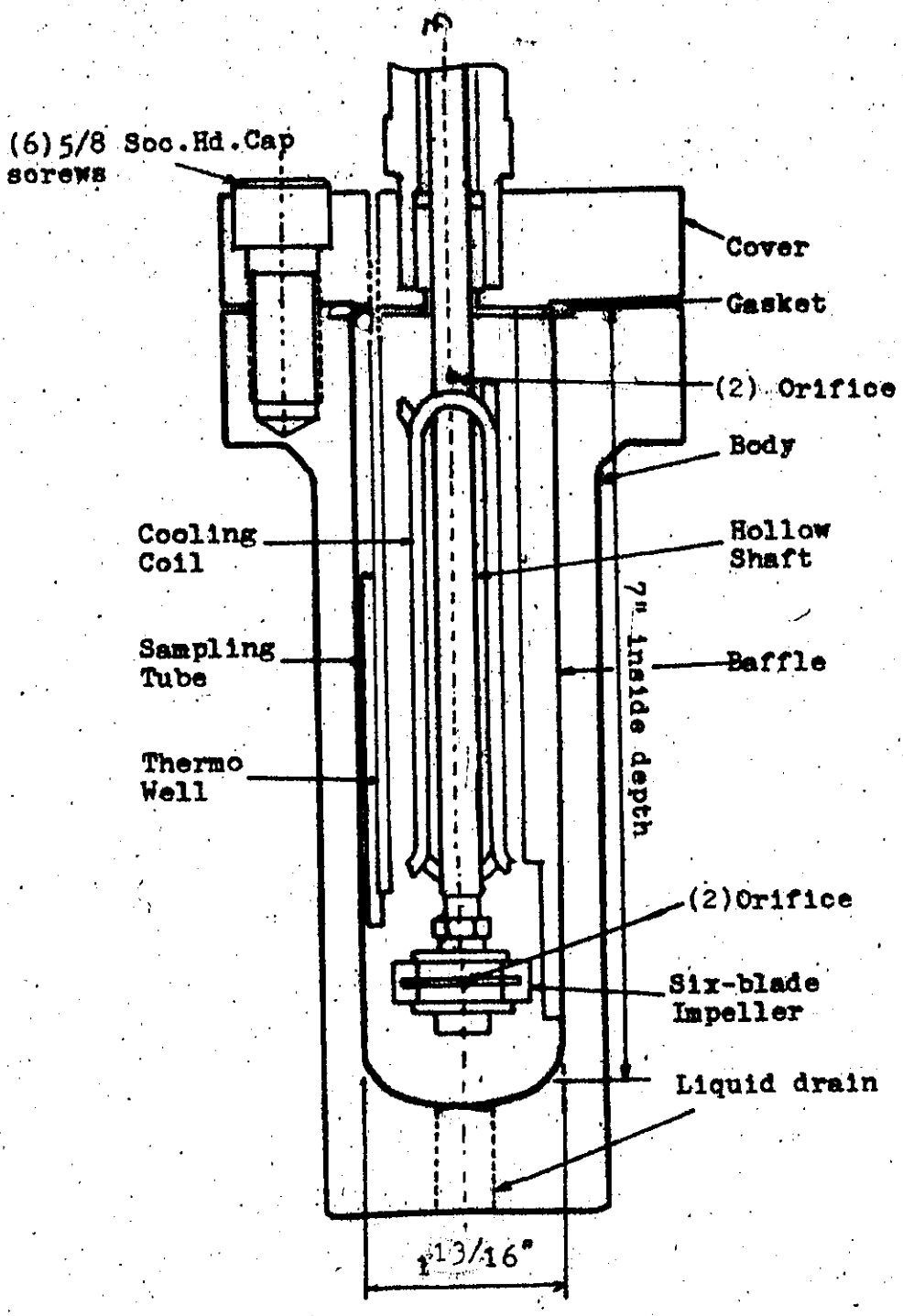



Fig. 3-2: THR REACTOR

through the tube to the bottom. The solvent liquid level was maintained high enough to prevent the liquid from carrying over and a volume of 230cc was found experimentally suitable.

Details of the vessel and the stirrer are shown in Fig.3-2 .

The solvent, 230 cc of dibutyl phthalate, was charged into the vessel before the catalyst was added. Specifications for the material are given in table 3-1

TABLE 3-1

Specifications for Dibutyl Phthalate

( Fisher Certified Reagent D-30 )

| | |
|---|---|
| Formula: | $C_6H_4 - 1,2\left[COO(CH_2)_3\ CH_3\right]_2$ |
| Molecular weight | 278.336 |
| Boiling point(1 atm) | 340°C |
| Specific gravity(20°C) | 1.047 to 1.049 |
| Dibutyl phthalate | 99.0% min by weight |
| Acidity as phthalic acid | 0.01% max by weight |
| Water | 0.1% max " " |
| Color | 15 apha max |
| Suspended matter | Substantially free. |

3-2 Pressure Measurement and temperature control system :

The pressure of the reactor was measured with a pressure gauge with a range from 0 to 200 psi. For mass transfer studies, the pressure versus time was monitored by a pressure transducer. The transducer was connected to a

Universal Transducer Readout model SC1001 and the voltage signal was recorded by a recorder, Honeywell model Electonik 194. The calibration of the transducer was carried out by plotting pressures versus voltage signals of the transducer readout .

An iron-constantan thermocouple, connected to a precision potentiometer (Leeds and Northrup model 8686 millivolt potentiometer) was used to measured the temperature within the reactor. It was inserted in the thermowell of the vessel. The temperature was controlled by using a variable transformer and a temperature controller, Honeywell model R-71644. The variable transformer was used to adjust the power of a heater covered outside the vessel.

Initial set-up of the temperature control system involved connecting a chromel-alumel thermocouple, which is located at the outside wall of the reactor, to the temperature controller. It was found that the temperature of the reactor cannot be controlled as desired. The new set-up described above, gave a good control of the liquid temperature, and a deviation of only $\pm$ 2$^{o}$C was observed through out the experiments. One hour was required before the temperature reached a steady state condition .

3-3 The Gas Flow System :

The feed to the reactor contained ethylene, oxygen and helium. Helium, rather than nitrogen, was used as an

inert diluent for two reasons. First, its high thermal conductivity and diffusivity were desirable for the purpose of eliminating the possible influence of heat or mass transfer on the reaction rate. Second, the use of helium simplified the gas chromatographic analysis considerably. This will be discussed further in the next section.

Gases supplied from standard gas cylinders, after pressure reduction with two stage regulators, were passed through line filters ( Matheson model 411X ). Flow rates were metered by capillary flow meters and controlled by precision needle valves in conjunction with flow controllers ( Moore model 63 BUL ). By using the flow controllers, the flow rates are unaffected by downstream pressure fluctuations. Pressures drops across the capillaries were measured by mercury manometers. Capillary flow meters were calibrated for each gas using soap bubble flow-meter, in which the time for a soap bubble to be displaced through a known volume was measured. The three capillaries were made from stainless steel and were all one meter long. Two of 0.2mm I.D. were for ethylene and oxygen, and one of 0.25mm I.D. was for helium. The design was based on the articles by Benton (9 ) and Whitwell (68) where flows are in laminar region. Calibration curves for each gas are given in the Appendix G.

The gases were mixed and the feed stream entered the reactor through the sampling tube directly into the slurry phase. The product stream leaving the reactor flowed

through a needle valve used to control the pressure of the reactor and through a liquid trap, where the vapour of the solvent was condensed. Water was used as coolant for the cold trap. In kinetic runs, 5 to 7 cc of the solvent was collected after a period of 8 hours. An equal amount was introduced back into the reactor to keep the volume constant. The product gas was then passed through a sample loop of a gas sampling valve before being vented. Valves are also included so that the reactor could be by-passed, if desired, and the feed diverted directly to the gas sampling valve.

It is interesting to note that before the cold trap was used , a reflux condenser was fitted to the exit of the reactor. Since it was found that water as a product could build up inside the reactor and have an inhibition effect on the reaction rates, the condenser was therefore withdrawn.

3-4 Product Analysis :

Gas chromatography was the method of analysis for this study. A Varian model 1420 gas chromatograph, equipped with a thermal conductivity detector was used. The product, in 0.5 cc sample, was injected by a gas sampling valve. A 1/8 inch, 6 foot long column packed with 80-100 mesh Porapack Q was used for the analysis. The helium carrier gas flow rate was maintained at 40.0 scc/min, and the column oven was maintained isothermally at 85°C. The detector current was 185 mA and the detector temperature was at 198°C .

The signal from the gas chromatograph was recorded on a Varian model A-25 strip chart recorder equipped with a disc integrator . The Porapak Q column gave a good separation of oxygen, carbon dioxide, ethylene , water and ethylene oxide, as shown in the sample chromatogram, Fig 3-3 on page 39.

Nitrogen and oxygen are not separable on this column. These two gases would appear as one peak in the chromatogram, and the presence of nitrogen would have made the determination of oxygen concentration impossible. This is one of the reasons why helium was used as the inert diluent in the reactor feed.

The chromatograph was calibrated directly for each gas species except $H_2O$. Mixtures of gases, usually binary mixtures with helium, were passed through the gas sampling valve and the sample was injected into the gas chromatograph. The composition of the gas was calculated from the measured flow rates. From the volume of the sample injected and its temperature, pressure and composition, the number of moles of each component could be calculated. The calibration curves were then prepared by plotting the number of moles of each component in the injected sample as a function of its peak area or peak height ( in the case of sharp, symmetric peaks) in the chromatogram. Peak heights were used for $O_2$ , $CO_2$ , and $C_2H_4$ , whilst peak area was used for ethylene oxide. Calibration curves are given in the Appendix G.

The concentration of water present was assumed

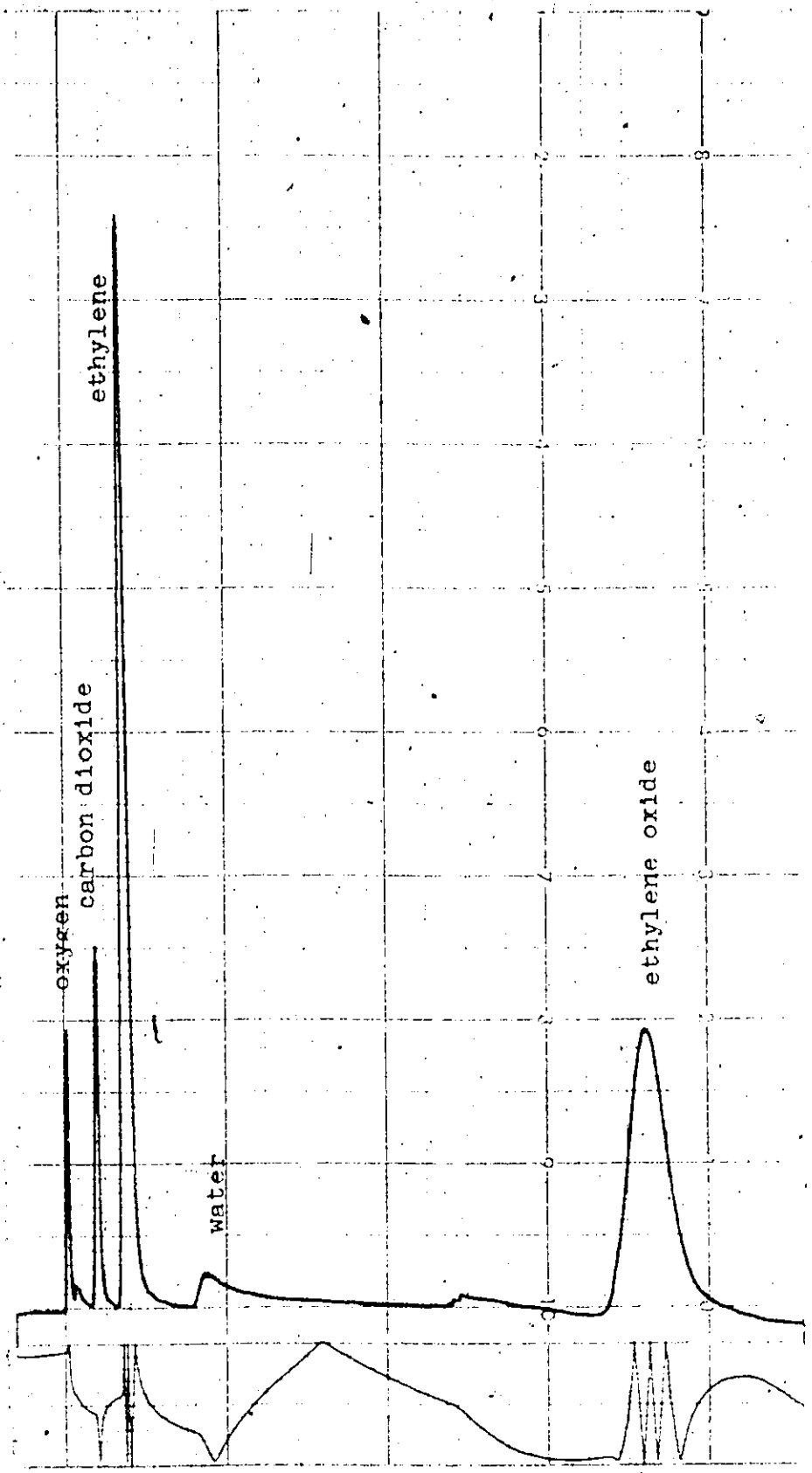



FIG. 3-3: GAS CHROMATOGRAM

to be equivalent to that for $CO_2$. This is due to the problem of analysis of water in the sample. This difficulty was reported by various workers (34). Water is apparently adsorbed very strongly on stainless steel at ambient temperatures. It was found that if the gas sampling valve was left for long in the inject position, the water peak in the chromatogram was extremely large. For this reason, measurement of the water concentration was not attempted. In order that the peak would not interfere with the later ethylene oxide peak, the valve was left in the inject position long enough for the full gas sample to be purged into the chromatograph. Twenty seconds were found to be satisfactory for the sample size and carrier gas flow rate used.

3-5 Catalyst Preparation and Description :

Silver, supported on low surface area $\alpha$- alumina, was the catalyst used in this study. Norton-38 alumina of 120 grit size was the catalyst support material; its properties are presented in table 3-2 on page 42.

The procedure followed in impregnating the catalyst support with silver was quite similar to that followed by Buntin (13) and Klugherz (34).

The alumina was washed several times with distilled water and dried in an oven at 120°C. Then, 80g. were weighed out into a beaker, placed in an oven and preheated to 95°C for later use. A solution of 60 g. of 85% lactic acid ( Fisher reagent grade) in 60 cc of distilled water was prepared

and heated to 93°C . While the hot solution was stirred, 30 g. of silver oxide (Fisher purified grade) was added slowly. The grayish yellow liquid was then filtered onto the preheated alumina by using a heated funnel. The mixture of alumina, immersed in the clear, yellow silver lactate solution was allowed to stand for one hour, in an oven maintained at 95°C. After impregnation, the excess liquid was removed by using a heated Buchner funnel set in a filter flask. The particles were allowed to cool in air, with occasional stirring to prevent caking. They were then poured in a porcelain dish and heated in a furnace for 16 hours at 360 - 380°C in order to decompose the silver lactate to metallic silver. After removal from the furnace, the catalyst was cooled in a nitrogen atmosphere and weighed. A weight gain of 6.33g.was noted. Thus, the catalyst contained 7.9% silver. The alumina which had originally been white, was now grayish brown. No further treament was given to the catalyst before its use in the reactor. The same batch of catalyst was used through out this study.

TABLE 3-2

Properties of Alumina Catalyst Support

Material: Norton 38, Alundum grain, 120 grit

$\alpha$- alumina form

Chemical Analysis: ( %, by weight )

| | |
|---|---|
| $Al_2O_3$ | 99.28 (by difference) |
| $Si\ O_3$ | 0.05 |
| $Fe_2O_3$ | 0.15 |
| $Ti\ O_3$ | 0.02 |
| $Na_2O$ | 0.50 |

Properties :

| | |
|---|---|
| True specific gravity | 3.97 |
| Average particle size | 0.004" |
| Approximate internal area | $0.015 m^2/g.$ |
| Approximate internal porosity | 40% |

## IV PROCEDURE AND PRELIMINARY EXPERIMENTS

In a three phase reaction system, studies of mass transfer and kinetics are equally important. In a system where the overall mass transfer resistance is negligible, a kinetic study is feasible and therefore can be investigated in the same manner as in gas phase reaction systems. As it was already mentioned in chapter II, before a reactant gas can reach the catalytic surface, several physical processes must occur and, therefore a mass transfer study is always a preliminary step in this type of reaction system.

### 4-1 Procedure for a Mass Transfer Study :

#### 4-1-1 Development of The Mass Transfer Equation:

The mass transfer from the bulk liquid to the external surface of the catalyst particles can be estimated by several correlations and will be discussed fully in the next chapter. For the mass transfer from the bubble liquid interface to the bulk liquid, a physical absorption experiment can be carried out and the coefficient $k_l a_g$ can be estimated. The absorption was carried out in a batch system which was closed for both gas and liquid. The term $k_l a_g$ rather than $k_l$ was of interest, since the main purpose of this study was not finding the mass transfer coefficfent $k_l$ , but to find the significance of the mass transfer resistance from the bubble liquid interface to the bulk liquid, which can be

evaluated by $1/k_l a_g$ .

For an unsteady state absorption without a chemical reaction :

$$\ln \frac{P - P_f}{P_i - P_f} = - \frac{P_i}{P_f} k_l a_g t \qquad (4\text{-}1)$$

where $P_i$ and $P_f$ are the initial and final pressure of the vessel, P is the pressure at time t. A plot of $- \frac{P_f}{P_i} \ln \frac{P - P_f}{P_i - P_f}$ versus time will be a straight line and the slope is equal to $k_l a_g$ . The result is shown in section 5-1, and the derivations of this equation is given in the Appendix A.

Several experiments were carried out with reactant gases and water at room temperature to test this equation. The results are reproducible; absorption curves of oxygen and ethylene in water are shown in Fig A -1 and A -2 of Appendix A.

4-1-2 General Procedure for Physical Absorption Study :

The reactor was filled with 230 cc of dibutyl phthalate. The liquid was then degassed by a vacumn pump and boiling. The gases withdrawnwere cold-trapped and the amount of solvent condensed was measured, which was usually small. The liquid was then maintained at 220°C, the same temperature used later in kinetic studies. The transducer readout and the recorder was turned on . The vessel was pressurized with one reactant gas , either oxygen or ethylene. The stirrer was started and the variation of pressure versus time was recorded. When the pressure inside

the reactor reached a steady state, the recorder was stopped, the outlet valve was opened and the remaining gas was withdrawn.

The same procedure was repeated with the second gas. The voltage signal with respect to time was converted to pressure-time with the help of a calibration curve.

## 4-2 Procedure for a Kinetic Study :

### 4-2-1 General Procedure :

In general, the procedure was the same for all kinetic experiments in this work. The reactor was filled with 230 cc of dibutyl phthalate, 0.5 g. of catalyst was added, then the reactor was closed. Reactant flow rates were set, and since they were run at atmospheric pressure, no pressure adjustment for the reactor was required. The temperature controller was set to give the desired temperature in the reactor, which was 220°C. The controller was working quite well since a variation within ± 2°C was observed during the experiments. The agitation was vigorous (1750 rpm), thus it can be assumed that the temperature inside the reactor was uniform through out.

Approximately forty five minutes was allowed for the system to reach steady state, and then the data for the run were taken. The capillary readings were recorded, as were the room temperature and the barometric pressure. Reaction conditions could then be changed to those desired

for the next run.

4-2-2- Preliminary experiment:

Prior to gathering kinetic data, a preliminary experiment was performed to test the stability of the solvent. Dibutyl phthalate was known to be very stable with respect to oxidation (16,17). The experiment was carried out by heating the solvent in the presence of catalyst particles, and only oxygen feed was introduced to the reactor. It was found by gas chromatographic analysis that the oxygen concentration in the product stream was the same as in the feed stream. Hence dibutyl phthalate was stable in the presence of oxygen and therefore suitable for the kinetic studies. The stability of dibutyl phthalate in the presence of the ethylene oxidation reaction will be discussed in the next chapter.

4-3 Treatment of Kinetic Data:

4-3-1 Method of Calculation:

The method of calculation is based on the assumption of a backmix reactor. A sample calculation is shown in the Appendix B.

