TH-435

# A KINETIC STUDY OF THE CATALYTIC OXIDATION OF BENZENE

TH-435

A THESIS SUBMITTED TO
THE UNIVERSITY OF BOMBAY
FOR THE DEGREE OF Ph.D. (Tech.)
BY

K. VAIDYANATHAN, B.Sc., B.Sc. (Tech.)

NATIONAL CHEMICAL LABORATORY, POONA.

# Statement required to be submitted under Rule 0.413 of the University of Bombay

No part of this thesis has been submitted for a degree or diploma or other academic award. The literature concerning the problem investigated has been surveyed, and all the necessary references are given in the thesis. The present work has been clearly indicated separately. The experimental work has been carried out entirely by me. In accordance with the usual practice, due acknowledgement has been made wherever the work presented is based on the results of other workers.

Waidyanallian

K. Vaidyanathan CANDIDATE

POONA May 1967

L. K. Doraiswamy RESEARCH GUIDE

# TABLE OF CONTENTS

Chapter .				
	SUMMARY	AND CONCLUSIONS	1	
1.	LITERAT	URE REVIEW AND PROBLEM OUTLINE	11	
	1.1	Introduction	11	
	1.2	Maleic anhydride from benzene oxidation - a general survey	12	
	1.3	Catalyst used in benzene oxidation	20	
	1.4	Mode of benzene oxidation	23	
	1.5	Kinetic models	27	
	1.6	Problem outline	31	
2.	EXPERIM	ENTAL	40	
	2.1	Experimental set up	40	
	2.1.1	General	40	
	2.1.2	Vaporizer	40	
	2.1.3	Reactor	42	
	2.1.4	Condenser	46	
	2.2	Catalyst	46	
	2.2.1	General	46	
	2.2.2	Catalyst preparation	48	
	2.3	Analytical techniques	49	
	2.3.1	Estimation of maleic anhydride	49	
	2.3.2	Estimation of benzoquinone	51	
	2.3.3	Estimation of carbon dioxide	51	
	2.3.4	Estimation of carbon monoxide	51	
	2.3.5	Estimation of water	52	

Cha	pter		Page
	2.4	Procedure	52
3.	INITIAL EVALUAT	TREATMENT OF DATA AND CATALYST	55
	3.1	Organisation of experiments	55
	3.2	Experimental data	56
	3.3	Preliminary evaluation of mass transfer	57
	3.4	Determination of first-order constants	60
	3.4.1	General	60
	3.4.2	Determination of rate constants	60
	3.5	Temperature dependence of first-order rate constants	64
	3.6	Accuracy of estimated constants	67
	3.7	Selection of catalyst composition	70
4.	PLAUS IB	LE MODELS	80
	4.1	General	80
	4.2	Hinshelwood models	81
	4.2.1	Applicability of Hinshelwood model	82
	4.2.2	Proposed (modified Hinshelwood) model	84
	4.2.3	Test of proposed model	88
	4.3	Probable controlling mechanisms	99
	4.3.1	General	99
	4.3.2	Controlling mechanism for the three reaction steps	112
	4.3.3	Comments	122
	4.3.4	Test of the models	123
	4.3.5	Temperature dependence of the	124

Chapter	Page					
5. CONTROLLING REGIMES IN BENZENE OXIDATIONS	130					
5.1 General theoretical development	130					
5.2 Identification of the controlling regimes in benzene oxidation	135					
NOMENCLATURE	156					
Appendices						
Appendix - A	160					
Appendix - B	200					
Acknowled coment						

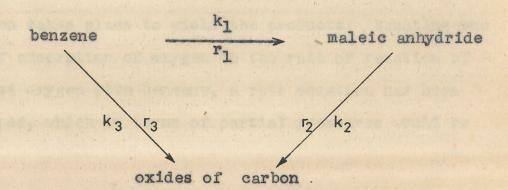
or the reaction was relieved and involved. It was observed that brough tempore exidation proceeds through a common of involved around the landston of involved around the proceeds the following and remonstrates are personally from the minutes around the personally from the process.

SUMMARY AND

CONCLUSIONS

#### SUMMARY AND CONCLUSIONS

The published literature on the oxidation of benzene to maleic anhydride in the vapour phase is quite vast, but only a small part of it relates to the kinetics of the oxidation process. As a first step in the present study, the available literature on the kinetics of the reaction was collected and tabulated. It was observed that though benzene oxidation proceeds through a number of intermediate steps (including the formation of phenol, hydroquinone and benzoquinone), for the kinetic analysis the following scheme has generally been accepted.



Moreover each of the three principal steps involved apparently follows first-order kinetics. According to Hammar (Svensk Kem. Tid., 64, 165 (1952); Chem. Abst., 46, 8945d (1952)) all these three steps have equal apparent activation energies, where as Ioffe and Lyubarskii (Kinetika i Kataliz, 3, 261 (1962);

Chem. Abst., 58, 55g (1963)) found the activation energies to be unequal.

Apparently no attempt has been made to postulate a plausible model for benzene oxidation, except the solitary attempt of Hayashi et al (Can. J. Chem. Eng., 41, 220 (1963)) who applied the Hinshelwood model to benzene oxidation, the scheme being,

In this model it is assumed that first oxygen is adsorbed over the catalyst surface, then benzene from the gas phase strikes the adsorbed oxygen whence the chemical reaction takes place to yield the products. Equating the rate of adsorption of oxygen to the rate of reaction of adsorbed oxygen with benzene, a rate equation has been developed, which in terms of partial pressures would be

$$\mathbf{r} = \frac{k_a k_r p_B p_0}{k_a p_0 + n k_r p_B} \qquad (1)$$

This rate equation is restricted to the overall reaction of hydrocarbon with oxygen and not to the individual steps involved. Also the equations are not of general applicability since the value of the specific

adsorption constant of oxygen has been found to vary for different hydrocarbons for a given temperature and catalyst, though the fact that only oxygen is assumed to be adsorbed would require that this constant should have the same value for all the hydrocarbons.

Hence a systematic study of the oxidation of benzene was carried out with the following objectives:

To establish the first-order rate constants and then to suggest a suitable composition of V<sub>2</sub>O<sub>5</sub> and MoO<sub>3</sub> (on silica gel) on the basis of a comparative assessment of the kinetic parameters for different catalyst compositions; to examine the Hinshelwood model proposed earlier; to propose plausible models of the Hougen-Watson type for all the principal steps involved; and to elucidate the effect (if any) of mass transfer and pore diffusion.

Experiments were carried out in an integral reactor with outside fluidized bed heating to obtain isothermal conditions. Rate data were collected at four different ratios of benzene to air (1:50, 1:80, 1:110 and 1:140) covering a temperature range of 310-400°C. and a contact time (W/F) range of 60-400 gm.hr./gm-mole. Results of all the runs are expressed in terms of the partial pressures of the products of oxidation, viz., unreacted

1 ....

benzene and oxygen, maleic anhydride, carbon dioxide and water (as benzoquinone and carbon monoxide were formed in traces, they were not included in the partial pressure calculations).

The rate data conform to pseudo first-order kinetics for all the catalysts employed. The first-order equations for the reaction scheme presented earlier are:

$$-\frac{dp_{B}}{d(W/F)} = (k_{1}+k_{3}) p_{B} \qquad .. \qquad (2)$$

$$\frac{\mathrm{dp}_{\mathrm{M}}}{\mathrm{d(W/F)}} = k_{1}p_{\mathrm{B}} - k_{2}p_{\mathrm{M}} \qquad .. \qquad (3)$$

$$\frac{dp_C}{d(W/F)} = (2k_1 + 6k_3) p_B + 4k_2 p_M .. (4)$$

The accuracy of the rate constants has been checked by back calculating the disappearance of benzene and formation of maleic anhydride and comparing them with the observed values. The deviation is about 8%. The temperature dependence of these constants has been expressed in the form of the usual Arrhenius relationship, which clearly showed that all the three steps involved have equal activation energies; but the value of the activation energies depends on the temperature region, being about

20 kcal./gm-mole in the region 310-350°C. and about 2 kcal./gm-mole in the region 350-400°C. The magnitude of the activation energy (2 kcal./gm-mole) in the higher temperature range (350-400°C.) suggests that in this region mass transfer might be the controlling step.

A comparative assessment of the kinetic parameters,  $k_1/(k_1+k_3)$  and  $k_2/k_1$ , for different catalyst compositions indicates that probably a total oxides content constant of 14% and  $V_2O_5$  to  $MoO_3$  ratio 1:1 is the most suitable composition for benzene oxidation.

As pointed out earlier, the Hinshelwood model is not of general applicability. Moreover, the present data also do not uphold this mechanism. Hence, starting from Bretton's postulate (Ind. Eng. Chem., 44, 594 (1952)) that hydrocarbon is adsorbed in preference to oxygen, a modified Hinshelwood model has been developed, according to which benzene is first adsorbed on the catalyst surface and oxygen from the gas phase then strikes the adsorbed benzene leading to chemical reaction. Equating the rate of adsorption of benzene to the rate of reaction of benzene at steady state, the rate equation developed is of the form,

$$r = \frac{k_B k_r p_B p_0}{k_B p_B + k_r p_0} .. (5)$$

This equation holds good for the initial conditions only.

An empirical correlation has been developed to extend the equation to other conditions by setting,

$$k_r = k_{ro} (1 - ax)$$
 .. (6)

where

a = empirical constant

The validity of the rate equation has been tested by calculating the rates and comparing them with the experimental values. The Arrhenius relationship developed for the specific rate constant  $k_{ro}$  (for the initial condition) yields an activation energy comparable with that obtained from first-order kinetics.

An attempt was then made to delineate the controlling steps for the reactions under study using the Hougen-Watson models. The models proposed after the usual elimination procedure are as follows:

For reaction step 1, adsorption of benzene is the controlling step, reaction occurring between adsorbed benzene and oxygen in the gas phase with carbon dioxide and water not adsorbed.

$$r_1 = \frac{k_{1s}}{(1 + K_M p_M)}$$
 .. (7)

anhydride is the controlling step, reaction occurring between adsorbed maleic anhydride and oxygen in the gas phase, with carbon dioxide and water not adsorbed.

$$\mathbf{r}_2 = \mathbf{k}_{2s} \, \mathbf{p}_{\mathbf{M}} \qquad \qquad \dots \tag{8}$$

For reaction step 3, adsorption of benzene is the controlling step, the reaction occurring between adsorbed benzene and oxygen in the gas phase, with carbon dioxide and water not adsorbed.

$$r_3 = k_{3s} p_B .. (9)$$

The equation developed for steps 2 and 3 are identical with the equation based on first-order kinetics, whose validity was established earlier. For reaction step 1, the accuracy of the constants,  $k_{ls}$  and  $k_{ls}$ , was checked by calculating the rates from the equation developed for this step and comparing with the observed rates. The deviation is about 13-15%.

The low activation energy (2 kcal./gm-mole) for the higher temperature range (350-400°C.) indicates that mass transfer might be the controlling step in this regime.

Since according to Petersen ("Chemical Reaction Analysis,"
Prentice-Hall, Inc., New Jersey (1965)) mass transfer
alone cannot be the controlling step, being always
accompanied by pore diffusional resistance, an attempt
was made to determine the influence of pore diffusion.
For this purpose rate constants were calculated for
different particle sizes, viz.,

-5 +12, -12 +22, -22 +36, -36 +60 (B.S.S. mesh)

Then, from a plot of the observed values of k (rate constant for total benzene disappearance) as a function of particle size, the intrinsic value of k was determined. In view of the similarity in the behaviour of all the rate constants this analysis has been restricted to the total disappearance of benzene. Using this value of k, the effectiveness factor  $\epsilon$  was calculated from,

$$\epsilon = \frac{\text{observed value of k}}{\text{intrinsic value of k}}$$
(10)

The Thiele modulus ( $\emptyset$ ) was estimated for different particle sizes from

$$\emptyset = L \sqrt{\frac{k \text{ (intrinsic)}}{D_e}} .. (11)$$

In the present case, the effectiveness factor was found to be practically unity, and in the plot of  $\varepsilon$  vs.  $\emptyset$  the experimental points also coincide with the theoretical  $\varepsilon$  -  $\emptyset$  curve.

Three regions can be identified in the curve:

(i) 
$$\emptyset$$
 < 0.2 where  $\varepsilon$  = 1;

(iii)  $0.2 < \emptyset < 2$ , the transition region; and (iii)  $\emptyset > 2$  where  $\varepsilon = 1/\emptyset$ .

Petersen has postulated a mass transfer factor ( $\epsilon$ ) and has established a relationship between this factor and the Thiele modulus ( $\emptyset$ ) for region (iii), which can be put in the form,

$$\delta = \frac{1}{1 + 30 \, (D_e/D)} \qquad .. \tag{12}$$

where the ratio  $(D_{\rm e}/D)$  is a measure of the tortuous diffusion inside the catalyst. This equation can be modified to provide

$$\delta = \frac{1}{1 + 30^{2}(D_{e}/D)} (13)$$

for region (i) where pore diffusion is absent. A scrutiny of Equation (13) shows that, in the case of benzene oxidation, the value of  $(D_{\rm e}/D)$  being  $5.102 \times 10^{-3}$ , the mass transfer factor (6) is unity. This fact, combined with the earlier observation that the effectiveness factor is also unity, suggests that neither external mass transfer nor pore diffusion offers any significant resistance in this reaction.

The above analysis was carried out for the high temperature range only since, in the low temperature range, chemical reaction is evidently the controlling step. It is a reasonable conclusion that in the high temperature range also chemical reaction is the controlling step, the unusually low value of the activation energy being attributable to a favourable change in the chemical structure of the catalyst.

Note: The nomenclature is given in pages 156-9.

# CHAPTER-1

PROBLEM OUTLINE

## Chapter 1

# LITERATURE REVIEW AND PROBLEM OUTLINE

# 1.1 INTRODUCTION

Maleic anhydride has uses in many branches of the chemical industry. This compound, an internal anhydride of an unsaturated dicarboxylic acid, with its enhanced reactive olefinic linkage, contributes (with its many derivatives) to the manufacture of a variety of chemicals ranging from oil additives to pharmaceuticals.

Maleic anhydride/acid may be obtained by the oxidation of benzene, biphenyl (28), \alpha-pinene (13,14), succinic acid (22), furfural (29,48,51,56), crotonaldehyde (2,7,11,15), butene (9,45,57,60), n-butane (6,35), furan (42), butadiene (6), furfuraldehyde (53), isobutylene (6), phenanthrene (50), cyclopentadiene (49), etc. The pyrolysis of diglycolic anhydride (38) and electrolytic oxidation of benzene (81) and cyclohexanone (27) also yield maleic acid. It is also obtained as a by-product in the production of phthalic anhydride from o-xylene (33) and naphthalene (24,25,73), of benzaldehyde/benzoic acid from toluene oxidation (62), and in the oxidation of ethyl benzene (61).

Attempts have been made to oxidize benzene in the liquid phase, but without success. Potassium permanganate has no marked effect on benzene in the liquid phase (74), hydrogen peroxide in the presence of iron salts yields a

mixture of phenol and diphenyl (16), and the action of air under pressure yields about 0.5 per cent phenol (37).

Of all the raw materials used benzene (25,58,59, 75,76), crotonaldehyde (5,12) and butene (55) are of commercial importance. However more than 90% of the total production of maleic anhydride is based on benzene oxidation.

In the following paragraphs a brief review is presented high lighting the general aspects of benzene oxidation, the various catalysts used, the mechanism of oxidation and the kinetic models proposed. Based on this survey the scope of the present work is outlined in Section 1.6.

# 1.2 MALEIC ANHYDRIDE FROM BENZENE OXIDATION - A GENERAL SURVEY

An account of the earlier papers dealing with the oxidation of benzene has been presented by Egloff (23) and by Marek and Hahn (46).

As early as 1870, Carius obtained a then unknown derivative of maleic acid as a result of treating benzene with perchloric acid. Kekule repeated this experiment, and identified this product to be  $\beta$ -trichloroacetocecrylic acid (CCl<sub>3</sub>COCH = CH - COOH). The mechanism of the reaction was explained by supposing that simultaneous exidation and chlorination of benzene led to a large number of

intermediate compounds, viz. chlorinated benzene, phenol, chlorinated phenols, quinones and finally chlorinated quinones.

In 1891 Zincke and his collaborators undertook a study of the action of chlorine (potassium chlorate + hydrochloric acid) on various derivatives of hydroxy benzenes. In their investigation they came across hexachloro-o-diketone, pentachloro-m-diketone derivatives and dichloro maleic acid. Further, the cleavage of the benzene ring by chlorine in alkaline solution was studied by Hantzsch.

Döbner oxidized phenol with potassium permanganate and obtained meso tartaric acid. It was presumed that hydroquinone, quinone and maleic acid were intermediate steps of oxidation.

In 1906, during a study connected with the structure of benzene, Kempf noted the formation of maleic acid as a result of the liquid phase oxidation of quinone with silver peroxide. He noted that this also resulted by the electrolytic oxidation of quinone.

However, the first step towards the oxidation of aromatics in the vapour phase was undertaken by Orloff in 1908. He obtained benzaldehyde by oxidizing toluene in the vapour phase over copper sieve contact mass. But in the case of benzene a number of unidentified compounds

were reported.

Further studies relating to the oxidation of hydrocarbons were conducted by Gilles and his associates, working at the Bureau of Chemistry in Washington and by Weiss and Downs and their associates, working in the laboratories of the Barret Company at Edgewater, New Jersey. The investigations carried out by them were said to have paralleled each other to a great extent. Very few details concerning the work were published. However, a number of patents were taken on the production of phthalic anhydride from naphthalene, anthraquinone from anthracene, phenanthrequinone from phenanthrene and benzaldehyde from toluene.

The first paper on the vapour phase oxidation of benzene was published in 1920 by Weiss and Downs (77). According to them the oxidation of benzene at high temperatures yielded diphenyl, tarry products and other products of complete oxidation. However, with certain catalysts, conversion to phenol to the extent of 0.3 per cent was possible, with quinone being formed in slightly larger amounts. In the case of a few catalysts, in particular with vanadium pentoxide, maleic acid was formed. Under their experimental conditions, the propertion of quinone to that of maleic acid formed remained almost unaltered. A small quantity of formaldehyde was also reported; but neither the amount nor the mode of its analysis

was indicated. The reaction velocity of the partial oxidation of benzene was said to be less than that of the oxidation rate of sulphur dioxide to sulphur trioxide or of ammonia to nitric acid. The apparatus used by these authors mainly consisted of a vaporizer through which air was bubbled and a 'U' tube reactor held in a bath of molten lead maintained at constant temperature. The reaction products were scrubbled with distilled water and analysed.

In an article published in 1926, Downs (19) had indicated that both alumina and iron, among other materials, were without catalytic activity. Several aspects of the laboratory scale investigations, including the mode of temperature control (through a molten lead bath) as well as the details of a commercial size reactor, consisting of a number of small diameter tubes inserted in a liquid mercury bath (heat exchanger type reactor) for controlling the temperature gradient, have been given. It has been indicated that a yield of 60 pounds of maleic acid per 100 pounds of benzene was feasible on a commercial scale.

Following the introduction of maleic anhydride in the market, Downs (26) published a paper on the possible plausible applications of maleic anhydride.

In 1929 Yabuta and Simose (82) reviewed the oxidation of benzene over vanadium oxide catalyst,

emphasizing the influence of diluent gases, mode of catalyst preparation and effect of other metallic oxides in the catalyst.

Zalkind (83) reported that, at the optimum temperature of 410-430°C., yields of 14 to 17 per cent maleic acid on the basis of benzene used could be obtained. The reaction probably took place via phenol to quinone, to maleic acid and subsequently to the complete oxidation products.

Pigulevskii (54) conducted experiments over ammonium meta vandate catalyst in atmospheres rich in oxygen. Working in the temperatures 370-450°C. with mixtures of benzene from 3 to 8 per cent and 19.7 to 89 per cent oxygen by volume, and at contact times (0.4 to 20.6 sec.) it was reported that a maximum yield of 38 per cent could be obtained.

Kiprianov and Shostak (44) obtained 24 per cent of maleic acid by weight of benzene fed over vanadium pentoxide deposited on pumice, and concluded that the yield could be doubled with 70 per cent vanadium oxide and 30 per cent molybdenum oxide catalyst. Moreover they ascertained, from experimental evidences, the effect of adding small amounts of some metallic oxides as promoters for their catalysts, and found that whilst cobalt enhanced the efficiency of oxidation, bismuth, tin and

lead were innocuous, and addition of iron, nickel, chromium or manganese was deleterious.

Takikawa (63) made use of multicomponent catalysts - vanadium and molybdenum oxides, vanadium, molybdenum and titanium oxides - for the oxidation of the parent compound.

In 1952, Hammar (34) published his studies on the reaction kinetics of the oxidation of benzene over vanadium - molybdenum catalysts deposited over alumina. The reactor consisted of a stainless steel tube heated both externally and internally with dowtherm. The only solid product identified was maleic anhydride and the gaseous products of oxidation were analysed by the conventional Orsat apparatus.

Fakuda (26) studied the relationship between the yield and the ratio of air to benzene, composition of the catalyst, etc., to evolve the optimum conditions for industrial production.

Norrish (52) and his collaborators conducted the oxidation of benzene at a higher temperature of 685°C. and at residence times up to two hours without a catalyst. The idea was to ascertain the mode of oxidation of benzene to the final products. According to the results published, the oxidation has been shown to proceed via successive hydroxylations of the ring to the dihydroxy

stage, whence the ring cleavage takes place, the fission products being rapidly degraded to C<sub>2</sub> hydrocarbons, formaldehyde, carbon oxides, hydrogen and water.

Bhattacharya and Venkataraman (2) have made a systematic study pertaining to the addition of various modifiers like oxides of cobalt, tungsten, uranium, cerium, thorium, zirconium and titanium to the vanadium - molybdenum mixed oxide catalyst over different catalyst supports like kieselguhr, pumice, kaolin, silica gel, metallic aluminium and calcium sulphate. Best yields of maleic acid (50 per cent conversion of benzene) were obtained with a vanadium pentoxide - molybdenum trioxide (ratio 1-2.3: 1) catalyst supported on kieselguhr with 5 per cent of cobalt oxide as promoter. According to them the mode of preparation of metal oxide and the pre-treatment of the supports also affected the yields.

Sherwood (59) has discussed the various processes used in maleic anhydride production, the significance of the oxidation step, the variables involved in the reaction, the composition of the catalyst used, the product recovery step and the different techniques used (viz. the fixed and fluidized bed techniques).

Due to the short supply of benzene, and the fact that out of 6 carbon atoms in benzene only 4 atoms are utilized in procuring maleic acid whereas the other 2 atoms are lost as oxides of carbon during the reaction, the

recent trends are to utilize hydrocarbons having 4 carbon atoms as the starting material, like butene (CH3-CH = CH-CH3) or crotonaldehyde (CH3-CH = CH.CHO).

Crotonaldehyde (4,5,12) is used by Germans in the production of maleic anhydride. The crotonaldehyde needed for this process is obtained from acetaldehyde by aldol condensation carried out in a continuous converter.

Irrespective of the starting materials used,
the reaction is highly exothermic. In order to prevent
the consequent temperature gradients in the catalyst bed,
which hamper the progress of the reaction to the
intermediate products of oxidation, many new ideas have
been put into practice.

At present, besides the conventional fixed bed technique for the maleic anhydride production, fluidized (58) and moving (64) bed techniques have also been employed.

A recent French patent (30) proposes a novel method which consists in packing the fixed bed reactor with three layers of catalyst of different compositions. The compositions of these catalysts are so adjusted that the reaction proceeds smoothly and a high yield of maleic anhydride is obtained.

Another method has been reported (10) in which

two catalytic reactors are operated in series. These two fixed bed reactors are packed with different quantities of the catalyst maintained at different temperatures and at specified conditions. The first reactor yields about 37.5 per cent and the second about 37.6 per cent, thus fetching a total of about 75 per cent of maleic anhydride per pass. This method appears to be in consonance with modern techniques of temperature optimization.

# 1.3 CATALYSTS USED IN BENZENE OXIDATION

A great variety of catalysts has been patented for use in the vapour phase oxidation of benzene to maleic anhydride. The use of the metals of the fifth and sixth groups of the periodic system or mixturesof these oxides has been particularly stressed. Vanadium pentoxide has been studied more in this connection than any other oxide because of its selective role in the oxidation of benzene.

Weiss, Burns and Downs (78) investigated the mechanism by which vanadium oxide catalyses the oxidation of benzene. It was found that the colour of the catalyst changed from reddish yellow in the initial condition to bluish green to grey after the reaction. Hence it was assumed that the pentavalent vanadium dissociates as

$$v_2 o_5$$
 benzene  $v_2 o_4 + o_4$ 

To verify this phenomenon, different catalysts of known composition were prepared and analysed at the end of the reaction. It was found that the equilibrium composition depended only on the ratio of air to benzene at a given temperature. But the proportion of vanadium pentoxide in the catalyst at equilibrium decreased with increase of temperature. At the same time, at higher temperatures, as the products of total oxidation from the reaction increased, it was suggested that the degree of complete oxidation was not solely dependent on the ratio of V<sub>2</sub>O<sub>5</sub> to V<sub>2</sub>O<sub>4</sub>. They attributed the relative proportions of the various products of oxidation from the parent compound to some other property of the catalyst, perhaps the structure of the crystalline lattice.

The effect of various promoters like molybdenum oxide (63), boric acid (63), chromic acid (39), tungstic oxide (65), in conjunction with the vanadium pentoxide, has been studied. Of these promoters, only molybdenum oxide is widely used.

loffe and his co-workers (39) have made a systematic study of the oxidation of benzene over a varied proportion of vanadium and molybdenum oxides. According to them, the increased activity of the catalyst is associated with the solid solution formation of  $MoO_3$  with  $V_2O_5$  lattice. Thus a 25 to 30 mole per cent of  $MoO_3$  with  $V_2O_5$  has been shown to form a good solid solution.

But according to others the ideal mixture proportion is 1:1 (2,66,67).

Addition of small quantities of "additives" or "modifiers" to V<sub>2</sub>O<sub>5</sub> - MoO<sub>3</sub> mixed oxide catalysts is said to enhance the reactivity to the formation of the intermediate products of oxidation. In other words, they are believed to inhibit the further oxidation of intermediate compounds to the ultimate oxidation products, as well as check the direct complete oxidation of benzene. Thus, additives like titanium dioxide (63), sodium salts (69), phosphorus pentoxide (65), potassium salts (70), nickel nitrate (31) and lithium oxide (32) have been studied in conjunction with the mixed exide catalysts of vanadium and molybdenum.

Inert materials like silica (79), alundum (68, 43) pumice (10,26), metallic aluminium (34), alumina (31, 71), quartz (67), fused corundum (40), silica gel (66) have been used as catalyst supports. However, it has been reported (66) that carriers like silica gel with high porosity have a deleterious effect on the conversion of benzene to maleic anhydride. On the other hand, carriers with low porosity (like quartz) are also not suitable, as the oxide coatings tend to peel off, especially in a fluidized bed, due to insufficient adhesion to the surface. Generally the best results are reported to be obtainable with carriers of medium porosity

like alundum (66).

Regarding the total oxides (molybdenum oxide plus vanadium oxide) required for the reaction, about 25% (on the carrier) has been found to be the best proportion by a few investigators (2,64,89). On the other hand, there are also patents (31,32,41) which claim about 15% total oxides to be the most suitable.

With respect to the size of the catalyst to be used in a fixed bed reactor, a range of about -3 +6 mesh (70,72) is considered to be the most favourable.

## 1.4 MODE OF BENZENE OXIDATION

A few references are available in the literature on the stepwise oxidation of benzene to the principal products of oxidation in the vapour phase.

The fact that Weiss and Downs (21,23,80) were able to isolate phenol in the products of reaction suggests a hydroxylation mechanism similar to that postulated in the case of vapour phase catalysis (3) in which the formation of monohydroxylated derivative is the first step. The hydroxyl group in phenol activates the para and ortho positions, so that the introduction of the second hydroxyl group would be expected to yield quinol (1:4 C<sub>6</sub>H<sub>4</sub> (OH)<sub>2</sub>) and catechol (1:2C<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub>) respectively, with a preponderance of the former. Quinol

was exidized further to quinone. However the amount of quinone formed was very little.

The mechanism of further oxidation of quinone to maleic anhydride is speculative, as none of the intermediate compounds in this step has been isolated. However the possibility of further hydroxylation of the quinone, and the formation of a polyketone due to rearrangement, may not be ruled out.

Further oxidation of this product results in ring rupture and formation of maleic anhydride

$$0 + 50 + 50 + 2CO_2 + H_2O$$

maleic anhydride

For the formation of phenol from benzene, atomic oxygen is necessary. Weiss, Downs and Burns (78) postulated that atomic oxygen formation occurs by the dissociation of pentavalent vanadium as shown in the following equation:

Thus they assumed that the function of the catalyst was to furnish 'active' oxygen. Zalkind and Zolotarev (83) also support the hydroxylation mechanism.

Recently Boocock and Cretonovic (8) have made an exhaustive study of benzene attack by atomic oxygen. According to them two modes of attack of atomic oxygen on benzene are possible: (a) abstraction of a hydrogen atom from the aromatic nucleus, or (b) addition to the aromatic nucleus.

Abstraction of a hydrogen atom would lead to the formation of hydroxyl radical and phenyl radical. Attack of benzene by hydroxyl radical would then be expected, with the subsequent production of phenol and diphenyl by radical association, according to the following scheme.

$$C_6H_6 + O$$
 —  $C_6H_5 + OH \cdot$ 
 $C_6H_6 + OH \cdot$  —  $C_6H_5 \cdot + H_2O$ 
 $C_6H_5 \cdot + OH \cdot$  —  $C_6H_5OH$ 
 $C_6H_5 \cdot + C_6H_5 \cdot$  —  $C_6H_5 - C_6H_5$ 

Alternatively, as with the olefines and cycloolefines, the oxygen atom may add directly to benzene molecule, which presents a large number of possibilites, as shown below:

However, none of these compounds is reported in the literature, although some derivatives are known. This is probably because I, II, III and IV isomerize quickly to the stable structure of phenol, whilst V and VI are undoubtedly prone to a variety of condensations, polymerizations and decompositions.

Norrish and Taylor (52) have carried out the complete oxidation (combustion) of benzene at a high temperature (685°C.) without a catalyst, but at long residence times reaching up to two hours. According to them, in the pyrolysis of benzene, small amounts of oxygen may catalyse the reaction leading to the formation of

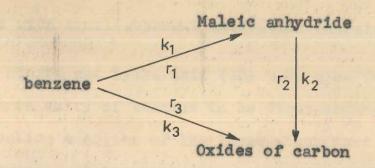
biphenyl (here oxidation is not involved). Thus :

During combustion (oxidation),

The further oxidation of these products takes place in a similar manner.

## 1.5 KINETIC MODELS

Numerous references pertaining to process studies on the oxidation of benzene are available (17,23,46), but only a few of them relate to the kinetics of the oxidation process, wherein rate equations have been given which can be used in reactor design. As pointed out earlier, the reaction proceeds through a number of intermediate steps, including the formation of phenol, hydroquinone and benzoquinone. Traces of formaldehyde and diphenyl have also been reported among the products. However, for the kinetic analysis of the reaction, the following scheme has normally been employed (17,34,40).



Hammar (34) has studied the oxidation of benzene over a number of catalysts consisting of V<sub>2</sub>O<sub>5</sub> and MoO<sub>3</sub> on metallic aluminium. He has interpreted the data according to the above scheme. The rate of the first step is said to be very fast, being limited only by the mass transfer rate. The fact that the activation energy for this step was of the order of 25 kcal. per gm-mole, which is inconsistent with mass transfer control, has been explained by assuming that the active area of the catalyst available for the reaction is itself temperature dependent.

The rate of total combustion of benzene (r<sub>3</sub>) was found to be almost independent of mass transfer, the rate determining step being either re-adsorption of maleic anhydride or surface reaction. However it is difficult to visualise the readsorption of maleic anhydride as a possible controlling step since maleic anhydride is not involved in the direct total combustion of benzene to carbon dioxide and water.

The three kinetic steps involved in the reaction were found by Hammar (34) to be uninhibited first-order

reactions with equal apparent activation energies.

Inffe and Lyubarskii (40) have also found the oxidation velocity of benzene to be first-order, but the activation energies of the three steps were found to be unequal. At benzene concentrations > 10 percent oxidation was found to be independent of oxygen concentration in the gas phase.

According to Bretton (9), initially the benzene is adsorbed over the catalyst surface with the abstraction of hydrogen to form a radical. Then the oxygen from the gas phase strikes over it and the chemical reaction proceeds through the formation and destruction of peroxy radicals.

Hayashi et al (36) have applied the Hinshelwood (steady-state) reaction mechanism to the oxidation of benzene, assuming:

- (i) oxygen is the only reactant adsorbed on the catalyst surface,
- (ii) the rate of desorption of oxygen from the catalyst is negligible.
- (iii) for reaction to occur, organic reactant in the gas phase must strike an adsorbed oxygen, and

(iv) a steady state is established in which the rate of removal of oxygen by chemical reaction equals the rate of adsorption of oxygen.

Equating the rate of adsorption of oxygen to the rate of chemical reaction, the final form of the equation developed, expressed in terms of partial pressure, was

$$r = \frac{k_a k_r p_B p_0}{k_a p_0 + n k_r p_B}$$

Mars and van Krevelen (47) have proposed a similar model for the oxidation of naphthalene. According to them the oxidation scheme is represented by the following two steps:

- (I) naphthalene + oxidized catalyst -->
  products + reduced catalyst
- (II) reduced catalyst + oxygen --> oxidized catalyst

The final rate equation developed by equating these two steps is identical in form with the Hinshelwood equation developed by Hayashi et al (36).

Recently Dmuchovsky et al (18) have studied the kinetics of the catalytic oxidation of benzene.

According to them also benzene is oxidized in two independent paths, one leading to maleic anhydride, which may be further oxidized and the other leading to the final products of oxidation as indicated in the scheme. A first-order rate low holds good up to 75 percent of the reaction range. This has been found to be true at various temperatures in the range 3190-3770c. The apparent activation energies for the two paths of oxidation of benzene are quite considerable and almost the same; whereas that required for the oxidative decomposition of maleic anhydride is found to be lower. It has been proposed that in the rate limiting step, benzene reacts with molecular oxygen either in a 1:2 or 1:4 fashion to yield activated complexes possessing considerable mobility.