The mole fractions of ethylene oxide and carbon dioxide in the product stream were obtained from the chromatogram with the aid of the calibration curves. The concentration of water was assumed to be equal to the measured concentration of carbon dioxide. Average reaction rates were then calculated from the equations:

$$r_{C_2H_4O} = \frac{y_{C_2H_4O}}{22414\left(\frac{W}{F}\right)\left(1 + \frac{1}{2} y_{C_2H_4O}\right)}$$

$$r_{CO_2} = \frac{\frac{1}{2} y_{CO_2}}{22414\left(\frac{W}{F}\right)\left(1 + \frac{1}{2} y_{C_2H_4O}\right)}$$

where $r_{C_2H_4O}$ and $r_{CO_2}$ are the average rates of ethylene oxidation to $C_2H_4O$ and $CO_2$, respectively, in gmoles of ethylene reacted/min.g.catalyst, $y_{C_2H_4O}$ and $y_{CO_2}$ are mole fractions of $C_2H_4O$ and $CO_2$ in the product gas stream; W is the weight of the catalyst in grams ; and F is the total feed flow rate in standard cc/min. It was assumed that all the $CO_2$ was formed directly from ethylene , and none was produced by the further oxidation of ethylene oxide (42). This is a reasonable assumption, especially since the ethylene oxide concentration was always low. The term $\left(1 + \frac{1}{2} y_{C_2H_4O}\right)$ is present in the denominator of the above equations because there is a change in the number of moles during reactions. Note that the equations pertain only to the situation in which no reaction product is fed to the reactor with the reactants.

The reaction rates computed above are assumed to correspond to the partial pressures of reactants and products in the reactor. Assuming that the mixing is complete, the properties of reaction mixture are uniform in all parts of the vessel and are the same as those in the exit stream. Hence the partial pressure of each component was computed

from its mole fraction in the exit gas stream and the reactor pressure.

Mass transfer resistance, both external and internal within the catalyst particles, was estimated to be small (See the next chapter). Therefore the reaction rates are kinetically controlled.

4-3-2 Catalyst Activity Variations :

The varying activity of silver catalysts used in the oxidation of ethylene is a problem which has plagued many investigators. Orzechowski and MacCormack ( 51) were the first to discuss the phenomenon in detail, but the subject has been brought up frequently since then. Orzechowski and MacCormack found that whenever reaction conditions, such as temperature, flow rate or feed composition, were changed, conversions to ethylene oxide and carbon dioxide changed as expected, but then continued to drift for many hours before reaching a steady state. Slow processes were also observed after the catalyst was pretreated under various coditions and then exposed to the reacting gases. They compared the observation of these slow processes with a calculation which indicated that the catalyst reached steady state within the first ten minutes after any change in reaction conditions. They explained the observation on the basis of the slow "rate of attainment of surface equilibrium" of non-reacting species. They concluded that two inhibiting species were present : (I) stably adsorbed oxygen atom and (II)

products of ethylene oxidation which build up slowly on the surface during the course of the reaction.

Nault et al. (47) and Buntin(13) also investigated the effects of catalyst pretreatment on the oxidation of ethylene . All studies noted that pretreatment with ethylene oxide results in a catalyst with unexpectedly high initial activity for both $C_2H_4O$ and $CO_2$formation . They also concluded that pretreatment with oxygen reduces catalytic activity slightly. Nault et al.also interpreted these results in terms of the mechanism of the reaction. They concluded that the catalyst site is at least partially reduced, especially since they observed the initial activity was higher after pretreatment with ethylene . Pretreatment with $O_2$ oxidized the catalyst, resulting in reduced activity. Furthermore it was believed that ethylene oxide, in some form , was involved in the catalytic site, since it had such a marked effect on the activity. Buntin also agreed with these conclusions. Harriott (27), using the same type of catalyst as in the present study, observed an increase in catalyst activity during the first few hours of operation, but an erratic decline in activity for overnight shutdowns or during a few days of test. The selectivity did not change much with catalyst age but was quite a bit lower at higher conversions.

Klugherz (34)' attempted to correlate the activity change with obvious variables such as conditions of overnight

treatment with different reactant gases, but the extent of change in activity was still variable and unpredictable. Furthermore, he observed the activities for the two parallel reactions forming $C_2H_4O$ and $CO_2$ varied independently as also observed by Buntin.

In agreement with previous works, the phenomenon was also observed in this study and could not be eliminated. Therefore such variations would be taken into account in planning and carrying out the experiments. The procedure for the treatment of kinetic data is described in the following section .

4-3-3 Treatment of Kinetic Data :

In order to study the kinetics of ethylene oxidation on silver, it was necessary to take into account the catalyst activity variations which were discussed in the preceding section. It was decided that all reaction rates would be compared with rates measured at a set of defined "standard conditions". The choice is arbitrary and in this work, the conditions selected for the standard run were :

| | |
|---|---|
| Reactor pressure | 1 atm |
| Reactor temperature | 220°C |
| Total feed flow rate | 73.8 scc/min. |
| Average partial pressure : | |
| of ethylene : | 0.5 atm |
| of oxygen : | 0.1875 atm |
| of helium : | 0.3125 atm |

A pair of runs at standard conditions bracket each "kinetic run" and are defined as "bracketing runs". This was easily achieved by alternating standard runs with runs at nonstandard conditions. The term "kinetic run" refers to those runs made at various gas composition and feed flow rates.

This practice was used by Sinfelt (60) to allow for the catalyst activity variations in the $C_2H_4$ hydrogenation and ethane hydrogenolysis, and by Buntin (13) and Klugherz (34) in their studies of ethylene oxidation on silver supported catalysts.

Throughout the course of the kinetic experiments, the rate of ethylene oxidation to ethylene oxide at the standard conditions was usually in the range 9.21 to $15.1 \times 10^{-6}$ gmoles ethylene reacted/gcatalyst.min. The corresponding range for carbon dioxide was 1.91 to $3.85 \times 10^{-5}$ gmoles ethylene reacted/gcatalyst.min. Conversion based on ethylene for the standard runs were primarily between 0.86 to 2.4 %, depending on the activity of the catalyst. The selectivity (moles ethylene converted to ethylene oxide per mole of ethylene reacted) ranged from 21.7 to 35.6%.

The kinetic results are expressed as relative rates of ethylene oxidation to ethylene oxide and carbon dioxide. Relative rate is defined as the ratio of the reaction rate for a kinetic run to an average of the corrected rates of standard runs made before and after the kinetic run. The significance of the term "corrected" rate must be

explained, but before doing so, it is necessary to present here the reason for using a relative rate approach.

In general, the rate of ethylene oxidation (to either $C_2H_4O$ or $CO_2$) can be expressed by the equation of the form :

$$r = \alpha f(P_E, P_O, P_{C_2H_4O}, P_{CO_2}, P_{H_2O}, T_R)$$

where r is the reaction rate and $\alpha$ is the activity factor, P's are the partial pressures of the reactants or products, respectively. $T_R$ is the reaction temperature.

It must be assumed that changes in the catalyst which result in variations in activity affect only the magnitudes of the reaction rates and not the dependence of rates upon the various reaction parameters (7 ). For example the number of active sites might be changing (39).

If rate measurement could be made at reaction conditions such that the average partial pressure of each component and temperature are always the same then $f(P_E, P_O, P_{C_2H_4O}, P_{CO_2}, P_{H_2O}, T_R)$ would be a constant. If $f_c$ is the value of this constant and $r_c$ is the reaction rate measured at such conditions, then :

$$r_c = \alpha f_c$$

Thus, $r_c$ would be a function of only the catalyst activity factor $\alpha$ . Runs could be made at these conditions both before and after a kinetic run. If one assumes that the catalytic activity during a kinetic run is equivalent to the average activity of the two bracketing runs at "constant"

conditions, any influence of activity variations would be eliminated by taking a ratio of the rate of the kinetic run to the average rate of the runs at constant conditions. That is :

$$\frac{r}{\bar{r}_c} = \frac{\alpha f\ (P_E\ ,\ P_O\ ,\ P_{C_2H_4O}\ ,\ P_{CO_2},\ P_{H_2O},\ T_R)}{\alpha f_c}$$

$$= \beta f\ (P_E,\ P_O,\ P_{C_2H_4O},\ P_{CO_2}\ ,\ P_{H_2O}\ ,\ T_R\ )$$

where $\beta$ is a constant , independent of activity variations. The form of the function f would then be determined from these rate ratios.

Since the activity of the catalyst is varying, it is impossible to select reaction conditions such that a reproducible gas composition can be achieved in the exit stream. At the same feed flow rate, variations in the activity result in widely different concentrations of products. Since the products significantly affect the rates of reactions, it is imperative that the same product concentrations always be used for computing the relative rates. To achieve this condition, all runs to be used for comparison with the kinetic runs would be made at fixed feed flow rate . Hence the "standard conditions" presented earlier were established; also the reaction rates for the standard runs were corrected for differences in concentrations of products.

The corrections to be applied to the standard runs to compensate for differences in product concentrations

were determined simply by measuring the rates of $C_2H_4O$ and $CO_2$ formation at several different conversions (i.e. various feed flow rates) with other conditions identical to those used in the standard runs.

The effects could not be evaluated separately for each of the three products. Therefore, the total pressure of the products would be used. $P_p$ was defined as the sum of the three product partial pressures:

$$P_p = P_{C_2H_4O} + P_{CO_2} + P_{H_2O}$$

and for a back-mixed reactor :

$$P_p = ( y_{C_2H_4O} + y_{CO_2} + y_{H_2O} ) P_t$$

where $P_{C_2H_4O}$, $P_{CO_2}$, and $P_{H_2O}$ are the partial pressures and $y_{C_2H_4O}$, $y_{CO_2}$, $y_{H_2O}$ are the mole fractions in the product gas stream, and $P_t$ is the total pressure of the reactor. Since both reactions involved in the ethylene oxidation were inhibited by the products, the variations in the selectivity were not too great. If the selectivity never varied, the partial pressure of each product would be a constant fraction of $P_p$. Determining the effect of $P_p$ on the reaction rates would then be equivalent to determining the effects of each of the products separately. Thus, the approximation is a good one if selectivity remains nearly constant. The use of $P_p$ is also a good approximation if the magnitudes of the effects of each of the products on the rates are similar.

The value of $P_p$ = 0.02 atm was chosen as the base to which the product concentrations of all standard runs are corrected. This value was chosen since it is close to an average of all those obtained for standard runs during the course of the experiments.

In many respects, the approach is similar to the one used by Buntin (13) and Klugherz(34). The relative rate (for either ethylene oxide or carbon dioxide formation) is now defined as the ratio of the rate of a kinetic run to an average of the rates of the standard runs, corrected to $P_p$= 0.02 atm, which bracket the kinetic run. If r is the actual rate measured during a kinetic run and $\bar{r}_s^o$ represents the average of the rates of the two bracketing runs at standard conditions ($r_s$), each of which has been corrected to $P_p$ = 0.02 atm ($r_s^o$), then the relative rate, R, is :

$$R = \frac{r}{\bar{r}_s^o}$$

$$= \frac{\alpha f(P_E, P_O, P_p, T_R)}{\alpha f(P_E=0.5\text{atm};\ P_O=0.1875\text{atm};\ P_p=0.02\text{atm},\ T_R=220^o)}$$

$$= \beta f(P_E, P_O, P_p, T_R)$$

The relative rates of ethylene oxidation to ethylene oxide and carbon dioxide are designated as $R_{C_2H_4O}$ and $R_{CO_2}$, respectively. Note that the relative rates are a function of $P_p$ as well as $P_E$, $P_O$ and $T_R$. Also, at standard conditions and at $P_p$=0.02 atm, the relative rates of both

reactions equal unity, by definition.

The correction factors used to adjust the reaction rates of the standard runs so that they correspond to rates measured at a total product concentration of $P_p$ = 0.02 atm are shown in Fig. F-1 and F-2 of the appendix F. The procedure used to obtained these curves is presented in the Appendix F.

The corrected standard rates for both $C_2H_4O$ and $CO_2$ are obtained by dividing the measured rates at standard conditions by the correction factors corresponding to the value of $P_p$ computed for the standard run under consideration.

4-4 Scope of Experimental Work :

In a three phase reaction system ; for a kinetic study to be feasible, the overall mass transfer resistances must be small, and therefore the reaction rate controls the rate of the overall process. Thus it is necessary to begin with a mass transfer study.

The rates of physical absorption into dibutyl phthalate of both reactant gases , ethylene and oxygen, were studied employing the method described in the previous section, at a temperature equal to the reacting temperature, and $k_l a_g$ was obtained. It will be proved in the next chapter that the mass transfer resistance from the gas bubble liquid interface to the bulk liquid and also the overall mass transfer resistance is small. Therefore a kinetic study is

possible under these conditions.

For a kinetic study, only partial pressure of oxygen was varied. The major variables of interest are the partial pressures of oxygen and the three reaction products, as characterized by $P_p$ . The term"partial pressure", as used here , always refers to the partial pressure within the reactor calculated with the assumption of a back-mix reactor.

The kinetics of ethylene oxidation at an ethylene partial pressure of 0.5atm are investigated. The oxygen partial pressures were varied from 0.115 to 0.282 atm. The agitator speed was also maintained constant at 1750 rpm, and the reactor temperature was kept at 220°C. In obtaining kinetic data with low conversions of ethylene, 500mg of catalyst was used.

The overall aim is to provide a preliminary step for a full study of the kinetics of ethylene oxidation on a supported silver catalyst in a liquid phase.

## V RESULTS AND DISCUSSION

### 5-1 Mass Transfer Studies :

In order to understand the kinetics of the catalytic slurry system and to interprete the relation of the overall rate with respect to the concentration of each reactant gas, it is necessary to evaluate the rates of transfer of reactants to the catalyst sites. As it was already mentioned in chapter II , the mass transfer from the bulk gas to the gas liquid interface is known to be rapid whereas the diffusion of the gaseous solutes in the liquid is relatively slow. In the following section, the mass transfer resistances from gas bubble liquid interface to the bulk liquid and from the bulk liquid to the catalyst surface will be discussed. The significance will be evaluated to determine reactant concentration at the external surface of the catalyst particles.

### 5-1-1 Gas Bubble Liquid Interface to Bulk Liquid : $k_l a_g$

Unsteady state physical absorption experiments were carried out for both reactant gases, oxygen and ethylene. By plotting $-\frac{P_f}{P_i} \ln \frac{P - P_f}{P_i - P_f}$ versus time, a straight line was obtained and the slope is equal to $k_l a_g$ . The result for dibutyl phthalate, at 220°C and at an agitation speed of 1750 rpm, is shown in Fig. 5-1 . Absorption time was fast for each gas . For ethylene, no further absorption was detectable after 7.5

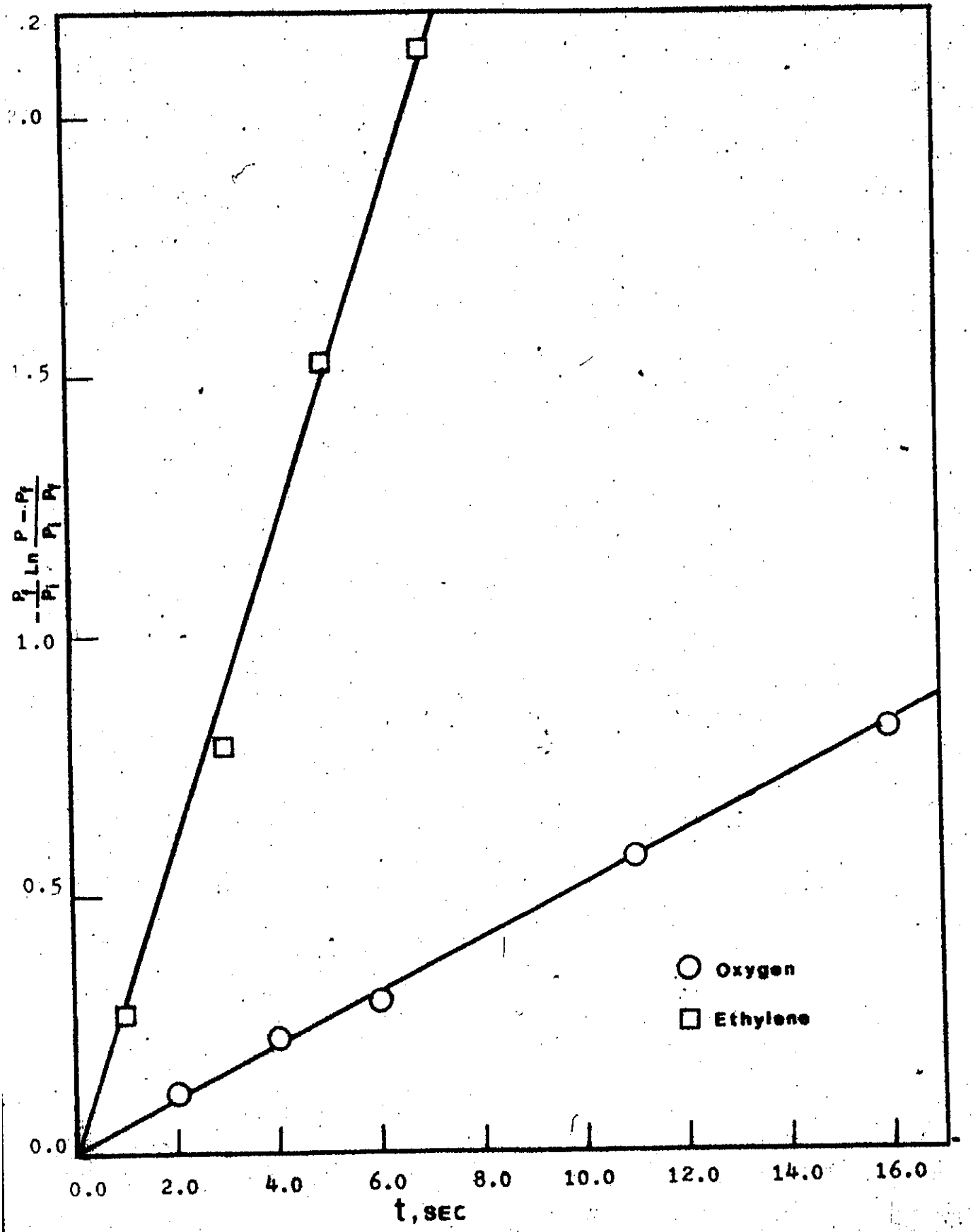



Fig 5-1 : PHYSICAL ABSORPTION OF REACTANT GASES IN DIBUTYL PHTHALATE

seconds, and for oxygen 16 seconds.

$k_l a_g$ evaluated by this method are found to be :

$$k_l a_g = 28.48 \times 10^{-2} \text{ sec}^{-1} \quad \text{for ethylene,}$$

$$k_l a_g = 5.03 \times 10^{-2} \text{ sec}^{-1} \quad \text{for oxygen.}$$

From the results shown, the $k_l a_g$ of ethylene is 5.7 times that of oxygen. It is also noted that the partial pressure of ethylene was always greater than that of oxygen, and that the molar flux of oxygen to the catalyst was a factor of about two greater than that of ethylene. From these observations it can be concluded that the concentration driving force needed to overcome mass transfer resistance for oxygen represented a greater fraction of the available driving force than was the case for ethylene. That is, if the reaction is significantly hindered by the mass transfer resistance, the condition will be more acute for oxygen than for ethylene. Therefore, to evaluate the significance of the mass transfer resistance, it is necessary only to assess the resistance due to oxygen. This procedure was used by Calderbank et al (15) in their study of hydrogenation of ethylene in an inert solvent. The mass transfer resistances were evaluated and hydrogen transfer rate became the determining factor.

The significance of the mass transfer resistance for absorption can then be demonstrated by the difference of the concentration of the solute gas in the bulk liquid $C_b$ and the concentration at the gas liquid interface $C^*$. With the assumption that there is no resistance across the gas liquid

interface, the concentration $C^*$ is always in equilibrium with the concentration of the gas at the surface of the gas phase. Therefore $C^*$ can be determined by Henry's law:

$$C^* = \frac{P}{H} \qquad (5 - 1)$$

where He is the Henry's law constant and P is the pressure of the corresponding gas. At steady state, the rates of all mass transfer steps and the kinetic step will be the same and equal to the global rate. Hence :

$$r_v = k_l a_g (C^* - C_b) \qquad (5 - 2)$$

Therefore the difference in concentrations can be evaluated by equation (5-2). Details of calculations are given in the Appendix C on page 106. For the highest actual rate, the significance of the difference in concentration represented by a percentage of $C^*$ is less than 5.7 %.