### 1.6 PROBLEM OUTLINE

The detailed review of the existing literature on the oxidation of benzene reported in the foregoing sections brings out the following salient features of this process:

- (1) Vanadium and molybdenum mixed-oxides are apparently the most suitable catalysts.
- (ii) The suitability of any particular catalyst composition has been established more from process data than from any rational interpretation of the kinetic

parameters of the reaction for various catalysts.

- (iii) First-order kinetic equations have been proposed for all the three principal steps involved.
- (iv) A solitary attempt has been made to postulate a model for the total oxidation of benzene according to the reaction,

Benzene + n0<sub>2</sub> Products

In this steady-state model it has been assumed that at equilibrium,

rate of adsorption of oxygen = rate of reaction of surface oxygen

- (v) Apparently no attempt has been made to postulate models for the three principal steps involved in benzene oxidation.
- (vi) The possibility of mass transfer being the controlling step at elevated temperatures has been suggested; but the magnitude of the activation energy is inconsistent with mass transfer control.

Thus, although considerable work has been done on benzene oxidation, there are still several aspects of the process which require elucidation and analysis. The present investigation was undertaken with the following principal objectives:

(1) To establish the first-order rate constants and then to suggest a suitable catalyst composition, using

V205 and Mo03 mixtures, on the basis of a comparative assessment of the kinetic parameters for different catalyst compositions, the object being to obtain a high selectivity to maleic anhydride.

- (2) To examine the Hinshelwood steady-state model for the total oxidation of benzene and to apply this model to the catalysts selected.
- (3) To establish plausible models (based on the Hougen-Watson approach) for each of the three significant steps involved in the oxidation of benzene.
- (4) To examine the role of pore diffusion for the selected catalysts and also the effect of external mass transfer (if any).

#### References

- 1. Acad. Vep. populare Ponune, Baza Cercetari stunt. Timisora, Studu Cercertari stunt. Ser. Chim. 6, 135-44 (1959); Chem. Abst., 55, 7005g (1961).
- 2. Bhattacharya, S.K. and Venkataraman, N., J. Appl. Chem. (London), 8, 728-37 (1958).
- 3. Bibb and Lucas, Ind. Eng. Chem., 21, 635 (1929).
- 4. BIOS Final Report No. 1650.
- 5. BIOS Final Report No. 739.
- 6. Bissot, T.C. and Benson, K.A., Ind. Eng. Chem., Prod. Res. Develop., 2, 57 (1963).
- 7. Bludworth, J.E. and Pearson, P.C. (Celanese Corporation of India), U.S. Patent, 2,462,938, Mar. 1, 1949; Chem. Abst., 43, 5034c (1949).
- 8. Boocock, G. and Cvetanovic, R.J., Can. J. Chem., 39, 2436 (1961).
- 9. Bretton, R.H., Wan, S.U. and Dodge, B.F., Ind. Eng. Chem., 44, 594 (1952).
- 10. British Patent 948,057, Jan. 29, 1964; Chem. Abst., 60, 11903a (1964).
- 11. Church, J.M. and Bitha, P., Ind. Eng. Chem. Prod. Res. Develop., 2, 61 (1963).
- 12. CIOS File No. XXVII 85.
- 13. Clark, C.K. and Hawkins, J.E., Ind. Eng. Chem., 33, 1177 (1941).
- 14. Clark, C.K. and Hawkins, J.E., Proc. Florida Acad. Sci., 4 (1939); 116 (1940); Chem. Abst., 35, 98 (1941).
- Consortium fur elektrochemisch Industrie G.m.b.H., Brit. Patent, 790,559; Chem. Abst., 52, 15572c (1958).
- Discussions Faraday Soc. No. 14, 160 (1953); Chem. Abst., 48, 10626h (1954).

- 17. Dixon, J.K. and Longfield, J.E., "Catalysis", (P.H. Emmett, ed.); Vol. VII, Chap. 3, Reinhold Publishing Corporation, New York (1960).
- Dmuchovsky, B., Freeks, M.C., Pierron, E.D., Munch, R.H. and Zienty, F.B., J. Catalysis, 4, (22), 291 (1965).
- 19. Downs, C.R. J. Soc. Chem. Ind., 45T, 188-93 (1926).
- 20. Downs, C.R., Ind. Eng. Chem. 26, 17-20 (1934).
- 21. Downs, C.R., J. Soc. Chem. Ind., 46T, 383-86 (1927).
- 22. Drossbach, O., German Patent 724,758, July 23, 1942; Chem. Abst., 37, 5736 (1943).
- 23. Egloff, G., Berkman, S. and Morrell, J.C., "Catalysis Inorganic and Organic", pp.280-81, 533-48, 800-2, Reinhold Publishing Corp., New York (1940).
- 24. Esso Research & Engineering Co., German Patent 943, 293, May 17, 1956; Chem. Abst., 53, 13113 (1959).
- 25. Faith, W.L., Keyes, D.B. and Clark, R.L., "Industrial Chemicals", 2nd Ed., pp.305-8, 500-4, Wiley, New York (1957).
- 26. Fakuda, T., J. Chem. Soc. Japan, Ind. Chem. Sect., 54, 111-13 (1951).
- 27. Falqui, M.T., Rand. Seminar. Fac. Sec. Univ. Cagliari, 23, 194 (1953); Chem. Abst., 49, 5157 (1955).
- 28. Faster, H.B. (National Aniline & Chemical Co.), U.S. Patent 2, 114, 798, April 19, 1938; Chem. Abst., 32, 4609 (1938).
- 29. Fedele Carello, Italian Patent, 461,821, Feb. 15, 1951; Chem. Abst., 46, 28421 (1952).
- 30. French Patent 1,340,392; Chem. Abst., 60, 6785 (1964).
- 31. French Patent 1,332,127; Chem. Abst., 59, 9807 (1963).

- 32. French Patent 1,262,809, Sept. 22, 1961; Chem. Abst., 56, 9975c (1962).
- 33. Gulati, I.B. and Bhattacharya, S.K., J. Sci. Ind. Research (India), 12B, 450 (1953); Chem. & Industry 1425 (1954).
- 34. Hammar, C.G.B., Svensk Kem. Tid., 64, 165-76 (1952); Chem. Abst., 46, 8945d (1952).
- 35. Hartig, M.J.P. (to E.I. du Pont de Nemours & Co.), U.S. Patent 2,625,519, Jan. 13, 1953 and U.S. Patent 2,691,660, Oct. 12, 1954; Chem. Abst., 47, 11226b (1953).
- 36. Hayashi, R., Hudgins, R.R. and Graydon, W.F., Can. J. Chem. Eng., 41, 220 (1963).
- 37. Hosaka, Y., J. Chem. Soc. Japan, Ind. Chem. Sect., 57, 197 (1954); Chem. Abst., 49, 115781 (1955).
- 38. Hurd, C.D. and Glass, H.G., J. Am. Chem. Soc., 61, 3490 (1939).
- 39. Ioffe, I.I., Ezhkova, Z.I. and Lyubarskii, A.G., Russ. J. Phys. Chem., 35, 1160 (1961).
- 40. Ioffe, I.I. and Lyubarskii, L.G., Kinetikai Kataliz, 3, 261-70 (1962); Chem. Abst., 58, 55g (1963).
- 41. Japanese Patent 14,213, Sept. 28, 1960; Chem. Abst., 55, 15356c (1961).
- 42. Kalnins, P., Hillers, S. and Tarvid, M., Latvijas, P.S.R., Zinatnu Akad., Vestis, 443 (1951); Chem. Abst., 48, 9994g (1954).
- 43. Kerr, R.O., Decker, W.R. and Dorsett, C.M., U.S. Patent 3,074,969, Jan. 22, 1963; Chem. Abst., 58, 11223c (1963).
- 44. Kiprianov, G.I. and Shostak, F.T., J. Appl. Chem. (U.S.S.R.), 11, 471 (1938); Chem. Abst., 32, 5788 (1938).
- 45. Krantz, K.W. (to E.I. du Pont de Nemours & Co.), U.S. Patent 2,605,238, July 29, 1952; Chem. Abst., 47, 4013e (1953).

- Marek, L.F. and Hahn, D.A., "Catalytic Oxidation of Organic Compounds in the Vapour Phase", pp.365-403, The Chemical Catalog Co., Inc., New York (1932).
- 47. Mars, P. and van Krvelen, D.W., Chem. Eng. Sci., 3, 41 (1954), Special Supplement.
- 48. Meszaros, L. and Foldeak, S., Szegedienesis Acta Phys., et Chem. (N.S.) 4, 144 (1958); Chem. Abst., 53, 15040d (1959).
- 49. Naboru Nagameguri and Mototaro Matsumoto, Japanese Patent 10,665; Chem. Abst., 52, 1557 (1958).
- 50. Nair, C.S.B., Bhatnagar, J.N. and Basu, A.N., J. Sci. Ind. Research (India), 13B, 220 (1954).
- 51. Nielson, E.R. (to the Quaker Oats Co.), U.S. Patent 2,421,428 June 3, 1947; Chem. Abst., 41, 5551d (1947).
- 52. Norrish, R.G.W. and Taylor, G.W., Proc. Roy. Soc. (London), 234A, 160-77 (1956).
- Novella, E.C., David, R.L. and Sanchez Lazano, V., Anales real soc. espan. fcs. of quim (Madrid), 52B, 63 (1956); Chem. Abst., 50, 13860g (1956).
- 54. Pigulevsku, V.V. and Yarzhemskaya, E.Y., J. Gen. Chem. (U.S.S.R.), 5, 1620 (1935); Chem. Abst., 30, 1978 (1936).
- 55. Plastics, 26, No. 283, 7 (1961).
- 56. Products Intermedios, S.L.E., Spanish Patent 193,998, July 31, 1951; Chem. Abst., 46, 19195f (1952).
- 57. Reid, J.C. (to Atlantic Refining Co.), U.S. Patent 2,773,838, Dec. 11, 1956; Chem. Abst., 51, 7408 (1957).
- 58. Research & Industry, 4, 3; 123; 149 (1959).
- 59. Sherwood, P.W., Petroleum Processing, 11, 82 (1956).
- 60. Skinner, W.A. and Tieszen, D., Ind. Eng. Chem., 53, 557 (1961).

- 61. Solomin, A.V., Suvorov, B.V. and Rafikov, S.R., Zhur. Obshchei Khim., 28, 133 (1958); Chem. Abst., 52, 12782h (1958).
- 62. Suvorov, B.V., Rafikov, S.R., et al., Dokalady Akad. Nank S.S.S.R., 88, 79 (1953); Chem. Abst., 48, 1977g (1954).
- 63. Takikawa, S., J. Soc. Chem. Ind. (Japan), 48, 31-9 (1945); Chem. Abst., 42, 6324 (1948).
- 64. Thampy, R.T. and Suri, I.K., Indian Patent 58756, June 4, 1958.
- 65. Trehan, B.S. and Thampy, R.T., Indian Patent 74,450, Nov. 3, 1962.
- 66. Trehen, B.S., Suri, I.K. and Thampy, R.T., J. Sci. Ind. Res., 18B, 147-51 (1959).
- 67. Trehan, B.S., Thampy, R.T. and Kiloor, N.R., Indian Patent 69164.
- 68. Trehan, B.S., Suri, I.K. and Thampy, R.T., Paintindia, 7, (1), 47-9 (1957).
- 69. U.S. Patent 2,777,860, Jan. 15, 1957; Chem. Abst., 51, 8131d (1957).
- 70. U.S. Patent 3,074,969, Jan. 22, 1963; Chem. Abst., 58, 11223c (1963).
- 71. U.S. Patent 2,967,185, Jan. 3, 1961; Chem. Abst., 55, 9727b (1961).
- 72. U.S. Patent 2,674,582; Chem. Abst., 48, 8258 (1954).
- 73. Ushakova, V.P., Korneichuk, G.P. and Roiter, V.A., Ukrain Khim. Zhur, 23, 310 (1957); Chem. Abst., 52, 4757hi (1958).
- 74. Vande Velde, A.J.J., Natuurw. Tijdschr., 20, 124 (1938); Chem. Abst., 32, 7900 (1938).
- 75. Weiss, J.M. U.S. Patent 2,209,908, 1941; Chem. Abst., 35, 135 (1941).
- 76. Weiss, J.M. and Downs, C.R., J. Am. Chem. Soc., 44, 1118 (1922).
- 77. Weiss, J.M. and Downs, C.R., Ind. Eng. Chem., 12, 228 (1920).

- 89. Senting to Targer every 13 to Salikova S.R. Shar Cobennati Phin. 28, 128 (1276) Comm. Abst., 29, 12739h (1669)
- CS. SEVETOP, S.V.) MAIIREY, S.M., CT 63., [Okel-by amo. Name S.C.S., St. 72 (1906)] Chem. Abst., 48, 1877g (1906).

. 50

.00

. 07

. 27

\*05

- Takitkava, C., J. Sop. Cham. Ind. (Jepen); and (Jepen); and (Jepen); date (Jepen); date (Jepen).
- Thomas B.T. and Surf. L.R., Indian Patent
- Ti. 250, inv. S. 1160.
- T. Sol. Ind. Res., 137, 187-01 (1959).
- Indian Private dense. T. T. and Silcon, B.D.
- Transmit, M. C., Durch, T. F. and Thurston, B. T., Ind. Thurston, B. T.,
- And Park to the Control of the last down
- T.S. Forest Store, yes, ten. 20, inda, onen.
- U.A. Petage Speck, 188, Jan. J. 1991; Char.
- And the state of t
- Unsation has been decided and horizon.
- Usquiove, V.F., Kornetchek, V. end Molter, V.A., Ukrain didn. Shire Es. 310 (189V); Oses. Abst., 35, Avivat (1998).
- Vanda Valida, A.J.J., Entrary. Elidadin. 20.
  - Wedge, J.S. U.S. Princet S. Str. J. L. Lands Coney, March., Sch. Land (1901).
- Total Jin (1938).

- 78. Weiss, J.M., Downs, C.R. and Burns, R.M., Ind. Eng. Chem., 15, 965-67 (1923).
- 79. Weiss, J.M., U.S. Patent 2, 154, 079, Apr. 11, 1939; Chem. Abst., 33, 5411 (1939).
- 80. Weiss, J.M. and Downs, C.R., J. Am. Chem. Soc., 45, 1003, 2341 (1923).
- 81. Winslow, N.M. and Heise, G.W. (to National Carbon Co.), U.S. Patent 2,427,433, Sept. 16, 19470 Chem. Abst., 42, 461 (1948).
- 82. Yabuta, T. and Simose, R., Inst. Phys. Chem. Res. (Tokyo), 8, 197-205 (1929); Chem. Abst., 23, 3441 (1929).
- 83. Zalkind, Y.S. and Zolotarev, S.J., J. Appl. Chem. (U.S.S.R.), 6, 781-4 (1933); Chem. Abst., 28, 4039 (1934); Chem. Abst., 30, 1978 (1936).

na managina impi

CALL CONCERN

.

The rank of the real party of

18-70 Clef. Apr., 52, 601 (1818). 18,

Value (in the stand of the stan

Ches. (C.S.S.A.), 6, 781-4 (4823) Ches. Last., 20, 1873 (1824).

Welson J.B. and Johns C.H., J. Am. Chan.

In shown in Picture 4.20 Meteored private six was fell absence a process of the control of the c

The Paper Iver

in stoom in Pigure 5.2 the vaportion positions in an arrange of some than one there is not a train of some than the train of the sound of the train of the train

CHAPTER-2

EXPERIMENTAL

#### Chapter 2

#### EXPERIMENTAL

### 2.1 EXPERIMENTAL SET-UP

#### 2.1.1 General

A diagrammatic sketch of the reactor assembly is shown in Figure 2.1. Metered primary air was fed through benzene vaporizer (A) where it was saturated with benzene, and met a stream of metered secondary air in mixing bulb (F). The mixed stream was then passed through preheater (B), which prevented the condensation of organic vapour to reactor (E). The preheater was heated by a fluidized bed of bauxite. The product stream was passed through a train of condensers cooled by ice-salt mixture, and finally through caustic bulbs where carbon dioxide was absorbed.

### 2.1.2 Vaporizer

As shown in Figure 2.2 the vaporizer consisted essentially of a narrow graduated tube (300 mm. long x 6 mm. diameter) with a stop cock at one end and a bulb at the other. A bead at the neck of the bulb prevented liquid benzene being carried away.

41

A - VAPORISER

B - PREHEATER

C - REACTOR

D - RECEIVERS FOR SOLID PRODUCTS

E - GAS ABSORBERS

F - MIXING BULB 0 PRIMARY

N THEOLOGIC

AND DESCRIPTION OF THE PARTY OF

TO-THE LANDSCRIPTION I.S.

Lansing I.I.S

A discrementia skutch of the reactor sessibly is equal in dignor on the session of the cast of the equal in the cast of the content of the cast contents of contents of contents of contents of cast contents of cast contents of the cast contents of cast cast contents of cast c

Total Total Sel. 8

bossioner marktonav and R.S. ornatt of mindt at a produce or the produce of the p

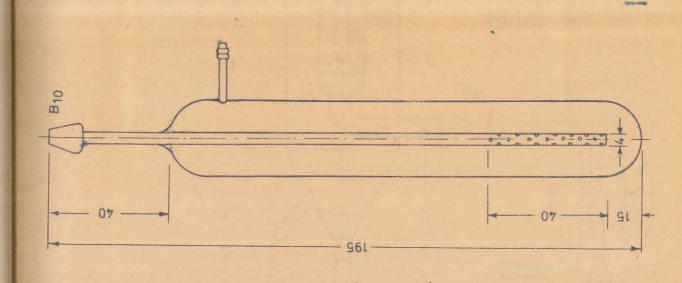
#### 2.1.3 Reactor

In the present study an integral type of reactor was used to get the kinetic data. Although a few studies have been carried out using a fluidized bed reactor for obtaining the kinetic data (in view of the high exothermicity of the reaction) (1), it must be emphasized that the use of a fluidized bed reactor is not warranted in any kinetic investigation, except where with appropriate stirring arrangements and baffles the fluidized bed could be made to approach a fully mixed reactor. In the reactor chosen for the present study, the diameter was small enough (25 mm.) to ensure plug flow conditions. A top-to-bottom feed was preferred to a bottom-to-top feed, since at high feed rates the top layers of the catalyst would tend to fluidize in the latter case. The reactor consisted of a 25 mm. diameter tube with a sintered disc at the bottom. The catalyst used was heated by a fluidized bed of bauxite. The advantages of such an arrangement are three-fold:

- (a) Initially when the reactor bed is at a temperature lower than the desired one, the fluidized bed acts as a heating medium.
- (b) During the reaction, when the temperature in the bed shoots up due to the exothermicity of the reaction, it serves as a coolant.

DISC SINTERED

SLT



TOTOLOGI E.L.T.

distributed by the reaction of the mark he

" saudior. In the restor closes for the present in .

the craim of (.ms ds) income line and retenal on they consistent. A top-to-bottom feed was produced to

TATOR IN . THE S TO RESELECT CONTENTS OF S IN IN. CLERKER taxintee with a more of the notion. The naturalist

only and the best building to be been say being

.uniber onivers a se eres and beathful.

(b) muchan the reaction, when the Compensions in

of the reachiety it serves as a decilent.

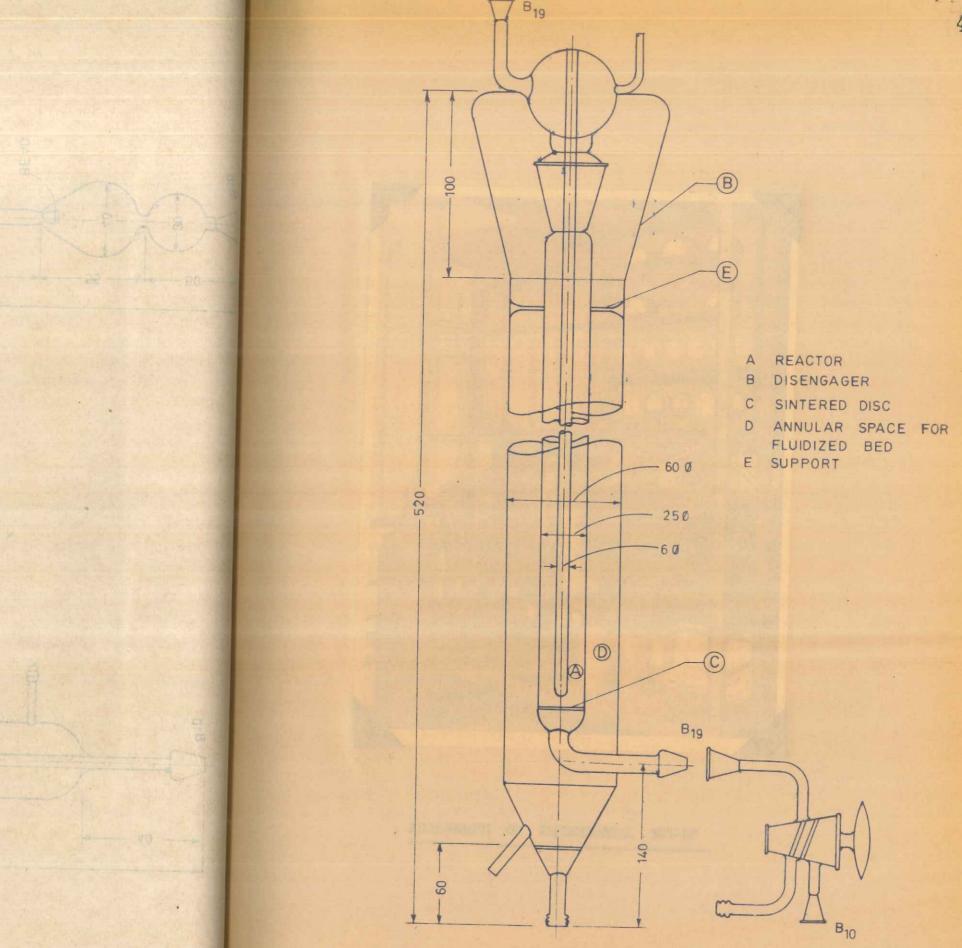
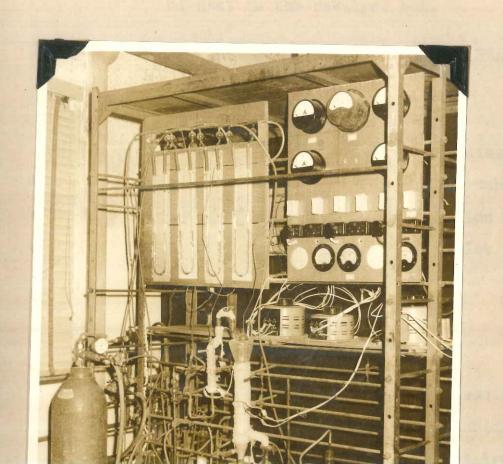


FIG. 2.3. REACTOR DETAILS



(c) It helps to maintain near isothermal conditions in the bed by quick dissipation of heat in the catalyst bed.

The other details of the reactor are shown in Figure 2.3.

### 2.1.4 Condenser

The details of the condenser are indicated in Figure 2.4. This consisted of a narrow 4 mm. tube connection, partly sintered at the lower portion and having a jacketed tube (25 mm. diameter) with an outlet.

### 2.2 CATALYST

### 2.2.1 General

TOTAL BRITEIN METERS TO STREET TOTAL

Egloff (3) of the catalysts used for the oxidation of benzene and also of the various methods of catalyst preparation (cf Section 3, Chapter 1). In general any catalyst required for a reaction can be prepared by the coprecipitation or coating technique. The coprecipitation technique is generally followed for hydrogenation catalysts, as in the case of reduction of nitrobenzene to aniline, for which the required copper catalyst is prepared by precipitating the copper hydroxide in the presence of the carrier.

The coating technique consists in evaporating

Learnedge Language of any animal and the control of the condition of the c

The details of the condenser are included in

P.l. & Condender

a jacketed wite (23 mm, diameter) with an outlier.

2.2.1 Comercial designation review has been presented by

Melofi (3). of the calalysis used for the cridation of beneated to calculation of the vertical solution (at souther 3 Charter 1). In a coord toy

estalyst required for a reaction can be propered by the

Recominge to constaily relieved for hydrogenation of categorists

to entition, for entitle the required order calcive is a proposed by precipitating the coppose hydroxide in the

anticipate at selected obstained actions out

presented of the cartier. The second to present the

the soluble salt solution of the required metal in the presence of the carrier, such that a uniform coating of the metallic salt is formed over the carrier.

Generally for oxidation catalysts the coating technique is followed.

For the vapour phase oxidation of benzene, vanadium-molybdenum mixed oxide catalysts are commonly used. These are generally prepared by the coating technique.

For benzene oxidation the metallic salts generally recommended are ammonium meta vanadate and ammonium molybdate. Ammonium molybdate is freely soluble in water, where as the meta vanadate is sparingly soluble. Hence ammonium meta vanadate is dissolved in an acid medium. The acid medium may be a mineral acid like hydrochloric acid (12) or an organic acid like oxalic acid (13). The advantages of oxalic acid are said to be three-fold: (1) the solubility of ammonium meta vanadate in water is greatly increased, thus eliminating the necessity for the evaporation of large quantities of water; (2) the activity of the catalyst is increased; and (3) the catalyst is said to dry to a "glass-like, greenish, amorphous mass" firmly attached to the catalyst support. Another advantage of oxalic acid over hydrochloric acid is that, unlike the latter, it does not evolve acidic fumes during catalyst preparation and activation. Hence

the catalysts studied have generally been prepared in oxalic acid medium. (Hydrochloric acid medium was used in certain cases to see whether it made any difference in product formation, but no marked effect was observed.)

A typical method of catalyst preparation containing 14% total exidescentent in the ratio of  $V_2O_5$ :  $MoO_3 = 7.2:6.8$  (approx 1:1) over silica gel is given below.

# 2.2.2 Catalyst preparation

one of I-res betteper out to methodos Ji. 8 biddles and

presidence were restricted and that a uniform conting

employeestalines end administration foldening to viletemol

or the matulate salters revised over the caption. . .

inlines are removedly prepared by the coalling

has stabeled when automic one palmenters vilousing.

wedding. The cold medium may be a minoral sold like.

sting said the single as as (42) bis single soid like oralite

seid (12). The edvintegment oxalde acid are deld to be

oreconey area melnosme to welltenior and (I) salet-or

Successions and files of forest views successions.

of an interest of the self over bear or and the self-one

nation deliver the letter, it does not evolve colife

copied application for northern property total action accept.

oldalor glassi ar simbly and policy of freely solable

. Didnice whereas of obstance the party world of

9.255 parts of ammonium meta vanadate (NH<sub>4</sub>VO<sub>3</sub>; m.wt. 117) and 8.343 parts of ammonium molybdate ( (NH<sub>4</sub>)<sub>6</sub> Mo<sub>7</sub>O<sub>24</sub>.4H<sub>2</sub>O; m.wt. 1235.95 ) were dissolved in 250 parts of hot 10% oxalic acid solution (10 gm. of oxalic acid in 100 ml. distilled water). To this solution 100 parts of silica gel (size -5 +12 B.S. standard) were added. The whole was evaporated to dryness with stirring over a water bath. This mass was then heated at 120-150°C. in a furnace for an hour, and the clusters formed in the mass were broken up and activated in a muffle at 400°C. for 8 hours. This was sieved to the required size.

The catalyst was then charged into the reactor and activated with air at 400°C. for 1½ hours, and for one hour more in the presence of air containing about 1% benzene vapour.

Several catalysts were prepared in accordance with the method outlined above, details of which are given in Table - 2.1. The compositions of these catalysts have been chosen to provide a near optimum value based on rate studies discussed in Section 3.7 Chapter 3. As pointed out in Chapter 3 surface area and pore volume have been determined for two of the catalysts which have been found to be satisfactory (Table - 3.6). The BET method was used for surface area determination and the pore volume was

determined by the usual displacement technique.

#### 2.3 ANALYTICAL TECHNIQUES

The products of the oxidation of benzene consist of both solid and gaseous components. They include maleic anhydride, oxides of carbon, water vapour and a little of benzoquinone. Other products mentioned, in particular by Weiss and Downs (14), include phenol, diphenyl and formaldehyde. However, none of these latter products was detected in the product obtained. Diphenyl is formed generally only at temperatures as high as 650°C. (11). The absence of phenol was assumed because of the FeCl<sub>3</sub> colour test being negative.

### 2.3.1 Estimation of maleic anhydride

The methods stated in the literature for the estimation of maleic anhydride include polarographic

Several calcalysts were prepared to advortages

given in action of the compositions of these estainsts and the beauty of the compositions of these estains and the beauty been also beauty and the composition is the composition in the composition is the composition in the composition is the composition in the composition in the composition is the composition in the composition in the composition in the composition is the composition in the

pointed out, in Charter 2 'carines and pore vulnes have

outlaidetony (Table - 3.6). The BET method see whee lor extraction and the pore volume wes determined by the west displacement technique.

empretour lablemente e.s

of hold solid and general or the callest on bensens on a little of holds of the callest of the c

of Dungoquinies, Olans products sentioned, in particular by Welski planet, depend of these parents of these letter products

descript of Principle Controls observed in Principle 19 Portugal

recently only at temperatures as high as 650 C. (11).

.ovkispon polski jani, meleo

etitbene stelar to neitestic 1.0.9

THE TENNE DANGER AN INCLUDING A

oldy meralos confent saturques pieles in solucites

Table - 2.1 Catalysts prepared

Particle size B.S.S. mesh	-12 + + + 12 -12 + + + 12 -36 + 60 -36 + 60 -12 - 12 -13 + 12 -13 + 13	
Ratio of V <sub>2</sub> 05 to Mo03	01000011	turo di desello i processi ditribili India in ter pre
Total oxides content,	44444488 8	
Catalyst	HWWWWWPP	chart or the com-
Serial	10040000	

estimation (4,5), potentiometric titration (9) and gravimetric estimation (6), apart from the usual alkali titration (2).

In the present work maleic anhydride was estimated by titration against standard alkali using phenolphthalein as indicator.

### 2.3.2 Estimation of benzoquinone

Benzoquinone in the presence of maleic anhydride (acid) can be estimated by potentiometric titration (10). A method analogous to this was followed in the present work. The solution containing benzoquinone was reacted with I in an acid medium. The liberated  $I_2$  was then titrated against  $S_2O_3$  by an indirect titration.

### 2.3.3 Estimation of carbon dioxide

Carbon dioxide was estimated by the conventional method of absorbing it in caustic bulbs and finding the difference in weight.

### 2.3.4 Estimation of carbon monoxide

The estimation of carbon monoxide generally consists in oxidizing it to carbon dioxide and estimating it as given above.

Hopcalite (7,8) is said to be an ideal catalyst

even at room temperature. Due to the non-availability of hopcalite catalyst, copper oxide at elevated temperature was used. However the results were not at all consistent. Hence the tail gas containing carbon monoxide was analysed in the conventional Orsat apparatus by absorbing it in ammonical cuprous chloride solution.

### 2.3.5 Estimation of water

No chemical methods were adopted for the estimation of water, and the water formed was calculated from material balance.

#### 2.4 PROCEDURE

The required quantity of the catalyst was charged into the reactor. Then the preheater and the reactor heaters were switched on, and the secondary air was also started. When the required temperature was attained, the primary air was turned on through the vaporizer. As the level of the manometer controlling the primary air was kept constant, the air rate passing through the vaporizer was constant; and hence the rate of benzene fed also remained steady.

Till steady-state conditions were reached, the product vapours from the reactor were vented out through

e inside of deficient of the control of the control

the analysis and the value formed was collectived.

The required cummilty of the desclyst was

dringed into the reactor. Then the presenter and the secondary eir reactor heaters were switched on, and the secondary eir was also started. When the required temperature was vitedned, the princer air was barned on through the vaporison. In the level of the namemoter controlling the princery air was kept penutant, the air rate passing through the vaporior was constant; and hence the rate passing through the vaporior was constant; and hence the rate

and the being war results the results were very the the through and the being very very tree the the results.

a bypass. When steady-state was reached, the primary air was stopped for a while, the level of benzene in the vaporizer noted down, the primary air restarted, and the three-way stop-cock turned on to the train of condensers previously adjusted to the required conditions. The duration of a run under steady conditions varied from 15 to 30 minutes, depending on the quantity and the ratio of air and benzene used. At the end of the run, the primary air was switched off first, then the three-way cock turned, the bypass. The level of benzene in the vaporizer was noted down, the difference in levels giving the quantity of benzene fed, and the manometer reading the quantity of air fed.

Whenever the bed height was changed, additional catalyst quantities were always taken from the same lot.

#### References

- 1. Badrinarayana, M.C., Ph.D. Thesis on oxidation of benzene submitted to the Indian Institute of Science, Bangalore.
- 2. Bhattacharya, S.K. and Venkataraman, N., J. Appl. Chem. (London), 8, 728-37 (1958).
- Egloff, G., Berkman, S. and Morrell, J.C.,
  "Catalysis Inorganic and Organic," pp. 280,800,
  Reinhold Publishing Corp., New York (1940).
- 4. Elcing, P.J., et al., J. Am. Chem. Soc., 71, 3616 (1949).
- 5. Elcing, P.J., Martin, A.J. and Rosenthal, I., Anal. Chem., 25, 1082 (1953).
- 6. Faith, W.L. and Shaible, A.M., J. Am. Chem. Soc., 60, 52 (1938).
- 7. Lamb, A.B., Bray, W.C. and Fraser, J.C.W., Ind. Eng. Chem., 12, 213 (1920).
- 8. Lamb, A.B., J. Am. Chem. Soc., 44, 738 (1922).
- 9. "Maleic Anhydride," Bulletin issued by Monsanto Chemicals (India).
- 10. Malyskev, A.I. and Ioffe, I.I., Zhur. Anal. Khim, 13, 374 (1958); Chem. Abst., 53, 133a (1959).
- U.S. Patent 1,322,983 (1919); (Marek, L.F. and Hahn, D.A., "The Catalytic Oxidation of Organic Compounds in the Vapour Phase," The Chemical Catalog Co., NY (1932) pp.367
- 12. U.S. Patent 2,967,185, Jan. 3, 1961, Chem. Abst., 55, 9727 (1961).
- 13. U.S.S.R. Patent 131,353, Sept. 10, 1960, Chem. Abst., 55, 6733 (1961).
- 14. Weiss, J.M. and Downs, C.R., Ind. Eng. Chem., 12, 228 (1920); J. Soc. Chem. Ind., 45T, 188 (1926).