This method was used by Kenney and Sedriks (32) in the determination of the significance of the mass transfer resistance from the gas bubble liquid interface to the bulk liquid in the hydrogenation of crotonaldehyde over palladium catalyst. They also reported a rapid approach to saturation of the solute gas in the solvent.

It can be concluded from this study that the mass transfer resistance from the gas bubble liquid interface to the bulk liquid is not the main and determining factor of the overall process. With a concentration difference already mentioned, this resistance can be considered small in the overall process.

5-1-2 Mass Transfer Resistance from the Bulk Liquid to the Catalyst Surface

There is no simple experimental method which can be used to show that the mass transfer resistance from the bulk liquid to the catalyst surface is negligible. However, from available correlations, the mass transfer coefficient can be estimated and the significance of the resistance can be evaluated.

For a first approximation, the mass transfer coefficient $k_p$ can be estimated for a sphere at its settling velocity. The terminal velocity of a small sphere is given by Stokes' law. For estimating $k_p^*$, the popular correlation of Harriott (26) can be used, the procedure involves estimating the Peclet number of the particle and using Brian and Hales' (56) curve. The Sherwood number can then be found ( $N_{Sh} = \frac{k_p^* . d_p}{D_{1m}}$ )

Details of calculations are given in the Appendix D . With the value of $k_p$ equals to 0.38 cm/sec , the mass transfer resistance due to this physical step is of 2.8 % of the equilibrium value of the concentration .

This approach was also used by Kenney and Sedriks (32) in their estimation of this mass transfer resistance in the system described in the previous section.

5-1-3 Internal Mass Transfer Resistance :

As was suggested by Smith (62), for fluidized

bed and slurry reactor, intraparticle transport process can usually be neglected. The significance of this resistance was first brought up by Satterfield, Ma and Sherwood ( 57) in the liquid phase hydrogenation of $\alpha$-methyl styrene. The effectiveness factor for the catalyst pellet was found to be in the same range as in gas phase study. Intraparticle resistance was also studied by Kenney and Sedriks (32). But in all cases, studies are concerning catalyst pellets and by a comparison the intrinsic rate constant of reactions using pellets and then catalyst in powder form. Thus they always assumed that the resistance is negligible in the case of catalyst powder. Therefore, for finely powdered catalyst, like in this study, the resistance also can be considered to be negligible.

Calculations were performed to find the effectiveness factor of the reaction using Satterfield method (56), by calculating the modulus $\Phi_s$ , and the effectiveness factor was read directly from the available chart. The result shows that, for highest available rate, the effectiveness factor approached unity and the resistance is therefore small in the overall process. ( Details of calculations are given in the Appendix E. ).

## 5-2 Kinetic Studies :

### 5-2-1 Presentation of results

The results obtained in this study of the kinetics of ethylene oxidation at 220°C are presented in Table A-1 in the Appendix B. Only data for the kinetic runs are included. The reaction rates have been corrected for variations in catalytic activity, as described in the preceding chapter.

The runs are limited to one partial pressure of ethylene ( $P_E$ = 0.5 atm ). At each set of oxygen partial pressure, the relative rate of ethylene oxidation to ethylene oxide ( $R_{C_2H_4O}$ ) and to carbon dioxide ( $R_{CO_2}$ ) are tabulated with the corresponding values of the sum of the product partial pressures, $P_p$ . The selectivity to ethylene oxide is also included, to indicate the relative contributions of the three products to $P_p$ . Due to the variation in conversion in each run, the oxygen partial pressure of each set was taken to be the average oxygen partial pressure of the set.

The kinetic data can be presented graphically by plotting the relative rates as a function of $P_p$ , for each set of oxygen partial pressures. The relative rates to ethylene oxide are shown in Fig. 5-2 and for carbon dioxide in Fig. 5-3. Smooth curves have been drawn through each set of data points corresponding to the different combinations of oxygen partial pressures.

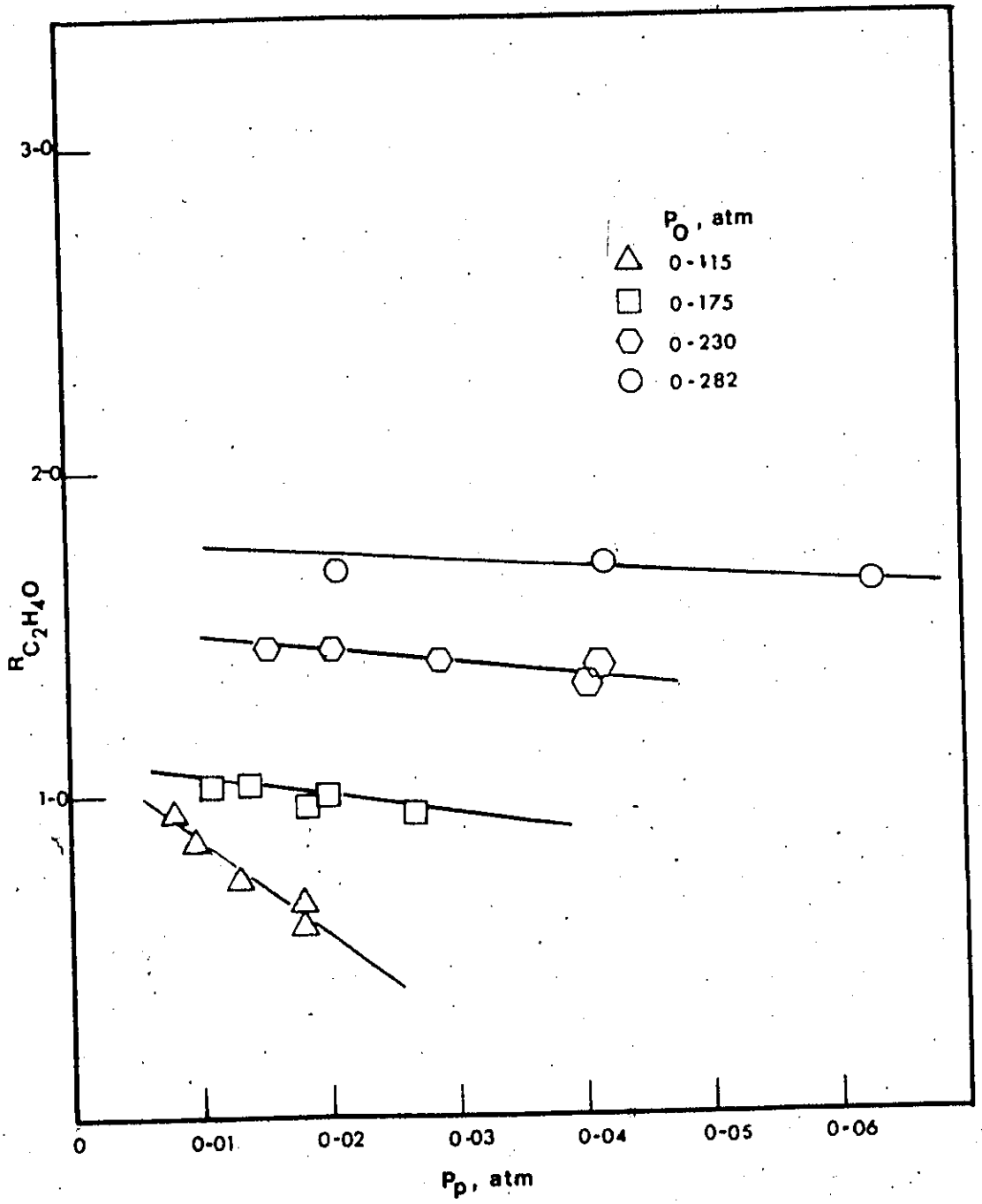



Fig 5-2 : EFFECT OF PRODUCT PRESSURE ON THE RELATIVE RATE OF ETHYLENE OXIDE FORMATION ($P_E$= 0.5atm)

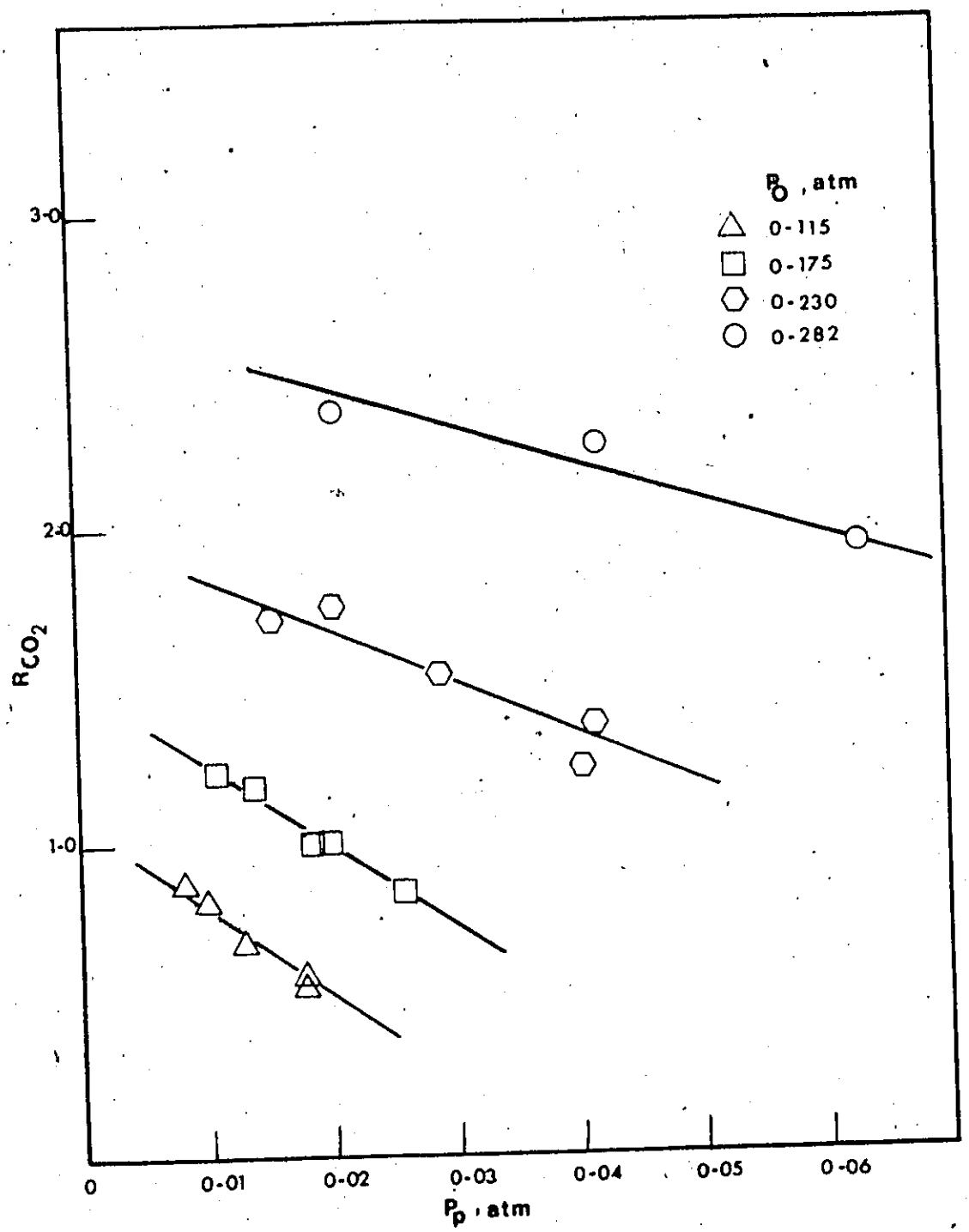



Fig 5-3 : EFFECT OF PRODUCT PRESSURE ON THE RELATIVE RATE OF CARBON DIOXIDE FORMATION ($P_E$=0.5atm)

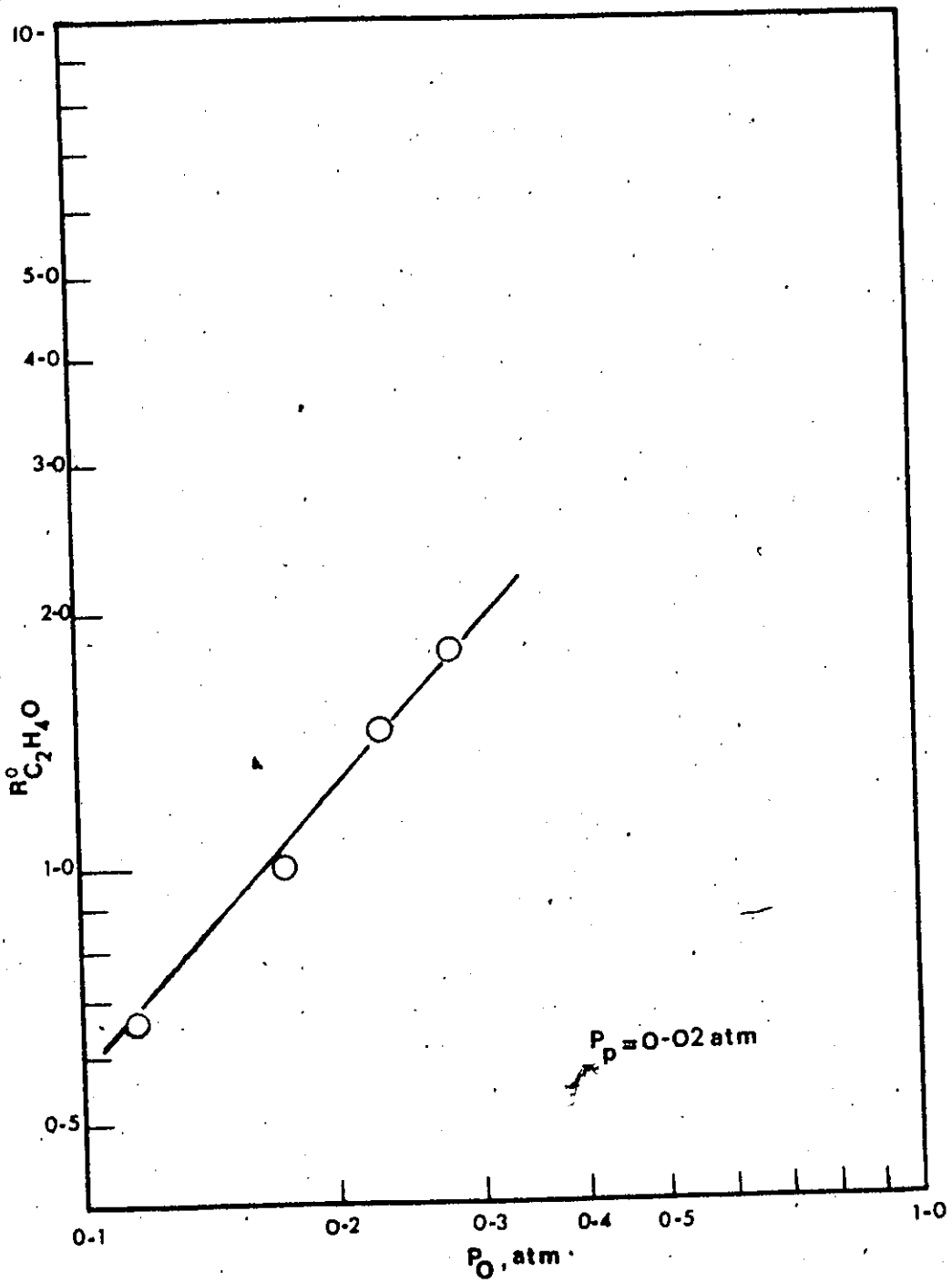



Fig 5-4 : EFFECT OF OXYGEN PRESSURE ON THE RELATIVE RATE OF ETHYLENE OXIDE FORMATION ($P_E$=0.5)

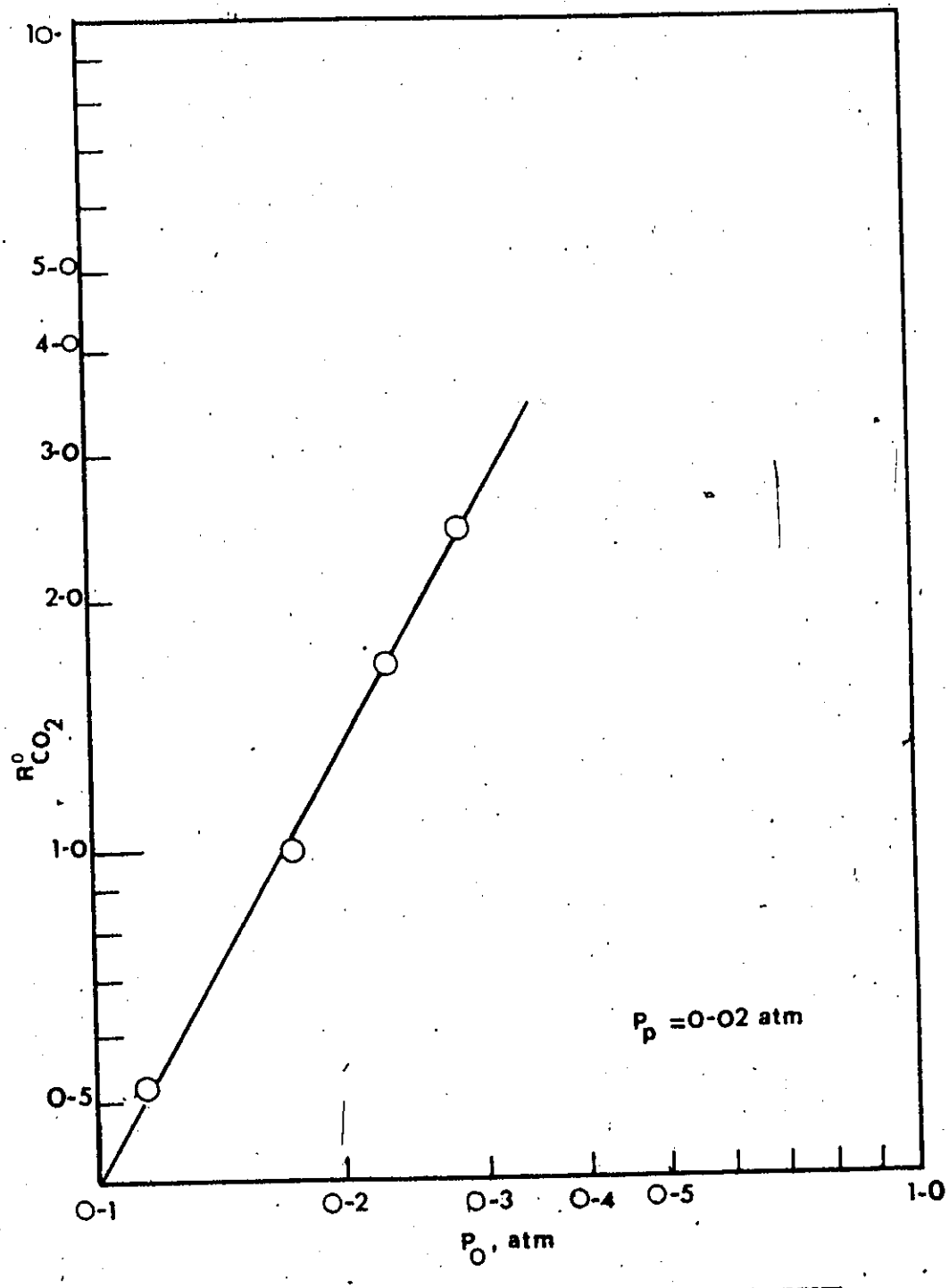



Fig 5-5 : EFFECT OF OXYGEN PRESSURE ON THE RELATIVE RATE OF CARBON DIOXIDE FORMATION ($P_E$=0.5atm)