Sadrinary and state of the ladies on callation of benegatives to the ladies institute of deleges, sangalors.

Restracted to the T. and Venketermen, E. J. Avender Tenketer (1808).

2 75

\*

.

+

. . . .

Related Partition of Corp., How York (1980).

Mindmer T. J. and All J. A. C. Comm. Ton. The Doctor (1919).

Auturn, J. F., Horting, A. S. and Rosenthal, I., and Mosenthal, I., and Mosenthal, I.,

Faith, W.L. and Sheible, E.H., J. Ac. Ches., 800., 60, 01 (1938).

Lamb, A.S., Brice, N.C. and France, J.C.2., Ind., Eng. Chep., 12, 412 (1920).

1000, 4.3., J. in. Chor. Soc., 45, 700 (1992).

(along a bemest significant enterprise obstate

Malyakov 1.1: and lefts, I.I.; Ser. and . Knin, 12, 374 (1956); Char. Abst., 55, 185s (1950).

Haben, D.A., The Catalyite exidetion of Strands Congenials Catalog Co., NY (1958) pp. 307

U.S. Patent 2, 967, 1851, 1851, Ches. 3, 1961, Ches.

9.5.5.2 Patent 131, 253, 3apt. 10; 10s0, Cani. Dat., 55, 6753 (1961).

tel , 78 , 151 , 150 , 1

the state of the same of the s

The real of blackers to ris I like to like

the realizable blue as here endeaded as the parties of the

The the south of the natural to ga, and T to buy

1977 to recombly entropy anther by the same too.

A statement, the lateral to never decrease. Service these of

CHAPTER-3

INITIAL TREATMENT OF DATA

### Chapter 3

### INITIAL TREATMENT OF DATA

### 3.1 ORGANISATION OF EXPERIMENTS

Any kinetic study entails the determination of conversions under different conditions. The principal variables studied and the ranges of these variables are given below:

Partial pressure of benzene : 0.61 x 10<sup>-2</sup> to 1.83 x

Temperature : 310-400°C.

Molar ratio of benzene to air : 1:50 to 1:140

Contact time (W/F) : 60-400 gm.hr./gm-mole

Catalyst size : -5 +12 to -36 +60

B.S.S. mesh

(The contact time is here defined as the ratio, W/F, where W is the weight of the catalyst in gm. and F is the hourly molar feed rate of benzene.)

weight of the catalyst (W) or by changing the feed rate (F), although the latter is more common. Nevertheless in this case, as very high molar ratios of benzene to air were used (and a small quantity of catalyst was taken to ensure isothermal conditions), from the practical point

The second secon conversions under the contract done. . The principal paint eral columnar and to accour end home tolbute actomicav. olos-malland nos-no z (The contest time is here defined as the ratio, Will, where Wits the solghtrof the catelydt iff gar, ind F. to and at W. med year a command to ofer best rafes virgen (F), although the Letter is more comment. Mevertheless in of meant our Jewlospe to william p liene a boat bear orang

of view the feed rate could not be varied over a wide range. Hence the entire range of WF values was covered by changing both W and F in an appropriate manner. The rate of benzene feed varied from 4 to 7.5 gm./hr. and the weight of the catalyst from 5 to 25 gm. Moreover, the catalyst for the kinetic runs was taken from a single stock prepared according to the method outlined in Chapter 2, thus avoiding discrepancies in the results due to variations in catalyst activity. Although there was no significant deactivation up to 60 hours, the catalyst in the reactor never exceeded 20 hours of usage in order to ensure the total absence of catalyst deactivation.

### 3.2 EXPERIMENTAL DATA

In order to establish the complete kinetics of this reaction and to propose plausible reaction models, over 300 experimental runs were carried out by a systematic variation of the significant variables listed earlier. The results of all these runs have been expressed in terms of the partial pressures of the products of reaction, viz, unreacted benzene and oxygen, maleic anhydride, carbon dioxide and water. Several tests showed that carbon monoxide and benzoquinone were formed in negligible quantities. Accordingly these have not been included in the partial pressure calculations. The

obly a payo believe ad don blico when boot ond welv to times. Hence the entire range of WF values was covered only the both warmen of the appropriate agreement. rate of bearing food verted from 4 to 7.5 go. Nov. and the weight of the estalyst from 5 to 25 cm. Morgover, the Chapter S, thus avoiding disorgenced in the country even a contrata . withvijos textidos at amoidateav at ano dwyladab to commade loted edd evices of testo al. SECRETARIES AND ATAG LARGE TARREST over 360 outportan terms were carried out byes a ser earlier. The comits of all those runs have been products of reaction, vis, unreacted bencence and oxygen. malolo eplydulige, derbon dioxida and solon, deverel test in negligible quartities. Recordingly these nave cot. been triglinged in the earliest procesure calculations. The

results of the experimental runs are presented in Appendix - A, Tables - A.1 to A.13. These runs cover the experimental programme listed in Table - 3.1.

Each of the Tables - A.1 to A.13 includes the results of the variation of residence time (W/F) and the molar ratio of benzene to air, both these factors together giving a considerable spread in the partial pressure values at any given temperature. These partial pressure values are necessary for formulating rate equations. At the same time the values of reaction rates also must be available, for which plots of conversion vs W/F are required. Thus Appendix - A, Tables - A.14 to A.29 give the derived values of x<sub>M</sub> and x<sub>C</sub> as functions of W/F for different ratios and temperatures.

Since the rates are normally derived by graphical differentiation or by differentiation of the analytical equations set up for the x - W/F curves, such curves were prepared for all ratios and temperatures listed in Table - 3.1. Representative plots at a few experimental conditions are shown in Figures B.1 to B.8 in Appendix - B. The rates were determined by graphical differentiation of these plots.

# 3.3 PRELIMINARY EVALUATION OF EXTERNAL MASS TRANSFER

In all kinetic studies it should be ensured

results of the experimental runs are presented in appendix - . . The A. 12. These runs cover the expendix - . . . The A. 12. These runs cover the expendimental programme listed in a ble - a. 1.

The of the variation of residence time (4/F) and the solar ratio of bename to air, both these issters together giving a considerable spread in the partial presents values at any given temporature. These partial presents values are necessary for formulating rate equations. At the same time the values of reaction rates also must be available, for which plots of conversion as W/F are required. Thus appendix "A, temporature of M/F are required. Thus appendix "A, temporature of M/F are required that appendix "A, temporature of M/F for aifferent ratios and temporatures of M/F for aifferent ratios and temporatures.

graphical dirigrantiation or by differentiation of the analytical equations set up for the x - WAF carves, which corves were prepared for all ratios and temperatures finted in imble - 2.1. Representative plots at a few appearance in appearance or about the Appearance of the rates were determined by graphical differentiation of these plots.

BETSKERT SEAR JAMESTER TO ROLLAULAUK YEARTELIESS S.S.

references to tables collected (with Table - 3.1 Appendix data experimental of

Table reference (of Appendix - A)	A.1, A.14.	A.2, A.3, A.4, A.5, A.6, A.15, A.16, A.17, A.18, A.19.	A.11, A.20, A.21, A.22, A.23, A.24.	A.25.	A.26.	A.27.	A.12, A.28.	A.13, A.29.
Temperatures studied	400	310, 330, 350, 350, 400	310, 330, 350, 375, 400	350	350	350	400	400
Particle size B.S.S.	- 5 +12	- 5 +12	- 5 +12	-12 +22	-22 +36	-36 +60	- 5 +12	- 5 +12
Ratio of V205 to Mo03	1:0	1:1	1282	1:2	1:2	1:2	1:1	121
Total oxides content	14	14	14	14	14	14	25	35
Catalyst	1	0	m	3A	33	30	4	D
Serial	1	00	m	4	S	9	7	80

that external film diffusion and pore diffusion are eliminated as far as possible. The gas film resistance can be overcome by operating at a high velocity and the resistance to pore diffusion by a proper choice of the catalyst size.

Hougen et al. (7) have developed charts by which the partial pressure difference between the flowing fluid and the exterior surface of catalyst particles in a packed bed can be evaluated as a function of a modified Reynolds number (Re) of the stream, a rate number (R") and the Schmidt number (Sc). Here,

$$R^{II} = \frac{G}{a_V \mu}$$

$$R^{II} = \frac{r}{a_M G_M}$$

$$Sc = \frac{\mu}{\rho D}$$

In the present study due to practical difficulties, the velocity of air was confined to the range, G = 50 to 145 lb./hr.ft.<sup>2</sup> (corresponding to Reynolds number 2 to 5). For the experimental condition the rate number was estimated to be about 1.0 x  $10^{-4}$  and the Schmidt number 0.7. Using these values in the above mentioned chart the partial pressure gradient  $(\Delta p/p)$  worked out to be about 0.001. This indicates that

that external film diffusion and pore diffusion are eliminated as far as possible. The cos film resistance we have overcome by operating at a high velocity and the resistance to pore diffusion by a proper choice of the

Hongon of all prosents difference between the flowing which the partiel presents difference between the flowing in the satisfact of carties of antieles in a packet be can be avalabled as a traction of a modified according to the street, a rate made (4.1) and the Schuldt makes (3.2). Here, a rate made (4.2)

of read the present study one to practical of read to the first of the the experimental condition

the Semilar number C.7. Uning these values in the shows mentioned chart the pertial processes gradient (A p/p) worked out to Se about 0.001. This indicates that

"Of x O.I trode od of botametes tow about 1.0 x 10"

the mass transfer coefficient is quite high and that external diffusion offers negligible resistance.

This should however be regarded only as indicative of the absence of mass transfer, since these charts may not be very reliable at low Reynolds numbers, and also diffusional falsification of reaction rates can occur under several conditions. Thus it was assumed, to start with, that mass transfer effects were absent and the data analysed subsequently (Chapter 5) to determine the exact controlling regimes in benzene oxidation.

It is also necessary to obtain rate data in the absence of pore diffusion. In the present study this was included in the mechanistic evaluation of the reaction and is discussed in Chapter 5.

# 3.4 DETERMINATION OF FIRST-ORDER CONSTANTS

### 3.4.1 General

Prior to the postulation of plausible kinetic models, it is essential to estimate the independent rates of the three reactions taking place. This may be done by developing empirical rate equations (which should be first-order equations according to the literature, in this case), determining the reaction velocity constants for all the steps from the corresponding integrated equations and then calculating the rates of individual steps at different residence times.

## 3.4.2 Determination of rate constants

For the kinetic analysis of the reaction, the

regimes in beneme exidetion.

absence of pere diffusion. In the precent study this wid

is disbuteed in Chapter J.

S. A DUTTERITURATION OF PIRST-ORDER CONSTANTS

Invento f.a.s.

the three reactions taking place. This may be done by

order equilibries according to the literature, in this case),

determining the reaction velocity west ante for all the steps

. weild en molitar.

allegation of a local managed c. b. S.

following scheme has been chosen (Chapter 1, page 38)

The reaction scheme presented may be stoichiometrically represented as follows:

carbon dioxide + water

$$C_6H_6 + 9/20_2 \xrightarrow{k_1} C_4H_2O_3 + 2CO_2 + 2H_2O$$
 (1)

$$C_4H_2O_3 + 3O_2 \xrightarrow{k_2} 4CO_2 + H_2O$$
 (ii)

$$C_6H_6 + 15/20_2 \xrightarrow{K_3} 6CO_2 + 3H_2O$$
 (111)

Dmuchovsky et al. (3) have assumed a slightly different stoichiometry since their data were better represented (for their catalyst) by that stoichiometry, which is.

$$c_{6}H_{6} + 40_{2} \xrightarrow{k_{1}} c_{4}H_{2}O_{3} + c_{0} + c_{0}C_{2} + c_{1}C_{2}$$

$$C_4H_2O_3 + 5/2O_2$$
  $\xrightarrow{k_2}$   $3CO_2 + CO + H_2O$  (v)

$$c_{6}H_{6} + 13/20_{2} \xrightarrow{k_{3}} 4c_{0} + 2c_{0} + 3H_{2}0$$
 (vi)

But the stoichiometry represented by reactions (i), (ii) and (iii) has been used in the present study as only traces of carbon monoxide were formed, and as shown later this stoichiometry represents the results remarkably well.

The rate equations for reactions (i), (ii) and (iii), based on pseudo first-order kinetics, are:

$$-\frac{dp_B}{d(W/F)} = (k_1 + k_3) p_B ... 3.1$$

$$\frac{d(W/F)}{d(W/F)} = k_1 p_B - k_2 p_M \qquad ... 3.2$$

$$\frac{dp_c}{d(W/F)} = (2k_1 + 6k_3) p_B + 4k_2 p_M \qquad ... 3.3$$

Equations (3.1), (3.2) and (3.3), on integration, give:

$$p_B = p_{Bo} e^{-(k_1 + k_3) (W/F)}$$
 ... 3.4

$$p_{M} = \frac{k_{1} b_{30}}{k_{2} - (k_{1} + k_{3})} \left[ e^{-(k_{1} + k_{3}) (W/F)} - e^{-k_{2}(W/F)} \right] ... 3.5$$

$$P_{e} = \frac{p_{Bo}}{k_{1} + k_{3}} \left[ -2k_{1} - 6k_{3} - \frac{4k_{1}k_{2}}{k_{2} - (k_{1} + k_{3})} \right]$$

$$\left[ -(k_{1} + k_{3}) (W/F) - 1 \right] + \frac{4k_{1}p_{Bo}}{k_{2} - (k_{1} + k_{3})} \left[ e^{-k_{2}(W/F)} - 1 \right]$$
3.6

The value of  $(k_1 + k_3)$ , which represents the velocity constant for the total disappearance of benzene, can be determined from the slope of the line obtained by plotting  $\log \frac{p_{BO}}{p_B}$  vs. W/F, in accordance with Equation (3.4). Such plots were prepared for all the catalysts and at all the different temperatures studied using the raw experimental data given in Appendix - A, Tables - A.1 to A.13. These plots appear in Appendix - B, Figures B.9 to B.16. It can be seen that the first order law holds good for the overall depletion rate of benzene up to 75 percent of the residence time (W/F) covered. Similar conclusions have also been drawn by other investigators working with different catalysts.

From a knowledge of the values of  $(k_1 + k_3)$  as outlined above, the individual values of  $k_1$ ,  $k_2$  and  $k_3$  can be ascertained by one or more of the following methods.

(a) Equation (3.5) can be recast into a more convenient form by multiplying both sides of the equation by

$$1/p_{Bo} \left[ \exp \left( - (k_1 + k_3) (W/F) \right) - \exp \left( - k_2(W/F) \right) \right]$$

From the experimental molar ratios  $(p_m/p_B)$  at two different residence times, together with the experimentally determined constant  $(k_1 + k_3)$ , the value of  $k_2$  can be found.  $k_1$  and  $k_3$  can then be evaluated from simple

algebraic procedures.

- (b)  $\frac{dp_M}{d(W/F)}$  can be evaluated for different values of W/F by finding the slopes of the curve of  $p_m$  vs. W/F, and then  $k_1$  and  $k_2$  can be calculated from Equation (3.2).
- (c) Equation (3.2) can be rewritten for the initial condition, i.e. at W/F=0, as

$$\left(\frac{dp_{M}}{d(W/F)}\right)_{0} = k_{1}p_{Bo} \qquad ... 3.7$$

From the value of  $\left(\frac{dp_M}{d(W/F)}\right)_o$  obtained from the plot mentioned in method (b), the value of  $k_1$  can be directly determined.

It has been found that  $k_1$ ,  $k_2$  and  $k_3$  calculated by the different methods listed above agree closely.

These values of  $k_1$ ,  $k_2$  and  $k_3$  for different catalysts are listed in Tables - 3.2 and 3.3 together with the activation energies. (Two other constants,  $k_{1S}$  and  $k_{M}$ , are also included in the table, and will be discussed in a subsequent section.)

### 3.5 TEMPERATURE DEPENDENCE OF FIRST ORDER RATE CONSTANTS

The effect of temperature on the rate constants has been studied in the range 310-400°C. In order to present the relationship in the form of the well known

<sup>\*</sup> This table contains all the kinetic constants for the two catalysts finally chosen (Section 3.7, Chapter 3, Page 70).

RATE AND ADSORPTION CONSTANTS FOR THE THREE SIGNIFICANT REACTIONS INVOLVED IN BENZENE OXIDATION TABLE - 3.2

						10.00		
	X X X X X X X X X X X X X X X X X X X	3.400	1 · 100	0.700	1	1	26.430	
м	k <sub>1s</sub> ×10 <sup>2</sup>	3.94	99.9	14 · 45	1	1	24 · 16	
CATALYST- 3	k3 X10 <sup>3</sup>	0.126	0 .229	0.453	0.477	0.519	23.860	2.270
CAT	k <sub>2</sub> X10 <sup>3</sup>	0.776	1 - 447	2 . 806	2.982	3 - 113	23.750	1 . 730
	k <sub>1</sub> × 10 <sup>3</sup>	0.368	969.0	1.358	1.455	1.513	23.730	1.800
Charles as a	KM X 10 <sup>-3</sup>	2.21	1.10	0.75	1	1	21 - 17	
	k <sub>1s</sub>	3.80	6.21	16.00	1	1	23.97	
-2	k <sub>3</sub> ×10 <sup>3</sup>	0.132	0.225	0.396	0.409	0.444	20.270	1.910
CATALYST-2	k <sub>2</sub> ×10 <sup>3</sup>	0.846	1.430	2.468	2 593	2.716	19.550	1.600
CA	k <sub>1</sub> ×10 <sup>3</sup>	0.403	0.675	1.141	1 .292	1.361	19 .060	2.920
	Temperature ° C.	310	330	350	375	400	Efor temp.range 310-350°C. kcal./gm-mole.	E for temp. range 350-400 °C. kcal./gm-mole.

Table - 3.3

Rate constants for different catalyst compositions at 400°C.

Catalyst number	k <sub>1</sub> x10 <sup>3</sup>	k <sub>2</sub> x10 <sup>3</sup>	k <sub>3</sub> x10 <sup>3</sup>
1 2	1.35 1.36	3.15 2.71	0.58
2 3 4 5	1.51 2.14 2.15	3.11 4.76 4.97	0.52 1.20 1.32

Arrhenius equation, plots of log k vs. 1/T were prepared (Figures 3.1 and 3.2). In this case each plot gave two lines of different slopes. In the high temperature region (350-400°C.), the activation energy was of the order of 2 kcal./gm-mole, where as in the lower temperature region (310-350°C.) the activation energy was 20+2 kcal./gm-mole. Moreover, it may be seen from Table - 3.2 that the activation energies for all the three steps are equal, as reported by Hammar (4).

The significance of the two activation energies is discussed in Chapter 5.

# 3.6 ACCURACY OF ESTIMATED CONSTANTS

The accuracy of the estimated constant has been checked as follows:

(i) Using the rate constants in Tables - 3.2 and 3.3 the total benzene disappearance (Equation (3.4)) and the expected conversion to maleic anhydride (Equation (3.5)) have been calculated and found to be in accordance with the experimental results, as shown in Figures B.17 to B.23 of Appendix - B. The average deviation is about 8%. The experimental points in these figures were plotted from the conversion data given in Appendix - A, Tables - A.14 to A.27.

(ii) The time required for reaching the maximum

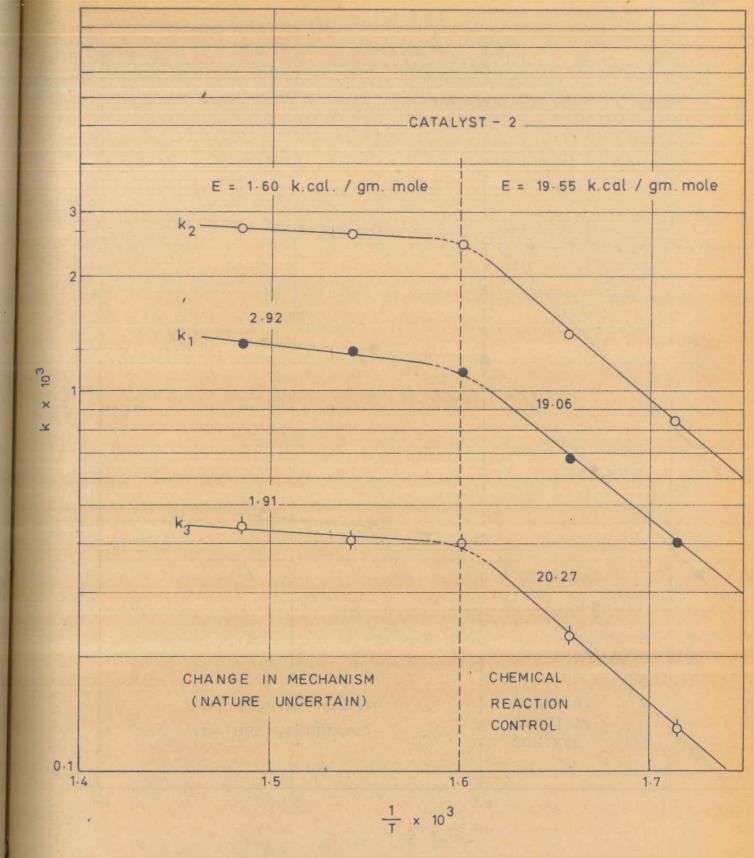


FIG. 3-1. IDENTIFICATION OF CONTROLLING REGIMES FROM

ARRHENIUS PLOTS FOR CATALYST - 2

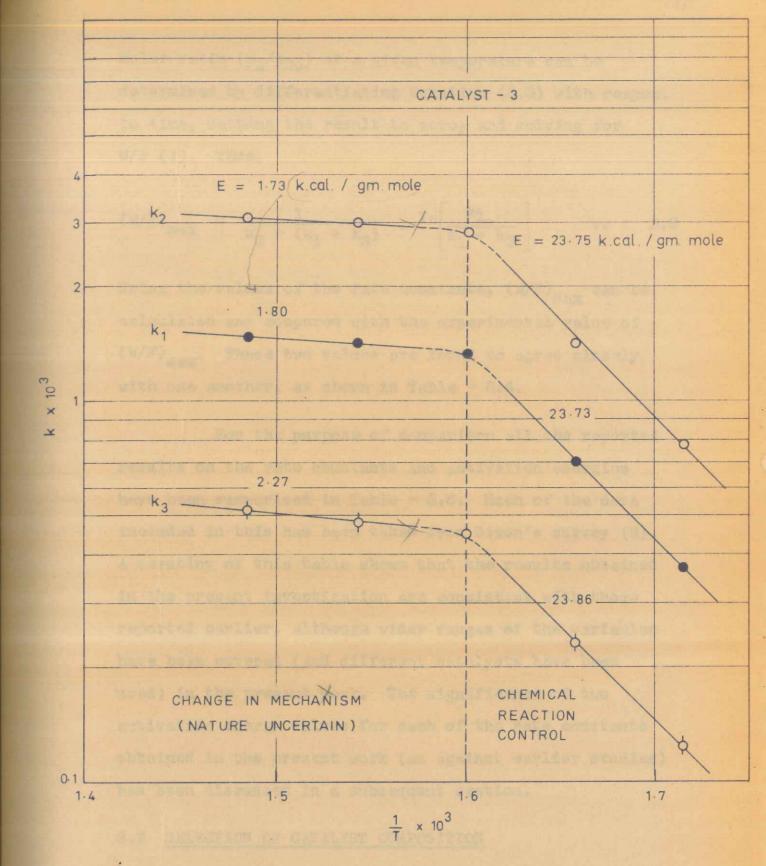


FIG. 3.2. IDENTIFICATION OF CONTROLLING REGIMES FROM

ARRHENIUS PLOTS FOR CATALYST-3

molar ratio  $(p_M/p_{Bo})$  at a given temperature can be determined by differentiating Equation (3.5) with respect to time, setting the result to zero, and solving for W/F (1). Thus,

$$(W/F)_{\text{max}} = \frac{1}{k_2 - (k_1 + k_3)} = \ln \left[ \frac{k_1}{k_1 + k_3} \right] \dots 3.8$$

Using the values of the rate constants, (W/F)<sub>max</sub> can be calculated and compared with the experimental value of (W/F)<sub>max</sub>. These two values are found to agree closely with one another, as shown in Table - 3.4.

For the purpose of comparison all the reported results on the rate constants and activation energies have been summarised in Table - 3.5. Much of the data included in this has been taken from Dixon's survey (2). A scrutiny of this table shows that the results obtained in the present investigation are consistent with those reported earlier, although wider ranges of the variables have been covered (and different catalysts have been used) in the present work. The significance of two activation energy values for each of the rate constants obtained in the present work (as against earlier studies) has been discussed in a subsequent section.

### 3.7 SELECTION OF CATALYST COMPOSITION

The optimum catalyst is one which yields a high

Table - 3.4

Test of rate constants by evaluation of (W/F)<sub>max</sub> from

Equation (3.8)

Catalyst	Temperature oc.	(W/F)max Exptl.	(W/F) <sub>max</sub>	Error,
1	400	255	292	-14.5
122222333345	310			
2	330	-		-
2	350	313	320	- 2.2
2	375	300	309	- 3.0
2	400	305	312	- 2.3
3	310	-		
3	330		**	
3	350	260	290	-11.5
3	375	265	270	+ 5.7
3	400	260	273	- 5.0
4	400	305	313	- 2.6
5	400	290	315	- 8.6

	PRESENT WOR	V <sub>2</sub> O <sub>5</sub> . MoO <sub>3</sub> on silica gel	310 - 400	4.5 - 14		- of an	Yes (in higher temp	22 ± 2 (in lower temp. range) ~0.75	Adsorption 22 controlled
DATION	DMUCHOVSKY et al.	V2 O5: MoO3 promoted with Ni Na-salts on carborundum	319-377	~ 8.75	status ali sens cara, /	1 0		~ 30	
ON BENZENE OXIDATION	HOLSEN	V <sub>2</sub> O <sub>5</sub> on Al <sub>2</sub> O <sub>3</sub>	325-450	7 - 14	mai-ab	oficial la r	n of mile 1 4 same th	19-20	2-10
KINETIC DATA ON E	MARS AND VAN	V205 · K2504	375	< 6 > 6 < 6 < < < < < < < < < < < < < <		da ma m sii hat ji o mal	ion gold neo wellyb afa annyd phiarable	It was Copening MANON Copening	1 1
SUMMARY OF KI	STEGER	A920 · V205 · Mo03 · A1203	720-530	~ 10 - 20 ~ 170	en (s.e. en vires en bein mu she.	V	Traiting of the state of the st	15 0.7	1.00.1
SUM	HAMMAR	V <sub>2</sub> O <sub>5</sub> · MoO <sub>3</sub> on aluminium	375 - 400	2.5 - 5.0		oda d	Yes	28 ± 4	0.2 - 0.5
	AUTHOR	CATALYST	Temperature range (°C.) Range of partial pressures	(mm. Hg.) a) Benzene b) Oxygen	a) with respect to benzene	oxygen	Dependence of rate on mass transfer	(kcal./gm-mole) Ratio, k <sub>1</sub> /(k <sub>1</sub> + k <sub>3</sub> )	Ratio, k <sub>2</sub> /k <sub>1</sub> Model proposed

proportion (with reference to the total benzene converted) of the desired product and is relatively cheaper than other catalysts. Here the catalyst selection was made by comparing the rate constant values. Thus the catalyst composition which gives a high  $k_1/(k_1+k_3)$  value (indicating a high yield of maleic anhydride) and a low  $k_2/k_1$  value (indicating low decomposition of maleic anhydride) may be considered suitable.

The catalyst parameters studied were the ratio of molybdenum oxide to vanadium oxide and the total concentration of these two oxides on silica gel. It was established from preliminary runs that pure molybdenum oxide gives negligible conversion to maleic anhydride, while pure vanadium oxide leads to a considerable wastage of benzene as oxides of carbon (i.e. low selectivity to maleic anhydride). Thus, with these two limiting values of catalyst composition being unsuitable, three different ratios of molybdenum and vanadium oxides were tried, and the total concentration of the two oxides was also varied. The rate constants, k<sub>1</sub>, k<sub>2</sub> and k<sub>3</sub>, were determined at 400°C. for each of the catalyst compositions selected, and the results are presented in Tables - 3.2 and 3.3.

Plots of  $k_1/(k_1 + k_3)$  and  $k_2/k_1$  as functions of the total oxides content at a fixed ratio of the oxides (vanadium oxide : molybdenum oxide = 1:1) are

shown in Figure 3.3. The experimental results on which this figure is based are given in Appendix - A, Tables - A.1 to A.13. From this plot it is clear that approximately 14% total oxides content is superior to the other compositions tried.

In a subsequent series of runs, the oxides content was fixed at 14% and the ratio of these oxides varied. The experimental data for this series is also given in Tables - A.1 to A.13 of Appendix - A. The variation of  $k_1/(k_1+k_3)$  and  $k_2/k_1$  with total oxides content is shown graphically in Figure 3.4, from which it may be concluded that a ratio of (1:1) is perhaps the most suitable in the oxidation of benzene.

From the discussion presented above it appears that the following composition of the catalyst would be nearly optimum for benzene oxidation.

Catalyst number - 2

Carrier - silica gel

 $(v_2o_5 + Moo_3)$  content - 14%

V205 : MoO3 - 1:1

Catalyst - 3 in which the total concentration of the oxides is the same as in catalyst - 2 but the ratio of vanadium oxide to molybdenum oxide is 1:2

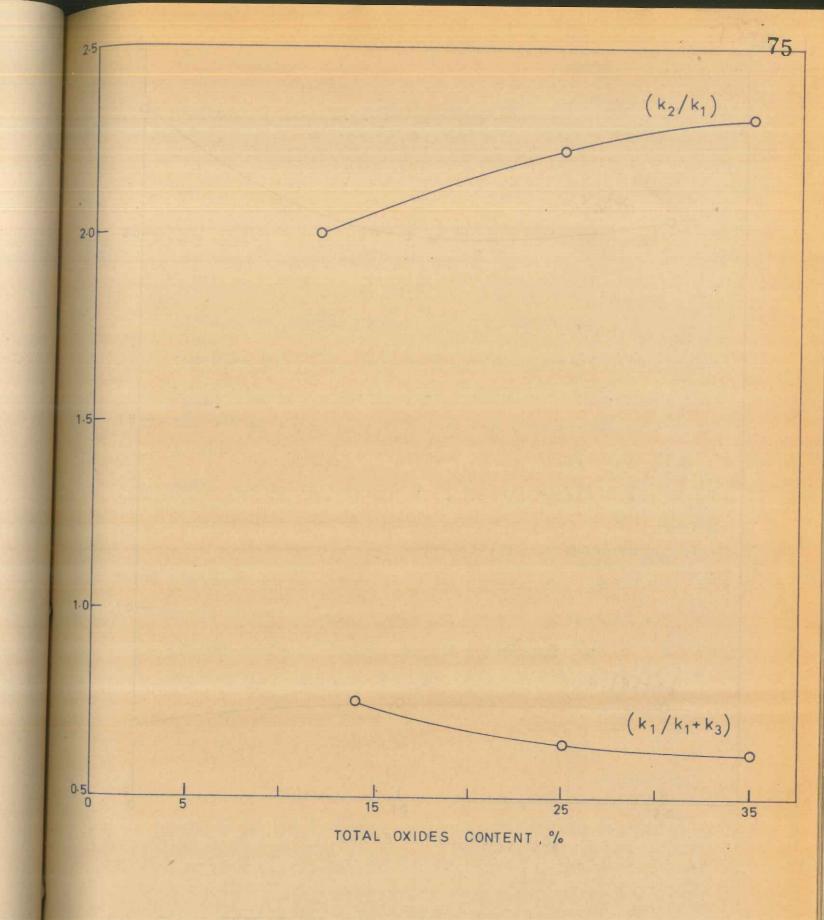


FIG. 3.3. EFFECT OF TOTAL OXIDES CONTENT ON SELECTIVITY

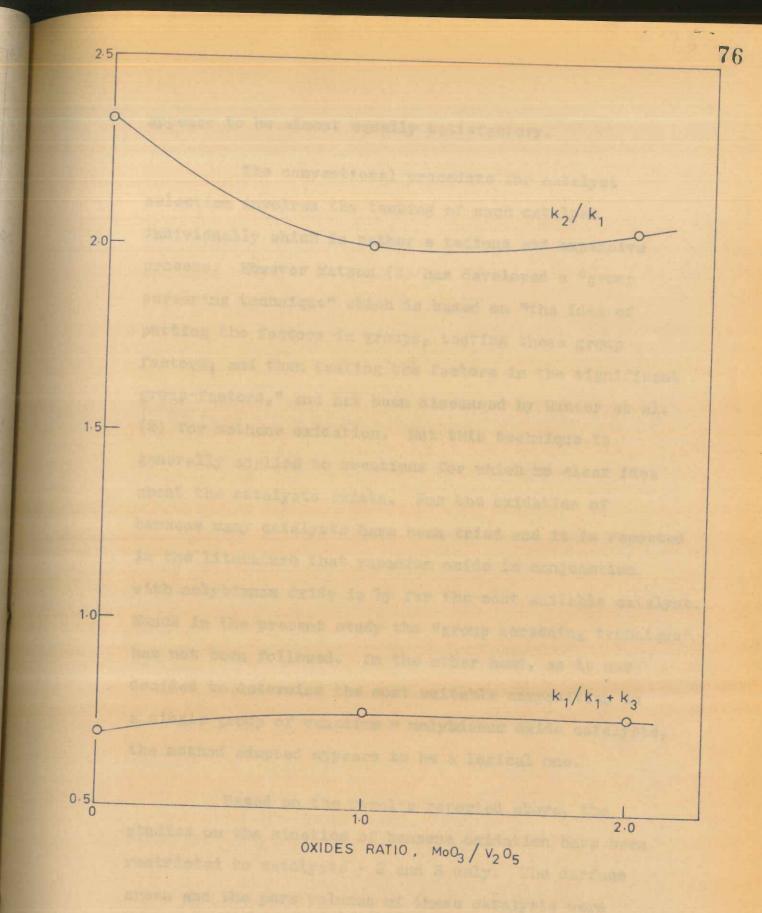


FIG. 3.4. EFFECT OF OXIDES RATIO (MOO3: V205) ON

SELECTIVITY

appears to be almost equally satisfactory.