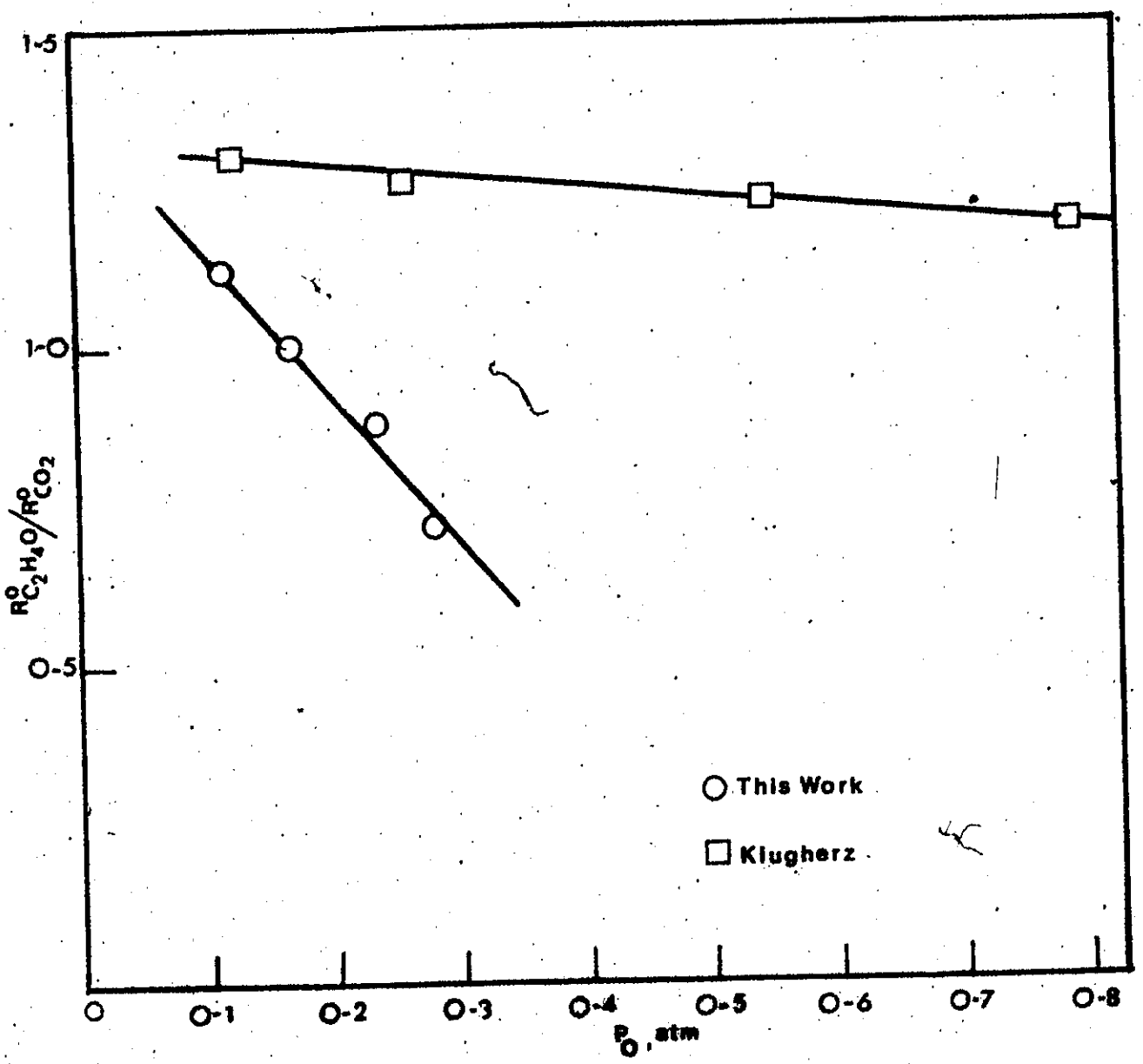



Fig. 5-6 : EFFECT OF OXYGEN PRESSURE ON THE SELECTIVITY OF ETHYLENE OXIDATION

5-2-2 Effect of the product partial pressures on the relative rates of ethylene oxidation :

It is obvious from Fig.5-2 and 5-3 ,that the product partial pressures have a considerable effect on the reaction rates.The rates decrease as $P_p$ is raised,regardless of the reactant concentrations,confirming the presence of strong inhibition by the reaction products.

Therefore the effect of the reaction products must be taken into account when determining the dependence of the relative rates upon the oxygen partial pressures. Buntin (13) approached this problem by correcting all his data to zero concentration of products,while Klugherz (34) corrected to a concentration of $P_p$ = 0.01 atm .Orzechowski and MacCormack (51) extrapolated their results back to zero conversion and contact time.However,it is often very difficult to graphically differentiate a plot of conversions versus contact time when the reaction is strongly inhibited by products.Nault,Bolme and Johanson (47),on the other hand, made no attempt to take the effect of the products into account in determining the effect of ethylene and oxygen partial pressures.

The inhibition of products can be explained as they absorb on the catalyst and compete with reactants for reaction sites.The interaction,therefore,should be less significant at high reactant pressures.Thus,from the curves of Fig.5-2 and 5-3 ,as the partial pressure of oxygen

increases, the slope decreases due to a diminishing effect of the product inhibition.

5-2-3 Dependence of relative rates on oxygen partial pressures

In order to determine the effect of oxygen pressures on the kinetics of ethylene oxidation, it was already decided that all relative rates would be compared at a single value of $P_p$. $P_p$ =0.02 atm. The relative rates have already been described by the relationship :

$$R = f(P_E, P_O, P_p, T_R)$$

Thus , with $P_E$, $P_p$ and $T_R$ constant ($P_E$=0.5 atm, $P_p$ = 0.02 atm and $T_R$=220°C ) the relative rates depend only on the partial pressure of oxygen. From the curves of Fig. 5-2 and 5-3, the relative rates of $R_{C_2H_4O}$ and $R_{CO_2}$ at $P_p$=0.02 atm are obtained. These relative rates, designated as $R^o_{C_2H_4O}$ and $R^o_{CO_2}$ are presented in table 5-1, along with the oxygen partial pressures to which they correspond.

The effect of oxygen partial pressures on the relative rates of ethylene oxidation are shown in Fig. 5-4 and 5-5. It is concluded that the relative rates increase with increasing oxygen pressures. The rates of ethylene oxidation to ethylene oxide is first order in oxygen pressures. The rates of ethylene oxidation to carbon dioxide appears to be higher than first order in oxygen pressures . A ln-ln graph was plotted for $R^o_{CO_2}$ versus $P_O$ ; and the apparent order of the reaction was found to be 1.73 .

TABLE 5-1

Effect of oxygen partial pressures on the relative rates of ethylene oxidation , for $P_p$ =0.02 atm

| $P_O$ | $R^o_{C_2H_4O}$ | $R^o_{CO_2}$ | $\frac{R^o_{C_2H_4O}}{R^o_{CO_2}}$ |
|---|---|---|---|
| 0.115 | 0.58 | 0.52 | 1.12 |
| 0.175 | 1. | 1. | 1. |
| 0.230 | 1.47 | 1.67 | 0.88 |
| 0.282 | 1.75 | 2.44 | 0.72 |

There is a wide contradiction reported on the reaction order related to oxygen pressures in the gas phase reaction system. Buntin (13), for instance, has concluded that the rates of the reaction to $C_2H_4O$ is proportional to $P_O^{\frac{1}{2}}$ . The apparent reaction order for oxidation to $CO_2$ is even lower than 1/2. On the other hand, results presented by Nault et al. (47) indicate that both reactions are nearly first order in oxygen at the particular ethylene pressure used (0.1 atm). Orzechowski and MacCormack (51) have concluded that at high oxygen concentrations, the rates are independent of oxygen pressures. The order equal to one or higher has been reported by Twigg , McKim and Cambron and Klugherz. Twigg (64) reported that the dependence on oxygen partial pressures could be represented by $P_O^{0.55}$ for ethylene oxide formation and $P_O^{1.1}$ for carbon dioxide formation at even low ethylene pressures. McKim and Cambron (41) reported that when ethylene

was present in excess, the rates were approximately proportional to oxygen concentrations. Klugherz (34) carried out his experiment in a wide range of ethylene pressures and reported that the apparent reaction order with respect to oxygen pressures varied widely, depending on the magnitude of the ethylene pressure. The reactions were definitely greater than 0.5 in the order of oxygen, even at moderate ethylene pressures. At an ethylene pressure of 0.526 atm, the relationship between reaction rates of both ethylene oxide and carbon dioxide production are approximately linear. Orders greater than one are also observed at higher ethylene pressures.

In summary, the contradiction may arise from the different partial pressures used for ethylene. As the ethylene pressures increase to more than 0.5 atm, the reaction order becomes unity or higher than one with respect to oxygen partial pressures. It is also able to conclude that, at ethylene partial pressure of 0.5 atm, oxygen is weakly adsorbed on the catalyst surface since the rates vary approximately linearly with oxygen pressures.

5-2-4 Effects of oxygen pressures on the selectivity of ethylene oxidation :

Differences in the selectivity were noted when the reactant compositions were varied. As already mentioned, the selectivities for the kinetic runs are included in table A-1 in the Appendix B on page 99 . The ratios of the relative

rates of $C_2H_4O$ and $CO_2$ formation at $P_p$ = 0.02-atm, that is $R^o_{C_2H_4O}/R^o_{CO_2}$ have been calculated and can be used as an indication for the selectivity of the two parallel reactions. These ratios are included in table 5-1. This approach is similar to the one used by Buntin (13) and Klugherz (34).

The effect of oxygen pressures on the ratios of rates is shown in Fig. 5-6, on page 69. The only available study that can be used for a comparison is that of Klugherz, where $P_E$ = 0.526 atm and $P_p$ = 0.01 atm. These data are included in Fig. 5-6.

The selectivity is found to decrease with oxygen pressure at moderate ethylene concentration, in agreement with what was observed by Klugherz. A sharp decrease in the selectivity in Fig. 5-6 is attributed to a higher rate of carbon dioxide formation at high oxygen concentration. It is also worth mentioning here that apparently at low ethylene pressure, the effect is reversed. It was reported by Klugherz (34) and Buntin (13) that the selectivity was found to increase with oxygen pressure at low ethylene concentration.

5-2-5 Comparison of the intrinsic reaction rates and selectivities for reactions in gas and liquid phases :

Some comparisons of the intrinsic reaction rates of this study showed that they were from two to three times higher than those obtained by Klugherz (34), which was done in a gas phase reaction system. For example, in Klugherz study, at $P_E$=0.526atm, $P_O$=0.263 atm, and $P_p$=0.0157 atm, the absolute

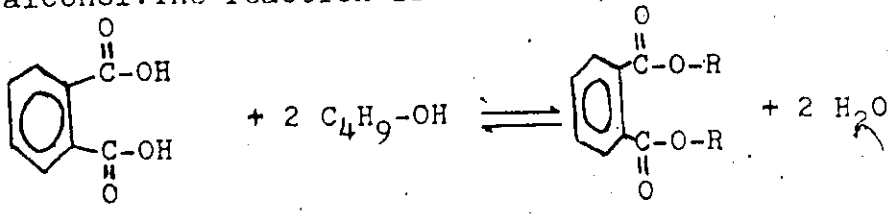
rate for ethylene oxide formation was $5.75 \times 10^{-6}$ gmole $C_2H_4$/min.g.catalyst and the selectivity was 61.2%. In this study, under nearly similar conditions, $P_E$=0.5, $P_O$=0.230, $P_p$=0.0156 atm, the rate was $15.3 \times 10^{-6}$ gmole $C_2H_4$/min.g.catalyst, and the selectivity was 30.7% . As it was already mentioned in Chapter II, the high activity of the catalyst may explain why a lower selectivity was obtained in a liquid phase system. Selectivities for ethylene oxide formation ranged from 20 to 40% in this study. Also , in view of the discussion given in section 2-6, the values are more reasonable than those given by Shingu (59). The effect of the solvent on the adsorption of various reactant and product gases on the catalyst surface is unknown, but it may play a part in the high activity of the catalyst. The solvent may act as an inhibitor in the ethylene oxide formation or the effect of any moderator present in the catalyst may have been neutralized by the solvent.

5-3 Stability of the solvent :

Dibutyl phthalate is known to be very stable with oxidising agents (See chapter IV ).However in the presence of the ethylene oxidation reaction,where water is formed, a saponification process of the ester can happen,as it was observed during the course of this study.

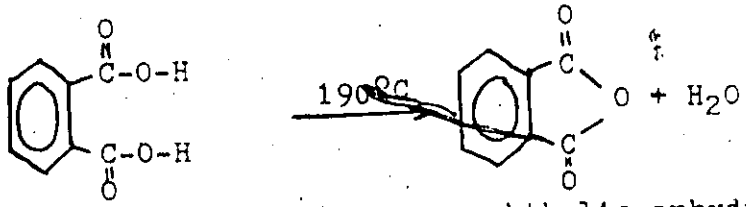
After operating the reactor consecutively for a few weeks,it was found that some white crystals,in needle form, were deposited on the upper wall of the reactor.Analyzing the substance by melting point and infra-red spectroscopy methods,it was identified as phthalic anhydride.The melting point of the crystals was 131°C and the I.R. result is shown in Fig. 5-7

Dibutyl phthalate is a diester of phthalic acid and n-butyl alcohol.The reaction is reversible as follow:




phthalic acid | n-butyl alcohol | dibutyl phthalate

Phthalic acid formed in the saponification process can become anhydride quite easily at the reaction temperature (17).




phthalic acid | phthalic anhydride

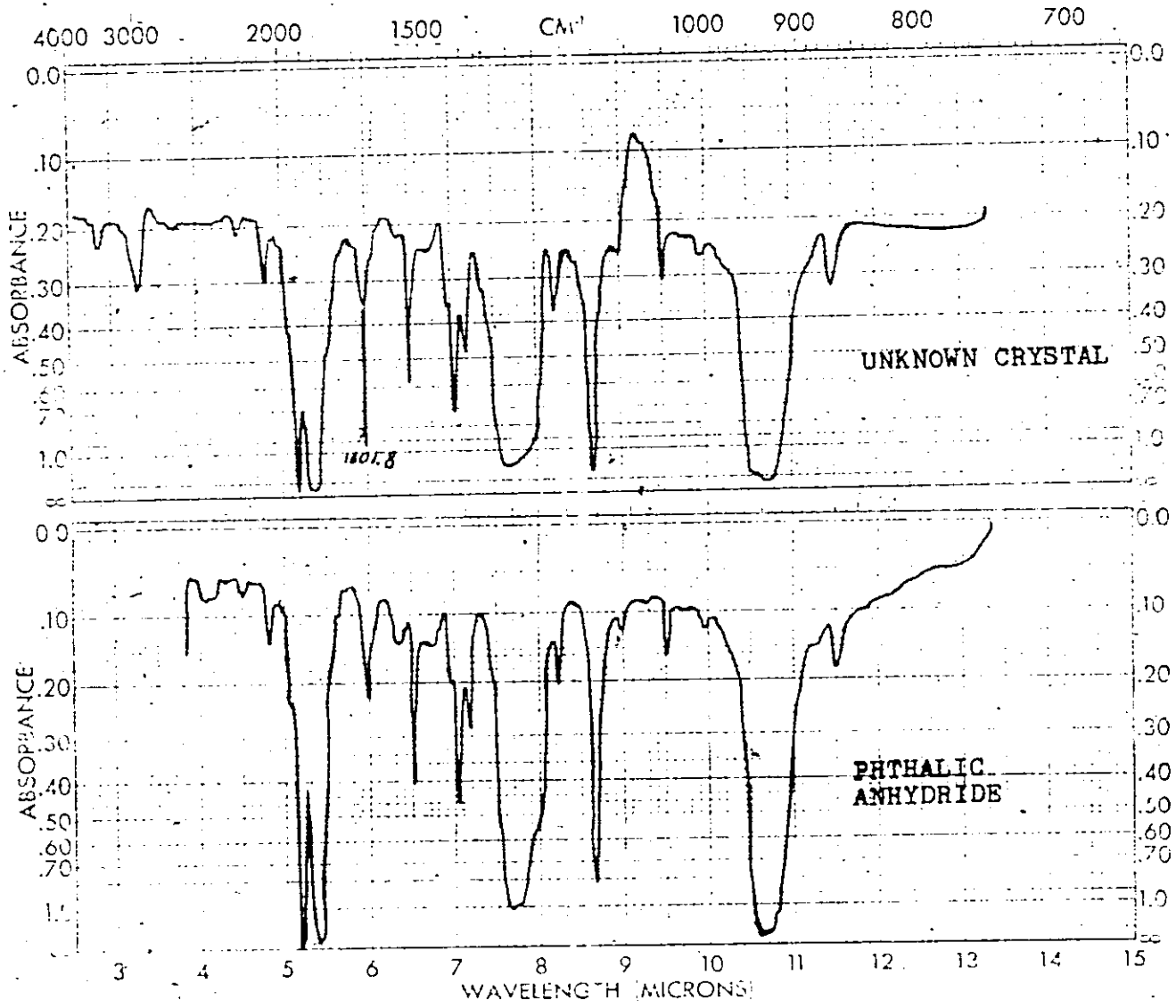



Fig. 5-7 : INFRA-RED ANALYSIS OF PHTHALIC ANHYDRIDE

The conversion in the ethylene oxidation is small, therefore the amount of phthalic anhydride formed is also small. But the decomposition of the solvent has caused some problem on the accuracy of the kinetic data obtained:

* The product partial pressure could be altered :

In the two reactions as described, 2 moles of $H_2O$ were reacted in step one and only one mole of $H_2O$ was recovered in step 2. Thus one mole of water in the product was consumed in the process. However, in the analysis, the number of moles of water was not measured and assumed to be equal to the number of carbon dioxide, therefore the problem does not affect the kinetic data.

* n-Butyl alcohol may react with oxygen which is a reactant in the ethylene oxidation:

The oxidation of n-butyl alcohol on a metal catalyst is not a well treated subject, only a few paper can be found. Cozzi (18) carried out the oxidation experiment with ethanol, propanol and butanol at 300 to 350°C . For ethanol, the main product is aldehyde and other side products are acid and some carbon dioxide and monoxide. He reported no reaction can happen below 200°C and aldehyde formation was noticed at 260°C. The conversion is even lower for butanol. Polyakov and Shalya (52) carried out the oxidation on a fluidized bed of silver and copper catalyst. Aldehyde was also formed as the main product with the concurrent formation of $CO_2$ and CO. The reaction temperature must be well above 220°C .

for butanol oxidation. Therefore, it is expected that at this temperature only a very small amount of oxygen is able to react with butanol to form carbon monoxide and carbon dioxide.

## VI CONCLUSION AND RECOMMENDATION

The kinetics of ethylene oxidation on a supported silver catalyst in dibutyl phthalate have been investigated over a wide range of oxygen pressures and at one constant ethylene pressure at 220° .The three mass transfer resistances : from bubble liquid interface to bulk liquid, from bulk liquid to the catalyst surface and intraparticle, are found to be negligible and therefore the system is feasible for a kinetic study .

For kinetic study , the data are expressed in terms of relative reaction rates to allow for observed variations in catalytic activity . Ratios of rates relative to rates at a defined set of reference conditions are calculated . Data corresponding to a constant sum of product partial pressure is of primary interest . The rates of formation of ethylene oxide are found to be first order with respect to oxygen pressure and higher than first order in the formation of carbon dioxide,at an ethylene partial pressure of .5 atm.Inhibition of the reaction by products is also observed .

The stability of dibutyl phthalate , when water is formed in the ethylene oxidation,causes some problem in assessing the accuracy of kinetic data.The saponification of the diester gives phthalic anhydride and butanol. It is an

important factor which was not reported by Shingu ( 59) can determined the feasibility of the process for industrial application.

It is recommended that other solvents which are stable to heat and oxidation,chemically indifferent and nonvolatile will be tried.In each case,the stability of the solvent must be investigated.

This study is a preliminary step in the investigation of the kinetics of a three phase reaction system.To obtain a full kinetic mechanism,a wider combination of ethylene and oxygen pressures must be used and it is recommended as the next step of the study of the process.