The conventional procedure for catalyst selection involves the testing of each catalyst individually which is rather a tedious and expensive process. However Watson (6) has developed a "group screening technique" which is based on "the idea of putting the factors in groups, testing these group factors, and then testing the factors in the significant group-factors," and has been discussed by Hunter et al. (5) for methane oxidation. But this technique is generally applied to reactions for which no clear idea about the catalysts exists. For the oxidation of benzene many catalysts have been tried and it is reported in the literature that vanadium oxide in conjunction with molybdenum oxide is by far the most suitable catalyst. Hence in the present study the "group screening technique" has not been followed. On the other hand, as it was decided to determine the most suitable composition in a single group of vanadium - molybdenum oxide catalysts, the method adopted appears to be a logical one.

Based on the results reported above, the studies on the kinetics of benzene oxidation have been restricted to catalysts - 2 and 3 only. The surface areas and the pore volumes of these catalysts were determined by the B.E.T. method and displacement technique respectively, and these values are included in Table - 3.6.

Table - 3.6

Properties of the catalysts selected for kinetic analysis

Catalyst number	Surface area sq.m./gm.	Pore volume ml./ml.
2 3	144 256	0.38

#### References

- Benson, S.W., "The Foundations of Chemical Kinetics," pp. 35, McGraw Hill, New York (1960).
- 2. Dixon, J.K. and Longfield, J.E., "Catalysis," (P.H. Emmett, ed.); Vol. VII, Chap. 3, Reinhold Publishing Corporation, New York (1960).
- Dmuchovsky, B., Freeks, M.C., Pierron, E.D., Munch, R.H. and Zienty, F.B., J. Catalysis, 4, (2), 291 (1965).
- 4. Hammar, C.G.B., Svensk Kem. Tid., 64, 165-76 (1952); Chem. Abst., 46, 8945 (1952).
- 5. Hunter, W.G. and Mezaki, R., Ind. Eng. Chem., 56, 38 (1964).
- 6. Watson, G.S., Technometrics, 3, 371 (1961).
- 7. Yoshida, F., Ramaswami, D. and Hougen, O.A., Am. Inst. Chem. Eng., Convention, Washington, D.C., December 1960.

-- HINELE

Described of sprooch are possible for possible for possible for the enterior of births in admired the twinty for the categories in a second of the atmosphere the categories of the same at a second of the same of the same at a second of the same of the same at a second or categories of the same at a second or categories in the second or categories in the second or categories in a second or categories in a second or categories at a second or categories in a second or categories at a second or categories of the same at a second or categories or categories at a second or categories at a second or categories or categories or categories at a second or categories at

socialists a second in anticomposity that Pinet machine - Transmitted in an anticomposity to machine the - Transmitted in an anticomposity to machine the - Transmitted in an anticomposity to machine the - Transmitted in the state of the production of the contract of

and the pridiction of binario as a smale, and ups ofth

CHAPTER-4

PLAUSIBLE MODELS

#### Chapter 4

#### PLAUSIBLE MODELS

#### 4.1 GENERAL

Two methods of approach are possible for postulating models for the oxidation of benzene (any hydrocarbon). In the first method it is assumed that only two steps are important, and that at steady state the rates of these two steps are equal (i.e. rate of adsorption of oxygen or benzene is equal to rate of reaction on the surface). In the second method the reaction is assumed to be controlled by the slowest step in a series of possible steps which occur during the catalytic reaction. All other steps are so fast as to have reached equilibrium.

while an attempt has been made in the past to postulate a model in accordance with the first method, apparently no attempt has been made to delineate the controlling steps in the three principal reactions occurring during the oxidation of benzene. Furthermore, these models (due to Hinshelwood) are only concerned with the oxidation of benzene as a whole, and not with the individual steps involved in the overall process. The Hinshelwood models are briefly analysed below, after which plausible controlling step models are developed for all the reactions.

#### 4.2 HINSHELWOOD MODELS

Hayashi et al (6) have applied the Hinshelwood reaction mechanism to the oxidation of benzene, assuming:

- (i) oxygen is the only reactant adsorbed on the catalyst surface,
- (ii) the rate of desorption of oxygen from the catalyst surface is negligible,
- (iii) for reaction to occur, organic reactant in the gas phase must strike an adsorbed oxygen,
- (iv) a steady state is established in which the rate of removal of oxygen by chemical reaction equals the rate of adsorption of oxygen.

Equating the rate of adsorption of oxygen to the rate of chemical reaction, the final form of the equation developed (expressed in terms of partial pressures) was

$$r = \frac{k_a k_r p_B p_0}{k_a p_0 + n k_r p_B} .. (4.1)$$

Mars and van Krevelen (16) proposed a similar model for the oxidation of naphthalene. They represented the oxidation scheme according to the following two steps:

- (I) naphthalene + oxidized catalyst products + reduced catalyst
- (II) reduced catalyst + oxygen \_\_\_\_ oxidized catalyst

The rate equation developed by them can be shown to be identical in form with Equation (4.1), based on the Hinshelwood model.

# 4.2.1. Applicability of the Hinshelwood model

If the Hinshelwood mechanism were to hold good, the adsorption constant  $k_a$  should have the same value for all hydrocarbon oxidations at the same temperature for a given catalyst, since they all would have one common step -- adsorption of oxygen on the catalyst surface. However, it may be noted from Table - 4.1 that the value of the adsorption constant depends on the hydrocarbon used (6). This would indicate that the mechanism suggested by Hayashi et al (6) and Mars and van Krevelen (16) is not of general applicability. Moreover, the present data also do not uphold the mechanism, as shown below:

Equation (4.1) may be rewritten in the form

$$\frac{p_{B}p_{0}}{r} = \frac{p_{0}}{k_{r}} + \frac{1}{k_{a}} np_{B} \qquad (4.2)$$

Table - 4.1

Reported specific adsorption constants at 324°C.(6)

Catalyst number	Hydrocarbon used	k <sub>a</sub> x10 <sup>5</sup>
11	Benzene Toluene Naphthalene	0.511 3.270 4.550
12	Benzene Toluene Naphthalene	0.650 4.340 6.010

Thus, a plot of  $\frac{p_B p_0}{r}$  vs.  $np_B$  should give a straight line with slope =  $1/k_a$  and intercept =  $p_0/k_r$ , considering  $p_0$  to be nearly constant.

However, in the present work, the above plot yields a curve and not a straight line as expected, indicating that the data do not uphold this mechanism (oxygen adsorption). This was found to be true at all the temperatures for both the catalysts. Representative plots are shown in Figures 4.1 and 4.2.

# 4.2.2 Proposed (modified Hinshelwood) model

According to Bretton (3), initially the hydrocarbon is adsorbed over the catalyst surface with the abstraction of hydrogen to form a radical. Then the oxygen from the gas phase strikes over it and the chemical reaction proceeds through the formation and destruction of peroxy radicals.

Based on Bretton's postulates (3), a rate equation similar to that suggested by Hayashi et al (6) and Mars and van Krevelen (4) (for naphthalene) can be developed with the following assumptions:

(i) benzene is the only reactant adsorbed on the catalyst surface,

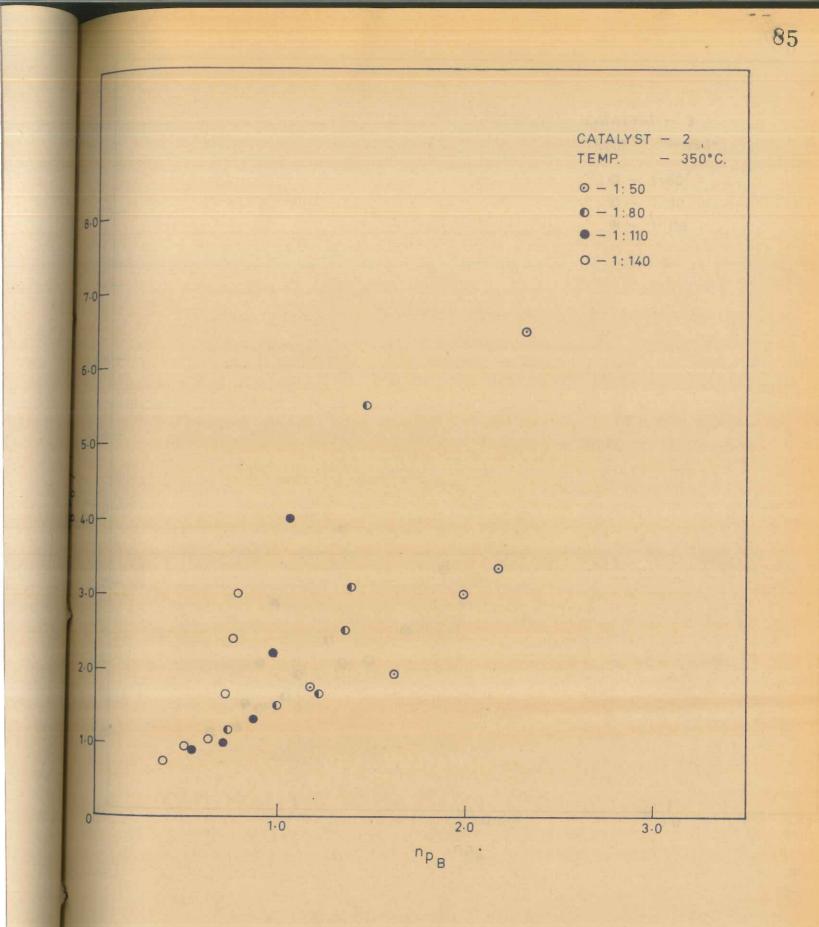


FIG. 4.1. HINSHELWOOD MODEL PLOT - OXYGEN ADSORBED

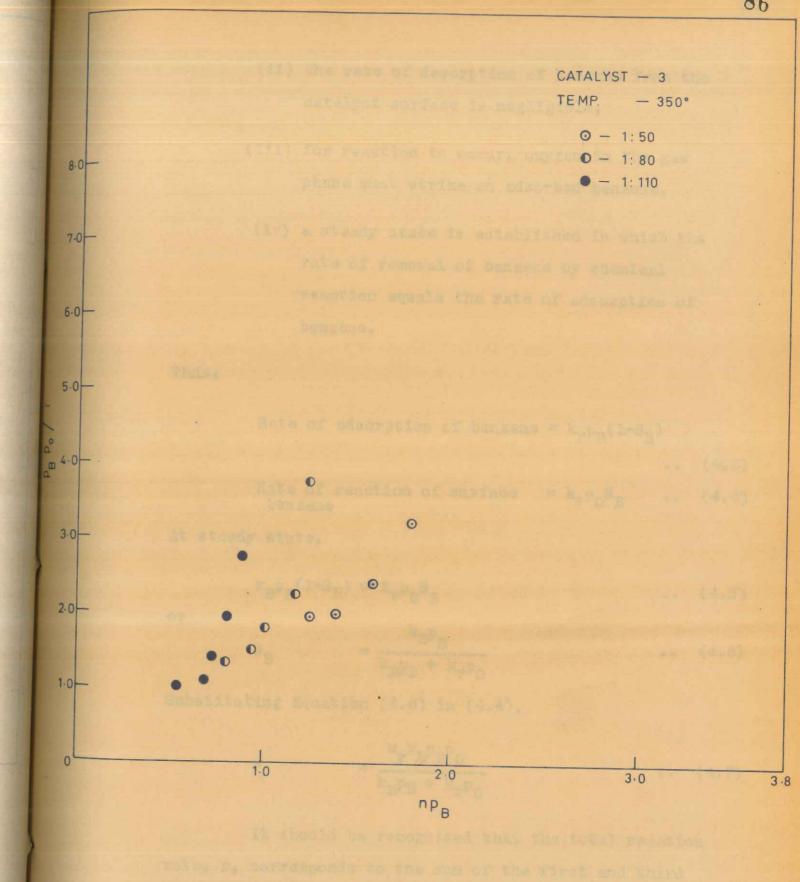


FIG. 4.2. HINSHELWOOD MODEL PLOT - OXYGEN ADSORBED

- (ii) the rate of desorption of benzene from the catalyst surface is negligible,
- (iii) for reaction to occur, oxygen in the gas phase must strike an adsorbed benzene,
- (iv) a steady state is established in which the rate of removal of benzene by chemical reaction equals the rate of adsorption of benzene.

Thus:

Rate of adsorption of benzene = 
$$k_B p_B (1-S_B)$$
.. (4.3)

At steady state,

$$k_B p_B (1-S_B) = k_r p_0 S_B$$
 .. (4.5)

or

$$s_B = \frac{k_B p_B}{k_B p_B + k_P p_O}$$
 .. (4.6)

Substituting Equation (4.6) in (4.4),

$$r = \frac{k_r k_B p_B p_0}{k_B p_B + k_r p_0} (4.7)$$

It should be recognised that the total reaction rate, r, corresponds to the sum of the first and third steps of the reaction scheme used, i.e.,  $r = (r_1 + r_3)$ 

(rate of total benzene conversion).

## 4.2.3 Test of proposed model

Equation (4.6) may be rewritten as,

$$\frac{p_{B}p_{O}}{r} = \frac{1}{k_{r}} p_{B} + \frac{p_{O}}{k_{B}} \qquad (4.8)$$

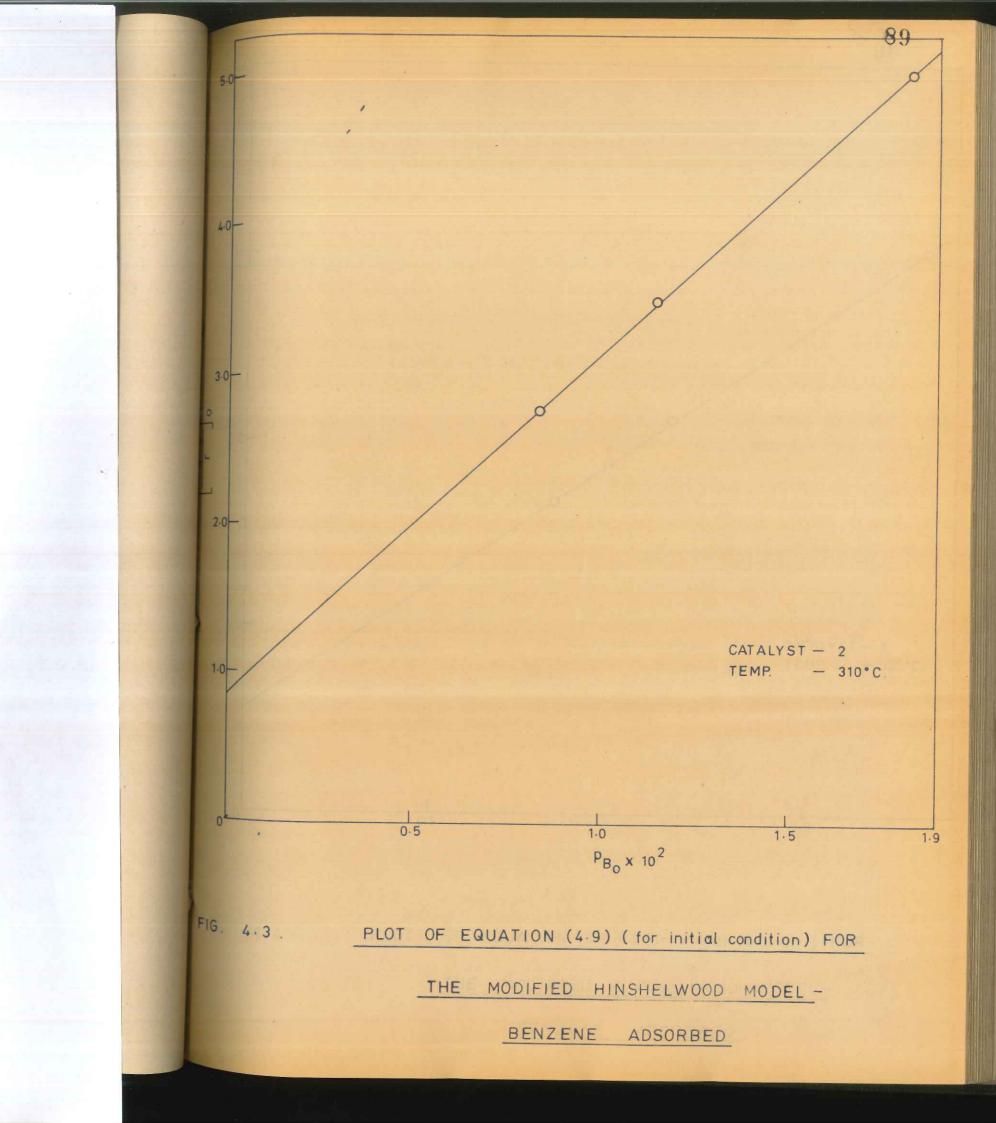
A plot of  $\frac{p_B p_0}{r}$  vs.  $p_B$  should give a straight line with  $1/k_r$  as slope and  $p_0/k_B$  as intercept, considering  $p_0$  to be nearly constant.

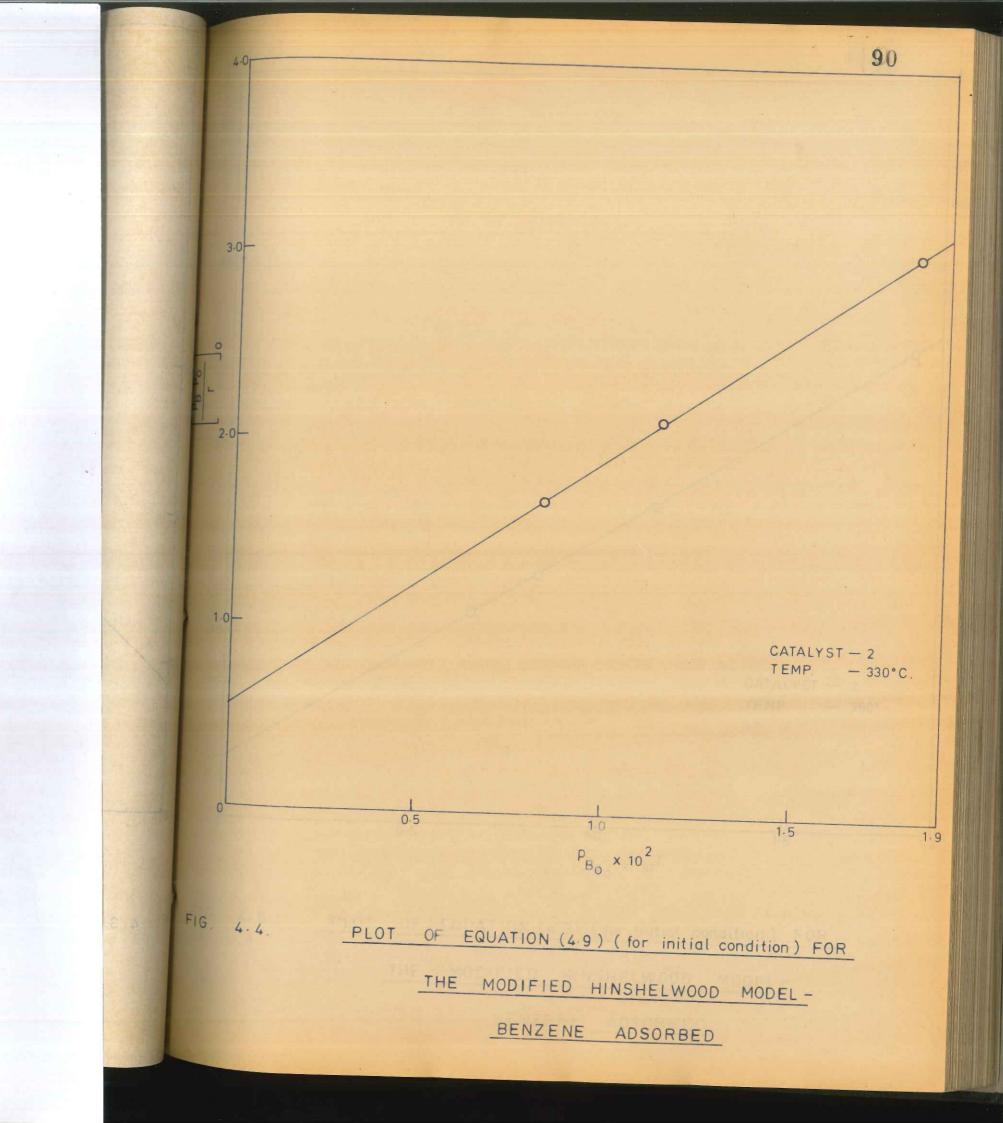
However in the present case, the above plot yields a straight line for the initial conditions only (i.e., W/F = 0), the corresponding equation being

$$\left(\frac{\mathbf{p}_{\mathbf{B}}\mathbf{p}_{\mathbf{0}}}{\mathbf{r}}\right)_{\mathbf{0}} = \frac{1}{\mathbf{k}_{\mathbf{r}\mathbf{0}}} \mathbf{p}_{\mathbf{B}\mathbf{0}} + \frac{\mathbf{p}_{\mathbf{0}}}{\mathbf{k}_{\mathbf{B}}} \dots (4.9)$$

Plots of this equation are presented in Figures 4.3 to 4.8 for both the catalysts. When data point outside the initial conditions are included a straight line is not obtained, as can be seen from the representative plots shown in Figures 4.9 and 4.10.

The fact that the proposed model holds good for the initial conditions, and fails completely as the conversion rises, could be due to a change in the order of the reaction with the formation of oxidation products.





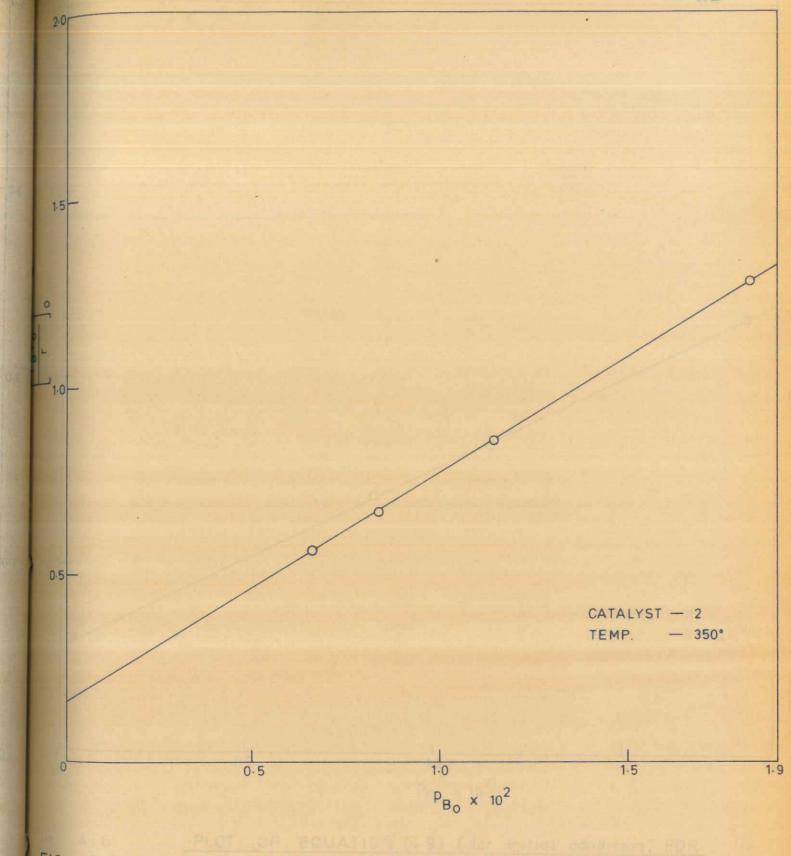
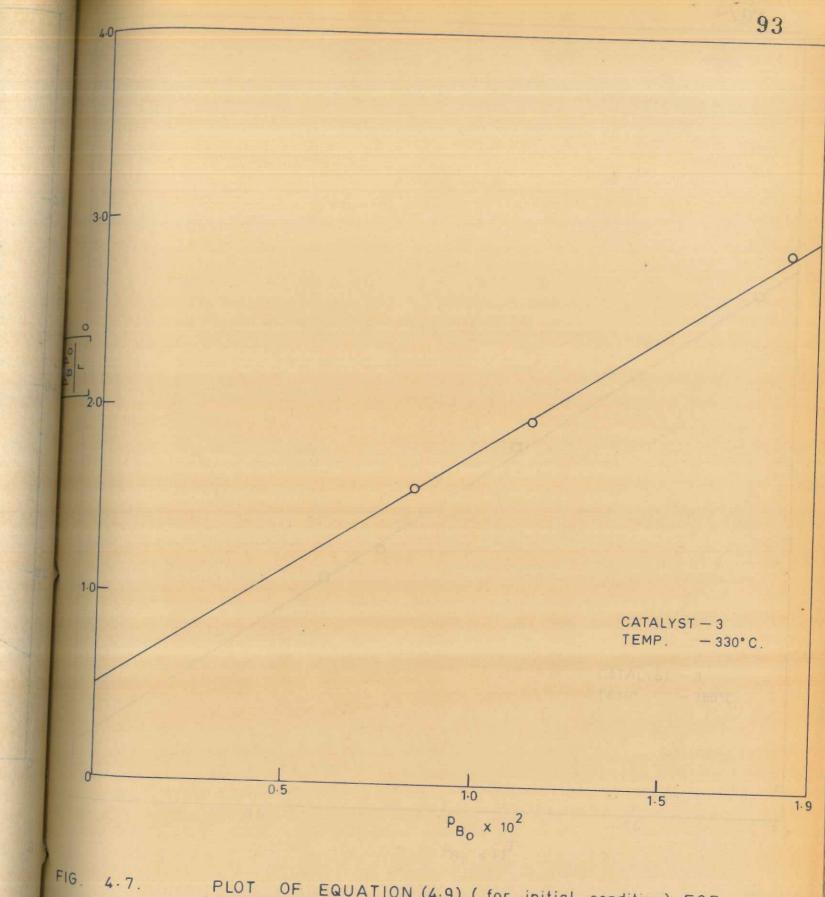


FIG. 4.5. PLOT OF EQUATION (4.9) (for initial condition) FOR

THE MODIFIED HINSHELWOOD MODEL -

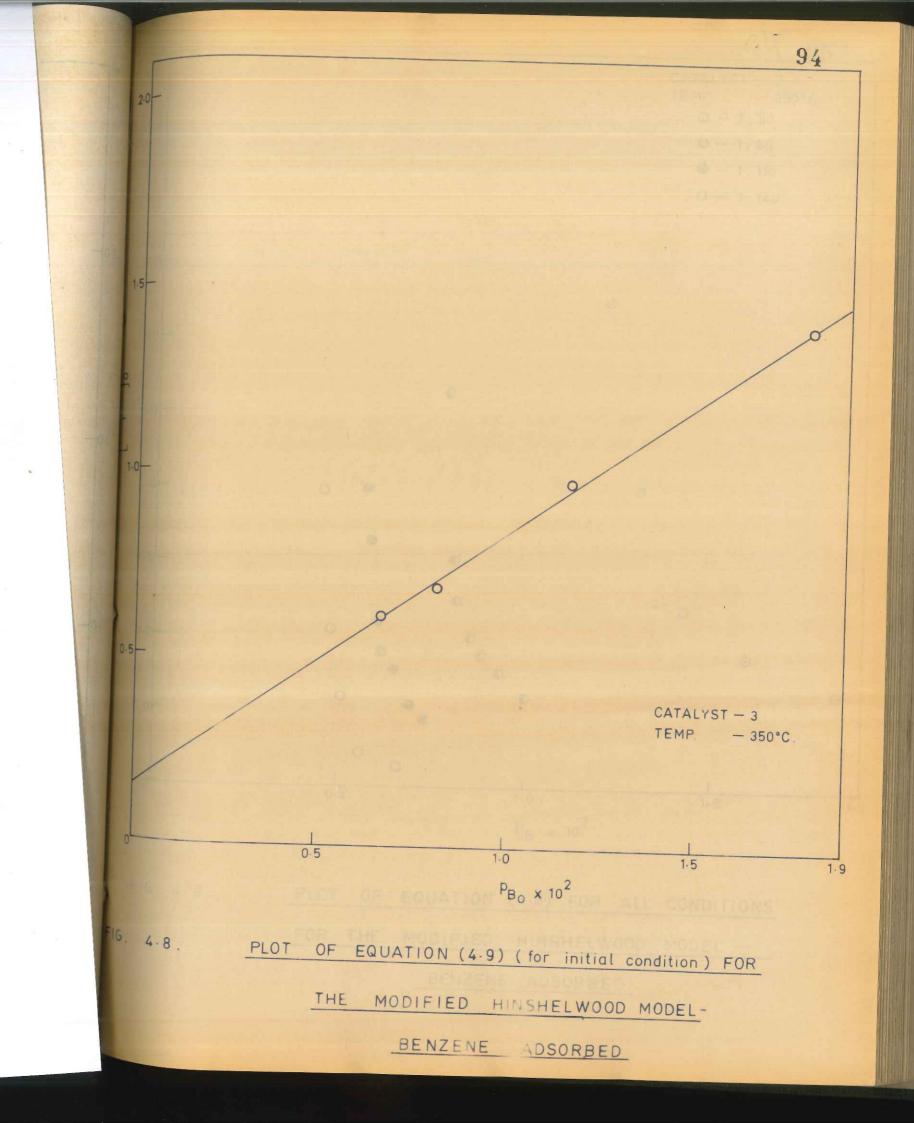
BENZENE ADSORBED



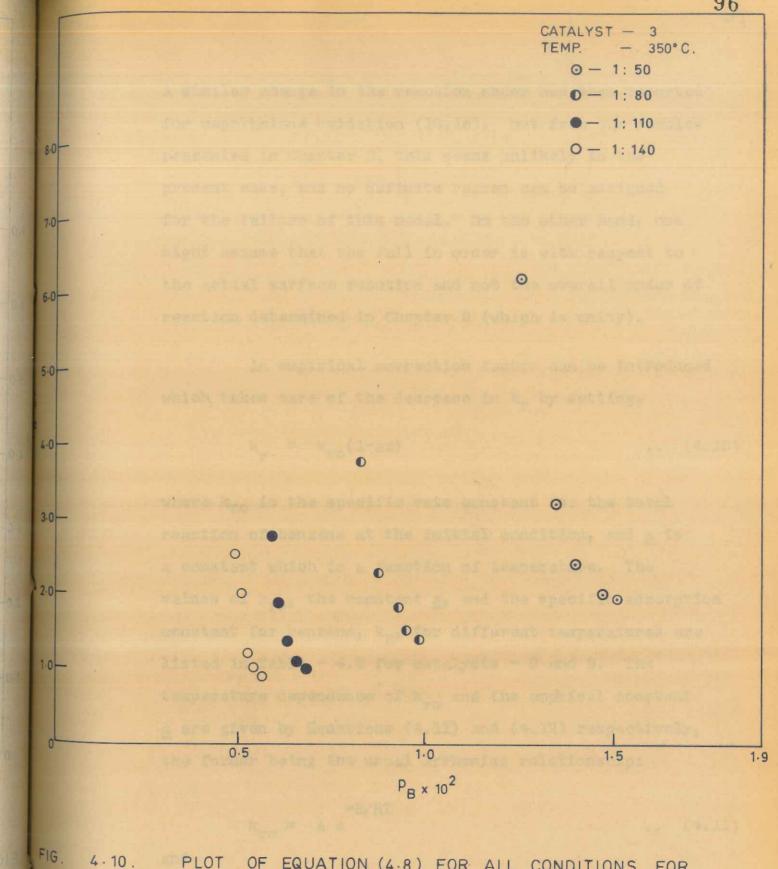
PLOT OF EQUATION (4.9) ( for initial condition) FOR

THE MODIFIED HINSHELWOOD MODEL-

BENZENE ADSORBED



BENZENE ADSORBED



4 - 10 . PLOT OF EQUATION (4.8) FOR ALL CONDITIONS FOR THE MODIFIED HINSHELWOOD MODEL -BENZENE ADSORBED

A similar change in the reaction order has been reported for naphthalene oxidation (10,16). But from the results presented in Chapter 3, this seems unlikely in the present case, and no definite reason can be assigned for the failure of this model. On the other hand, one might assume that the fall in order is with respect to the actual surface reaction and not the overall order of reaction determined in Chapter 3 (which is unity).

An empirical correction factor can be introduced which takes care of the decrease in k<sub>r</sub> by setting,

$$k_r = k_{ro}(1-ax)$$
 .. (4.10)

where  $k_{ro}$  is the specific rate constant for the total reaction of benzene at the initial condition, and a is a constant which is a function of temperature. The values of  $k_{ro}$ , the constant a, and the specific adsorption constant for benzene,  $k_{B}$ , for different temperatures are listed in Table - 4.2 for catalysts - 2 and 3. The temperature dependence of  $k_{ro}$  and the empirical constant a are given by Equations (4.11) and (4.12) respectively, the former being the usual Arrhenius relationship:

$$k_{ro} = A e$$
 .. (4.11)

and

$$\mathbf{a} = \alpha \mathbf{T}^{\beta} \qquad (4.12)$$

Table - 4.2

Values of the specific rate constant k<sub>ro</sub> (for the initial condition) and the specific adsorption constant k<sub>B</sub> at different temperatures for the modified Hinshelwood model\*

Catalyst number	Temperature oc.	k <sub>ro</sub> x10 <sup>2</sup>	a	k <sub>B</sub>	
2	310 330 350	0.448 0.741 1.538	10.60 4.76 2.63	0.230 0.345 1.762	
3	310 330 350	0.515 0.781 1.450	11.10 4.77 2.99	0.179 0.387 1.283	who Table

<sup>\*</sup>As stated in the text, these are for total benzene disappearance.

The graphical representation of Equations (4.11) and (4.12) appears in Figures 4.11, 4.12 and 4.13, 4.14 respectively, and the values of the constants A, E,  $\alpha$  and  $\beta$  are listed in Table - 4.3 for both the catalysts.

As in the case of the activation energies for the first-order rate equations developed in Chapter 3, two distinct regions of the activation energy values were observed. But Figures 4.11 and 4.12 show the results in the lower temperature range only (310-330°C.). The correlation for the higher temperature range (350-400°C.) was equally satisfactory and the corresponding values of A, E,  $\alpha$  and  $\beta$  are also included in Table - 4.3.

Equations (4.8) and (4.10) were verified by back calculating the rates and comparing them with the observed values. The results for the low temperature range are shown in Figures 4.15 and 4.16. Representative data for the two catalysts appear in Tables - A.30 and A.31 of Appendix - A. The average error is 8-10%.