## VII NOMENCLATURE

| | |
|---|---|
| $a_g$ | Gas liquid interfacial area per unit volume of liquid, $cm^2/cc$ |
| $a_p$ | External particle surface area per unit volume of liquid, $cm^2/cc$ |
| A | A constant in the overall rate equation. |
| b | A constant in the rate equation. |
| $C_b$ | Bulk concentration of solute gas in liquid, gmole/cc |
| $C_g$ | Concentration of solute gas in the bulk gas, gmole/cc |
| $C_s$ | Concentration of solute gas at the external surface of the catalyst particle, gmole/cc |
| $C^*$ | Equilibrium concentration of solute gas in liquid, gmole/cc |
| $d_p$ | Catalyst particle diameter, cm |
| $\mathcal{D}_{bulk}$ | Bulk diffusivity, cm/sec. |
| $\mathcal{D}_{eff}$ | Effective diffusivity within the catalyst particle, cm/sec. |
| $\mathcal{D}_{bulk,eff}$ | Effective bulk diffusivity within the catalyst particle, cm/sec. |
| $\mathcal{D}_{K,eff}$ | Effective Knudsen diffusivity within the catalyst particle, cm/sec. |
| $\mathcal{D}_{12}$ | Bulk diffusivity of the solute gas in liquid, cm/sec |
| f | Functional relationship between reaction rate and partial pressure excluding activity factor. |
| $f_c$ | Value of function at constant conditions. |
| F | Feed flow rate, scc/min. |
| g | Gravitational constant, 980.665 $cm/sec^2$ |
| H | Henry's law constant, atm/cc/gmole. |
| $k_l$ | Gas liquid absorption constant, cm/sec. |
| $k_o$ | Overall rate constant in a slurry reactor, cm/sec. |
| $k_g$ | Bulk gas to bubble liquid interface mass transfer coefficient |

| | |
|---|---|
| $k_p$ | Liquid particle mass transfer coefficient, cm/sec |
| $k_p^*$ | Liquid particle mass transfer coefficient due to free fall, cm./sec . |
| $k_1$, $k_2$, $k_3$, $k_4$ | Constant in rate equations |
| $k_E$, $k_O$, $k_p$, $k_s$ | Rate constants for adsorption. |
| $K_1$, $K_2$ | Adsorption equilibrium constants. |
| $K_E$, $K_O$, $K_p$, $K_s$ | Adsorption equilibrium constants. |
| M | Molecular weight of solvent, gm/gmole. |
| n, N | Total number of mole of gas in adsorption. |
| $N_{Pe}$ | Peclet Number. |
| $N_{Re}$ | Reynold number. |
| $N_{Sh}$ | Sherwood number. |
| P | Pressure of absorbed gas, atm |
| $P_i$, $P_f$ | Initial and final pressure of absorbed gas, atm |
| $P_E$, $P_O$, $P_p$ | Partial pressure of ethylene, oxygen and product respectively, atm |
| $P_{C_2H_4O}$, $P_{CO_2}$, $P_{H_2O}$ | Partial pressure of ethylene oxide, carbon dioxide, and water, respectively, atm |
| $P_t$ | Reactor pressure, atm. |
| q | Amount adsorbed, Elovich equation. |
| r | Rate of $C_2H_4O$ or $CO_2$ formation. |
| $r_c$ | Reaction rates measured at "constant" conditions |
| $r_{C_2H_4O}$ | Rate of $C_2H_4O$ formation, gmole $C_2H_4$/min., g.catalyst. |
| $r_{CO_2}$ | Rate of $CO_2$ formation, gmole $C_2H_4$/min., g.catalyst. |
| $r_s$ | Rates of $C_2H_4O$ or $CO_2$ formation measured at standard conditions |
| $r_s^o$ | Rates at standard runs corrected to $P_p$ = 0.02 atm |
| $r_v$ | Overall reaction rate in slurry reactor, gmole/cc.min. |

| | |
|---|---|
| $R$ | Ideal gas law constant. |
| $R_{C_2H_4O}$, $R_{CO_2}$ | Relative rates, relative to rates at standard conditions corrected to $P_p$ = 0.02 atm |
| $R^o_{C_2H_4O}$, $R^o_{CO_2}$ | Relative rates corresponding to $P_p$ = 0.02 atm |
| $S_g$ | Surface area per unit weight of catalyst, $cm^2/gm$ |
| $t$ | Time |
| $T$ | Reaction temperature, $^oC$ |
| $U_t$ | Terminal velocity in free fall , cm/sec. |
| $V_l$ | Volume of solvent , cc |
| $V_g$ | Volume of the gas space, cc |
| $V_1$ | Molecular volume of solute at normal boiling point, cc/ gmole. |
| $W$ | Weight of catalyst, gm. |
| $y_{C_2H_4O}$, $y_{CO_2}$, $y_{H_2O}$ | Mole fraction of products in the product stream. |
| $y^o_E$ , $y^o_O$ | Mole fraction of ethylene and oxygen in feed. |

Greek letters :

| | |
|---|---|
| $\alpha$ | Activity factor. |
| $\beta$ | Constant. |
| $\Phi_s$ | Modulus |
| $\phi_s$ | Thiele Modulus. |
| $\varepsilon$ | Porosity. |
| $\eta$ | Effectiveness factor. |
| $\mu$ | Viscosity, cp |
| $\rho_p$ | Density of the catalyst, g/cc. |

| | |
|---|---|
| $\tau$ | Tortousity |
| $\chi$ | "Association"parameter for solvent. |

Subscripts

| | |
|---|---|
| E | Ethylene |
| O | Oxygen |
| p | product |
| t | total . |

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# IX APPENDICES

## APPENDIX A

### Mass Transfer Studies :Physical Absorption

The resistance to mass transfer in the liquid phase may be determined by observations of the rate of absorption or desorption of a sparingly soluble gas into or out of liquid,and physical absorption is a method which has been used extensively in the determination of the mass transfer coefficient.

The absorption technique can be a flow system in which a sparingly soluble volatile solute is stripped out of its liquid solution into an insoluble gas bubble stream or where a sparingly soluble gaseous solute is dissolved by a liquid from an admixture with an insoluble gas bubble stream. A batch technique can also be used,in which a certain volume of an initially solute-free liquid was brought in contact with a pure gas phase of the solute under consideration.The rate of the solute uptake with respect to time was then monitored.The batch absorption technique presents some drawbacks as suggested by Kozinsky and King (35).Under conditions of high agitation,the liquid tends to approach saturation very quickly,thus reducing the time available for measurement.Also,some gases,such as hydrogen,are highly insoluble gases,consequently the total volume of gas absorbed is quite small.There is thus a possibility of significant error due to small temperature change or leaks.

The method used in this study employs a transducer read-out, therefore , even with a fast absorption, the solute uptake versus time can always be recorded with high efficiency. The prevention of leaks was also undertaken by pressurizing the vessel overnight to detect any possible leak. Before physical absorption data were taken for Dibutyl Phthalate, the method was tested with a system of water and each of the reactant gases. The reproducibility of result was good under repeated test. The results of $O_2$ and $C_2H_4$ in 230cc of water at 23°C are shown in Fig.A-1 and A-2 on page 97 and 98.

Derivation of equation of batch absorbtion

Henry's law constant can be expressed as:

$$H = \frac{P}{C^*}$$

where P is the instantaneous pressure of the gas and $C^*$ is the corresponding value of the equilibrium concentration of the solute gas in the liquid.

The bulk concentration $C_b$ of the solute gas in the liquid :

$$C_b = \frac{V_g}{V_l \cdot RT} ( P_i - P )$$

Where $P_i$ is the initial pressure, $V_g$ is the volume of the gas space and $V_l$ is the volume of the liquid. Then:

$$C^* - C_b = \left( \frac{1}{H} + \frac{V_g}{V_l RT} \right) P - \frac{V_g}{V_l RT} P_i \qquad (9\text{-}1)$$

The rate of the solute uptake is related to the rate of change in pressure by means of the ideal gas law:

$$\frac{dN}{dt} = \frac{V_g}{RT} \times \frac{dP}{dt} \qquad (9\text{-}2)$$

also :

$$-\frac{dN}{dt} = V_l k_l a_g ( C^* - C_b) \qquad (9\text{-}3)$$

Hence from equations (9-1), (9-2) and (9-3):

$$-\frac{1}{RT}\frac{dP}{dt} = k_l a_g \frac{V_l}{V_g}\left[\left(\frac{V_l}{H\ V_g} + \frac{1}{RT}\right)P - \frac{1}{RT}P_i\right], \qquad (9\text{-}4)$$

Let $\alpha = \frac{V_l}{H\ V_g} RT$, then equation (9-4) becomes:

$$-\frac{dP}{dt} = k_l a_g (\alpha + 1)P - P_i \qquad (9\text{-}5)$$

Integrate equation (9-5) :

$$-\int_{P_i}^{P} \frac{dP}{(\alpha + 1)P - P_i} = (\alpha + 1)\, k_l a_g t$$

$$-\ln \frac{(\alpha + 1)P - P_i}{P_i} = (\alpha + 1)\, k_l a_g t \qquad (9\text{-}6)$$

At equilibrium, the final pressure is $P_f$ and the final concentration of the solute is $C^*$ where $C^*$ is equal :

$$C^* = \frac{V_g}{V_l\ RT}( P_i - P_f )$$

and $$C^* = \frac{P_f}{H}$$

Hence $$\frac{P_f}{H} = \frac{V_g}{V_l RT}( P_i - P_f)$$

or: $$\frac{P_i - P_f}{P_f} = \frac{V_l\ RT}{H\ V_g}$$

$$= \alpha$$

Therefore equation (9-6) becomes :

$$-\frac{P_f}{P_i} \ln \frac{P - P_f}{P_i - P_f} = k_l a_g t \qquad (9\text{-}7)$$

A plot of $-\frac{P_f}{P_i} \ln \frac{P - P_f}{P_i - P_f}$ versus t is a straight line and $k_l a_g$ is equal to the slope of the curve .

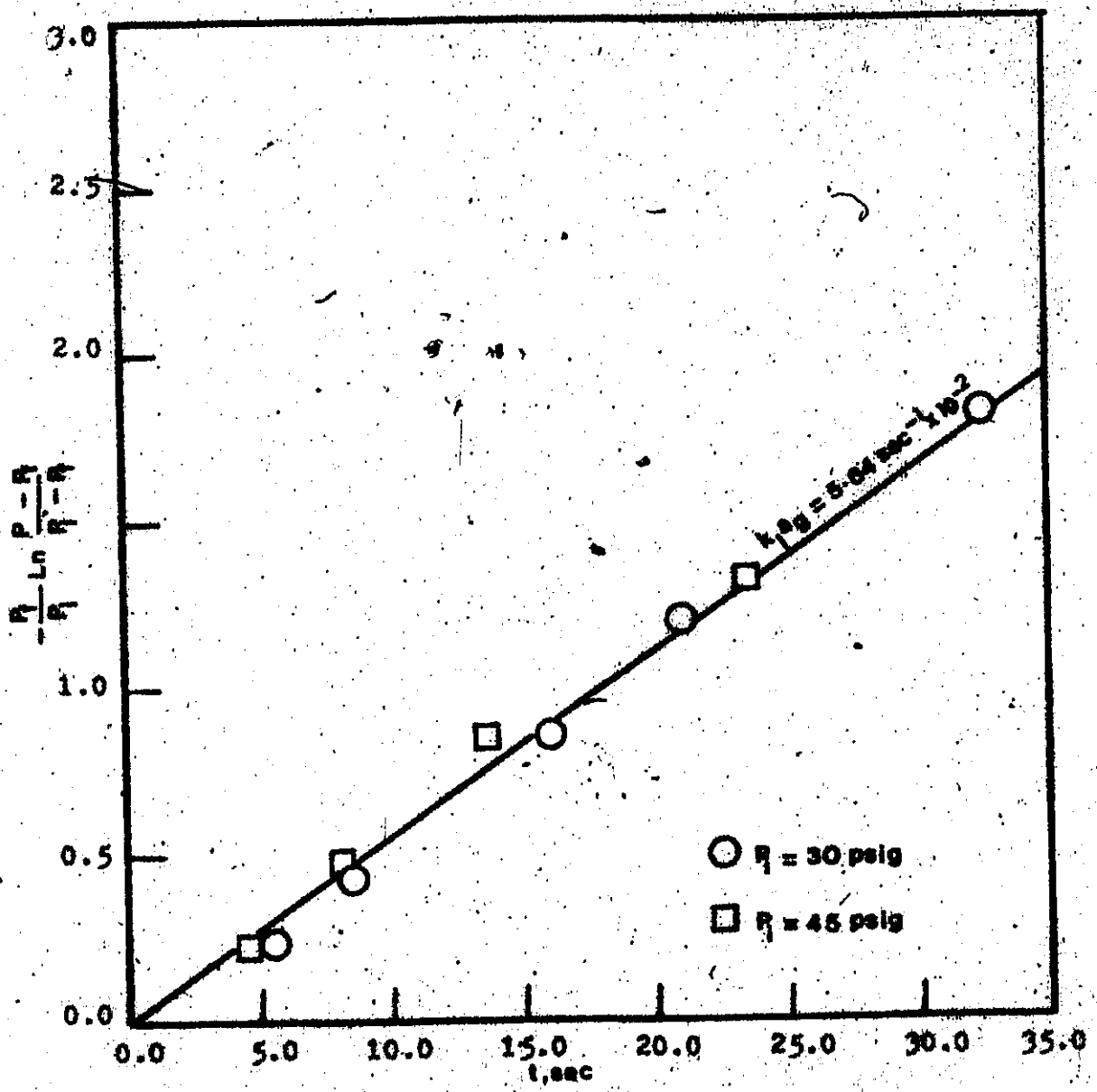


Fig A-1 : PHYSICAL ABSORPTION OF OXYGEN IN WATER

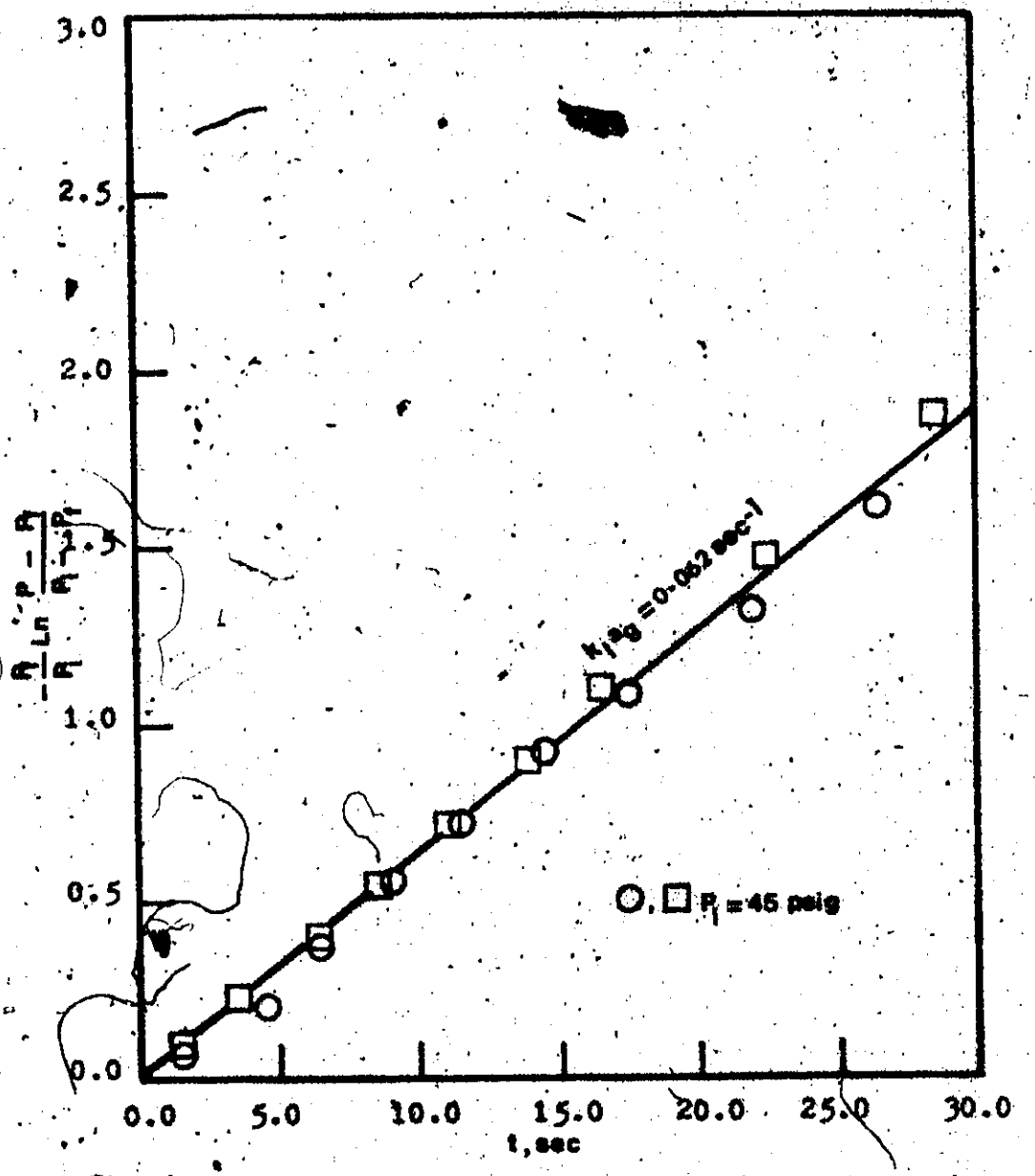


Fig A-2 : PHYSICAL ABSORPTION OF ETHYLENE IN WATER

## APPENDIX B

## Kinetic Runs: Experimental Results and Sample Calculations

### TABLE A-1

Tabulation of experimental data on kinetics of ethylene oxidation at 220°C , $P_E$=0.5 atm

| Run No. | $P_O$ atm | $P_P$ atm | Relative Rates $R_{C_2H_4O}$ | Relative Rates $R_{CO_2}$ | Sel. % | Conv. % |
|---|---|---|---|---|---|---|
| 19 | 0.118 | 0.0098 | 0.855 | 0.819 | 31.3 | 0.6 |
| 17 | 0.119 | 0.0082 | 0.940 | 0.878 | 35.7 | 0.6 |
| 15 | 0.116 | 0.0128 | 0.733 | 0.668 | 29.3 | 0.8 |
| 13 | 0.112 | 0.0179 | 0.667 | 0.538 | 26.8 | 1.1 |
| 11 | 0.112 | 0.0181 | 0.594 | 0.600 | 29.8 | 1.2 |
| | $P_O$ average = 0.115atm | | | | | |
| 29 | 0.177 | 0.0140 | 1.026 | 1.192 | 27.3 | 0.9 |
| 27 | 0.179 | 0.0111 | 1.034 | 1.220 | 30.6 | 0.7 |
| 25 | 0.174 | 0.0186 | 0.956 | 0.991 | 24.6 | 1.1 |
| 23 | * | 0.0200 | 1. | 1. | * | * |
| 21 | 0.169 | 0.0257 | 0.942 | 0.841 | 31.9 | 1.7 |
| | PO average = 0.175 atm | | | | | |

(*) standard runs

TABLE A-1 (cont.)

| Run No. | $P_O$ atm | $P_p$ atm | Relative Rates $R_{C_2H_4O}$ | Relative Rates $R_{CO_2}$ | Sel. % | Conv. % |
|---|---|---|---|---|---|---|
| 39 | 0.235 | 0.0205 | 1.452 | 1.751 | 26.6 | 1.3 |
| 37 | 0.239 | 0.0156 | 1.453 | 1.710 | 30.7 | 1.0 |
| 35 | 0.230 | 0.0289 | 1.410 | 1.531 | 25.7 | 1.8 |
| 33 | 0.220 | 0.0406 | 1.332 | 1.232 | 24.2 | 2.5 |
| 31 | 0.220 | 0.0416 | 1.395 | 1.374 | 29.7 | 2.7 |
| | $P_O$ average = 0.230 atm | | | | | |
| 47 | 0.297 | 0.0212 | 1.691 | 2.366 | 27.1 | 1.3 |
| 45 | 0.282 | 0.0422 | 1.710 | 2.260 | 22.1 | 2.5 |
| 43 | 0.266 | 0.0627 | 1.643 | 1.933 | 20.1 | 3.7 |
| | $P_O$ average = 0.282 atm | | | | | |

TABLE A-2

Average values of rates at standard conditions that bracketed runs of indicated run number.

| Run No. | Rate x $10^{-5}$ gmole/min.g catalyst $r_{C_2H_4O}$ | $r_{CO_2}$ | Average Sel. % | Average Conv. % |
|---|---|---|---|---|
| 19 | 1.166 | 3.282 | 26.2 | 1.36 |
| 17 | 1.495 | 3.337 | 31.0 | 1.47 |
| 15 | 1.310 | 3.340 | 28.2 | 1.42 |
| 13 | 1.350 | 2.590 | 34.4 | 1.20 |
| 11 | 1.295 | 2.930 | 30.6 | 1.29 |
| 29 | 1.347 | 3.092 | 30.4 | 1.35 |
| 27 | 1.053 | 2.023 | 34.1 | 0.94 |
| 25 | 1.350 | 3.569 | 27.4 | 1.50 |
| 23 | * | * | * | * |
| 21 | 1.413 | 3.371 | 29.6 | 1.46 |

(*) Standard runs

TABLE A-2 (cont.)

Average values of rates at standard conditions that bracketed runs of indicated run number.

| Run No. | Rate x $10^{-5}$ gmole/min.gcatal. $\bar{r}_{C_2H_4O}$ | $\bar{r}_{CO_2}$ | Average Select. % | Average Conversion % |
|---|---|---|---|---|
| 39 | 1.358 | 3.081 | 30.7 | 1.40 |
| 37 | 1.060 | 2.016 | 34.6 | 0.90 |
| 35 | 1.409 | 3.380 | 29.4 | 1.50 |
| 33 | 1.250 | 3.850 | 24.5 | 1.60 |
| 31 | 1.347 | 3.572 | 27.4 | 1.50 |
| 47 | 1.150 | 3.009 | 27.7 | 1.27 |
| 45 | 1.111 | 2.529 | 30.5 | 1.11 |
| 43 | 1.280 | 2.674 | 32.5 | 1.20 |

Sample Calculation:

The sample calculation shown below related to one of the runs at standard conditions. The calculation based on the assumption of a back-mix reactor : assuming that the mixing was complete, so that the properties of the reaction mixture were uniform throughout the vessel and were the same as those in the exit ( or product ) stream .

Feed flow rates :

Helium = 23.06 scc/min

Oxygen = 13.83 scc/min

Ethylene = 36.89 scc/min

Total F = 73.78 scc/min

Weight of catalyst, W= 0.5 g.

Reactor pressure = 1atm

Feed composition calculated from the flow rates:

$y_E^o$ =0.50

$y_O^o$ =0.1875

Mole fraction of the reaction products in the exit stream ( from gas chromatographic analysis ):

$y_{C_2H_4O}$ = 0.0018

$y_{CO_2}$ = 0.0100

As presented on page 47 , the equation for calculating the rate of formation of $C_2H_4O$ is:

$$r_{C_2H_4O} = \frac{y_{C_2H_4O}}{22414\left(\frac{W}{F}\right)\left(1 + \frac{y_{C_2H_4O}}{2}\right)}$$

$$r_{C_2H_4O} = \frac{0.0018}{22414\left(\frac{0.5}{73.78}\right)\left(1 + \frac{0.0018}{2}\right)}$$

$$= 1.184 \times 10^{-5} \text{ gmole } C_2H_4O/\text{min.gcatalyst}$$

Similarly for $CO_2$ :

$$r_{CO_2} = \frac{\frac{1}{2} y_{CO_2}}{22414\left(\frac{W}{F}\right)\left(1 + \frac{y_{C_2H_4O}}{2}\right)}$$

$$= \frac{\frac{1}{2} 0.01}{22414\left(\frac{0.5}{73.78}\right)\left(1 + \frac{0.0018}{2}\right)}$$

$$= 3.29 \times 10^{-5} \text{ gmole } CO_2 / \text{min.gcatalyst}$$

Calculation of partial pressure:

$$P_E = \left[y_E^o - \left(y_{C_2H_4O} + \frac{y_{CO_2}}{2}\right)\right] \times P_t$$

$$= \left(0.5 - \left(0.0018 + \frac{0.01}{2}\right)\right) \times 1$$

$$= 0.493 \text{ atm}$$

$$P_O = \left[y_O^o - \left(\frac{y_{C_2H_4O}}{2} + \frac{3}{2} \times y_{CO_2}\right)\right] \times P_t$$

$$= \left(0.1875 - \left(\frac{0.0018}{2} + \frac{3}{2} \times 0.010\right)\right) \times 1$$

$$= 0.172 \text{ atm}$$

$$P_p = \left(y_{C_2H_4O} + y_{CO_2} + y_{H_2O}\right) \times P_t$$

Assuming $y_{H_2O} = y_{CO_2}$

$$P_p = \left(0.0018 + 2 \times 0.01\right)$$

$$= 0.0218 \text{ atm}$$

Selectivity :

$$= \frac{y_{C_2H_4O} \times 100}{\left( y_{C_2H_4O} + \frac{y_{CO_2}}{2} \right)}$$

$$= \frac{0.0018 \times 100}{0.0018 + \frac{0.01}{2}}$$

$$= 26.5\ \%$$

Conversion :

$$= \frac{\left( y_{C_2H_4O} + \frac{y_{CO_2}}{2} \right) \times 100}{y_E^o \left( 1 + \frac{y_{C_2H_4O}}{2} \right)}$$

$$= \frac{\left(0.0018 + \frac{0.01}{2}\right) \times 100}{0.5 \left( 1 + \frac{0.0018}{2} \right)}$$

$$= 1.4\ \%$$

## APPENDIX C

### The Significance of Mass Transfer Resistance from Bubble Liquid Interface to Bulk Liquid ( $1/k_l a_g$)

Henry's law constant based on the physical absorption study :

$P_i$ = initial pressure of oxygen

= 69.7psia

$P_f$ = final pressure

= 30.2 psia

$V_l$ = volume of liquid solvent.

= 230 cc

$V_g$ = gas volume

= 300 - 230

= 70 cc

T = 473 K

Number of moles of oxygen absorbed

$$n = \frac{P.V}{R.T}$$

$$= \frac{39.5}{14.7} \times 70 \times \frac{1}{82.06} \times \frac{1}{473}$$

$$= 4.85 \times 10^{-3} \text{ gmole}$$

Concentration of $O_2$ in the liquid at saturation :

$$C^* = \frac{n}{V_l}$$

$$= 2.11 \times 10^{-5} \text{ gmole/cc}$$

Henry's law :

$$H = \frac{P_f}{C^*}$$

$$= \frac{2.054}{2.017 \times 10^{-5}}$$

$$= 9.75 \times 10^4 \quad \text{atm.cc/gmole}$$

The Significance of The Mass Transfer Resistance :

At steady state, the rate of mass transfer from the bubble liquid interface to the bulk liquid is equal to the rate of the reaction. To estimate the deviation from the saturated concentration, it is necessary to use the highest reaction rate in kinetic runs . This is at $P_O$= 0.3125atm and:

$$r_{C_2H_4O} = 2.30 \times 10^{-5} \text{ gmole } C_2H_4/\text{gcatal. min.}$$

$$r_{CO_2} = 8.10 \times 10^{-5} \quad "$$

Consider the oxidation reaction of ethylene :

$$C_2H_4 + \frac{1}{2}O_2 \longrightarrow C_2H_4O$$

$$C_2H_4 + 3\ O_2 \longrightarrow 2\ CO_2 + 2\ H_2O$$

Hence, the rate of oxygen reacted is equal to 1/2 of the rate of ethylene converted to $C_2H_4O$ and 3 times the rate of ethylene converted to $CO_2$ .

The global rate can be expressed as :

$$r_v = k_l a_g \ ( C^* - C_b )$$

where $C_b$ is the bulk concentration . From this equation ( $C^* - C_b$ ) can be estimated and the percentage of deviation from $C^*$ can be obtained .

The total rate of $O_2$ converted per unit volume of solvent, $r_v$ , can be expressed as :

$$r_v = \frac{(\frac{1}{2} . r\ C_2H_4O + 3.r_{CO_2}) \times W}{V_l}$$

where W = 0.5 g. is the amount of the catalyst used .

$$r_v = \frac{(\frac{1}{2} \times 2.30 \times 10^{-5} + 3 \times 8.10 \times 10^{-5}) \times 0.5}{230}$$

$$= 5.53 \times 10^{-7} \text{ gmole } O_2/\text{cc.min.}$$

$$C^* - C_b = \frac{r_v}{k_l a_g} \quad , \ k_l a_g = 5.03 \times 10^{-2} \text{ sec}^{-1}$$

$$= \frac{5.53 \times 10^{-7}}{5.03 \times 10^{-2} \times 60}$$

$$= 1.83 \times 10^{-7} \text{ gmole/cc.solvent}$$

$$C^* = \frac{P_O}{H}$$

$$= \frac{0.3125}{9.75 \times 10^4}$$

$$= 3.21 \times 10^{-6} \text{ gmole/cc.solvent}$$

% chage of concentration due to resistance :

$$\frac{C^* - C_b}{C^*} = \frac{1.83 \times 10^{-7}}{3.21 \times 10^{-6}}$$

$$= 5.7 \times 10^{-2} \text{ or } 5.7\%$$

## APPENDIX D

### Estimation of the mass transfer coefficient from bulk liquid to catalyst surface ( $k_p$ )

Diffusion coefficient of oxygen in dibutyl phthalate :

Kinematic viscosity of dibutyl phthalate at 200°C (12):

$\eta$ = 0.375 c.stokes.

$= 0.375 \times 10^{-2}$ $cm^2/sec$

The Wilke and Chang equation (58) for diffusion coefficient :

$$D_{12} = 7.4 \times 10^{-8} \frac{(\chi_M)^{\frac{1}{2}} \, T}{\mu . V_1^{0.6}}$$

where $D_{12}$ is the diffusion coefficient of solute 1 in dilute solution in solvent 2 at temparature T , $cm^2/sec$ .

M = molecular weight of solvent

= 278.336 g.

T = absolute temp.

= 473 K

$\mu$ = viscosity of solution .

$= 0.375 \times 10^{-2} \times 1.0426$

= 0.391 c.poise

$V_1$ = molecular volume of solute at normal boiling point

= 27.9 cc/gmole for $O_2$ (30)

$\chi$ = "association" parameter for solvent, the recommended value is 1 (58)

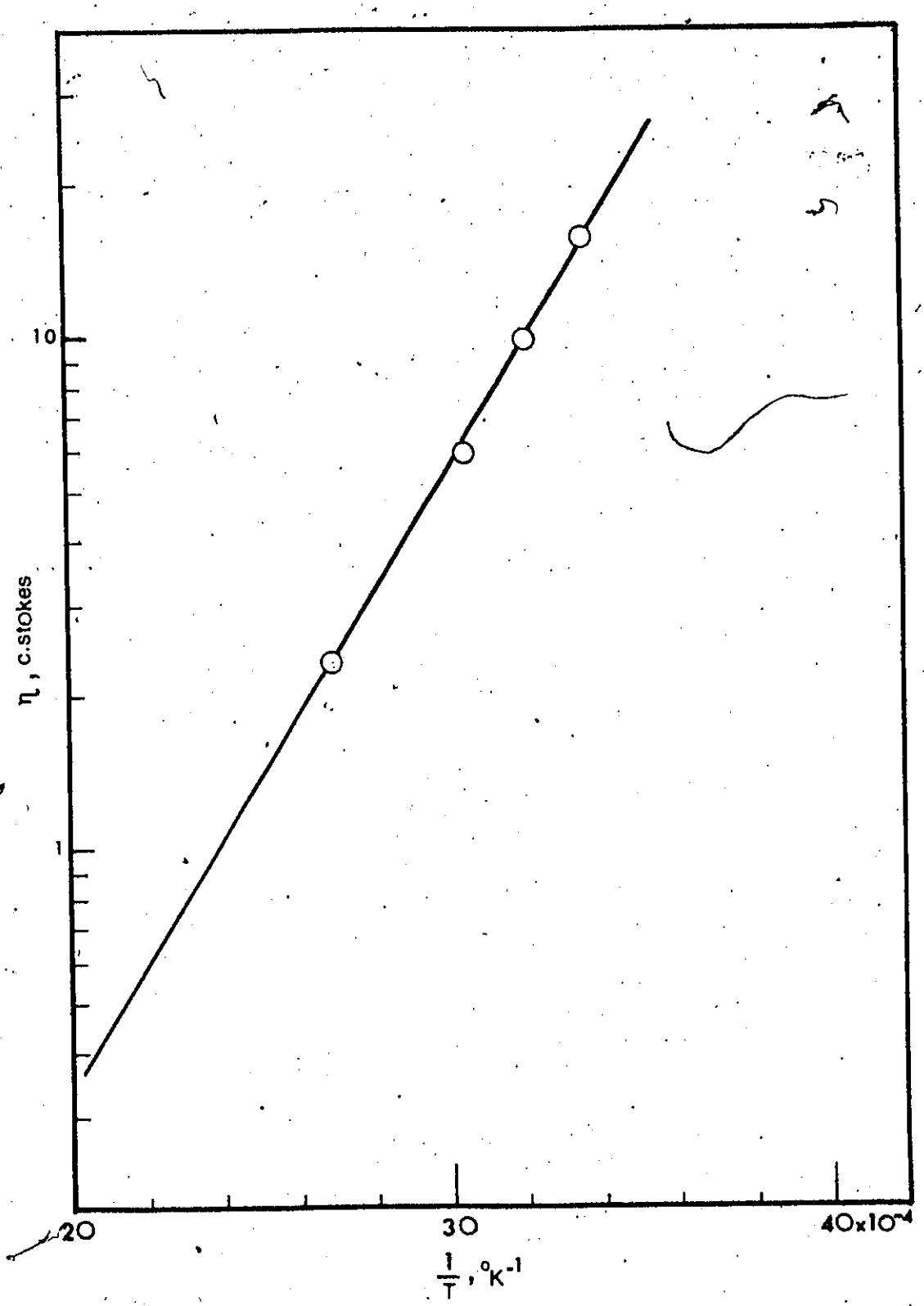


Fig D-1 : KINEMATIC VISCOSITY OF DIBUTYL PHTHALATE

$$D_{12} = \frac{7.4 \times 10^{-8} \times (1 \times 278.34)^{\frac{1}{2}} \times 473}{0.391 \times (27.9)^{.6}}$$

$$= 20.27 \times 10^{-5} \text{ cm}^2/\text{sec}$$

Estimation of the mass transfer coefficient ($k_p$) by Harriott's method (26, 56).

The method was also used by Kenney and Sedrik (32) in their estimation of the deviation from saturation of hydrogen concentration in solvent .

Using Stokes'law to estimate the terminal velocity due to free fall :

$$U_t = \frac{d_p^2 \Delta\rho . g}{18 \mu}$$

$\Delta\rho$ = difference in density of the particle and the fluid

= 4.27 - 1.043

= 3.227 g/cc

$d_p$ = diameter of the particle

= 0.004"

= $1.016 \times 10^{-2}$ cm

$g$ = 980.665 cm /sec$^2$

$\mu$ = $0.391 \times 10^{-2}$ cm$^2$/sec

$$U_t = \frac{(1.016 \times 10^{-2})^2 \times 3.227 \times 980.665}{18 \times 0.39 \times 10^{-2}}$$

= 4.65 cm/sec

The Peclet number :

$$N_{pe} = \frac{d_p U_t}{D_{12}}$$

$$N_{pe} = \frac{1.016 \times 10^{-2} \times 4.65}{20.27 \times 10^{-5}}$$

$$= 0.233 \times 10^{3}$$

Using Brian and Hales' curve, the relation between Sherwood number $N_{Sh}$ and Peclet number $N_{pe}$

$$N_{Sh} = \frac{k_p^* d_p}{D_{12}} = 8.5$$

Hence $k_p^*$ due to free fall is equal :

$$k_p^* = \frac{N_{Sh} \cdot D12}{d_p}$$

$$= \frac{8.5 \times 20.27 \times 10^{-5}}{1.016 \times 10^{-2}}$$

$$= 0.1[illegible] \text{ cm/sec}$$

Slurries of catalyst particle suspended in a liquid are necessarily and vigorously agitated both to keep the solids in suspension and to promote absorption of reacting gases . The turbulence that results promotes mass transfer and the actual value of $k_p$ is greater than $k_p^*$ . The difference is not great as the particles tend to follow the motion of the fluid. Harriott's comparison of his own showed : $1 < k_p/k_p^* < 4$

As a first approximation $k_p$ may be estimated as twice the calculated value, $k_p = .34$ cm/sec .

<u>The significance of the mass transfer resistance</u> :

At steady state, the rate equation may be written as:

$$r_v = k_l a_g ( C^* - C_b )$$

$$= k_p a_p ( C_b - C_s )$$

The two mass transfer processes are in series .

Therefore the significance of the mass transfer resistance from the bulk liquid to the catalyst surface $1/k_p a_p$ can be obtained by a comparison with the mass transfer resistance $1/k_l a_g$ .

$\rho_p$ = density of the catalyst

= 4.27 g/cc

$$\frac{\text{Total area}}{\text{g.catalyst}} = \frac{6}{d_p \rho_p}$$

$$= \frac{6}{1.016 \times 10^{-2} \times 4.27}$$

$= 138.3 \text{ cm}^2/\text{g}$

$a_p$ = total area per unit volume of solvent

$$= \frac{m \times 183.3}{230}$$

$= .301 \text{ cm}^2/\text{cc solvent}$

$$\frac{1}{k_p a_p} = \frac{1}{0.34 \times 0.301}$$

$= 9.77$ sec

$$\frac{1}{k_l a_g} = \frac{1}{5.03 \times 10^{-2}}$$

$= 19.88$ sec

While the resistance due to $1/k_l a_g$ contributes a deviation from the equilibrium concentration of 5.7 % ( See Appendix C ) , the resistance $1/k_p a_p$ in turn , contributes a further deviation of:

$$\frac{5.7\ \% \times 9.77}{19.88} = 2.8\ \%$$

The total external resistanes, therefore create a total change of $5.7+2.8 = 8.5\ \%$ of the equilibrium concentration. Thus, it can be concluded thatthey are not significant in the overall process.

## APPENDIX E

## Internal Mass Transfer

Because the kinetics of the reaction are extremely complex , it would be difficult to calculate an effectiveness factor for the porous catalyst directly . Klugherz (34) assumed an effective diffusivity $D_{eff} = \varepsilon D_{bulk}/\tau$ , where $\varepsilon$ is the porosity and $\tau$ is the tortousity and used a Sherwood number of 2 for calculating the mass transfer coefficient . It is reasonable in the case of gas phase reaction since the Knudsen diffusivity in the pore is very high , and the Sherwood number is of minimum value . The value of $\varepsilon = 0.4$ and $\tau = 2$ are typical of $\alpha$-alumina support. It was foud that the intraparticle mass transfer resistance was negligible.

Satterfield (56) suggested a method for the determination of the effectiveness factor by using a modulus $\Phi$ when the reactant concentration at the catalyst surface is known, for a sphere :

$$\Phi_s = \frac{R^2}{D_{eff}} \left(-\frac{1}{V_c}\frac{dn}{dt}\right) \frac{1}{C_s}$$

The parentheticalexpression is the observed rate of the reaction per unit volume of catalyst pellets , $C_s$ is the reactant concentration at the outside surface of the catalyst pellets , R is the radius of the catalyst and $D_{eff}$ is the effective diffusivity . For any interger power rate equation:

$$\Phi_s = \eta . \phi_s^2$$

where $\phi_s$ is the Thiele modulus and $\eta$ is the effectiveness factor . The relationship between $\Phi_s$ and $\phi_s$ is more complex for a more complicated kinetic expression.