# 4.3 PROBABLE CONTROLLING MECHANISMS

## 4.3.1 General

the

Two methods of determining controlling mechanisms are available. One is due to Hougen-Watson (9) and the other due to Balandin and his coworkers (1,2). Both

Table - 4.3

Constants of Equations (4.11) and (4.12) for the modified Hinshelwood model

Catalyst	Constant	Temp. range		
number		310 - 350°C.	350 - 400°C	
	A	9.92x10 <sup>5</sup>	7.08x10 <sup>-2</sup>	
	E	-22.39	-1.90	
2	α	6.24x10 <sup>39</sup>	6.24x10 <sup>39</sup>	
	β	-14.02	-14.02	
	A	1.06x10 <sup>5</sup>	3.35x10 <sup>-1</sup>	
	E	-19.73	-6.67	
3	α	6.84x10 <sup>40</sup>	6.84x10 <sup>40</sup>	
	β	-14.39	-14.39	

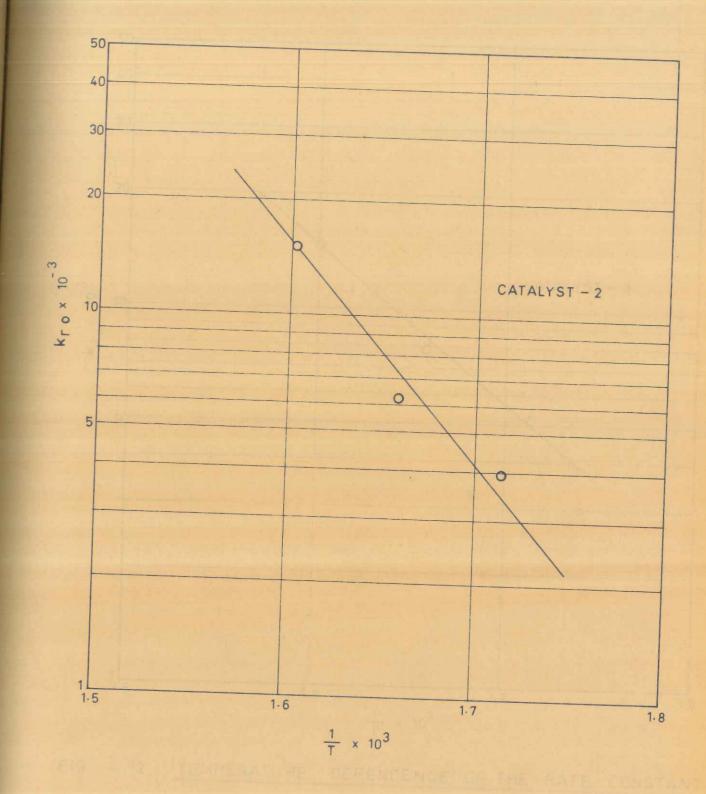


FIG 4.11. TEMPERATURE DEPENDENCE OF THE RATE CONSTANT

kro AT INITIAL CONDITION FOR THE MODIFIED

HINSHELWOOD MODEL

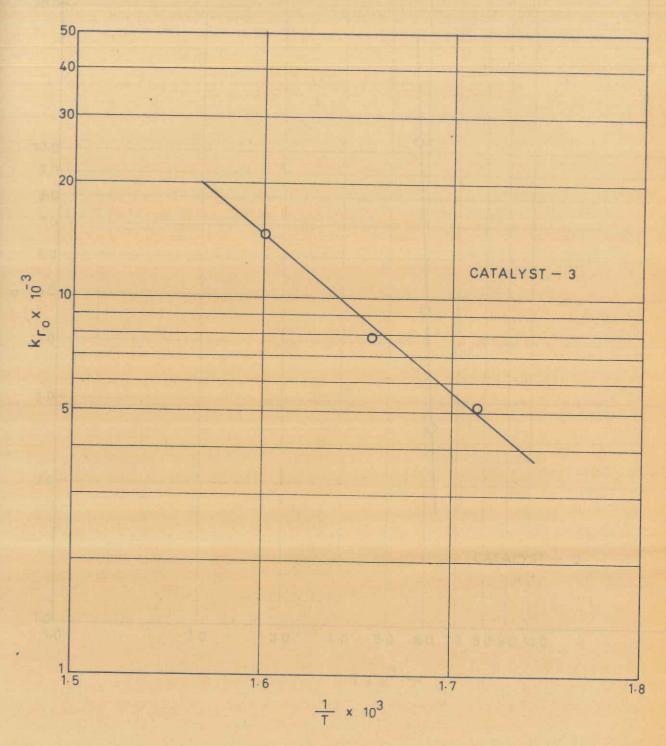


FIG. 4-12. TEMPERATURE DEPENDENCE OF THE RATE CONSTANT

kro AT INITIAL CONDITION FOR THE MODIFIED

HINSHELWOOD MODEL

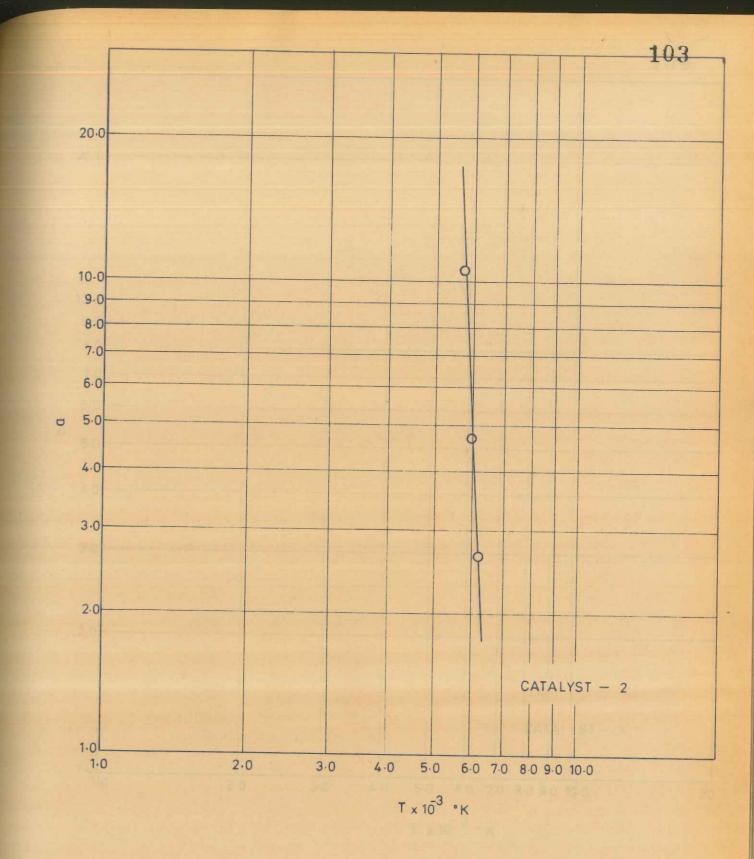


FIG. 4.13. EMPIRICAL CORRELATION OF CONSTANT 'a' WITH

TEMPERATURE FOR THE MODIFIED HINSHELWOOD

MODEL FOR CATALYST-2

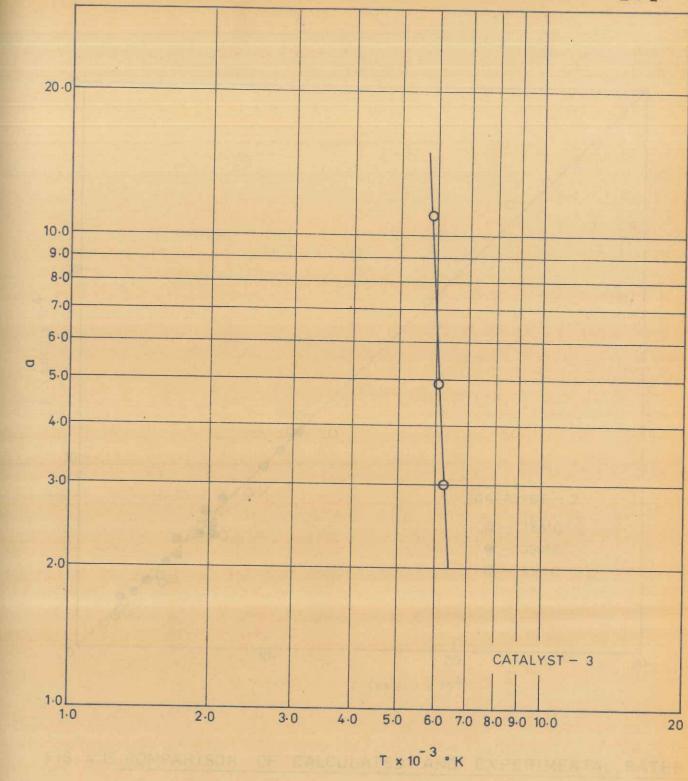


FIG. 4-14. EMPIRICAL CORRELATION OF CONSTANT 'a' WITH

TEMPERATURE FOR MODIFIED HINSHELWOOD

MODEL FOR CATALYST-3

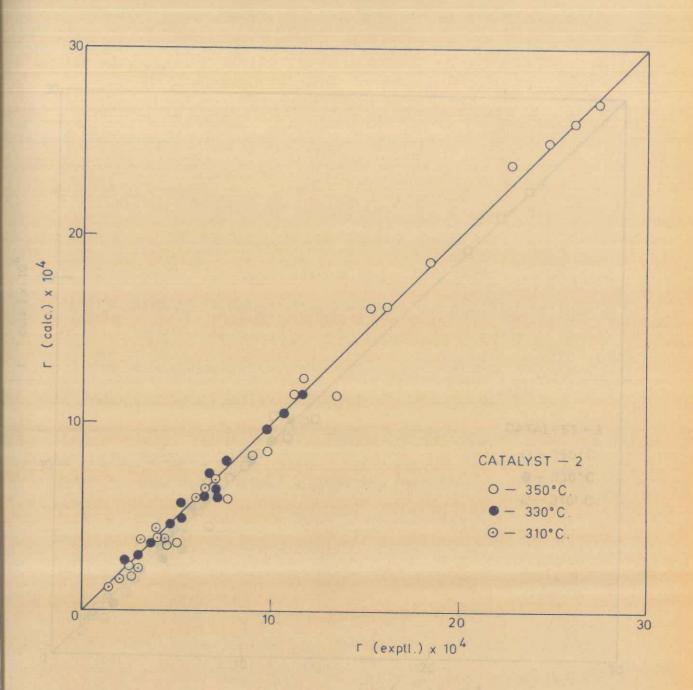


FIG. 4-15. COMPARISON OF CALCULATED AND EXPERIMENTAL RATES

FOR THE MODIFIED HINSHELWOOD MODEL

[Equations (4-8) & (4-10)]

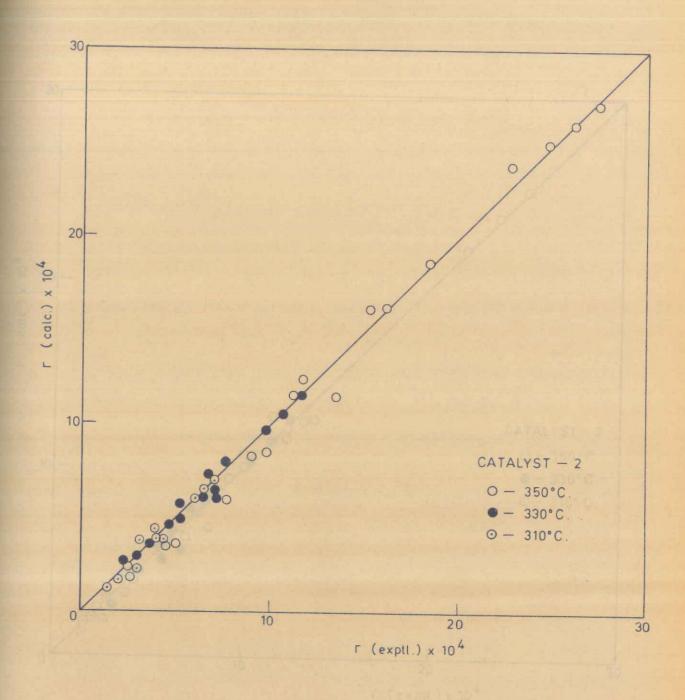


FIG. 4-15. COMPARISON OF CALCULATED AND EXPERIMENTAL RATES

FOR THE MODIFIED HINSHELWOOD MODEL

Equations (4.8) & (4.10)

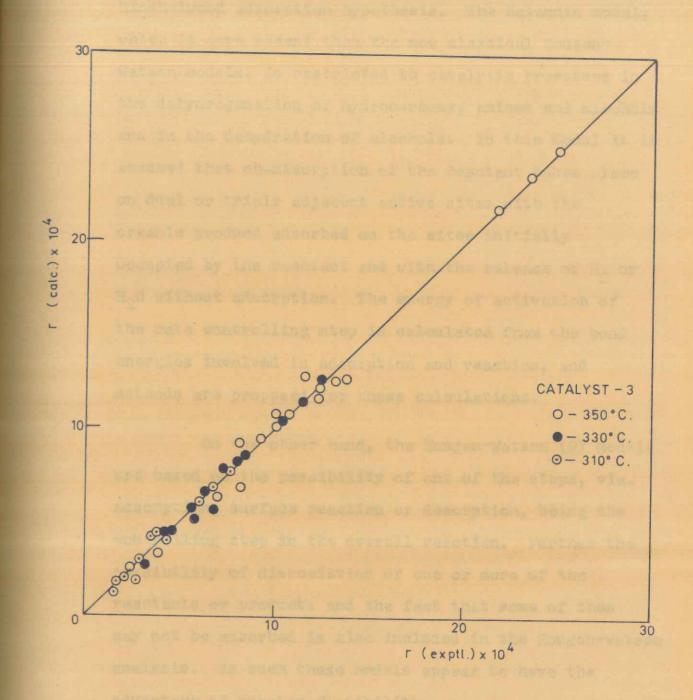


FIG. 4.16. COMPARISON OF CALCULATED AND EXPERIMENTAL

RATES FOR THE MODIFIED HINSHELWOOD MODEL

[ Equations (4.8) & (4.10) ]

Hinshelwood adsorption hypothesis. The Balandin model, which is more recent than the now classical Hougen-Watson models, is restricted to catalytic processes in the dehydrogenation of hydrocarbons, amines and alcohols and in the dehydration of alcohols. In this model it is assumed that chemisorption of the reactant takes place on dual or triple adjacent active sites with the organic product adsorbed on the sites initially occupied by the reactant and with the release of H<sub>2</sub> or H<sub>2</sub>O without adsorption. The energy of activation of the rate controlling step is calculated from the bond energies involved in adsorption and reaction, and methods are proposed for these calculations.

On the other hand, the Hougen-Watson (9) models are based on the possibility of one of the steps, viz. adsorption, surface reaction or desorption, being the controlling step in the overall reaction. Further the possibility of dissociation of one or more of the reactants or products and the fact that some of them may not be adsorbed is also included in the Hougen-Watson analysis. As such these models appear to have the advantage of greater flexibility.

In the original Hougen-Watson method the rate and adsorption constants were determined by linearising the equation which, for a reaction involving two reactants

A and B (and for chemical reaction controlling), is usually of the form:

$$\mathbf{r} = \Delta k p_{\mathbf{A}} p_{\mathbf{B}} \qquad (4.13)$$

where

$$\Delta = \frac{1}{(1 + \leq p_i K_i)^n} \qquad (4.14)$$

p<sub>i</sub> = partial pressure of the ith component,

and

K<sub>i</sub> = adsorption constant constant of the ith
 component.

The form of the denominator in the  $\Delta$  expression would be different for adsorption and desorption models. The term,  $\Delta$ , represents the effect of adsorption on the chemical reaction.

In their studies on the dehydrogenation of butane and butenes over chrome-alumina catalyst, Happel et al (5) have extended the theory of Horiuti (7) and showed that the term  $\Delta$  can be regarded purely as an empirical function of the partial pressures. According to them the rate equation can be expressed as,

$$\mathbf{r} = \Delta' \mathbf{k}_{\mathbf{S}} \mathbf{p}_{\mathbf{A}} \mathbf{p}_{\mathbf{B}} \cdots (4.15)$$

where

γ = stoichiometric number, which is defined as the number of times an elementary

step in a sequence occurs during a single occurrence of the overall reaction as represented by the overall chemical equation,

and

$$\Delta' = \frac{1}{(1 + \leq p_1^m K_1)^n} \qquad .. \quad (4.16)$$

If  $\gamma$  and m are both assumed to be unity, Equation (4.15) becomes identical with the Hougen-Watson equation for surface reaction. With this restriction the expression for  $\Delta$  given in Equation (4.14) can be extended to several models, and based on a statistical analysis of the data a suitable model then selected.

The evaluation of  $\gamma$  is often quite difficult, and a procedure has been outlined by Horiuti et al (8) which assumes that  $\gamma$  for the overall reaction is the same as that for the controlling step in the series of elementary steps involved. Thus the exponent  $1/\gamma$  in Equation (4.15) represents the reciprocal of the stoichiometric number of the rate controlling step. Considering a simple reaction of the type,

$$A + 2B \longrightarrow 3C,$$
 (4.17)

the various elementary steps in accordance with the Hougen-Watson model and the corresponding values of stoichiometric numbers are given below:

step	stoichiometric number
A + 1 Al (where 1 is an active site)	1
B + 1 -> B1	2
Al + Bl -> Cl	3
C1 C+1	3

It can be seen that the rate controlling elementary step is probably the adsorption of A. But this can be stated with certainty only after fitting up model equations for different steps. Thus there is no need a priori to eliminate  $\gamma$  from the equations, and it should be possible to estimate  $\gamma$  along with the other constants involved in the  $\Delta$  expression from suitable linear or non-linear procedures.

In the present reaction system the determination of  $\gamma$  by the simple method described for reaction (4.17) is not possible since the reaction is complex and several products are involved. Thus one could include  $\gamma$  in the usual Hougen-Watson equation and estimate its value as mentioned above, or assume it to be unity as has been done in the original Hougen-Watson method and which has been shown to be largely true by the successful application of these models. It is significant that a value of unity for  $\gamma$  gave reasonably satisfactory results for the dehydrogenation of butane and butenes over

chrome-alumina catalyst (5) (although from statistical methods a value of between 1 and 2 was found to be the best).

In the present study  $\gamma$  was assumed to be unity and the constants of the Hougen-Watson models estimated by the usual linearisation methods. In the last few years several non-linear methods of estimating the Hougen-Watson constants have been reported, principally by Lapidus (15) and Watson and collaborators (11,12,13,14). In these methods the restraint imposed by linearising the models is removed and more meaningful constants are obtained. However, since the non-linear methods are best applicable to integrated rate equations or to rate data obtained in differential reactor, their use is not called for in the present case where the rates have been determined by an indirect procedure as follows.

The reaction rates for each of the three steps were calculated from the values of k<sub>1</sub>, k<sub>2</sub> and k<sub>3</sub> given in Tables - 3.2 and 3.3 and from the partial pressures of benzene, oxygen, maleic anhydride, carbon dioxide and water at different residence times (Tables - A.1 to A.13 of Appendix - A). Then it was a matter of fitting the data in accordance with the linearised Hougen-Watson procedure. For the present complex reaction this method of obtaining individual rates was considered superior to

that based on a material balance of the rates of formation or disappearance of reaction components.

# 4.3.2 Controlling mechanism for the three reaction steps Reaction step 1

The various mechanisms considered and the corresponding equations for surface reaction controlling are given below (in all these equations the possibility of a triple site mechanism was not considered and therefore it was throughout assumed that one or more of the reactants or products was not adsorbed):

- (I) Surface reaction controlling; water not adsorbed.
- (a) When reaction occurs between adsorbed benzene and adsorbed oxygen,

$$r_1 = \frac{k_{1s}p_Bp_0}{(1 + K_Bp_B + K_0p_0 + K_Mp_M + K_Cp_C)^2} \dots (4.18)$$

(b) When reaction occurs between adsorbed benzene and oxygen in the gas phase,

$$r_1 = \frac{k_{1s}p_B}{(1 + K_Bp_B + K_Mp_M + K_Cp_C)^2}$$
 .. (4.19)

(c) When reaction occurs between benzene in gas phase and adsorbed oxygen,

$$r_1 = \frac{k_{1s}p_0}{(1 + K_0p_0 + K_Mp_M + K_Cp_C)^2}$$
 .. (4.20)

- (II) Surface reaction controlling; carbon dioxide not adsorbed.
- (a) When reaction occurs between adsorbed benzene and adsorbed oxygen,

$$r_1 = \frac{k_{1s}p_Bp_0}{(1 + k_Bp_B + k_0p_0 + k_Mp_M + k_Wp_W)^2} .. (4.21)$$

(b) When reaction occurs between adsorbed benzene and oxygen in gas phase,

$$r_{1} = \frac{k_{1s}p_{B}}{(1 + k_{B}p_{B} + k_{M}p_{M} + k_{W}p_{W})^{2}} \qquad (4.22)$$

(c) When reaction occurs between benzene in gas phase and adsorbed oxygen,

$$r_1 = \frac{k_{1s}p_0}{(1 + K_0p_0 + K_Mp_M + K_Wp_W)^2}$$
 .. (4.23)

(III) Surface reaction controlling; maleic anhydride not

adsorbed.

(a) When reaction occurs between adsorbed benzene and adsorbed oxygen,

$$r_1 = \frac{k_{1s}p_Bp_0}{(1 + k_Bp_B + k_0p_0 + k_Cp_C + k_Wp_W)^2} .. (4.24)$$

(b) When reaction occurs between adsorbed benzene and oxygen in gas phase,

$$r_1 = \frac{k_{1s}p_B}{(1 + K_Bp_B + K_Cp_C + K_Wp_W)^2}$$
 .. (4.25)

(c) When reaction occurs between benzene in gas phase and adsorbed oxygen,

$$r_1 = \frac{{^k_{1s}}^p_0}{(1 + K_0 p_0 + K_C p_C + K_W p_W)^2} \qquad .. \qquad (4.26)$$

(IV) Surface reaction controlling; carbon dioxide and water not adsorbed.

(a) When reaction occurs between adsorbed benzene and adsorbed oxygen,

$$r_1 = \frac{k_{1s}p_Bp_0}{(1 + k_Bp_B + k_0p_0 + k_Mp_M)^2}$$
 (4.27)

(b) When reaction occurs between adsorbed benzene and oxygen in gas phase,

$$r_1 = \frac{k_{1s}p_B}{(1 + K_Bp_B + K_Mp_M)}$$
 .. (4.28)

(c) When reaction occurs between benzene in gas phase and adsorbed oxygen,

$$r_1 = \frac{k_{1s}p_0}{(1 + K_0 p_0 + K_M p_M)}$$
 (4.29)

- (V) Surface reaction controlling; carbon dioxide and maleic anhydride not adsorbed.
- (a) When reaction occurs between adsorbed benzene and adsorbed oxygen,

$$r_1 = \frac{k_{1s}p_Bp_0}{(1 + K_Bp_B + K_0p_0 + K_Wp_W)^2}$$
 .. (4.30)

(b) When reaction occurs between adsorbed benzene and oxygen in gas phase,

$$r_1 = \frac{k_{1s}p_B}{(1 + K_Bp_B + K_Wp_W)}$$
 (4.31)

(c) When reaction occurs between benzene in gas phase and adsorbed oxygen,

$$r_1 = \frac{k_{1s}p_0}{(1 + K_0p_0 + K_Wp_W)} \qquad (4.32)$$

(VI) Surface reaction controlling; maleic anhydride and water not adsorbed.

(a) When reaction occurs between adsorbed benzene and adsorbed oxygen,

$$r_1 = \frac{k_{1s}p_Bp_0}{(1 + K_Bp_B + K_0p_0 + K_Cp_C)^2}$$
 (4.33)

(b) When reaction occurs between adsorbed benzene and oxygen in gas phase,

$$r_1 = \frac{k_{1s}p_B}{(1 + K_Bp_B + K_Cp_C)}$$
 .. (4.34)

(c) When reaction occurs between benzene in gas phase and adsorbed oxygen,

$$r_1 = \frac{k_{1s}p_0}{(1 + K_0p_0 + K_Cp_C)}$$
 (4.35)

None of these equations (4.18) to (4.35) 7 yielded all positive constants.\* Hence none of the mechanisms considered above would be plausible.

As a next step, similar equations were developed for adsorption of reactant controlling and desorption of product controlling, and their validity ascertained.

It was found that for reaction step 1, the acceptable model would be: adsorption of benzene controlling with carbon dioxide and water not adsorbed on the catalyst surface, the reaction occurring between adsorbed benzene and oxygen in the gas phase. The corresponding equation is given by,

$$r_1 = \frac{K_{1s}p_B}{(1 + K_M p_M)}$$
 ... (4.36)

The adsorption mechanism also seems to be indicated by the initial rate plot in accordance with the method of Yang and Hougen (17). In this plot the initial rate is plotted as a function of total pressure or molar

ratio of the reactants in the feed. Representative plots of the initial rate as a function of molar ratio of benzene and air in the feed are shown in Figures 4.17 to 4.19. From the nature of these curves it appears that adsorption of one of the reactants might be the controlling step, a fact borne out by the least square analysis of the data described earlier.

Note: In the reaction models given above the constant appearing in the numerator (the so-called kinetic term) is expressed as a single constant, although it may contain an adsorption constant as in the original Hougen-Watson model. This has been done in accordance with the simplified procedure suggested by Corrigan (4).

# Reaction step 2

An analysis similar to the one carried out for reaction step 1 was also made for this step. Based on this analysis the following model is proposed:

Adsorption of maleic anhydride controlling, with carbon dioxide and water not adsorbed and reaction occurring between adsorbed maleic anhydride and oxygen in the gas phase. The corresponding equation is

ratio of the release in the charles of solar felicity of the initial rate as a function of solar felicity for the fall of the felicity of the felicity for the felicity of the felicity of the felicity of the felicity of the salars of these curves it appears the felicity of the felicity

Months to a separation and the separation (the so-called normalia) is expressed as a single constant, alticogn to an also spital constant as in the criticinal nough water and accel. This has been done in necordance with the single sea along the necordance with the single that procedure started by Corrigin (4).

Resettion aven R

not you deliver was not not reliable absolute on.

no beautiful code bind you show only was I year noticeen to the code of the

arbiteser has bedroom to reter in adiable reduced and resolution of mayon but address minimum states bedroom about an extension at address and antitude antitude antitude and corresponding states as and

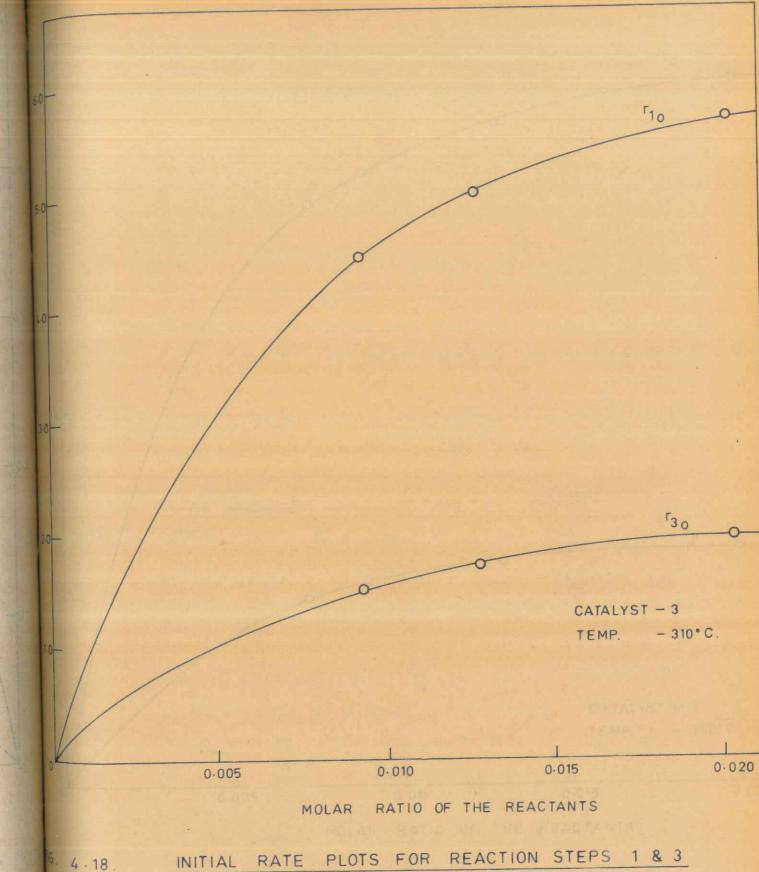
PYB. PY ... KK

119 710 r30 CATALYST - 2 - 310°C. TEMP. 0.020 0.015 0.010 0.005 MOLAR RATIO OF THE REACTANTS

FIG. 4-17. INITIAL RATE PLOTS FOR REACTION STEPS (1) & (3)

FOR CATALYST - 2

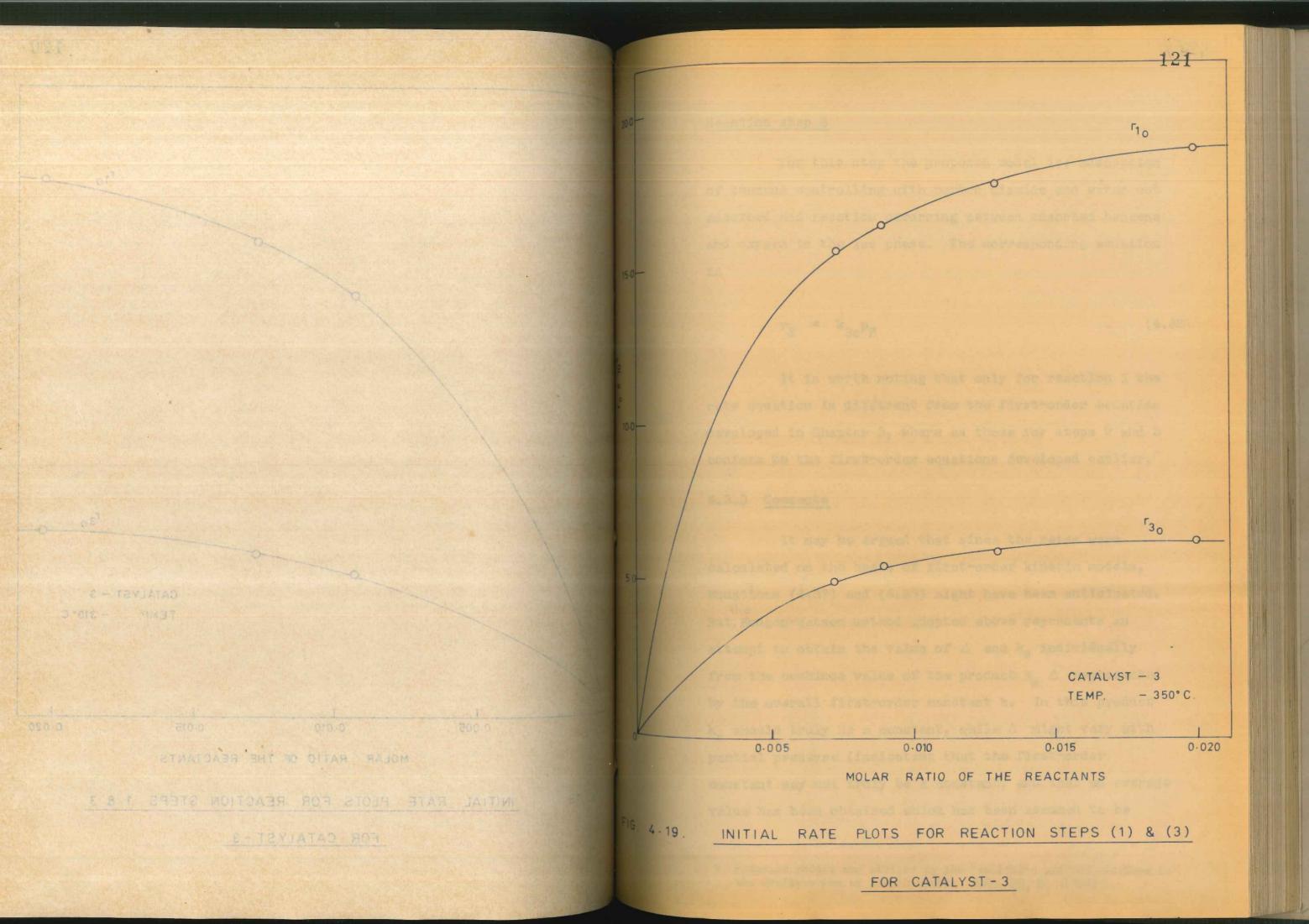




INITIAL RATE PLOTS FOR REACTION STEPS 1 & 3

FOR CATALYST - 3

MOLAR RATIO OF THE REACTANTS 4 477. INITIAL RATE PLOTS FOR REACTION STEPS (1) 8 (3)



## Reaction step 3

For this step the proposed model is: adsorption of benzene controlling with carbon dioxide and water not adsorbed and reaction occurring between adsorbed benzene and oxygen in the gas phase. The corresponding equation is

$$r_3 = k_{3s}p_B$$
 (4.38)

It is worth noting that only for reaction 1 the rate equation is different from the first-order equation developed in Chapter 3, where as those for steps 2 and 3 conform to the first-order equations developed earlier.\*

# 4.3.3 Comments

It may be argued that since the rates were calculated on the basis of first-order kinetic models, Equations (4.37) and (4.38) might have been anticipated. the But, Hougen-Watson method adopted above represents an attempt to obtain the value of  $\Delta$  and  $k_{\rm s}$  individually from the combined value of the product  $k_{\rm s}$   $\Delta$  represented by the overall first-order constant k. In this product  $k_{\rm s}$  should truly be a constant, while  $\Delta$  might vary with partial pressure (indicating that the first-order constant may not truly be a constant, and that an average value has been obtained which has been assumed to be

CATALYST - 3

CODS 0 000 0.015

MOLAR MATIC OF THE REACTANTS

INITIAL RATE PLOTS FOR REACTION STEPS (1) & (3)

FOR CATALYST - 3

<sup>\*</sup> Proposed models are similar to the "splitting off" of olefines in the dealkylation of alkylbenzenes (CEP, 50, 35 (1954)).

constant within certain limits of error). The above analysis has shown that  $\Delta$  is unity for reaction steps 2 and 3 and is a variable quantity for reaction step 1.

It is apparent from the controlling step models as well as the modified Hinshelwood model that benzene is adsorbed in preference to oxygen (which is probably weakly adsorbed if at all). Since the desorption of oxygen is generally rather a slow step, models based on hydrocarbon adsorption appear to be more plausible.

It has been postulated that water is not adsorbed on the catalyst. In the case of silica gel water is present in various forms. But it is unlikely that at the temperature involved (310-400°C.) it would be present in the adsorbed form, as it has been found that the loss in weight of silica gel is hardly 1-2% at the temperatures involved. Hence it is a reasonable conclusion that no water is present in silica gel at these temperatures (i.e. water is not adsorbed as proposed in the models).

# 4.3.4 Test of the models

and ony on in the sam where. The corresponding senation

C hos C scele upl esond as eveny . TulgedD of begoloveb

(alettern (4.37) and (4.38) at eat have been settented at

the the countil first-order constant it. In this product

on significant avoid beigges bonden mestale-manuel ins

(60.4) year organization of the second of the

Among the constants  $k_{1s}$ ,  $k_{2s}$ ,  $k_{3s}$  and  $K_{M}$ , the validity of  $k_{2s}$  and  $k_{3s}$  (which are identical with the first-order rate constants,  $k_{2}$  and  $k_{3}$ ) has already been confirmed in Chapter 3. The values of the constants,  $k_{1s}$  and  $K_{M}$ , are given in Table - 3.2, and the accuracy of

constant necessions to the contract and the second of the

one and land land boowledness betatem on the boosest of the allowed to consider the control of the description of the descripti

Les notite to case on the case postulated that water is not. In les notite to case of the case of the postulate of the case of

temperatures (i.e. water is not adapted as proposed in

Stands the constants has keep the constant the characters of the constant and the characters and the characters are constanted by the characters of the constants of the constant of the constants of the constant of the const

these constants has been tested by calculating the reaction rates using these constants and comparing with the experimental rate values, as shown in Figures 4.20 and 4.23. Representative data for the two catalysts appear in Tables - A.30 and A.31 of Appendix - A. The average error is 13-15%.

# 4.3.5 Temperature dependence of the constants

constant,  $K_M$ , and the surface reaction constant,  $k_{1s}$ , can be expressed in the usual Arrhenius form. These plots are shown in Figures 4.22 and 4.23. These constants have been evaluated for the lower temperature range only since (as shown later) this range corresponds definitely to chemical reaction control. The constants in the high temperature range may not be meaningful and are therefore not included in the table (in spite of the evidence that high temperature range also may be chemically controlled).

and .. - midwigh to 18.1 box 06.1 - belief of uponess

simplement of the pendagonal authoriginal C.S.

services and to selection the transfer of the transfer of

be expressed in the transmitted of the second of the secon

which the standards of the terms of the terms of

if it responsible rango has not be meaningful and are

so the bale spec contamined dill fail combive

dinascalis controlicis).

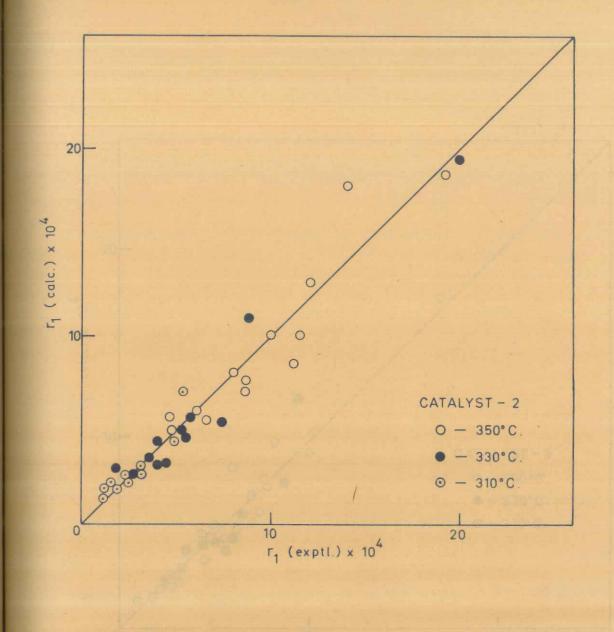


FIG. 4.20. COMPARISON OF CALCULATED AND EXPERIMENTAL

RATES FOR HOUGEN-WATSON MODEL FOR

MALEIC ANHYDRIDE FORMATION [Equation (4.36)]

MALEIC ANHYDRIDE FORMATION LEGISLION (4-38)

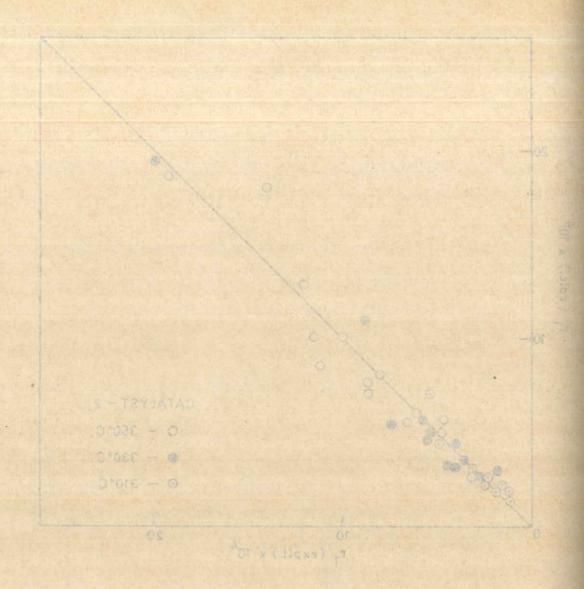


FIG 4.20 COMPARISON OF CALCULATED AND EXPERIMENTAL RATES FOR HOUGEN-WATSON MODEL FOR MALEIC ANHYDRIDE FORMATION [Equation (4.36)]

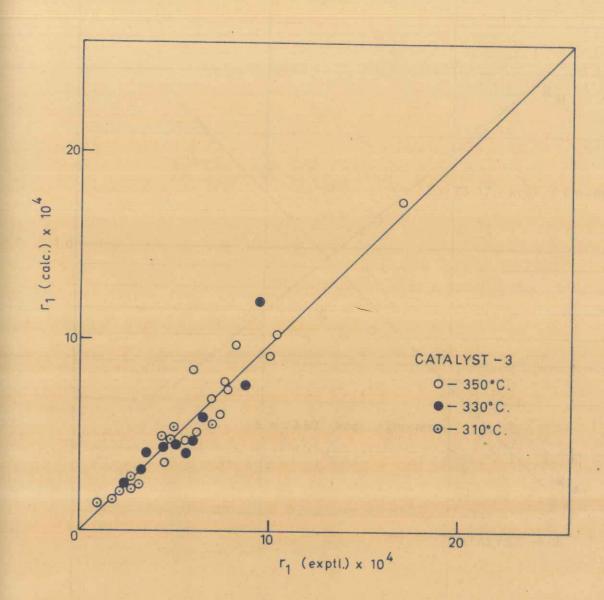
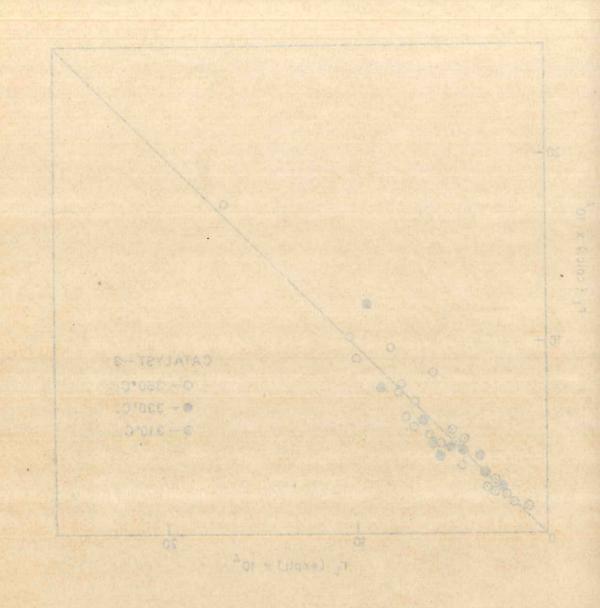


FIG. 4.21. COMPARISON OF CALCULATED AND EXPERIMENTAL

RATES FOR THE HOUGEN-WATSON MODEL FOR

MALEIC ANHYDRIDE FORMATION [Equation (4.36)]



G 4.21. COMPARISON OF CALCULATED AND EXPERIMENTAL RATES, FOR THE HOUGEN-WATSON MODEL FOR MALEIC ANHYDRIDE FORMATION Equation (4.36)

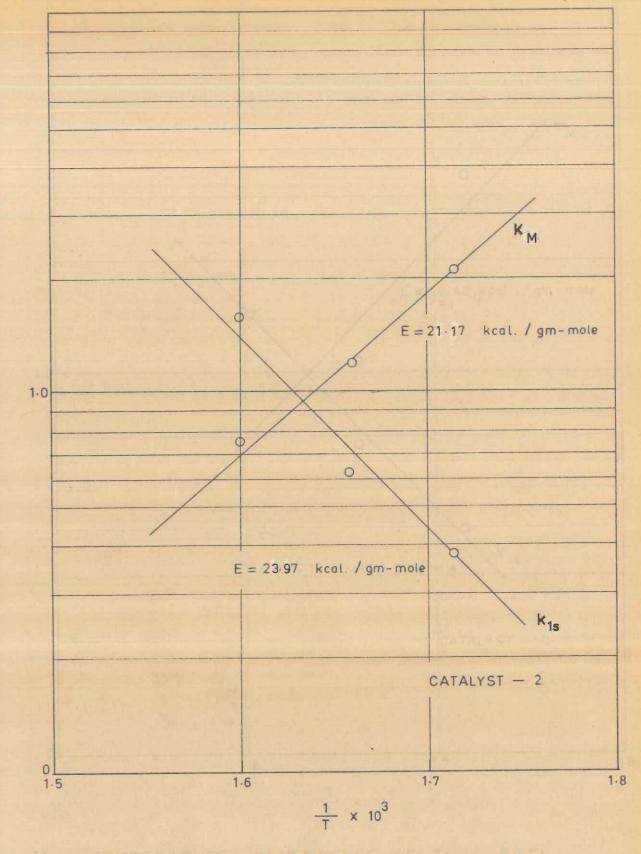
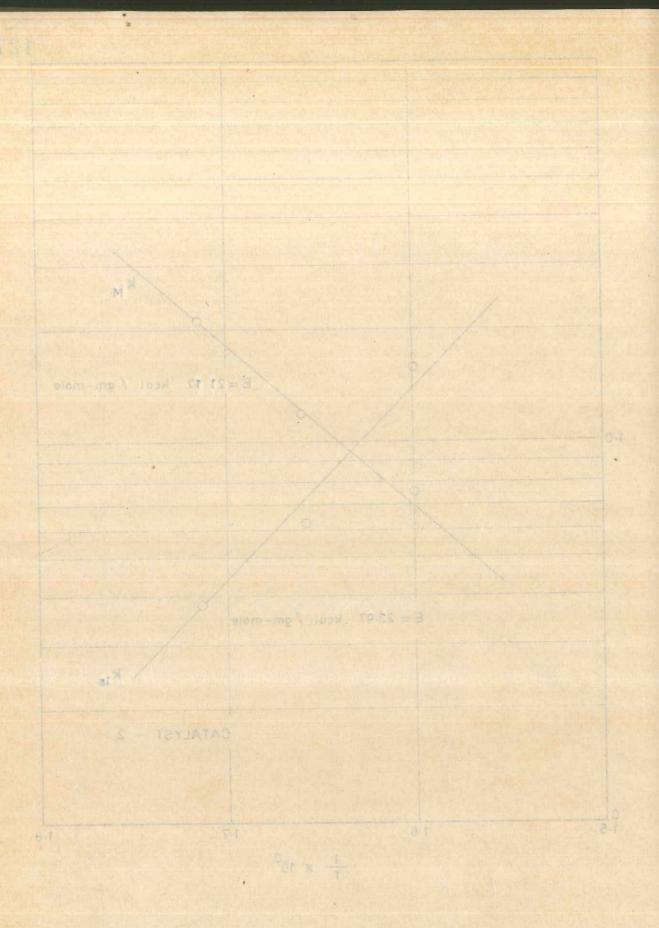


FIG. 4.22. TEMPERATURE DEPENDENCE OF THE RATE

CONSTANT k<sub>1s</sub> AND THE ADSORPTION CONSTANT K<sub>M</sub>

(maleic anhydride) FOR THE ADSORPTION CONTROL

MODEL WITH CATALYST-2



TEMPERATURE, DEPENDENCE OF THE RATE
CONSTANT KIS AND THE ADSORPTION CONSTANT KM
( maleic abovered abovered on constant Km

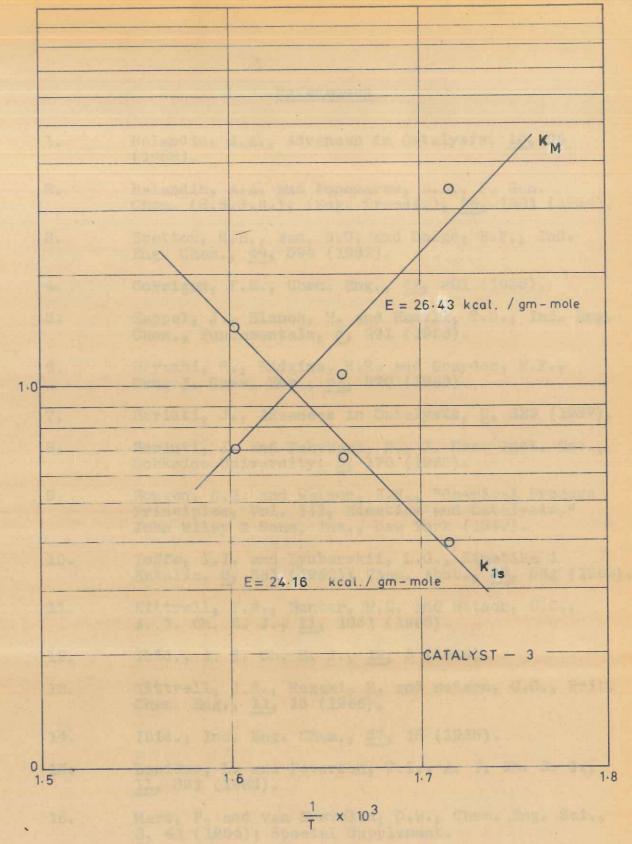
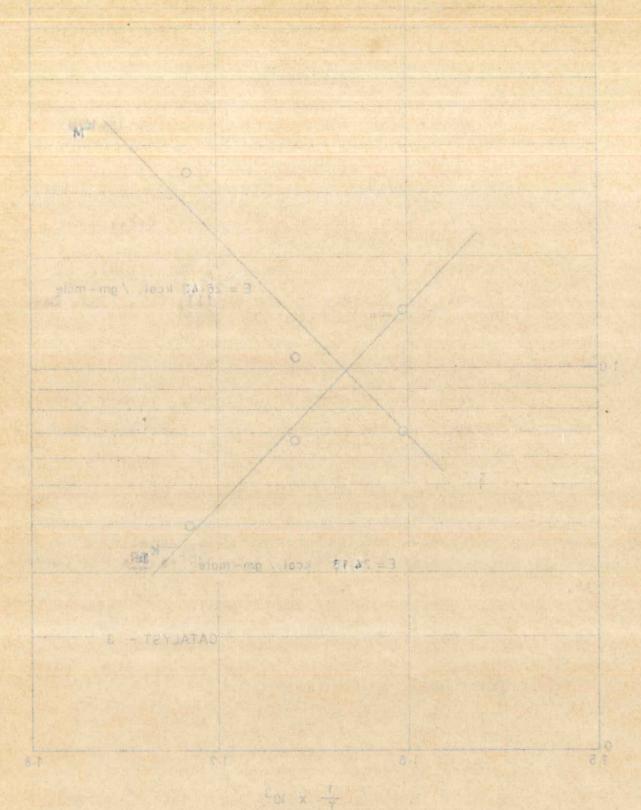


FIG. 4-23. TEMPERATURE DEPENDENCE OF THE RATE

CONSTANT k<sub>1s</sub> AND THE ADSORPTION CONSTANT K<sub>M</sub>

(maleic anhydride) FOR ADSORPTION CONTROL MODEL

WITH CATALYST-3



TEMPERATURE DEPENDENCE OF THE RATE CONSTANT KM CONSTANT KM (moleic anhydride) FOR ADSORPTION CONTROL MODEL

#### References

- 1. Balandin, A.A., Advances in Catalysis, 10, 96 (1958).
- 2. Balandin, A.A. and Ponomarev, A.A., J. Gen. Chem. (S.S.S.R.), (Eng. Transl.), 26, 1301 (1956).
- 3. Bretton, R.H., Wan, S.U. and Dodge, B.F., Ind. Eng. Chem., 44, 594 (1952).
- 4. Corrigan, T.E., Chem. Eng., 62, 201 (1955).
- 5. Happel, J., Blanck, H. and Hamill, T.D., Ind. Eng. Chem., Fundamentals, 5, 291 (1966).
- 6. Hayashi, R., Hudgins, R.R. and Graydon, W.F., Can. J. Chem. Eng., 41, 220 (1963).
- 7. Horiuti, J., Advances in Catalysis, 9, 339 (1957).
- 8. Horiuti, J. and Takezawa, N., J. Res. Inst. Cat., Hokkaido University, 8, 170 (1960).
- 9. Hougen, O.A. and Watson, K.M., "Chemical Process Principles, Vol. III, Kinetics and Catalysis,"
  John Wiley & Sons, Inc., New York (1947).
- 10. Ioffe, I.I. and Lyubarskii, L.G., Kinetika i Kataliz, 3, 261 (1962); Chem. Abst., 58, 55g (1963).
- 11. Kittrell, J.R., Hunter, W.G. and Watson, C.C., A. I. Ch. E. J., 11, 1051 (1965).
- 12. Ibid., A. I. Ch. E. J., 12, 5 (1966).
- 13. Kittrell, J.R., Mezaki, R. and Watson, C.C., Brit. Chem. Eng., 11, 15 (1966).
- 14. Ibid., Ind. Eng. Chem., 57, 18 (1965).
- 15. Lapidus, L. and Peterson, T.I., A. I. Ch. E. J., 11, 891 (1965).
- 16. Mars, P. and van Krevelen, D.W., Chem. Eng. Sci., 3, 41 (1954); Special Supplement.
- 17. Yang, K.H. and Hougen, O.A., Chem. Eng. Prog., 46, 146 (1950).

Cook. (C. J. J. ), (Mar. Trans.), Apr. 1303 (1908)

Therefore, R.S., Man, S.C. and Dodge, S.F., Man.

-. Cappingum, T.E., Church, St. 201 (1956).

Happel, J., Blanck, E. and Hartil, T.D., Ind. Reg.

Cas. J. Chom. Edg. 200 (1908).

Hortant, S., Mayanosa in Catalysis, S. 830 (1807).

Horizon University, E. 170 (1860).

9. Housen, C.S. and Watson, C.M., Schiertes Proque Relacipies, Vol. III, Kinglies and Cabelyons, C. John Maley & Sons, Tho., New York (1987).

10. Totag 1,1. and Iveneratel, 1.1. Minorika i (1002) (1002) Chau. Abst., 58, 588 (1002)

18. Isid., A. J. On. E. J., 18, 5 (1960).

13. Wittensell, J.S., Maraki, R. and Watson, C.C., Brit. (Usam. 12.5.) 13 (1986).

A. Ibid. Day, Comp. Chec. 37, 38 (1985).

in the second of the second for the second s

15. Hore, P. und van Wrevelan, D. M., Chan, Bur. 3ci.,

17. Yours Ell, and Housell D. L., Ollen, Ent. Props.

CONTRACTOR ANYTHER IN PROCESS OF THE PERSON

THE RESERVE OF THE PARTY OF THE

one form a matimal high for distinguishing between the resides of mentral high for distinguishing between the resides of mentral in a december resident of relatively los temperatures chemical remarks in normally the combroling measures, since the reaction rate is quite low (being an important distinction of temperature). This is characterized by an antivation imargy of ever 10 hostographs (frequently > 20 hostographs) in the mean, irehering plot a steep line therefore results for the chemical control regime, as shown by like (1) of Frequent 6, 1

depositions of rate on imparature leads to a minutest constraint of the constraint becomes extraordy that and too rest of measures of the constraint to the reaction one becomes the controlling stap. In this tage the effect of temperature board on mathematically its offset on the physical proposition (value of the offset) which considered the physical proposition (value of the offset) which considered the physical proposition (value of the offset) which considered the physical proposition (value of the offset) which considered the case the offset of the off

CHAPTER-5

CONTROLLING REGIMES IN
BENZENE OXIDATION

## Chapter 5

### CONTROLLING REGIMES IN BENZENE OXIDATIONS

## 5.1 GENERAL THEORETICAL DEVELOPMENT

The effect of temperature on the rate constants can form a rational basis for distinguishing between the regimes of control in a chemical reaction. At relatively low temperatures chemical reaction is normally the controlling mechanism, since the reaction rate is quite low (being an exponential function of temperature). This is characterized by an activation energy of over 10 kcal./gm-mole (frequently > 20 kcal./gm-mole). In the usual Arrhenius plot a steep line therefore results for the chemical control regime, as shown by line (1) of Figure 5.1

As the temperature is raised the exponential dependence of rate on temperature leads to a situation where chemical reaction becomes extremely fast and the rate of transfer of the reactants to the reaction zone becomes the controlling step. In this case the effect of temperature would be reflected by its effect on the physical properties (mainly diffusion) which characterize mass transfer. Thus a line with a considerably lower slope, corresponding to an activation energy of about 2 kcal./gm-mole (usually < 1 kcal./gm-mole), is obtained

CONTROLLING REGIMES IN

#### C respect

# SHOTTERING RESPECT OF RESIDENCE OF LIGHTNESS

## THE PROPERTY OF THE PARTY OF TH

the effect of temperature on the rate constants and constants are constants and constants are control to a chemical reaction. At relatively regimes of control to a constant reaction is normally the controlling sechantary since the reaction rate is quite for (being an expenseble) function of temperature). This is characterized by an activation energy of ever 10 weel. As well (frequently > 20 Keel. As well). In the usual arrhentus plot a steep line therefore results.

dependence of rate on temperature lands to a situation dependence of rate on temperature lands to a situation share chees extremely fast ad the state of transfer of the resolution becomes the controlling stop. In this case the effect of properties would be reflected by its sitect on the physical properties (mainly diffusion) which observed estate transfer. Thus a line with a considerably lower slope, sorresponding to an activation energy of shout sions. Stop to an activation energy of shout sions. Stop to an activation energy of shout.

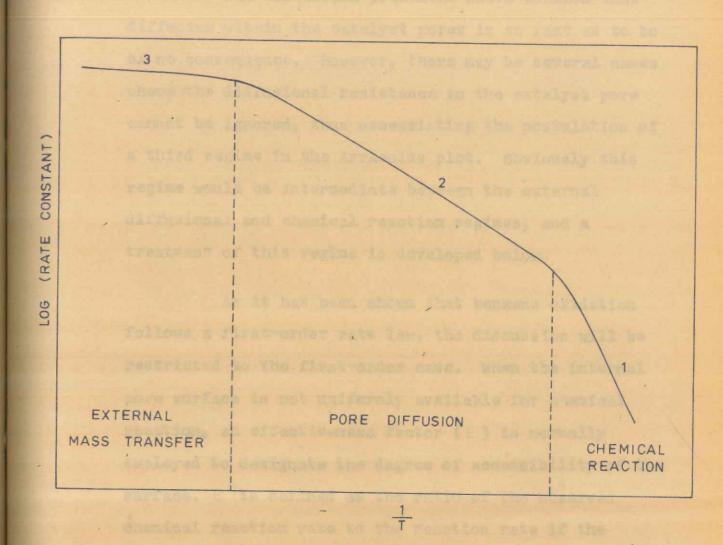


FIG. 5.1. REGIMES OF CONTROL IN A GAS-SOLID REACTION

It has been appear that I is a fundation of the Tatalo

PORE DIFFUSION CHE

EXTERNAL MASS TRANSFER

16. 6 1: REGIMES OF CONTROL IN A GAS-SOLID REACTION

in the Arrhenius plot as shown by line (3) of Figure 5.1.

The discussion presented above assumes that diffusion within the catalyst pores is so fast as to be of no consequence. However, there may be several cases where the diffusional resistance in the catalyst pore cannot be ignored, thus necessiating the postulation of a third regime in the Arrhenius plot. Obviously this regime would be intermediate between the external diffusional and chemical reaction regimes, and a treatment of this regime is developed below.

As it has been shown that benzene oxidation follows a first-order rate law, the discussion will be restricted to the first-order case. When the internal pore surface is not uniformly available for chemical reaction, an effectiveness factor (6) is normally employed to designate the degree of accessibility of the surface. 6 is defined as the ratio of the observed chemical reaction rate to the reaction rate if the concentration of the reactant within the pores is uniformly equal to the concentration at the surface. Thus the reaction rate (expressed in concentration units) can be represented as

$$\mathbf{r}_{\mathbf{c}} = \mathbf{c} \, \mathbf{k}_{\mathbf{c}} \, \mathbf{C} \qquad \qquad .. \qquad (5.1)$$

It has been shown that  $\epsilon$  is a function of the Thiele

in the Arrhenius plottisk shownessy line (3) of Figure 5.1.

Jeni commes evoda bejmbreng mbresserb eni

of to definational registering on the catalyst pore

dernot be ignored, thus necessian plot, postulation of a third regime in the Arthenius plot, obviously this regime vould be intermediate between the external

diffusional and chemical reaction regimes, and a

motosotro amazono Jenis myone meed ash ii ah

follows a lirst-order rate law, the discussion will be restricted to the first-order usse. When the inversal

pers surises is not uniformly available for dissided reaction, an effectiveness feator (E) is normally of the castley of acceptance of acceptance of the castley of the

bevreade of to obtan out as bantist at 3 .cominue

concentration of the redefant within the poren is

uniformly south to the concentration at the sarrane. Thus

the reaction rate (expressed in concentration units) den

an hetmaniqui

oroter and to nothered a at 3 Jeff mont good and fi

modulus, which for a first-order reaction is defined by,

$$\emptyset = L \sqrt{k_c/D_e} \qquad .. \qquad (5.2)$$

where

L =characteristic length defined by  $v_p/a_p$ 

The general nature of the  $\epsilon$  -  $\emptyset$  plot for a first-order reaction is shown in Figure 5.3. For values of  $\emptyset$  greater than 2, one may write,

$$\epsilon = \frac{1}{L \sqrt{k_c/D_e}} \qquad ... (5.3)$$

OI

$$\epsilon = 1/L \sqrt{D_e/k_c} \qquad .. \qquad (5.4)$$

Substituting Equation (5.4) in Equation (5.1),

$$r_c = 1/L \sqrt{D_{e}k_c} \cdot C$$
 .. (5.5)

The effective diffusion coefficient  $D_e$  and the reaction velocity constant  $k_c$  can be expressed in the form of the usual Arrhenius equation:

$$k_c = A_r e^{-E_r/RT} .. (5.6)$$

modulate, which for a figure-order resulton is defined by,

Dan Kono

and the second s

yd henileb diamel planietherend = d

The second secon

Tebro-Janki a vol Joly 0 - 9 ont to parden fatons; off

resetten te skoum in Figure 5.3. For values of 6 greater

(8.8)

Substituting Equation (5.4) in Equation (8.1),

nolinear est ham of installmon moterate by and the resolution of the valouity constant is eas be expressed in the formula supplied;

(6.8) ... 28\100 4 = 4

$$D_{e} = A_{D} e^{-E_{D}/RT} \qquad (5.7)$$

where E<sub>r</sub> and E<sub>D</sub> are the activation energies for reaction and diffusion respectively.

Substituting Equations (5.6) and (5.7) in (5.5),

$$r_{c} = 1/L \left[ A_{D} A_{r} e^{-E_{r}/RT} - E_{D}/RT \right]^{\frac{1}{2}} C \qquad (5.8)$$

or

$$r_{c} = K' e \frac{(E_{r} + E_{D})}{2RT} \qquad ... \qquad (5.9)$$

where

$$K' = 1/L (A_D A_r)^{\frac{1}{2}}$$

Comparing Equation (5.9) with the standard form,

$$r_c = A e^{-E/RT}$$
 ... (5.10)

we obtain

$$E = \frac{E_{D} + E_{r}}{2}$$
 .. (5.11)

pare E, and E are the sotivation emergies for resolion and diffusion respectively.

substituting Equations (5.6) and (6.7) in (5.6),

THE TENT

(4.6)

(40 04) a 1/2 (20 04)

commented Equation (5.9) with the standard form,

OL. 6)

atado e

 $E = E_r/2$  (if  $E_D$  is low compared to  $E_r$ )

Thus the value of the activation energy, E, in the pore diffusion region tends to be half the value for the chemical control regime.

Line (2) of Figure 5.1 represents the regime where internal pore diffusion is operative. It is thus possible to have all the three regimes of control with a suitable variation of temperature or catalyst properties (like pore size and characteristic length).

It has been pointed out by Petersen (6) that external mass transfer can never by itself be the controlling step in a chemical reaction, and that whenever experimental results indicate external mass transfer control, there is also a simultaneous diffusional resistance, the magnitude of which is invariably greater than the mass transfer resistance. This concept will be developed further in the next section for the oxidation of benzene.

# 5.2 IDENTIFICATION OF THE CONTROLLING REGIMES IN BENZENE OXIDATION

Arrhenius plots of the different rate constants for the two catalysts employed in this study are shown

E = E/2 (if  $E_0$  is low compared to  $E_1$ )

Thus the value of the setivation energy, is, in the pore diffrience region tends to be helf the value for the chemical control regime.

where internal pore difficult to represent the regime where internal pore difficulties of description of control with possible to have all the three regimes of control with a suitable variation of temperature or catalyst.

It has been pointed out by Peterson (5) that extensed mest treated and treat outered at a controlling step in a chemical results results indicate external mass transfer nontrol, there is also a simultaneous diffusional resistance, the mignitude of which is invertibly greater than the mass transfer resistance. This concept will be developed further in the next section for the concept will be developed further in the next section for the caldetion of beniane.

Aprhantus plots of the different rate constants for the two catelysts caployed in this study are shown

in Figures 3.1 and 3.2. It will be seen that for all the constants the activation energy in the higher temperature range is considerably lower than for the lower temperature range. The temperature ranges and the corresponding activation energies are:

310 - 350°C. -- 20 kcal./gm-mole. 350 - 400°C. -- 2 kcal./gm-mole.

Obviously in the lower temperature range (310-350°C.) chemical reaction controls, where as in the higher temperature range (350-400°C.) external diffusion (mass transfer) would appear to be the limiting resistance. The transition from one region to another is generally not as abrupt as has been found in this case. It is likely that, if the transition region is studied more closely, a gradual shift in the mechanism would be observed. This was not done in the present study since the shift in the mechanism was unmistakable.

The magnitude of the activation energy in the high temperature range appears to be somewhat higher than for external diffusion control (for which it should generally be less than 1 kcal./gm-mole), but too low for pore diffusion alone to be the controlling step (for which the magnitude of the activation energy should be E (chemical)/2, or about 10 kcal./gm-mole). Therefore

in Figures 8.1 and 3.5. It will be seen that for all the constants the constants on energy in the higher the range is considerably loser than for the lover tamperature range. The temperature ranges and the corresponding activation energies and

and - and -

Obviously in the lover temperature range (310-3600c.)
chemical resoltion controls, where as in the hisher
imagerature range (800-900°0.) external distusion (dapa
tromater) would appear to be the limiting resistance.
The transition from one resion to specimen is generally
not as abrupt as has been found in take case. It is
likely that, if the transition region is studied note
closely, a gradual shift in the mechanism would be
chaseved. This was not done in the present study since
the shift in the mechanism was uncharacteric.

The magnitude of the colivation energy in the night compensation energy in the sign compensation compensation of the second than for external diffusion control (for which it should generally be less than 1 worl./gr-wols), but too low for pose diffusion along to be the control of the step of the magnitude of the activation energy should be it (chemical)/2, or about 10 worl./gr-wols). Therefore

it appears desirable to examine this regime further. As a first step in this direction, the effect of pore diffusion was experimentally determined and also evaluated from the criterion proposed by Weisz and Prater (9).

Experiments were carried out at 350°C. with catalyst - 3 of the following size ranges:

-5 +12, -12 +22, -22 +36, -36 +60 (B.S.S. mesh)

It was found that the data obtained for each of these size ranges followed first-order kinetics. In order to elucidate the role of pore diffusion it is necessary to express the observed rate constants as a function of the particle size. For this purpose the rate constant  $(k_1+k_3)$  for the total oxidation of benzene was used in all the calculations since the behaviour of the individual constants,  $k_1$ ,  $k_2$  and  $k_3$ , is similar to that of the rate constant for total benzene disappearance  $(k_1+k_3)$ . Henceforth the rate constant for total benzene disappearance,  $(k_1+k_3)$ , will be designated as k.

Since the absence of pore diffusion cannot be assumed a priori the rate constants determined would be  $\epsilon$  k (and not merely k) in accordance with Equation (5.1). A plot of  $\epsilon$  k vs. particle size should give a line which levels off as the particle size is decreased, the

it appears depireble to exemine this regime inviter. As a first step in this direction, the pirect of pere diffusion was experimentally determined and also evaluated from the oritarion proposed by weigh and Freier (9).

Experiments yers carried out at 350°C. with catelyst - 3 of the following size ranges:

(meda .2.2.m) Da+ as- ,as+ ds- ,as+ dr- ,as+ as-

It was found that the data obtained for such of these size ranges followed first-order Mineties. In order to eliminate the redge of pose difficulty it is necessary to express the observed rate constants as a function of the particle size. For this purpose the rate constant (Minetic) for the total oxidation of benzene was used in all the calculations since the behaviour of the individual constants, My. My and My. Is similar to that of the individual constant for total benzene disappearance (My My).

assumed o prior the rate constants determined would sammed o prior the rate constants determined would be for (and not marely k) in accordance with Senation (5.1).

A plot of c k vu. particle size should give a line which levels off as the particle size is decreased, the

asymptotic value corresponding to the intrinsic rate constant, k. The effectiveness factor, , for any size can then be determined from the relation,

$$\varepsilon = \varepsilon \, k/k \qquad .. \qquad (5.12)$$

A plot of k (experimentally determined value of the rate constant for different particle sizes) as a function of particle size is shown in Figure 5.2. The values of 6 for the different particle sizes were determined in accordance with Equation (5.12), and are listed in Table - 5.1. It can be seen that 6 is practically unity for all the catalyst sizes, leading to the conclusion that pore diffusion is not significant. This is further examined below.