Estimation of $\Phi_s$ :

$$-\frac{1}{Vc}\frac{dn}{dt} = \frac{r_v \rho_p}{60 \text{ sec}}$$

where for highest actual rate :

$$r_v = \frac{1}{2} \times 2.3\times10^{-5} + 3\times8.1\times10^{-5}$$

$$r_v = 25.45 \times 10^{-5} \frac{\text{gmole } O_2 \text{ reacted}}{\text{min. g catalyst}}$$

( See Appendix C )

$$-\frac{1}{Vc}\cdot\frac{dn}{dt} = \frac{25.45 \times 10^{-5} \times 4.27}{60}$$

$$= 1.81 \times 10^{-5} \frac{\text{gmole } O2}{\text{sec. cc catal.volume}}$$

$$C_s = \frac{6.25 \times 10^{-6} \times (100 - 8.5)}{100}$$

$$C_s = 5.72 \times 10^{-8} \frac{\text{gmole } O2}{\text{cc solvent}}$$

( See Appendix C )

$$R = \frac{d_p}{2}$$

$$= 5.08 \times 10^{-3} \text{ cm}$$

$$\frac{1}{D_{eff}} = \frac{1}{D_{K,eff}} + \frac{1}{D_{12,eff}}$$

$$D_{12,eff} = \frac{D_{12} \times \varepsilon}{\tau}$$

$$= \frac{20.27 \times 10^{-5} \times 0.4}{2}$$

$$= 4.05 \times 10^{-5} \frac{\text{cm}}{\text{sec}}$$

$$D_{K,eff} = 19400 \frac{2}{\tau_m S_g \cdot \rho_p} \sqrt{\frac{T}{M}}$$

Where :

$\tau_m$ is the value of tortousity factor obtained when $D_K$ is calculated for mean pore radius , $\tau_m = 2$

$S_g = 0.5\ m^2/g$ catalyst surface per gm.

$\rho_p$ = density of catalyst

$= 4.27\ g/cc$

M = molecular weight of oxygen

$= 16\ g$

$$D_{K,eff} = 19400 \frac{(0.4)^2}{2 \times 0.5 \times 10^4 \times 4.27} \sqrt{\frac{473}{16}}$$

$$= 0.395 \text{ cm/sec}$$

The Knudsen diffusivity is very high in comparison to the bulk diffusivity , the Knudsen diffusion can be considered to be negligible .

$$D_{eff} = 4.045 \times 10^{-5} \text{ cm/sec}$$

$$\Phi_s = \frac{R^2}{D_{eff}} \left(- \frac{1}{V_c} \frac{dn}{dt}\right) \frac{1}{C_s}$$

$$= \frac{(5.08 \times 10^{-3})^2}{4.054 \times 10^{-5}} \times 1.81 \times 10^{-5} \times \frac{1}{5.72 \times 10^{-6}}$$

$$= 2.01$$

In the range of ethylene pressure used , the rate of oxidation reaction is nearly first order in oxygen pressure For a first approximation , the order can be taken as 1

$$\phi_s = \left(\frac{\Phi_s}{\eta}\right)^{\frac{1}{2}}$$

The method of estimating $\eta$ involves successive approximation , by assuming value of $\eta$ .(56)

The final value of $\eta$ was found to be 0.93 , the effectiveness factor approaching 1 . It can be therefore concluded that the internal mass transfer resistance is negligible .

## APPENDIX F

### Procedure for obtaining factors used to correct rates at standard conditions

The factors used to correct the rates of runs at standard condition to $P_p$ = .02 atm were obtained and applied in the following manner . Separate calculations were performed for the two parallel reactions to $C_2H_4O$ and $CO_2$ .

a/ As mentioned in chapter IV , runs were made at various feed flow rates with ethylene and oxygen pressures in feed of 0.5 and .1875 atm respectively . These runs were bracketed by runs at standard conditions, as defined on page 50 . By varying the flow rate, the value of $P_p$ ranging from about 0.01 to 0.03 atm were obtained . During these experiments, the $P_p$'s for standard runs varied within the relatively narrow limits of 0.0168 to 0.025 atm .

b/ As a first approximation , therefore , the standard runs were considered to have been measured at $P_p$=0.02 atm . Relative rates were calculated using this approximation. If the rate at the pressures and temparatures of the standard conditions, but at various flow rates , is represented by $r_p$ and the rate at standard conditions by $r_s$ , then the approximate relative rate , R' , is :

$$R' = \frac{r_p}{\overline{r_s}}$$ , where $\overline{r_s}$ is the average of the two $r_s$ of two bracketing runs.

c/ The values of ( $r_p/\overline{r_s}$ ) were plotted as a function

of the $P_p$'s of the non-standard runs.

d/ A preliminary correction of the rates of each standard run to $P_p = 0.02$ atm was then applied using these plots of ( $r_p/\bar{r}_s$ ) versus $P_p$ . For each standard run, a particular value of $P_p$ has been obtained. The rate of each standard run ($r_s$) was corrected, approximately, to $P_p = 0.02$ atm (i.e. to $r_s^o$ ) on the basis of the equation :

$$r_s^o = \frac{r_s}{(r_s/r_s^o)}$$

the term $(r_s/r_s^o)$ in the denominator of this equation can be approximated by the value of $(r_p/\bar{r}_s)$ corresponding to the particular $P_p$ obtained when the rate of the standard run is $r_s$

$$(r_s^o)_{approx.} = \frac{r_s}{(r_p/\bar{r}_s)}$$

e/ These approximate values for the rates of standard runs corrected to $P_p = 0.02$ atm were then used to calculate better estimates of the relative rates $\left[ r_p/(\bar{r}_s^o)_{approx.} \right]$

f/ Next, plots of this quantity as a function of $P_p$ were prepared.

g/ Final estimates of the corrected standard rates $r_s^o$ were obtained by dividing $r_s$ by the value of $\left[ r_p/(\bar{r}_s^o)_{app.} \right]$ corresponding to the particular $P_p$ involved .

h/ From the final estimates of $r_s^o$ , final values of $(r_p/\bar{r}_s^o)$ can be calculated and plotted as a function of $P_p$. These plots are shown for $C_2H_4O$ and $CO_2$ in Figs. F.

If these curves are now used to repeat the above calculation, identical values of $(r_p/\bar{r}_s^o)$ are generated, since $(r_p/\bar{r}_s^o)$ is equivalent to $(r_s/r_s^o)$ (See step d) . It should be mentioned that the curves shown in Fig. F1 are not too different from the preliminary curves originally obtained in step (c).

i/ These curves for $(r_p/\bar{r}_s^o)$ as a function of $P_p$ are used to correct the reaction rates for all the standard runs to a total product concentration of $P_p$=0.02atm. The corrected standard rates, $r_s^o$, for both $C_2H_4O$ and $CO_2$ are calculated from:

$$r_s^o = \frac{r_s}{(r_s/r_s^o)}$$

$$= \frac{r_s}{(r_p/\bar{r}_s^o)}$$

The values of $(r_p/\bar{r}_s^o)$ to be used in this equation are obtained from Figs F , at $P_p$ equal to that computed for the standard run under consideration.

As a numerical example of how these correction factors were obtained, the ethylene oxide data for run 29 together with run 28 and 30 at standard conditions can be used .

The calculated rates and corresponding values of $P_p$ are :

| Run No. | $r_{C_2H_4O}$ (gmole/min.g.catalyst) | $P_p$, atm |
|---|---|---|
| 28 | $1.184 \times 10^{-5}$ | 0.0218 |
| 29 | $1.381 \times 10^{-5}$ | 0.0140 |
| 30 | $1.510 \times 10^{-5}$ | 0.0199 |

As a first approximation, the value of $(r_p/\bar{r}_s)$ at

$P_p$= 0.014 atm is:

$$\frac{r_p}{\bar{r}_s} = \frac{1.381 \times 10^{-5}}{\frac{1}{2}(1.184 \times 10^{-5} + 1.510 \times 10^{-5})}$$

$$= 1.025$$

The values of $(r_p/\bar{r}_s)$ such as this are plotted as a function of $P_p$ . This plot can then be used to correct the rates of the standard runs to $P_p$= 0.02 atm . At $P_p$ = 0.0218 atm, $(r_p/\bar{r}_s)$=0.99 and at $P_p$= 0.0199atm, $(r_p/\bar{r}_s)$=1.01. Thus , $(r_s^o)_{approx.}$ for run 28 is $1.196 \times 10^{-5}$ and for run 30 is $1.495 \times 10^{-5}$ .

Then :

$$\frac{r_p}{(r_s^o)_{approx.}} = \frac{1.381 \times 10^{-5}}{\frac{1}{2}(1.495 \times 10^{-5} + 1.196 \times 10^{-5})}$$

$$= 1.026$$

The value of $(r_p/r_s^o)_{appr.}$ are plotted versus $P_p$ . The above calculations are repeated using this plot to obtain the final values of $(r_p/r_s^o)$ thus :

$$\frac{r_p}{r_s^o} = \frac{1.381 \times 10^{-5}}{\frac{1}{2}\left(\frac{1.184 \times 10^{-5}}{.985} + \frac{1.510 \times 10^{-5}}{1.01}\right)}$$

$$= 1.026$$

Finally, this value for $r_p/r_s^o$ at $P_p$ = 0.014 atm is included in Fig.F1 on page 122 .

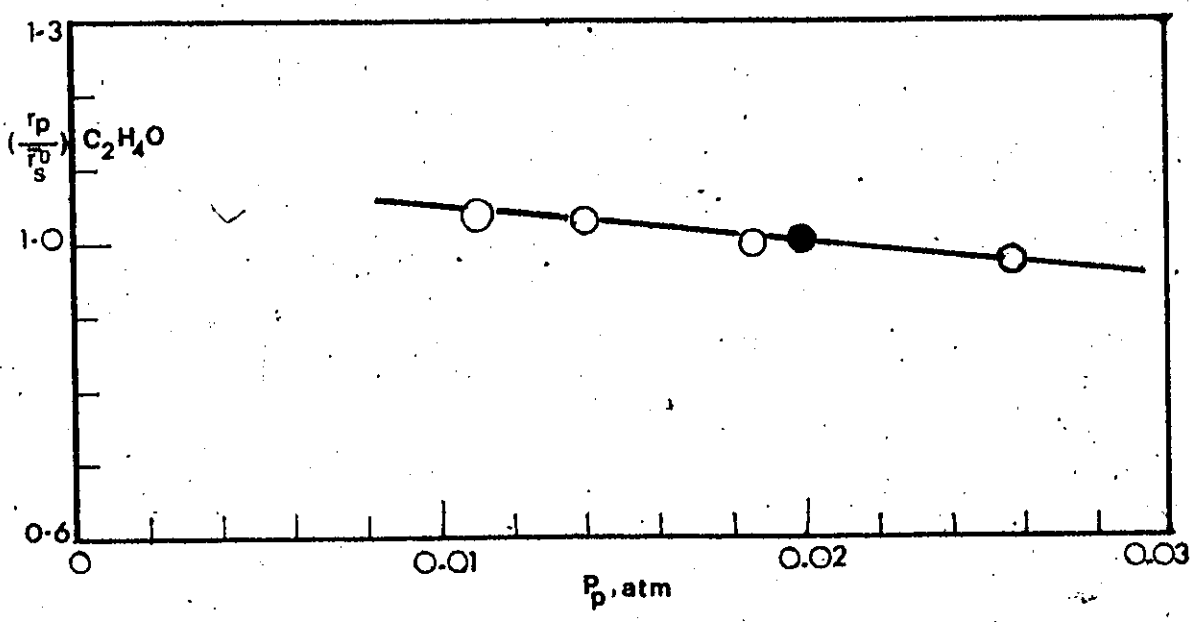


Fig F-1 : CORRECTION FACTOR FOR RATES OF ETHYLENE OXIDATION TO ETHYLENE OXIDE TO $P_p$=0.02atm.

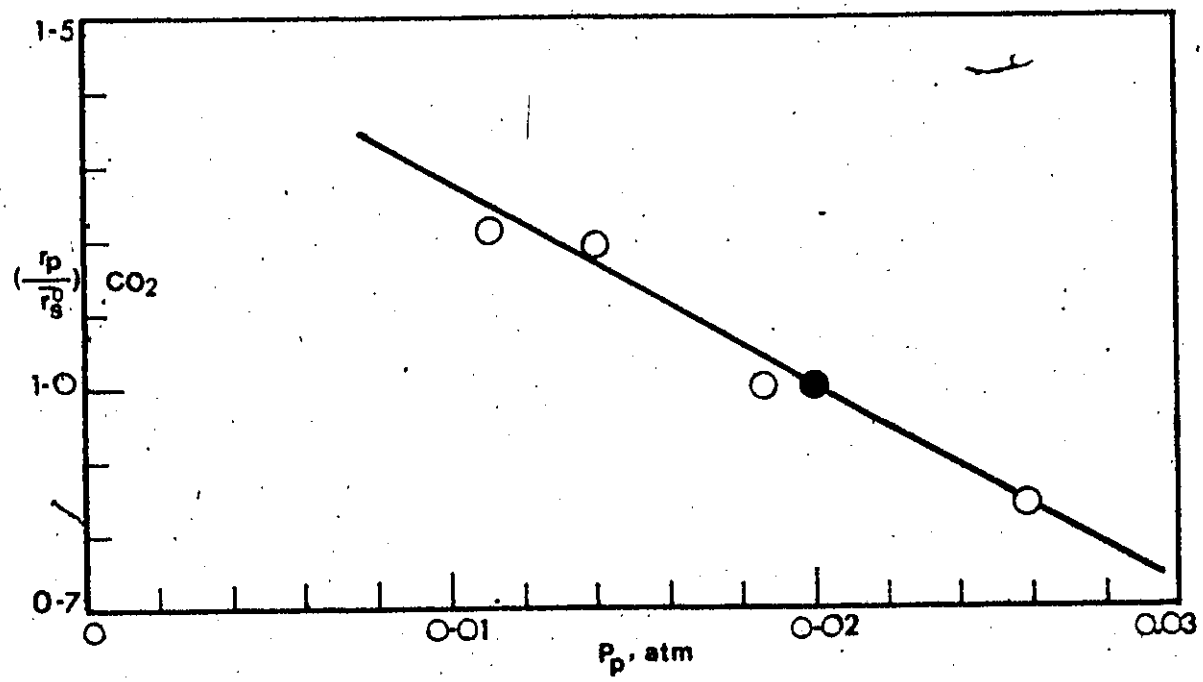


Fig F-2 : CORRECTION FACTOR FOR RATES OF ETHYLENE OXIDATION TO CARBON DIOXIDE TO $P_p$=0.02 atm.