The Thiele modulus,  $\emptyset$ , for the present catalyst (catalyst - 3) was evaluated as follows: The effective diffusivity,  $D_e$ , was first calculated from the equation presented below (8) (since unpelletted silica gel particles were used, it was assumed that Knudsen flow was operative):

$$D_{e} = 19,400 \frac{\theta^{2}}{\gamma s \rho_{p}} \sqrt{T/M}$$
 .. (5.13)

Assuming a tortuosity factor (T) of 1.2 and using the

asymptotic value corresponding to the intrinsic vate constant, i. The effectiveness factor, . for any size can then the detrained from the relation,

constant for different particle wises) as a function of an emarcant for different particle wises) as a function of a particle size of 2. The values of 1 particle size of 2. The values of 1 for the different particle of sea were determined in accordance with Equation (3.12), and are listed in Table - 5.1. "It can be seen that ( as procionally unity for all the details at a gracification for all the details at a gracific to the fourther that committees are listed in formal formal formal and at a funther

The This Jesus on the contract of the process that cally of the process of the contract of the

and anter box f. I to ( T ) ander tyteoproof a anteresa

Table - 5.1

Experimental effectiveness factors for different values of the Thiele modulus

Particle size B.S.S. mesh	kx10 <sup>3</sup>	€	0
- 5 +12	1.811	0.873	0.1612
-12 +22	2.033	0.977	0.0713
-22 +36	2.043	0.984	0.0379
-36 +60	2.081	1.000	0.0228

L.B. - eldal

abulav Jurattii toi svoježi seemavijoelie laimaminegas

0			Paytigle
	-		B.S.S. mout
6.1812	0.875	1.871	
0.0372	0,934	2.081	-28 +36 -26 +60

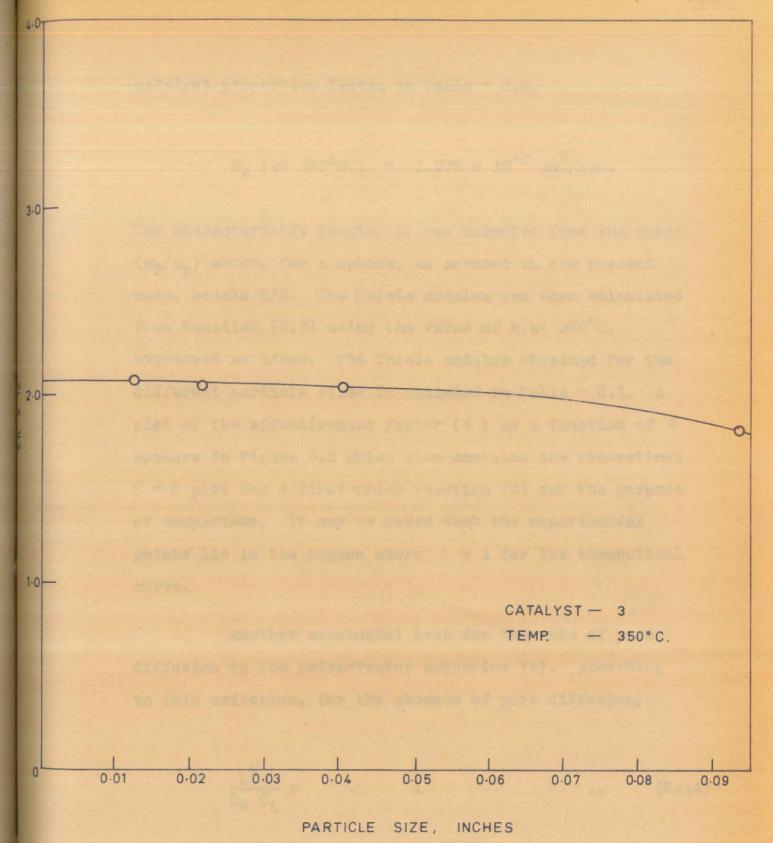


FIG. 5.2. EFFECT OF PARTICLE SIZE ON OBSERVED RATE CONSTANT

catalyst properties listed in Table - 3.6,

$$D_e$$
 (at 350°C.) = 1.575 x 10<sup>-3</sup> cm<sup>2</sup>/sec.

The characteristic length, L, was computed from the ratio  $(v_p/a_p)$  which, for a sphere, as assumed in the present case, equals R/3. The Thiele modulus was then calculated from Equation (5.2) using the value of k at  $350^{\circ}$ C. expressed as 1/sec. The Thiele modulus obtained for the different particle sizes is included in Table - 5.1. A plot of the effectiveness factor ( $\epsilon$ ) as a function of 0 appears in Figure 5.3 which also contains the theoretical  $\epsilon$  - 0 plot for a first-order reaction (8) for the purpose of comparison. It may be noted that the experimental points lie in the region where  $\epsilon$  = 1 for the theoretical curve.

Another meaningful test for the rate of pore diffusion is the Weisz-Prater criterion (9). According to this criterion, for the absence of pore diffusion,

$$\frac{L^2}{D_e C_i} r < 1 ... (5.14)$$

Making use of the following representative values,

CATALYST - 3
TEMP - 380°C

PARTICLE SIZE, INCHES

REGION (III)



FIRST-ORDER

V

FOR

CURVE

(E)

FACTOR

EFFECTIVENESS

VALUES

EXPERIMENTAL

THE

ALSO

SHOWING

ontalyst properties listed in Table - 0.0, .

open, equals No. The Totale compute was then delculated .500cc de d lo enlav and gates (C.C) soldanes mori ent vol bentafdo animbon afeldT off . seaVI as besserque A .f.C - older of bession of assis elaborate thousand in To notional a as ( 3 ) reduct assemulatedlin out to toly faritoroads ont antatuco cala dalme E. & sammit nt emerga istusmiraque ent fant beten od yen fi . mostramace to -DVt.ike

uniformula . (0) actually notard-mates and at notartith andreatith over to comerce out for molarative sing of

EXPERIMENTAL

0

THEORETICAL

1.0

REGION

FIG

3 5

REACTION,

THEORETICAL

L = 0.04 cm.

 $C_1 = 5.5 \times 10^{-7} \text{ moles/cc.}$ 

 $r = 7.8 \times 10^{-7} \text{ moles/cc/sec.}$ 

the inequality is estimated to be 0.943 for catalyst - 2 and 1.44 for catalyst - 3. As this is close to the marginal value of unity, it may be inferred that pore diffusion (if at all present) should be insignificant.

Since, according to Petersen (6), mass transfer alone cannot be the controlling mechanism, and external diffusional resistance is always accompanied by pore diffusional resistance, an analysis of the combined effect of the two resistances is necessary before the influence of pore diffusion in benzene oxidation can be discarded. For this purpose the rate of reaction occurring inside a porous particle can advantageously be expressed in terms of the rate per unit external surface area of the catalyst, since mass transfer is based on the external surface only.

Considering a single porous sphere of radius, R, the rate per unit volume of the catalyst particle is given by,

$$r_c = \epsilon k_c c_s \qquad .. \qquad (5.15)$$

.mo 40.0 = a

C4 = 3.5 x 10-7 moles/cc.

r = 7.8 x no-7 moles/ed/sec.

the inequality is estimated to be 0.943 for estalyst - 2 and 1.44 for detalyst - 3. As this is close to the end 1.44 for detalyst - 3. As this is close to the energinal value of unity, it may be infarred that pore diffusion (if at all present) should be insignificant.

alone cannot be the controlling mechanism, and external
diffusional resistance is always accompanied by pore
diffusional resistance, as analysis of the condition
diffusional resistance, as analysis of the condition
effect of the two resistances is necessary before the
influence of pore diffusion in benzene exisation can be
discarded. For this purpose the rete of resetion eccurring
discarded a percus perticle can advantageously be expressed
in term of the rate per unit external cartace eres of
the catalyst, since mass transfer is based on the external
entrane entry.

Considering a single porous sphere of radius, the rate per unit volume of the catalyst particle is twen by,

re e kg dg

where,

C<sub>s</sub> = surface concentration of the reactant

re = reaction rate based on concentration

If the rate is expressed as gm-mole/hr.cc. of catalyst (r'c),

$$r'_{e} = r_{e} \rho_{p}$$
 .. (5.16)

giving

$$\mathbf{r}_{\mathbf{c}}^{\prime} = \mathbf{c} \, \mathbf{k}_{\mathbf{c}} \, \mathbf{p} \, \mathbf{c}_{\mathbf{s}} \qquad .. \qquad (5.17)$$

If the reaction velocity constant is now expressed in terms of unit surface area of the catalyst,

$$k_c = k_s S$$
 ... (5.18)

where k<sub>s</sub> has the units (cm./hr.) and S is the surface area (cm<sup>2</sup>) per unit weight (gm.) of the catalyst. Substituting Equation (5.18) in Equation (5.17),

$$\mathbf{r}_{\mathbf{c}}^{\prime} = \epsilon \, \mathbf{k}_{\mathbf{s}} \, \mathbf{S} \, \boldsymbol{\rho}_{\mathbf{p}} \, \mathbf{c}_{\mathbf{s}} \qquad (5.19)$$

For a single particle of spherical shape, the

r = resulten rate based on condensration |

unite, en cet.

ke = velocity constant, m. co. cet.

Jevistas to .oo. wileieneng as hearestone at star and if

(FI. 0) .. (O. 17)

If the concilon velocity quartent is now expressed in terms,

. Jayleter out to some section that to

. Kg = kg S .. (5.18)

where kg has the units (on./hr.) and S is the surface area

(caf) per unit weight (gm.) of the catalyst. Substituting Soustion (5.18) in Equation (5.17),

For a single particle of spherical shape, the

rate is given by,

$$r_p' = 4/3 \pi R^3 (k_s S \rho_p C_s) \in ... (5.20)$$

Since the surface area is  $4\pi R^2$ , the rate (rpe) for a spherical particle per unit external surface area will be given by,

$$r_{pe}^{!} = R/3 (k_s S \rho_p C_s) \in$$
 .. (5.21)

This may be expressed as,

$$r'_{pe} = k'_{s} C_{s}$$
 .. (5.22)

where

$$k_s^! = \frac{R k_s S \rho_p}{3} \in ... (5.23)$$

The constant, k's, is obviously a rate constant based on external surface area (as against ks based on the total surface area) and has the units of length/time (cm./hr. bn this case).

The basic differential equation for a non-porous spherical catalyst pellet immersed in a large medium of stagnant reactant is (6):

$$D \frac{d}{dR^{\dagger}} \left[ R^{\dagger 2} \frac{dC}{dR^{\dagger}} \right] = 0 \qquad .. \quad (5.24)$$

the street with the state of th

T = 4/3 T R (16 8 P 06) F . . . (6.80)

Since the surface area is 4 NE, the rate (rge) for a spherical particle per unit external muriace area will be given by.

(15.8) .. (5.81) E .. (5.21)

This may be expressed as,

(8.0a) .. (8.0a)

(65.83) .. (5.83) .. (5.83)

The sourtant, kd, is obviously a rate constant based on external surface area (so against kg based on the total surface area) and has the units of langth/time (co./hr. bn this case).

The braid of transmit all the start of the a large medium of starment of the start of the start

(26.8) ..  $0 = \frac{06}{105} \frac{8}{10} \cdot 9 \cdot \frac{6}{105} \cdot 9$ 

where R' represents the radial coordinate. The boundary condition for this equation is given by,

$$\mathbf{r}_{pe}^{t} = \mathbf{D} \left( \frac{d\mathbf{C}}{d\mathbf{R}^{t}} \right)_{\mathbf{R}^{t} = \mathbf{R}} \qquad (5.25)$$

This condition denotes that the heterogeneous rate based on external surface area should be equal to the rate of diffusion at the surface of the particle. Equation (5.25) can be made dimensionless by the following transformations:

$$\overline{C} = \frac{C - C_b}{C_b} \qquad .. \qquad (5.26)$$

and

$$\bar{R} = R'/R$$
 .. (5.27)

the resulting equation being

$$r_{pe}^{\dagger} = \left(\frac{D C_b}{R}\right) \left(\frac{d\overline{C}}{d\overline{R}}\right)_{\overline{R}=1}$$
 (5.28)

Equation (5.22) can also be expressed in dimensionless form,

$$r_{pe}' = k_s' C_b (1 + \overline{C}_s)$$
 .. (5.29)

by using the transformation,

where E' represents the redist coordinate. The boundary ...

This condition denotes that the heterogeneous rate based on external surface area should be equal to the rate of differentian at the surface of the porticle. (Equation (5.95) and the made dimensionies by the following transformations:

Das

galad molf-wee salilisees add

Equation (5.82) can also be expressed in dimensionless form,

by using the transferential,

$$\overline{C}_{s} = \frac{C_{s} - C_{b}}{C_{b}} \qquad (5.30)$$

Combining Equations (5.28) and (5.29),

$$\left(\frac{d\overline{C}}{d\overline{R}}\right)_{\overline{R}=1} = \left(\frac{k_s^{\prime} R}{D}\right) (1 + \overline{C}_s) \qquad .. \qquad (5.31)$$

or

$$\left(\frac{d\overline{c}}{d\overline{R}}\right)_{\overline{R}=1} = \theta \left(1 + \overline{c}_{s}\right) \qquad ... \qquad (5.32)$$

where

$$\Theta = \left(\frac{k_s! R}{D}\right) \qquad .. \qquad (5.33)$$

From Equations (5.33) and (5.23),

$$\Theta = \frac{R^2 k_s S \rho_p}{3D} \in ... (5.34)$$

This may be written as,

$$\Theta = \frac{R^2 (k_s s /_p)}{3D_e} (\frac{D_e}{D}) \in ... (5.35)$$

OF

2 - 3 = 3

From Equations (5.33) and (5.33),

Combining Resettons (8.98) and (8.39),

 $\left(\frac{5}{a^5}+1\right)\left(\frac{8}{a}\frac{1}{a}\right)=\left(\frac{5}{8a}\right)$ 

$$\theta = 3 0^2 \left(\frac{D_e}{D}\right) \in ... (5.36)$$

where,

$$\emptyset = R/3 \sqrt{\frac{k_s S \rho_p}{D_e}}$$
 .. (5.37)

Equation (5.36) represents the relationship between the dimensionless group,  $\theta$  (calculated on the basis of unit external surface area), the Thiele modulus,  $\theta$  (which is a measure of internal pore diffusion) and a tortuosity term represented by  $(D_{\rm e}/D)$ . It now remains to eliminate  $\theta$  from this equation, so that a relationship can be obtained exclusively between  $\theta$  and  $\theta$  for a given ratio of  $(D_{\rm e}/D)$ .

One can identify three regions in the  $\varepsilon-\emptyset$  plot:

- (1)  $\emptyset$  < 0.2, where  $\varepsilon = 1$ .
- (ii)  $0.2 < \emptyset < 2$ , transition region.
- (iii)  $\emptyset \geqslant 2$ , where  $\varepsilon = 1/_{\emptyset}$ .

Region (iii) has been discussed by Petersen (6) in detail.

The present reaction, however, falls in region (i). In
the following paragraphs, the development of Petersen for

The state of the s

(18.87) eva = 0

Equation (5.30) represents the relationship between the dimensionless group, 8 (calculated on the beats of unit external surface area), the Thiele sodulus, 9 (which is a measure of internal pore diffusion) and a cortuosity to term represented by (D\_/D). It now remains to climinate from this equation, so that a relationship can be obtained exclinively between 8 and 6 for a given ratio of (D\_/D).

plot;

(1) \$ < 0.2, where \$ = 1.

(11) 0.2 < 0 < 2, transition region.

(111) \$ > 2, where \$ = 1/.

Region (iii) has been disquested by Peterson (a) in detail.
The present reaction, however, Talla in region (i). In
the following peragraphs, the development of Peterson for

region (iii) is briefly summarized, and the treatment is then extended to region (i).

#### Region (iii)

As mentioned above, for this region  $\varepsilon = 1/\emptyset$ , and Equation (5.36) reduces to,

$$\theta = 3\emptyset \left(\frac{B_e}{D}\right) \qquad .. \qquad (5.38)$$

Let us now consider Figure 5.4 in which concentration gradients are shown both for external diffusion and internal pore diffusion. The existence of a concentration gradient inside the pore is accounted for by the introduction of the effectiveness factor,  $\epsilon$ . Similarly the existence of an external mass transfer gradient can be accounted for by a mass transfer factor,  $\epsilon$ . If this is done, the reaction rates can be expressed in terms of the bulk concentration (which is the concentration measured experimentally). Thus we may define a mass transfer factor,  $\epsilon$ , as

$$C_s = 6 C_b$$
 .. (5.39)

 $\mathcal{E}_{s}$  can be expressed in terms of the dimensionless concentration,  $\overline{C}_{s}$ , by combining Equations (5.30) and (5.39). Thus,

C<sub>b</sub>

C<sub>c</sub>

C<sub>b</sub>

C<sub>c</sub>

FIG. 5.4. CONCENTRATION PROFILES IN A SYSTEM WHERE

EXTERNAL MASS TRANSFER AND PORE DIFFUSION

ARE SIMULTANEOUSLY OPERATIVE

region (111) is briefly summarized, and the transmist is them extended to region (1).

### (111) noiseE

As mentioned above, for this region E = 1/0 , and Equation (5.36) reduces to,

(58.6) .. 
$$\left(\frac{e^{it}}{a}\right)$$
06 = 0

Let us now consider figure 5.8 in which concentration gradients are shown both for external diffusion and insernal powe diffusion. The externos of a concentration gradient inside the pore is accounted for by the introduction of the effectiveness factor, c. Similarly the externes of an external mass transfer gradient can be exceeded for by a mass transfer factor, . If this is done, the resultion rates can be expressed in terms of the bulk concentration (which is the concentration that as any define a mass transfer factor, c. as

can be expressed in turns of the dimensionless concentration, \$\overline{\alpha}\_{a}\$ by combining Equations (5.36) and (5.38). Times

CONCENTRATION PROFILES IN A SYSTEM WHERE
EXTERNAL MASS TRANSFER AND PORE DIFFUSION
ARE SIMULTANEOUSLY, OPERATIONS

$$6 = 1 + \overline{C}_{s}$$
 .. (5.40)

The solution of the differential equation represented by Equation (5.32) provides the following relation for  $\overline{C}_s$ :

$$-\overline{C}_{s} = \frac{\theta}{1+\theta} \qquad .. \qquad (5.41)$$

Combining Equations (5.40) and (5.41)

$$6 = \frac{1}{1+\theta} \qquad (5.42)$$

Then, from Equations (5.42) and (5.38), the mass transfer factor can be expressed in terms of Thiele's modulus as,

$$\delta = \frac{1}{1 + 30 \, (D_{e}/D)} \qquad .. \quad (5.43)$$

Equation (5.43) fulfills the objective of this development, viz., to relate the mass transfer factor (6) with the Thiele modulus ( $\emptyset$ ).

It must be emphasised that Equation (5.43) holds good for region (iii) only, and is not operative for benzene oxidation, where  $\epsilon$  is almost unity. Extrapolation of Equation (5.43) to  $\epsilon = 1$  is not warranted since one

vd. bedreserger notinupe Latinevellib ent to notinue ent

(IF.8) .. = 5-

Combining Endaltons (6.40) and (5.41)

Them, from Countions (0.49) and (0.38), the mans transler to them. Santon oan he expressed in terms of Thiele's modulus say

(cl.a) ... (c) as + 1

Houstion (8.48) Initials the objective of this development, viz., to relate the mass transfer factor (6) with the Thiele modulus (8).

It must be emphasised that Equation (5.33) told good for vegion (111) only, and is not operative for bensens exidetion, where 6 is sladet unity. Extrapolation of Equation (5.43) told = 1 is not warranted since one

would then cross over to region (i).

## Region (i)

As stated earlier, the present study on the oxidation of benzene falls in region (i) of the  $\varepsilon-\emptyset$  curve, where  $\varepsilon$  is unity. For this region, Equation (5.36) can be written as,

$$\theta = 30^2 \frac{D_e}{D}$$
 .. (5.44)

Combining this with Equation (5.42),

$$6 = \frac{1}{1 + 30^2 \, (D_e/D)} \qquad (5.45)$$

In this region  $\emptyset$  is always less than about 0.2, and since  $(D_e/D)$  is of the order of 0.1 or less, from Equation (5.45) it may be seen that & is also substantially unity. In the case of benzene oxidation,

$$\frac{D_e}{D}$$
 = 5.102 x 10<sup>-3</sup>

and therefore  $\delta$  is far closer to unity than in cases where (D<sub>e</sub>/D) is of the order of 0.1.

would then erous over to region (1). It is the state of t

oxidation of benzene falls in region (i) of the C - D carter oxidation of benzene falls in region (i) of the C - D carve, where E is unity. For this region, Equation (5.36) can be written as,

Combining this with Equation (5.42),

In this region  $\theta$  is always less than about 0.2, and since  $(0_{\phi}/\Omega)$  is of the order of 0.1 or less, from Equation (0.45) it may be seen that ( is also substantially unity. In the case of benzene oxidation,

g-or x sor s = od

and therefore a factor closer to unity than in cases where (0,0) as of the order of 0.1.

From the development presented above it would appear that in region (i), where the effect of pore diffusion is absent, the effect of mass transfer is also absent. This fact, combined with the conclusion in respect of region (iii), suggests that external mass transfer cannot be operative in the region where  $\varepsilon$  is unity and that, when it becomes operative (in the region  $\varepsilon < 1$ ), the resistance due to pore diffusion is of a higher order. In the case of benzene oxidation, since  $\varepsilon = 1$ , it follows that external mass transfer is also negligible. It may be recalled that this was anticipated in Chapter 3, where external mass transfer was estimated to be negligible from the charts of Hougen et al (10).

In the lower temperature range one can conclude from the magnitude of the activation energy that chemical reaction is the controlling step. In spite of the low activation energy observed in the higher temperature range, it may be concluded (in view of the absence of diffusional effects) that in this region also probably chemical reaction controls, the fall in activation energy being due to a change in the structure or chemical character of the catalyst used. A similar fall in the activation energy at higher temperatures has been reported by Pinchbeck (7) and Ioffe et al (5) in the oxidation of naphthalene; by Dixon (1) in his review on the oxidation of maleic anhydride carried out by Holsen (4); and by

histor it evode between the received and many server and the received and received the received

sonts contaction or beneath of the case of beneath oxidation, since the case of beneath asset to the case that see the case the c

negligible. It may be recalled that this was anticipated in Chapter 3, where caternal mass transfer was estimated to be negligible from the charts of Housen et al (10).

In the lower temperature range one can conclude from the magnificate of the activation emergy that onemical reaction is the controlling step. In spite of the low activation energy observed in the higher temperature range,

activation energy observed in the higher temperature remi

chesteal remotion controls, the fall in activation energy coint due to a change in the structure or chemical character of the catalyst used. A similar fall in the activation energy at higher temperatures has been removie by Pinchbeck (?) and loffe at al (5) in the exidation of maphibalene; by Dimon (1) in his review on the exidation of aspatches and other carried cut by Helener (4), and lower temperature on the exidation of aspatches and other carried cut by Helener (4), and lower temperature of the most by the second of the carried cut by Helener (4), and by Helener (5) and the carried cut by Helener (6), and the carried cut by the carried cut by

Hedden (3) in the oxidation of coal by air.

Hammar (2) reported mass transfer to be the controlling step in the oxidation of benzene, though a high value of the activation energy (28 ± 4 kcal./gm-mole) was obtained. In view of this inherent discrepancy, it would be logical to speculate that chemical reaction is the limiting step.

On the basis of the findings reported in this chapter, it may be concluded that:

- (1) Chemical reaction appears to be the controlling resistance over the entire temperature range.
- (2) While in the temperature range, 310-350°C., this conclusion is substantiated by the magnitude of the activation energy (which is about 20 kcal./gm-mole), in the higher temperature range (350-400°C.) an activation energy of 2 kcal./gm-mole seems to suggest mass transfer control.
- (3) A detailed analysis of external diffusion and pore diffusion indicates that neither of these is operative and that the low activation energy in the higher temperature range is attributable to a favourable change in the structure or orientation of the catalyst.

"leader (3) In the oxidation of coal by air.

deman (3) reported was transfer to be the control of the control o

min's at betrough manifest the findings reported in this

objection of the contract of t

(1) Chemical resultion appears to be the controlling resistance over the entire temperature range.

(2) While in the temperature range, 210-25000., this conclusion is substantiated by the magnitude of the activation energy (which is about 20 keel./ga-mole), in the higher temperature range (250-40000.) an activation energy of 2 keel./ga-mole seems to suggest mass transferences.

(8) a derailed analysis of external diffusion and pore diffusion indicates the party of the state of the state of the indicate operative and that the low detivities to a develope to a favourable counts of the structure of orientation of the estalyst.

#### References

- 1. Dixon, J.K. and Longfield, J.E., "Catalysis," (P.H. Emmett, ed.); Vol. VII, Chap. 3, Reinhold Publishing Corporation, New York (1960).
- Hammar, C.G.B., Svensk Kem. Tid., 64, 165 (1952);
   Chem. Abst., 46, 3945d (1952).
- 3. Hedden, K., Chem. Eng. Sci., 14, 317 (1961).
- 4. Holsen, J.N., Ph.D. Thesis, "An investigation of the catalytic vapour phase oxidation of benzene," Washington Univ., St. Louis, Missouri (1954).
- 5. Ioffe, I.I. and Sherman, Yu. G., J. Phys. Chem., (U.S.S.R.), 28, 2095 (1954); Chem. Abst., 50, 10691 (1956).
- 6. Petersen, E.E., "Chemical Reaction Analysis," Prentice-Hall, Inc., New Jersey (1965).
- 7. Pinchbeck, P.H., Chem. Eng. Sci., 6, 105 (1957).
- 8. Satterfield, C.N. and Sherwood, T.K., "The Role of Diffusion in Catalysis," Addison-Wesley Publishing Co. (1963).
- 9. Weisz, P.B. and Prater, C.D., Advances in Catalysis, 6, 144 (1954).
- 10. Yoshida, F., Ramaswamy, D. and Hougen, O.A., Am. Inst. Chem. Eng., Convention, Washington, D.C., December 1960.

#### NOTES TO AND REAL PROPERTY.

## Soul rolls grantalist

## welst more velocity, percents/hy.end

## " reaction valuelty constants for the other

## Is 3 and 5 shows in the reaction remove

### ground of (low.) (see, eat.) (see,

### , aposific value of alexantion of an see an

### benezes retrectively, perchaptively (go, or

# NOMENCLATURE

mar (hr.) Limb cut. ).

## \$000001012

	Biron, J.R. and Longiteld, J. E.	
28, 32	(P. H. Bandtt, od.): Yol. VII, Che	
	Windows, C.C.T., Sween's New Tite.,	27.7
	Manuar, C.S.J., Syshek New. IId., Chom. abut., 46, 89456 (1968).	
TOAT ) LTD	Hodden, A., Chet. Rot. Bol., 16,	
	Holawn, J.H., Ph.D. Theads, An is	
	bungane," Maghington Univ., St. Is	
	of any for the property of the first of the	
	Masouri (1954).	

				. 66			
E	ter.		Amusio P	. 3.3	. magn		

A CAMPAGE S.	· - The second	

*			· C. C	*	********	harrie.	4 6			
		200								
		of the same								

Serterfield, C.F. and Shorwood, L.M., "The Hole of Diffusion is Satalysis," Address Wesley Fablishing Co. (1963).

il soomyba	M Pretery		

<sup>10.</sup> Yourism, F., Immersing, D. and Hongan, O.S., ... An. Inst. Chem. Eng., Convention, Hambington, Dogomber 1860.

## NOMENCLATURE

a	- constant.
am	- external surface area of pellet per unit
	mass, cm <sup>2</sup> /gm.
a <sub>v</sub>	- external surface area per unit volume of
	catalyst bed, cm2/cm3
A	- Arrhenius constant.
C	- concentration, gm-mole/cc.
₹	- dimensionless concentration, $\frac{C-C_b}{C_b}$ .
c <sub>b</sub>	- bulk concentration, gm-mole/cc.
Cs	- surface concentration, gm-mole/cc.
dp	- particle diameter, cm.
D	- bulk diffusion coefficient, cm <sup>2</sup> /sec.
De	- effective diffusion coefficient, cm2/sec.
E	- activation energy, kcal./gm-mole.
F	- feed rate, gm-mole/hr.
G	- mass velocity, gm./hr.cm2
Gm	- molal mass velocity, gm-mole/hr.cm?
k1, k2, k3	- reaction velocity constants for the steps
	1, 2 and 3 shown in the reaction scheme,
	gm-mole/(hr.) (gm. cat.) (atm.).
ka, kB	- specific rate of adsorption of oxygen and
	benzene respectively, gm-mole/(hr.) (gm. cat.) (atm.).
ke	- reaction velocity constant,
	ec./(hr.) (gm. cat.).

NOMENCLATURE

constant, who should AND ADDRESS OF THE PARTY OF THE catalyst dedy on! / om. . Imstence cutastence -- Goodsetration, garage/co. - dimmesionless concentration, Lilling. bulk concentration, percola/co. surfece condentration, garanta/co. particle singeter, on. affective diffusion coefficient, ont/sed. setivation energy, kest./gareole. ... Toed rate, part peul -Ton. will and a ville of or a new wolst mass velocity, savedle/mr.ou. I, 2 and 3 shows in the reaction achters, (ata) (ata .og) (ata) (ata.). - septime two of alternation of caveen and ben sene respectively, darwels/(hr.) (st. cak.) con/(her) (em. cat.).

specific rate of total reaction of benzene, gm-mole/(hr.) (gm. cat.) (atm.). kro specific rate of total reaction of benzene at the initial condition, gm-mole/(hr.) (gm. cat.) (atm.). reaction velocity constant per unit surface area, cm./hr. reaction velocity constant based on external surface area, cm./hr. kls, k2s, k3s rate constants in the Hougen-Watson models. K constant. KB, KC, KM, adsorption constants for benzene, carbon dioxide, maleic anhydride, oxygen Ko, Kw and water, respectively. 1 active site. characteristic length, cm. order of reaction. molecular weight. moles of oxygen used per mole of the hydrocarbon reacted; also number of active sites. partial pressure, atm. reaction rates for steps 1, 2 and 3 shown r1, r2, r3 in the reaction scheme, gm-mole/(hr.) (gm. cat.). reaction rate, gm-mole/(hr.) (gm. cat.). rt reaction rate, gm-mole/(hr.) (cc. cat.).

		appealing rate, of total reaction of benchman
		garmole/(mr.) (ms. cat.) (atm.)-
100	*	specific rate of total reaction of benesses
		of the initial condition, of
		guencle/(lus.) (gm. est.) (ntm.).
		resortion velocity constant per unit.
	-	surface area, ca./hr.
10		no bessed instance viloolev molitoses
		external surface area, cr./hr.
	*	. rate constant at the Medger-Watson bear .
		constant.
		edeception constants for Nontones,
ON TO TEST		carbon dioxide, salete saludedes, onygen
10.		- Tievidosquat , Totay bas
		estive site.
		characteristic length, ca.
	*	order of reaction.
		. Justow to Lawston
		moles of oxygen ased per mole of the
		nydrogarion reading also maker of active
		The same of the sa
TARRATA		resolted rates for stage 1, 2 and 8 shows
E. C. C. I.		in the reaction senso, sersole/(m.) (sm.
		reaction rate; garagle/(hr.) (pr. cat.).
San		reschion rate, garmole/(hr.) (not cat.).

ro	- total reaction rate at the initial condition,
	gm-mole/(hr.) (gm. cat.).
R	- gas constant, cal./oK./gm-mole;
	also radius of the pellet, cm.
R*	- radial coordinate.
R"	- rate number, $\frac{r}{a_m G_m}$ .
The state of the	
Re	- Reynolds number, G
S	
THE PERSON NAMED IN	surface area per unit weight of catalyst,
C C	cm <sup>2</sup> /gm.
SB	- fraction of catalyst surface covered with
	benzene.
Se	- Schmidt number, MP
T	- temperature, OK.
W	- weight of the catalyst, gm.
x	
	mole of benzene converted to products per
	mole of feed.
*c	- mole of benzene converted to carbon dioxide
	per mole of feed.
× <sub>M</sub>	- mole of benzene converted to maleic
	anhydride per mole of feed.
GREEK LETTER	S
α,β	- constants.
	constants.

stoichiometric number of the rate controlling step.

total remarken rate at the initial condition,		1 02
garmelt/(hr.) (gm. cut.).		
gas comenant, dal./em-scies		
also reduce of the police, on-		
radial coordinate.		1.5
rate number, 2		*9
Seynolds number,		
autings, area per unit weight of catchyst,		
Francism of estalyst surface ofvered with		-
*onsenod		
Annalda nimbor, 200		
besperature, or.		
weight of the catalyst, to.		
req ajordory of bejusymen susaned to slow		
. beel to elow		
mole of bename converted to curben dioxide		ox
per mole of feet.		
plefem of betraynes emerned to slow		
converted per mole of feet.		
	England.	表现的
constants.		
salitorion sign and to redman sintemplately		

C reciprocal of the adsorption term.
 E effectiveness factor.
 B dimensionless group, ks R D
 B pore volume, cc./cc.
 C density, gm./cc.
 C mass transfer factor.
 E summation.
 T tortuosity factor.
 M Thiele modulus, L √k/De.
 M Viscosity, gm./cm. hz.

A — reciprocal of the adsorption turns,

a discoliveness incier.

b discoliveness fronts,

c discolives fronts,

c density, gu./oc.

c assa transfer factor.

c tortuesity factor.

d thisle soculms, I / WE.