## Appendix G

## Calibration Curves

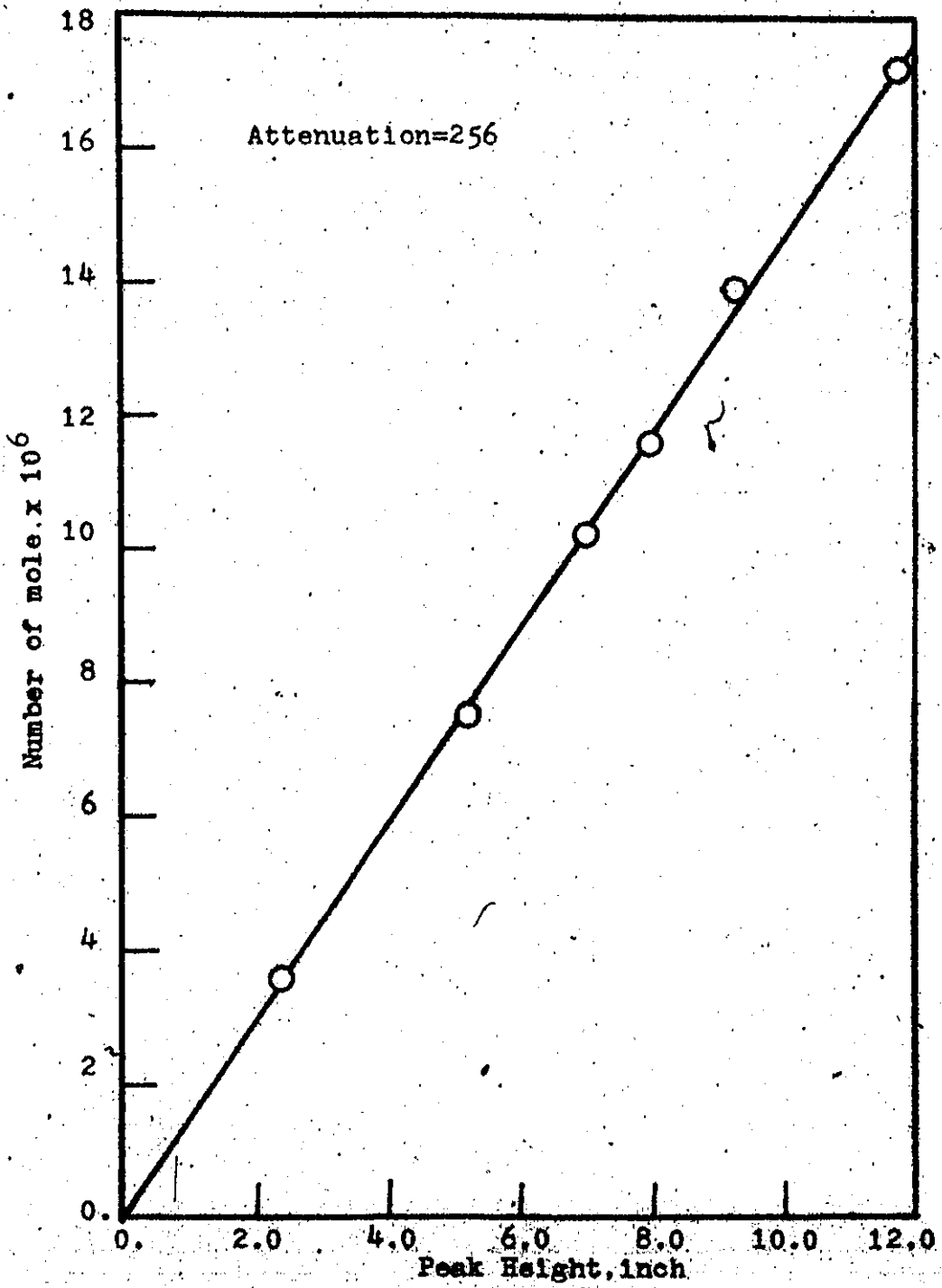


Fig. G-1 : CALIBRATION OF OXYGEN

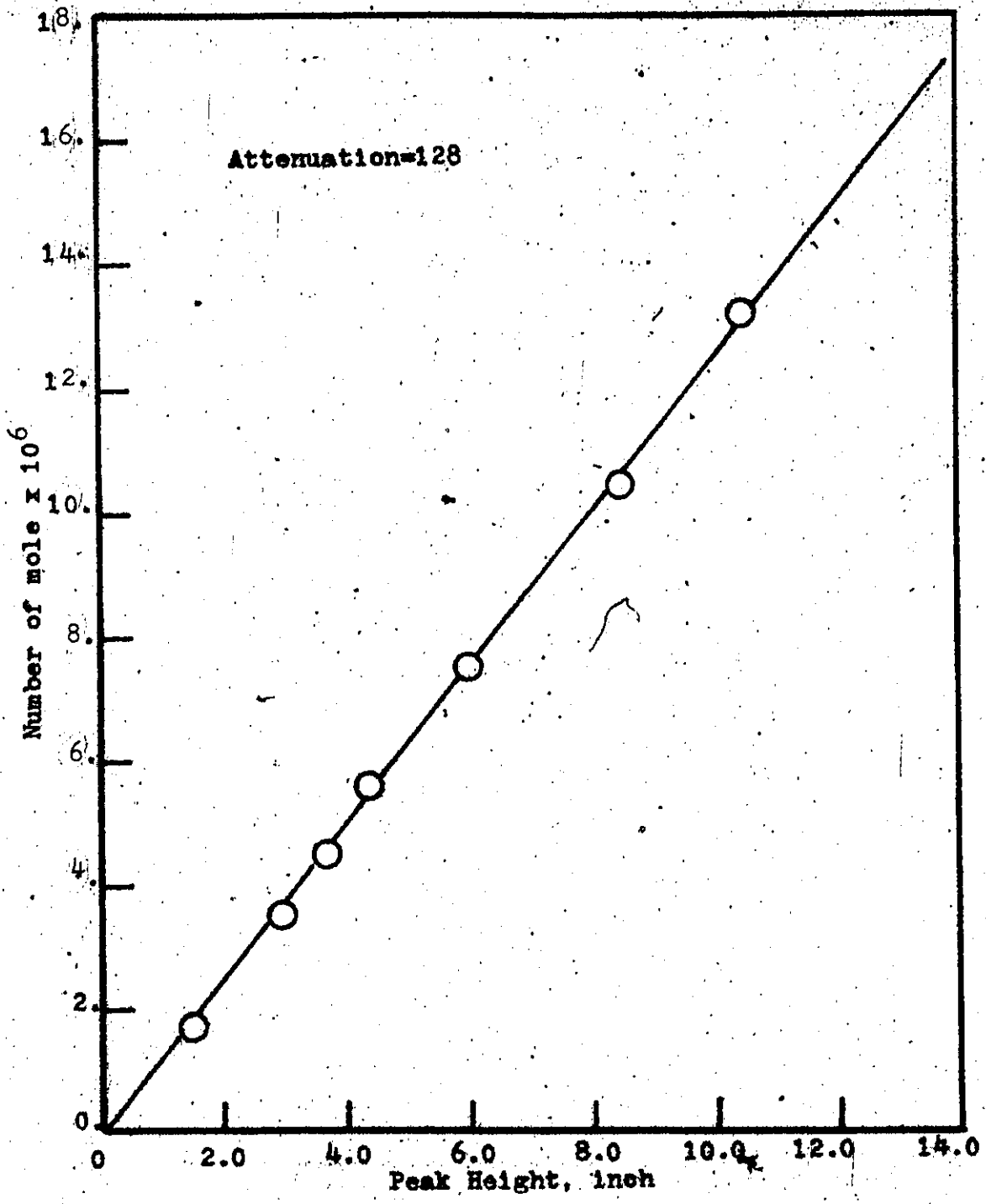


Fig. G-2 : CALIBRATION OF ETHYLENE

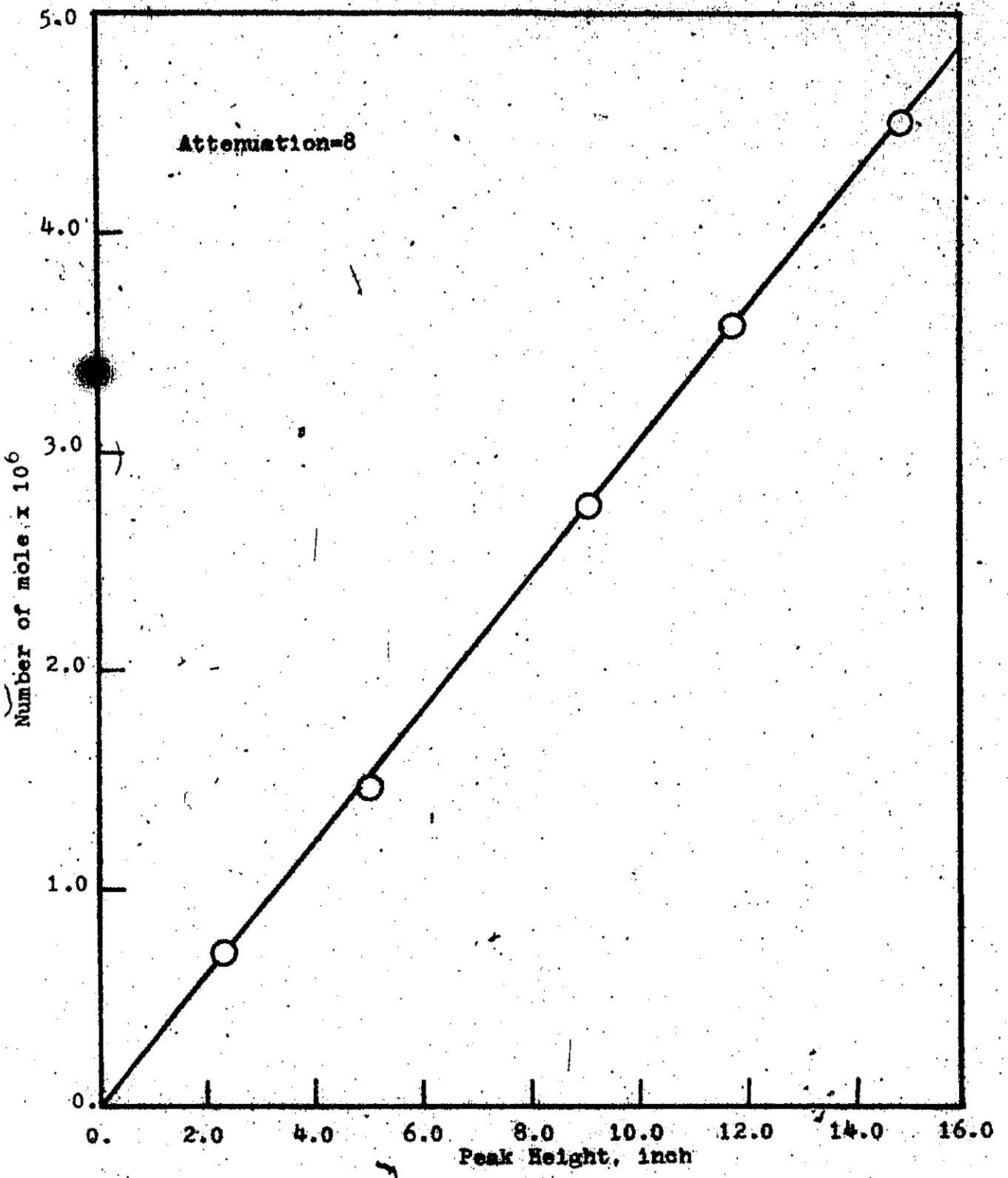


Fig. G-3 : CALIBRATION OF CARBON DIOXIDE

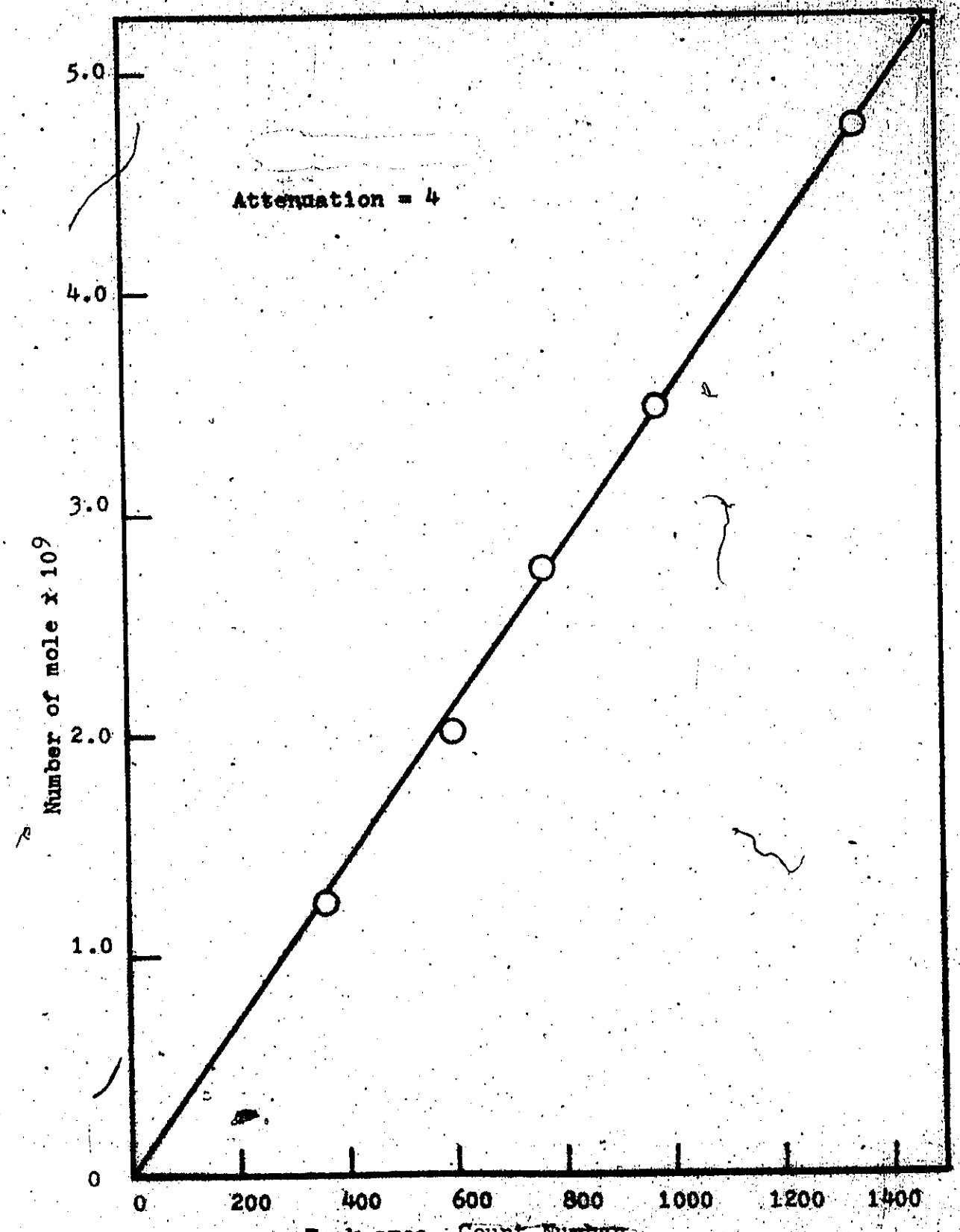


Fig. G-4 : CALIBRATION OF ETHYLENE OXIDE

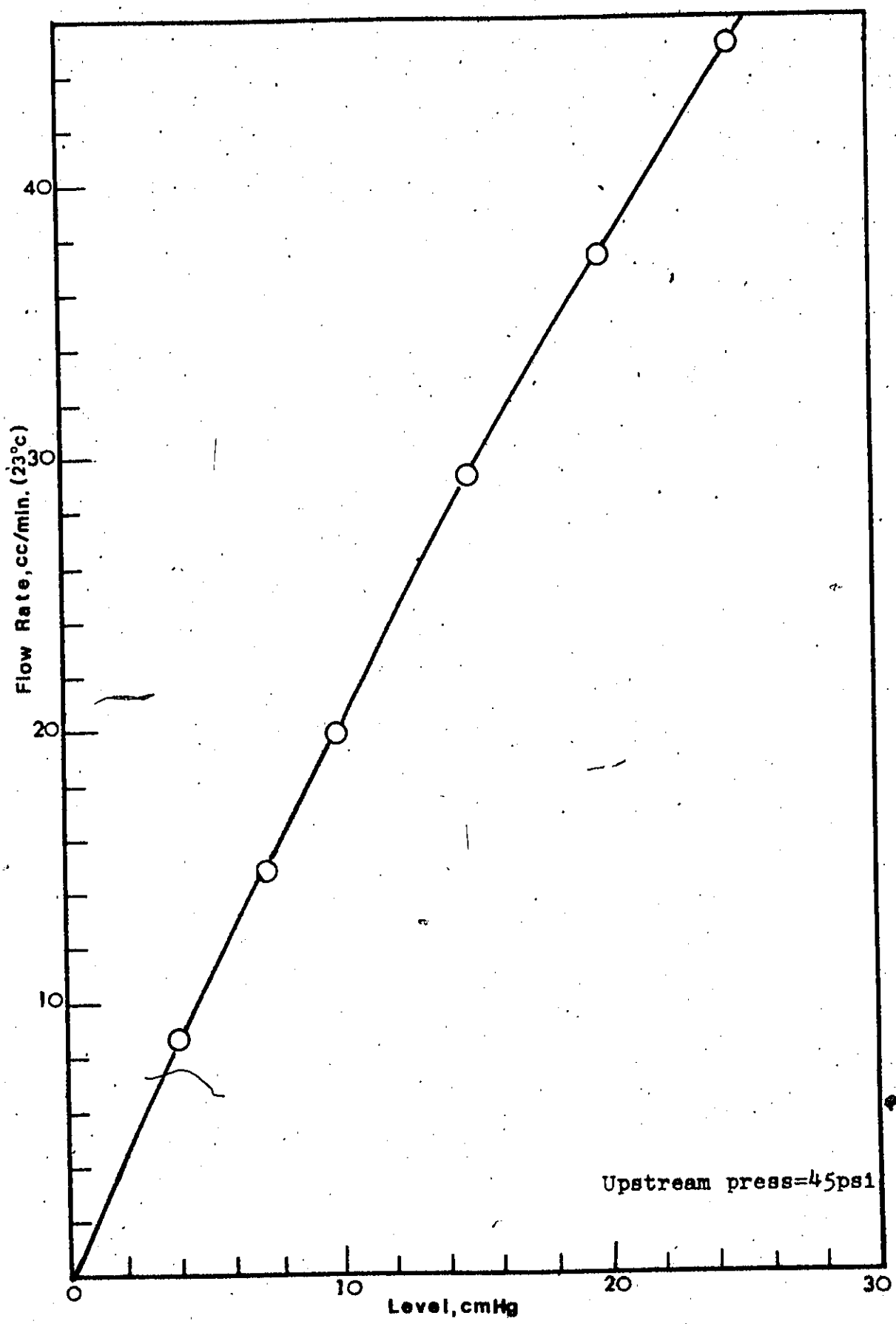


Fig G-5 : FLOW CALIBRATION OF OXYGEN

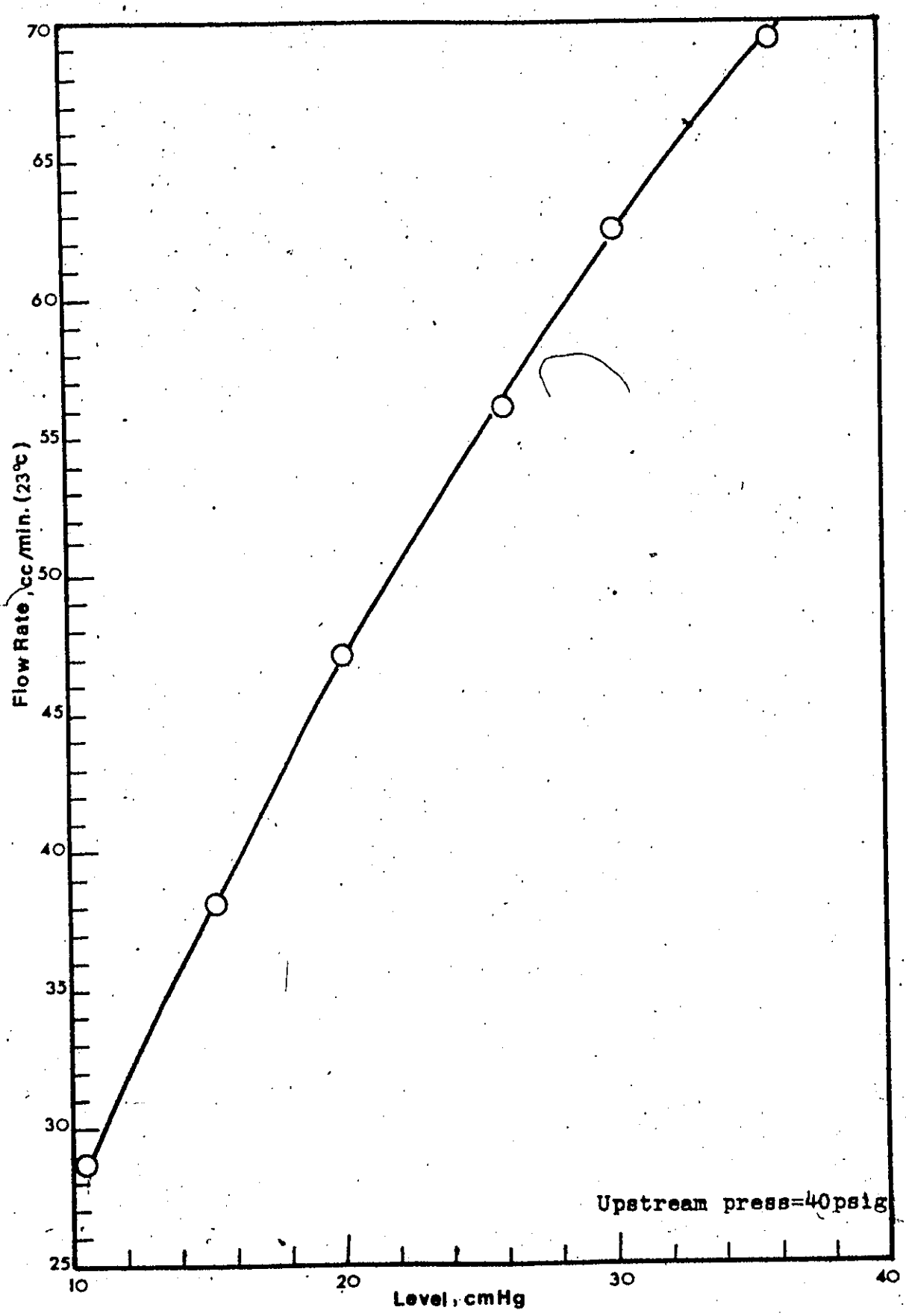


Fig G-6 : FLOW CALIBRATION OF ETHYLENE

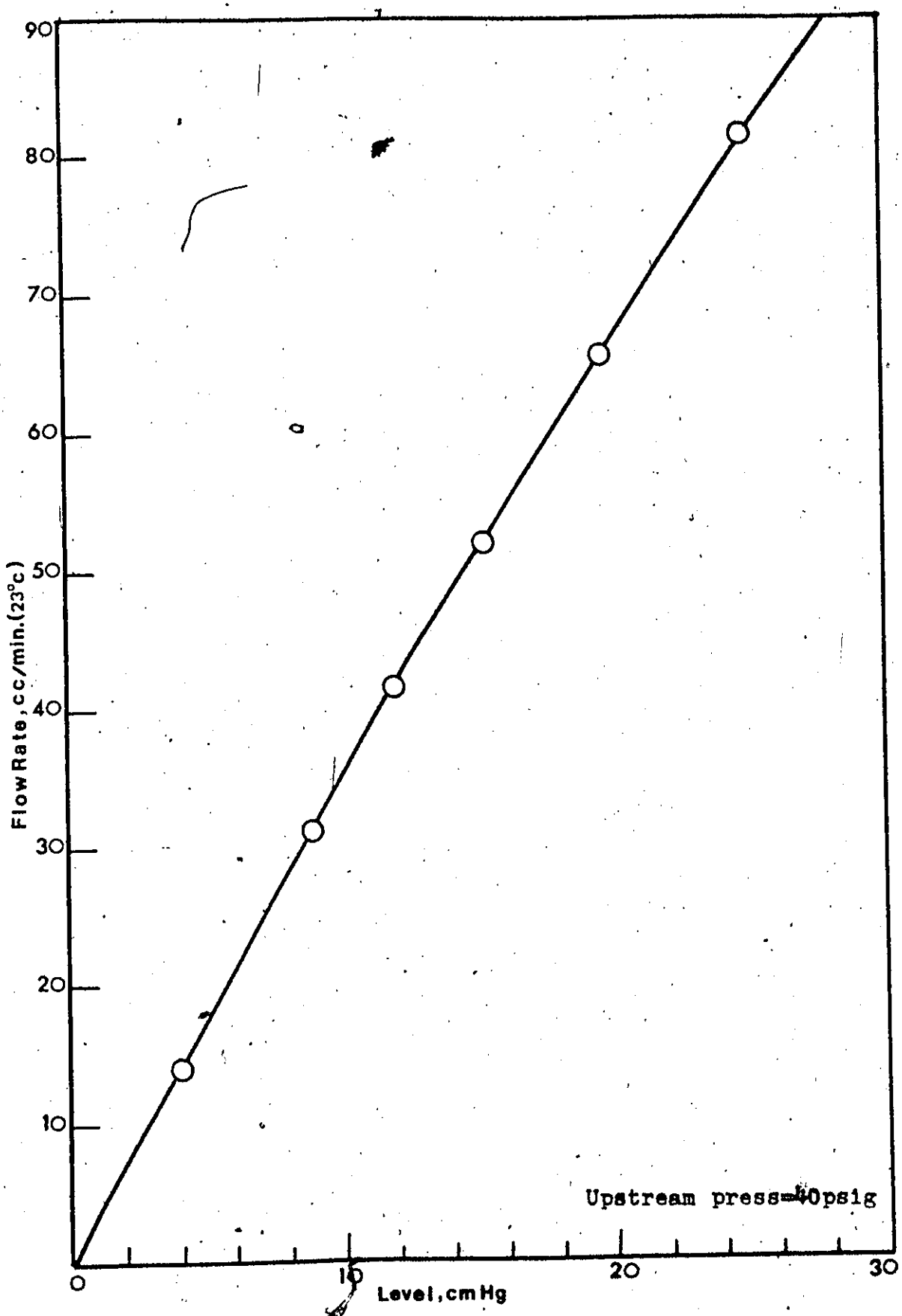


Fig G-7 : FLOW CALIBRATION OF HELIUM

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