APPENDED TO A

Tables or owner toners) Name

APPENDICES

APPENDIX - A

Tables of experimental data

APPENDICES

Experimental data for catalyst - 1 at 400°C.

benzene:air	1					1:50									1:80			
W/F	63	0	09	93	132	162	190	228	280	•	0 (	20	06	132	160	192	204	250
PBx102	m	1.785	1,518	1.400	1,312	1,258	1.220	1,185	1.170	1 10.4	1. 10#	0.987	0.932	0.871	0.830	0.798	0.792	0.20
Pox101	4	1.927	1.762	1.688	1.652	1.594	1.568	1,542	1.529	000	1.930	1.827	T. 788	1.723	1.719	1.695	1.691	1.688
P <sub>M</sub> x103	55		1.187	1.651	1.713	2.052	2,106	2,124	1.963			0.865	1.038	1,304	1,471	1.557	1.592	1.673
Pcx102	9		1,1389	1,6635	1.9402	2,3534	2,5582	2.7666	2.9067			0.6504	0.9141	1,1741	1.3475	1.5085	1,5362	1.5108
Pwx102	7		0.6889	0.9979	1,1425	1,3833	1,4911	1.5970	1.6509			0.4117	0.5608	0.7174	0.8208	0.9099	0.9273	0.9803

-		
	v	
	1	
-	ъ	
rent.	ø	
.0	я	
4.3	2	
-	×	
-	s	
-		
0	ε	
~		
O	×	
1000		
-	я.	
	×	
	٠	
-	æ	
	æ	
	8	
	a	
-42	2	
	ŧ	
	1	
-	8	
G)		
-	٨.	
-	1	
-	8	
- 0	N.	
-	1	
400	в.	
	8	
-	8	

ERRESTES SERVICES

**国的是自身的特别,** 是是是各种的是,

-	O.	8	4	ıo	9	7
	0		0			
	19	0.718	1.874	0.538	46	00
	107		00		79	47
	154		00		86	53
1:110	183		-		90	63
	212		-		10	.66
	230		-	1,135	1.1177	
	321	0.550	-	-	03	0.7356
		The state of the s				
	0		- 0	100		
	19	0.574	1.901	4.	.36	
	86			.57	52	
	124			0.649	0.6268	0.3783
1:140	155		1.00	6	.71	
	180		- 0	00	.76	
	203			00	.80	
	242			0.	.86	
	337	-	-	0	00	

Experimental data for catalyst - at 310°C.

CVI

\$861989B.

. . . . . . . . . . .

DECEMBER :

- E888888888

\*\*\*\*\*\*

\* \* \* \* \* \* \* \* \*

HARAGO HARAGO

LEALERLE

\*\*\*\*\*\*\*\*\*\*\*

SECTION SECTION

benzene:air	WF	pBx102	Pox101	PMx103	Pcx102	Pwx102
	002	1.8317				
1:50	149	1.7091	1,8520			
	230	1.6659		0.9579	0.5653	0.3784
	0				1	
	175			57		
1:80	164			47		
	240	1.0528	1.8764	0.5570	0.3798	0.2456
	0		1.9440		A	
	69	0.8155	1.9290			0.0632
1:110	154		00 0			0.0801
	190		1.9130	0.3341	0.1951	0.1122
	238		0			0.1671

Experimental data for catalyst - at 330°C.

CO

35839 35839

HARRIE WHATEL BRIDE

December of the second

	WF	p <sub>B</sub> x10 <sup>2</sup>	Pox101	D.x103	2012 0	201- "
			,	- M	- C	PWALO
	0	1.8317	1.9234			
	69	1.7067	1.8525	LO27 0	0 4454	1
1	104	1.6593	1.8950	7000	#0##°0	0.2987
1:50	149	1,5954	1.787.1	1.0294	0.6224	0.4141
	194	1.5791	1 2000	Today.	0.9202	0.5844
	2000	1 2000	T. (020	1,4213	1.0568	0.6705
	3	T. 0000	L. 1473	1.5789	1,1554	0.7356
	0	1,1533	1.9375			
	72	1.0770	1.8947	0 4500	2020	
	113	1.0415	1.8738	00000	0.2737	0.1828
1:80	155	1,0088	1.8522	0.000	0.4029	0.2683
	209	0.9957	1.8447	00440	2000-0	0.3575
	250	0.9606	1 2000	0.00 O	0.00.0	0.3882
			2000°+	0.9941	0.7579	0.4780
	0	0.8416	1.9441			
	89	0.8005	1.9207	0.9401	0 1400	
	111	0.7567	1.9003	1040 O	10%T*0	0.0983
1:110	149	0.7408	1.8845	0.000	6675.0	0.1837
	195	0,7235	1.8763	0.000	0.09 LS	0.2489
	235	0.7133	1.0680	00000	02440	0,2835

7			
4			
-1			
	一位就是是第二 世纪英雄姓 第五五五世	F 1	
-	· 的是有关的   一种的数据的   一种的		
	· 新教育者 · · · · · · · · · · · · · · · · · · ·		
-1			
-1		8	
		1	
	· 表面只以图。		
	NESSES DESCRIPTION OF SERVICE OF	ST.	
	1. 在的以外的		
	그런데 이 있게 그 그가 빨 맛 뿐 뿐 그 것 뭐 뭐 맛 뭐		
3		Power of the second	
	·····································		
	1、福河西西西西西,西南河河南西 唯新期限保险。		
	26555 54555 BESSS		
	一直接近海岸 正是出来对方 澳洲东西市的		
	一分子不知道 古古古古古 有重点不可的	1 20 1	
		100	
		3	
		the sale	
	COURTED SOCIETY MERKING		
	SERLED SOCIAL BELLES		
		1111111	
		1	
		SUN SUN SUN	
		1 2 1	
		BRANCH OF	

Experimental data for catalyst - 2 at 350°C.

benzene:air	WF	pBx102	Pox101	PMx103	PCx102	
1	63	es	4	22	9	
	0	1,8318	1.9233			
	19	1.5969	1.7879	1,3555	0.8668	
	66	1.4899	1,7230	1.8666	1,3042	
C to	131	1.4213	1.6814	2,1982	1.5837	
OCIT	173	1.3485	1.6421	2,7055	1.8171	
	199	1,3188	1,6245	2.8612	1.9329	
	230	1.2965	1.6148	3,0957	1.9732	
	313	1.2267	1.5741	3,4822	2.2373	
	0	1,1533	1.9375			
	65	1.0090	1,8551		0.5376	
	107	0.9345	1.8072	1,1267	0.8619	
1.00	001	0.8878	1.7799		1.0393	
Tien	LYS	0.8649	1.7667		1,1242	
	ST2	0.8311	1.7470		1.2508	
	44.0	0.8144	1.7358		1.3367	
	STS	0.7892	1.7204	-	1.4363	

. . . . .

	Э.
-	- 2
- 5	-2
2000	1 2
.0	
1.3	9
7	44
- 6	88
24	21
0	м
~ ~	
	п
_	4
and it	
A.	ж
72	
	•
-	8
-	
	8
-	8:
- 4	
	1
	8
200	
W	9
- 1	ŧ.
Land.	
0	2
photo	R
625	
40	
Eur's	
70.7	

SECOLOGICA PROPERTY OF A STATE OF

STANDARD CARLES OF THE STANDARD CO.

TALES SERVICE SERVICE

STATE OF STA

1	2523 3632 4688 5379 5557 6079 6423	25 25 25 25 25 25 25 25 25 25 25 25 25 2
1	00000	0.1819 0.2232 0.3260 0.4083 0.4393
9	0.3831 0.5714 0.7408 0.8601 0.8796 0.9665 1.0266	0.2817 0.4069 0.5079 0.5769 0.6308 0.6758
5	0.5823 0.7894 0.9846 1.0789 1.1588 1.2473	0.4108 0.5545 0.7209 0.8415 0.9296 1.0137
4	1.9441 1.8839 1.8573 1.8150 1.8110 1.7984 1.7900	1.9479 1.8864 1.8700 1.8589 1.8504 1.8431 1.8333
8	0.8416 0.7381 0.6942 0.6525 0.6263 0.6177 0.5973 0.5845	0.6626 0.5882 0.5595 0.5298 0.5103 0.4954 0.4823 0.4652
CO .	68 104 149 187 222 267 302	0 102 138 178 215 252 334
1	1:110	1:140

Experimental data for catalyst - at 375°C.

O

benzene:air W/F P <sub>B</sub> x10 <sup>2</sup> P <sub>O</sub> x10 <sup>1</sup> P <sub>M</sub> x10 <sup>3</sup> P <sub>C</sub> x10 <sup>2</sup> I = 2 3 4 5 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6							
0       1.8318       1.9233       -       6         1.4       1.5749       1.7751       1.5332       0.9496         144       1.3665       1.6538       2.6469       1.3521         182       1.2861       1.6042       3.0041       2.0747         245       1.2863       1.5849       3.2807       2.1823         245       1.2267       1.5715       3.4584       2.2450         301       1.1868       1.5715       3.4584       2.2450         103       0.9939       1.8448       0.8961       0.5978         103       0.9939       1.8448       0.8961       0.5978         140       0.8857       1.7873       1.4508       1.0251         187       0.8342       1.7489       1.6918       1.2379         250       0.8144       1.7391       1.8591       1.2894         250       0.7634       1.7286       1.9214       1.3634	benzene:air	W/F	PBx102		P <sub>M</sub> x103	Pcx102	P <sub>w</sub> x10 <sup>2</sup>
62 1.5749 1.7751 1.5332 0.9496 0.1.4760 1.7751 1.5332 0.9496 0.1.4760 1.7145 1.9508 1.3521 0.9496 1.2861 1.2861 1.6042 3.0041 2.0747 1.2861 1.2867 1.5715 3.4584 2.2450 1.7313 1.5715 3.4584 2.2450 1.1868 1.5501 3.6819 2.3954 1.5715 1.868 1.9375 0.8961 0.5978 0.9318 1.8773 1.4508 1.0251 0.8659 0.7674 1.7286 1.9214 1.2379 0.7674 1.7286 1.9214 1.3634 0.8644 1.7286 1.9214 1.3634	1	63	8	4	5	9	1
96 1.5749 1.7751 1.5332 0.9496 0 1.44 1.3665 1.6538 2.6469 1.7313 1.5845 1.5849 3.2807 2.0747 1.5865 1.5849 3.2807 2.0747 1.5865 1.5849 3.2807 2.0747 1.5865 1.5867 1.5716 3.6819 2.2450 1.1533 1.9375 0.8961 0.5978 0.8957 1.7873 1.4508 1.0251 0.8857 1.7873 1.4508 1.0251 0.8844 1.7391 1.8591 1.2379 0.322 0.8144 1.7391 1.8591 1.2379 0.7874 1.7286 1.9214 1.3634 0.		00		1.9233			-
144 1.3665 1.6538 2.6469 1.3521 0.1.2861 1.2861 1.6538 2.6469 1.7313 1.5849 3.2807 2.1823 1.5849 3.2807 2.1823 1.5849 3.2807 2.1823 1.5849 3.2807 2.1823 1.5849 3.2807 2.3954 1.5501 3.6819 2.2450 1.8650 0.9939 1.8448 0.8961 0.5978 0.8857 1.7873 1.4508 1.0251 0.8859 0.7879 1.7891 1.8591 1.2379 0.8144 1.7391 1.8591 1.2379 0.8144 1.7391 1.8591 1.3634 0.8141 1.3634		7 90		1.7751	1.5332	0.9496	1 8
182 1.2861 1.6042 3.0041 2.0747 1.2297 1.5849 3.2807 2.1823 1.5849 3.2807 2.1823 1.5715 3.4584 2.2450 1.5501 3.6819 2.3954 1.5501 1.8691 1.8591 1.2379 0.8857 1.7286 1.9214 1.2379 0.7524 1.7286 1.9214 1.3634 0.894		144		1.7145	1.9508	1,3521	0.88
245 1.2267 1.5849 3.2807 2.1823 1.5715 3.4584 2.2450 1.5715 3.4584 2.2450 1.5501 3.6819 2.3954 1.5501 1.9375 0.8961 0.5978 0.8957 1.7873 1.4508 1.0251 0.8557 0.8144 1.7286 1.9214 1.2379 0.7524 1.3534 0.7524 1.3534 0.7524	00:1	182		1.6042	3.0041	1.7313	1.13
301 1.1868 1.5501 3.4584 2.2450 1.1868 1.5501 3.6819 2.3954 1.5501 103 0.9939 1.8448 0.8961 0.5978 0.8857 1.7873 1.4508 1.0251 0.8559 0.8144 1.7391 1.8591 1.2379 0.322 0.7534 1.7286 1.9214 1.3634 0.3634		219		1.5849	3.2807	2.0747	1,33
0 1.1533 1.9375 - 3.6819 2.3954 1.0939 1.0939 1.8448 0.8961 0.5978 0.8957 1.1567 0.8659 0.98342 1.7873 1.4508 1.0251 0.8559 0.8144 1.7391 1.8591 1.2379 0.322 0.7524 1.7286 1.9214 1.3634 0.3634		240		1,5715	3.4584	9.9450	J. 41
65 0.9939 1.8448 0.8961 0.5978 0.8961 0.5978 140 0.8357 1.7873 1.4508 1.0251 0.8144 1.7391 1.8591 1.2379 0.850 0.7879 1.7286 1.9214 1.3634 0.8591		705		1.5501	3.6819	2.3954	7.56
65 0.9939 1.8448 0.8961 0.5978 0.8957 0.8957 0.8857 1.7873 1.4508 1.0251 0.8559 0.855 0.8144 1.7391 1.8591 1.2894 0.855 0.7979 1.7286 1.9214 1.3634 0.8591		0	7.1522	1000	The same	The state of the	0
103 0.9318 1.8061 0.8961 0.5978 0.140 0.8357 1.7873 1.4508 1.0251 0.8559 0.8342 1.7391 1.8591 1.2379 0.7634 1.7286 1.9214 1.3634 0.7634		65	00000	1.9373			
140 0.8857 1.7873 1.4508 1.0251 0.8659 0.8342 1.7391 1.8591 1.2379 0.850 0.7979 1.7286 1.9214 1.3634 0.		103	0.000	1.8448	0.8961	0.5978	
222 0.8342 1.7489 1.6918 1.2379 0.850 0.7979 1.7286 1.9214 1.3894 0.322 0.7979 1.7286 1.9214 1.3634 0.		140	0.0000	1,8061	1.1567	0.8659	
0.8144 1.7391 1.8591 1.2379 0.07979 1.7286 1.9214 1.3634 0.07634	1:80	187	0.8349	1 7400	1.4508	1,0251	
0.7979 1.7286 1.9214 1.3634 0.		222	0.8144	1 7203	1.6918	1,2379	
0.7634 1.3634 0.		250	0.7970	T. 7000	1.8591	1.2894	
		322	0.7634	1.7000	1.9214	1.3634	

-	
	3
-	а
- 4	п
	d
- 2000	ı
- 0	8
1.3	я
- April	8
-	и
- 19	ı
	н
-	я
- 9	я
83	а
0	и
30,000	ø
-	n
	я
	3
	3
IO	,
153	4
	9
	п
-	в
~44	а
-	я
	ı
400	
-	в
-	в
	8
	ø
200	в
(13	r
-	5
-	п
100	и
0	ш
galed.	п
	н
CD3	п
100	ы
P .	ы

Treation of the state of the st

Shhimbah bahanaha

PAZJU.

1			1:110					1.140			
63	620	107	181	212	322	0	190	140	208	250	010
m	0.8416							0.5167			
4	1.9441		1.8288			. 6	800	1.8616	00 00	80	00
ıcı			1.0435					0.7692			
9	1	6.4	0.7556	9	000			0.5673	20	- 1-	w
	1	24	0.4822	9	64			0.3033			

THE STATE OF STATE OF

Experimental data for catalyst -2 at 4000C.

benzene;air	W/F	PBx102	P <sub>0</sub> x101	PMx103	PCx102	pwx102
1	03	e	4	0	9	2
	0	1,7965	1.9223			
	46	1.6026	1.8144	1.257	0.6600	0.4557
	2001	1.5629	1,7875	1.347	0.8623	0.5655
	135	2) 14-1	1.6997		1.4508	
1,50	189	70000	1.6538		1.7640	
	900	1.0000	1.09.79		2.0944	
	940	TOTAL L	1.5746		2.2492	
	208	1.1.04	1.5584		2.3642	
	246	1. 1484	1.5488		2.3897	
	020	1.1246	1.5282		2,5655	
	0	1,1533	1.9375			
	53	1.0113	1.8578	0 800	1000	
	119	0.9157	1.7962	1.234	TSA# 0	
1.80	147	0.8856	1.7815	1.496	1,0085	0.6533
-	000	0.8419	1.7533	1.643	1.2109	
	0000	0.0000	1.7275	1.836	1.3864	
	300	2007.0	1.7164	1.978	1.4474	
	000	0. (DOL	1.7003	2.099	1.5615	

10000000 10000000	293922153 2111111555		
11.000 11	0.00 to 10.00 to 10.0	Posta a	
STREETS STREETS STREETS	TORRESSE.	607.00	The state of
	2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	to to to	200 XXX 100 XX
		S. S. S.	
222222	-18888888888	70 2	
		T. T. State of the	

- 1	
-	
post	
7603	
-	
4.5	
2000	
204	
1,000	
Proj	
49	
(3)	-
-	
-	
- 63	
~	
2757	
100.00	•
200	
14.2	
796	
1701	
1246	
15233	
200	
Carry.	
an an	
100	
10000	
-	
- 4546	
	-
ALC:	
543	
100	
- The second	
- proof	

-	0	c		U	0	ı
	3	,		•	0	
11111111	0	0.8341				
	70	0.7140			48	
	117	0.6668	1.8426	0.817	67	
The second second	175	0.6260			80	
:110	190	0.6172			00	
	240	0.5872			96	
	266	0.5720	-		02	
	322	0.5438	1.7730	1,451	1,1311	0.7106
			A LEGISLAND			
	0	0.6625				
	09	0.5800			0.3187	
	86	0.5471		-	0.4539	
	140	0.5099			0.6686	0.3959
:140	222	0.4750	1.8364	0.976	0.7344	0.4648
	234	0.4660			0.7851	
	272	0.4529			0.8360	
	346	0.4385			0.8873	K

	6.9
	1
	catalyst
Table - A.7	Experimental data for catalyst -

9

THE STATE OF THE S

SECTION PROPERTY.

Panalan, Panalana.

BURE STATE STATE OF S

coccesso encicación

. . . . . .

. . . . .

benzene: air	W/F	PBx102	Pox101	PMx103	PCX102	PWX102
	0	1.8317	1.9232	. 1		. 0
	000	1.7454	1.8741	0.5165	0.3110	0.2071
CHAL	100	1.7212	T-8609	0.6832	0.3894	0.2630
OCIT	130	1.7040	1.8505	0.7656	0.4597	0.3064
	Ton	1. 66888	1.8396	0.8279	0.5371	0.3513
	2007	4.0000	100001	1.0001	0.5880	0.4022
	0	1.1533	1.9375			
	64	1.1092	1.9122	0.2584	0.1610	0.1063
	107	1.0812	1.8965	0.4336	0.2590	0.1728
1:80	132	1.0679	1.8888	0.5097	0.3081	0.2050
	194	1.0497	1.8779	0.6032	0.3801	0.2504
	236	1.0413	1.8733	0.6585	0.4084	0.2701
	0	0.8416	1.9441			
	20	0.8136	1.9279	0.1607	0.1033	0.0677
	110	0.8022	1.9210	0.2154	0.1501	0.0966
	140	0.7947	1.9170	0.2709	0.1728	6.1135
1:110	190	0.7847	1.9111	0.3206	0.2125	0.1383
	248	0.7779	1,9075	0.3425	0.2447	0.1566

		11 kende
	0. 3441. 0. 1158 0. 1288 0. 1081 0. 1081 0. 1081 0. 1081 0. 1081 0. 1081 0. 1081	bearos.
	0.3483 0.3483 0.6083 0.	Paro
		p <sup>0</sup> zzro <sub>j</sub>
	1.08.18 1.08 1.0	1.02Z10g
	Sala sala salas	W.E.
San	21.28	parkenergy.

Experimental data for catalyst - 3 at 330°C

A Charles on the last of the l		0				
Denzene: alr	W/F	PBx10	Pox104	PMx103	PCx102	Pwx102
	0	1.8317	1.9233			
	63	.70	1.8522	0.8151		0 9047
-	104	61	1.7978	1.2089		
00:1	130	59	1.7867	1.2748		
	168	57	1.7766	1.4393	0.0000	CT CO
	220	53	1.7491	1 4704		
				00.00		
	0	1,1533				
	20	1.0783	1,8957	478		
	107	1.0411		0.7769		-
1:80	132	1.0935		10		
	187	0 07777		OTO		-
	000	1000		982		-
	202	0.9640		039	1717.0	0.4624
	(	0 0000				
	0	0.8416	1,9441			
	89	0.7891	1.9132			
	211	0 7580	1 00000	•	•	
7:110	120	00000	07.00		-	- 92
	100	しまっこっこ	1.8812		-	- 6
W.H.	TAS	0.7262	1.8763			
	244	0.7072	1,8654	0.7423	0.5095	0.3080

	The state of the s		
	1000 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	1	
	1 2 1 2 2 7		
	1 00000 00000 00000		
	l cosso cobbb babbb	100	
	0.000 0.000	10	
	1000000 100000 000000 0000000000000000	9	
	TOTAL TOTAL PROPERTY	1	
	DODGO GOOGO HOOGO	DC x 10	
		100	
	1282 1282 1282 1282 1282 1283 1283 1283	P. Tros	
	1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	15	
	TOTAL SOUTH IN DAMES OF	N.	
	oppoor hoppo hhaha	200	
	Papada hacada hadaaa	la para	
	1. 见见法实识比 一世间企业负责 经电路设施员	0	
	TOBER TOBER		
	British habital Habita	0	
	debelah debelah debelah	60x20g	
*			
	· 多思克思克思 图 1 见 1 见 2 见 2 见 2 见 2 见 2 见 2 见 2 见 2 见	_50	
	000000 00000 000000 000000000000000000	2	
	TOTAL DECOME SECURE	.24	
	0.100.0 0.000.0 0.000.	Brrus	
	Ponuno vinion smarra	-50	3
- 8	TREE OF THE STATE	2	
	CHRIST MANA SALA	26	
		- 4	
		4 1	
		The second	
	182 98		
		5 1	
		100	
		. 55	
		15	
		sh 9	

devision to 1800 to design to pair

Experimental data for catalyst - 3 at 350°C.

	benzene:air W	1				1:50	100	24	31		C	To	OT.	1:80	20	255	
	WF	co l	0	50	20	33	200	44	101		0;	TS	200	2	33	50	0
	pBx102	60	1.800	1.516	1,404	1.370	1.345	1.050	1,262		1.171	0,000	2000	0.880	0.858	0.831	100
	P0x101	4	1.925	1.775	1.760 1.727	1.700	1.684	7.005 7.005	1.640		1,942	1,845	1.024	1.001	1 780	783	T. 100
	P <sub>M</sub> x103	نۍ		1,583	1,655	2.415	2.540	2.845	2.850	200:1		1.053	1,147	1,310	T. 032	T. 720	T'ATR
	Pcx102	Ø		0.9126	1.0384	1.3725	1.4605	1.6635	1,7713	T. 1038		0.6025	0,7309	0.7928	0.9726	1.0053	1.0742
94	pwx102	4		0.6934	0.7671	0.9557	1,1102	1.2575	1,3276	1.3204		0.3888	0.5371	0,5926	0,6642	0.7601	0.8944

																	114		3.1	
75 1								41		11 0			100							
1881.0			-								A	3.4	Cons.						1000	
200																				
							1				S I					- 1		15 -41		
		7	4	Η.		100 h		200			8 7	3						35 B 10		
-			7			-			W 30		- 1	- 1		•					104	
															*					
																			100	
0988						OI.							T-MANTO				31 7		50x70	
						178			30.0	4.0										
400 -										45 0		30 -								
							1									3 1			24-	
4 4				*	*			11 4						-					0	
1-3																				
																			1 / SW	
																			1. 9	
																			1 50	
					-		2									3 1		62		
						*		30				F 9		-					1 100	
1.088					T								STATE OF							
																			Totag	
																			1	Contract of
100															2.5				9	
													0.0							
																			1 1	
			0.		-			13	-				. B		*			Little State of	1	
7* 3.80		n.			L		las.						0000							
						1/3														
						100	27									W.C.	3		100	
	10%					388	LAI		362	100	Second		370			N. C.	200	V CX	TOS.	
087	168	888	088	988	202	988	1771		2002	10000	2000	200	320	100	MAN.	1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	200	52	Salas.	
0.830	1.891	* 353	058	.888	1.888	320.0	1771		2002	1000	2000	1.40	078	100	- MODE		200	5 CX	Parros.	
0.830	0.891	0.858	0,880	0.988	0.398	0.988	1777		1,000	10000	1 1000 P	2.50	278.1	100	Table of the same	No. of Contract of	200	C2.	Salanos	
0.530	0.891	0.853	088.0	0.985	0.888	0.982	1,157		1.068	1000 P	1,3088	200	078.1	100	T-STORY	NAME OF THE PARTY	2000	C2	16 Extos	
0.530	0.891	6358	088,0	0.988	0.398	0.982	7.757		1.068		2000	7.955	7.350	100	2.000	No. of the last of	200	62	Solva	
0.530	0.831	6353	058.0	0.988	200.0	0.982	1,141		7.068	10000	2,200%	3.55	1.340	100	T-MAN	NAME OF THE PARTY	200	2.02	Solve Salve S	
0.530	168.0	6888.0	0,880	0.988	208.0	0.988	1,141		7.000	10000	2000	7.30	1.340	100	2000	NAME OF THE PARTY		CX.	\$2Lxgs	
																		E CO	19 <sup>25</sup> arro <sub>S</sub>	
																			Solvanos S	
																			NS SETTOS	
																		CX.	N.S. 1925 TOS	
							1.171						135						N.S. 15Trug	
																			N.S. SERIOS	
																			IN/8 19 <sup>25</sup> arrog	
																			N.S. SATIOS	
																			N.B. SEETOS	
																			NAS 1975/208	
																			NAS SPITOS	
																			N.S. SEETOS	
																			1	
																			1	
																			1	
			772																1	
			772										130						1	
			772										130						1	
			772										130						1	
													130						1	
			772																1	
			772										130						1	
			772										130						1	
			772										130						1	
			772		The state of the s								130						penrepereta M.S. SETOS	
			772										130						1	
			772		The state of the s								130						1	

	•
	•
-	
773	
-	•
100	
1.3	
-	
and the last	
2-4	
-	•
- 63	
-	
-	
2.3	
~	
-	3
-	•
-	
C23	
~	
-	
-	
<b>S31</b>	
-	
-	
-633	
740	
general.	-
-	
5.3	
general .	-
-	
623	
***	
-	
-	

				1		
1	83	8	4	D.	9	2
	0					
	75	0.686	1.820		0.4258	- 0
	102			0.880	0.5026	0.3871
1	150			-	0.6003	
1:110	211				0.7083	
	270			-	0.7322	
	294			-	0.7331	
	338				0.7607	- 0
	•		CHO			
	>					
**	62			0.517		
	96			0.610		
	147			0.755		- 0
1:140	168			0.802	- 6	
	215	0.510	1.870	0.901	0.4638	
	280			0.940		
	346			0.982	0.5791	0.4101

FER	<b>其的是数</b> 。	图图 经有限 图 图 1	
7 000	6000	0000000	
0.0389	0.3556	7007.0 9887.0 9887.0	0
1000 1000 1000 1000 1000 1000 1000 100	8484		4
1.850	27868	2899988888 8899988888888888888888888888	
1980	1866	200000000000000000000000000000000000000	.60
1000		0000000	
285	27899	8kate2a	2/3
	ž.		

Experimental data for catalyst - 3

p <sub>M</sub> x10 <sup>3</sup> p <sub>C</sub> x10 <sup>2</sup> p <sub>W</sub> x10 <sup>2</sup>	5 6 .7	.560 1.0328 0.6689 .750 1.1902 0.7755 .365 1.6867 1.0878 .880 1.9860 1.2717 .050 2.0725 1.3469 .740 2.1556 1.3547	.122 0.7319 0.4863 .183 0.7589 0.4875 .650 0.9472 0.6399 .835 1.2392 0.8093 .988 1.2841 0.8439
PBx102 Pox101 P	8	735 1.930 1.768 1.768 1.768 1.720 2.06 1.600 2.188 1.583 2.291 1.583 1.940	980 1.825 1.990 1.821 1.787 1.785 1.785 1.745 1.728 1.738 1.728 1.728
benzene:air W/F p	1 2		1:80 124 0. 202 0. 246 0.

-	
-	ŧ.
	и.
1000	
- 100	ш
_	
3:5	
The state of	
- 200	
0	
- 50	
63	2
-	
-	a .
7	2
-	8
-	
200	
the same	
	а.
- 4	ĸ۸
1000	
<b>S</b>	
	8
	я.
100	2
-	2
- 5	R
	5.
	ь.
193	8
W	2
-3	9
-	
-	
phid.	2
and.	
60	
4	
Bird.	

STREET, STREET

SECRETAL SEC

Hardes Sassass

SECRETARY PRESERVED A

STREET SERVICES

-

1	63	က	4	IQ.	9	4
	0	0.842				
	22	0.710	1.867	0.736		0.3217
	116	0.677	-			
1:110	135	0.642	-	-		
	202	0.630	-	-		
	270	0.614	-	1,238	0.8579	0.5496
	360	0.602	1.807	-	0.9157	
	0		-			
	73	0.573	1.890			
	65		-	0.560	0.4369	0,2756
1:140	141		FF (26)		- 0	
	183					
	283					
	312					

1.0

		10, 10	
	TOTAL		
	1 0 0 0 0 0 0 0 0 1 0 0 0 0 0 0 0 0 0 0		
	The second secon		
			1
1	Militario de la marca della ma		
	States a seed as		
3	hoodso - hhhhoo	*	
j			
3			
1	TERROTO MEGACIONO		
	Edeles Seese		
1	Chilippinia hiphippini		
3	CONTRACTOR OF THE PROPERTY OF THE PARTY OF T		
			100
1			
į			
1	The second secon		
2			
1	Bandaga shering		
3	100000000000000000000000000000000000000		
1	The second and the second seco		
ì			
9			
į	The second secon		
-	1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	100	
0	688689° 588664°		
į			
-			
1000		1	
I			

Experimental data for catalyst - 3 at 400°C.

penzene:alr	W/F	pBx102	Pox101	PMx103	Pcx102	PWX102
1	83	m	4	2	9	7
	0	1.760	1.920		-	
	74.	1.418	1.720	1.740	1.3731	0.8729
	123	1.317	1.665	2.720	1.6834	1.0922
OCIT	143	1.298	1.670	2.510	1.5899	1,1238
	224	1.200	1.608	3.440	2.0201	1,3564
	280	1,165	1.576	3.380	2.2404	1,4593
	308	1.162	1.574	3.270	2.2932	1.4761
	0	1.140	1.940			
the standard are by	95	0.910	1.180	1.220	0.8966	0.5739
1.00	128	0.894	1.179	1.460	0.8904	0.5924
1:80	180	0.843	1.177	1.778	1.0527	0.7092
	222	0.820	1.176	1.925	1,1370	0.7667
	280	0.790	1.174	1.998	1.2942	0.8506
	305	0.791	1,173	1.955	1.3062	O DECK

W. P. W. B. C. S.		18 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2		1 1	
		ALL DO THE COLUMN TO			
		ES AS TO SELECT A			
THE REAL PROPERTY.		-02 PER SER SER SER			
(C) (C) = () = ()	- FIR 20 4	B B B C C C C C C C C C C C C C C C C C	- AS		
				100	
The Real Property lies	and the later of t	The San		1 1 1 1	
	And And a line of	penenn		ACTUAL DE	
				1	
				- 2	
				1	
	-				
2000 2000 2000 2000 2000 2000 2000 200		STORES .		200.2	
		THE RESERVE THE PARTY OF THE PA		Signal Signal	
				Same B	
	The state of	in to to and set a			
1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	The one of	THE REAL PROPERTY AND ADDRESS OF			
hhhh	* * 1			- E	
				1 11 1	
		THE RESIDENCE OF THE PARTY OF T	OUR ALL SHAPE		
			-		
				1	
				- 3	
				(C) 2	
				1 1 1 1	
		288888		S OFF	
				Trees of	
	Section 1	1000 400 -0-01		39 1	
	THE PARTY	THE REAL PROPERTY AND ADDRESS OF THE PERSON	DE THE	100	
1 0880 1 0880 1 0880 1 0880					
		20 20 20 10 to im-			
	and the same of	The second second second second		1	
			4		
				100	
				-	
		3999888		E	
				3.7	
		0 0 0 0 0 0 0		. 34 1	
				Total B	
From Factor	by by by	description by her bit his			
hhhh	be bedre	bibbbbbb		400	
hinhih	balada.	bhhhhhhh		- FR	
hichh	ha ha ha	bishhibbh		and the	
hishib	ba baba	bbbbbbb	and the last	400	
hinhih	ba baba	blabblabb		- Ch	
hinhih	h haha	beliebele le le le		- C - C - C - C - C - C - C - C - C - C	
hinhih	la haba	beliebeliebeliebelie		Si .	
				- Di	
				6. 29	
				80	
				80	
				10,5	
MAD CONTRACT	140	200 Sept 200		80	
1000 END	320	200 Sept 200		10,5	
1000 END	320	28.28.28.28.28.28.28.28.28.28.28.28.28.2	65	10,5	
MAD CONTRACT	320	200 Sept 200	65	10,5	
1000 END	320	28.28.28.28.28.28.28.28.28.28.28.28.28.2	65	10,5	
1000 END	320	28.28.28.28.28.28.28.28.28.28.28.28.28.2	65	10,5	
1000 END	320	28.28.28.28.28.28.28.28.28.28.28.28.28.2	65	10,5	
1000 END	320	28.28.28.28.28.28.28.28.28.28.28.28.28.2	65	10,5	
1000 END	320	28.28.28.28.28.28.28.28.28.28.28.28.28.2	65	10,5	
1000 END	320	28.28.28.28.28.28.28.28.28.28.28.28.28.2	65	10,5	
00.00 00	1.140		65	10,5	
00.00 00	1.140		65	10,5	
00.00 00	1.140		65	10,5	
00.00 00	1.140		65	10,5	
00.00 00	1.140	28.28.28.28.28.28.28.28.28.28.28.28.28.2	65	10,5	
00.00 00	1.140		65	10,5	
00.00 00	1.140		65	10,5	
00.00 00	1.140		65	10,5	
00.00 00	1.140		65	10,5	
00.00 00	1.140		65	10,5	
00.00 00	1.140		65	10,5	
00.00 00	1.140		65	10,5	
00.00 00	1.140		65	10,5	
00.00 00	1.140		65	10,5	
00.00 00	1.140		65	10,5	
00.00 00	1.140		65	10,5	
00.00 00	1.140		65	MAR DEXTOR	
00.00 00	1.140		65	MAR DEXTOR	
00.00 00	1.140		65	MAR DEXTOR	
00.00 00	1.140		65	MAR DEXTOR	
00.00 00	1.140	308 389 384 1.189 148 1.888 1.888 1.888 1.888 1.888 0 1.888	65	MAR DEXTOR	
00.00 00	1.140	308 389 384 1.189 148 1.888 1.888 1.888 1.888 1.888 0 1.888	52	MAR DEXTOR	
00.00 00	1.140	308 389 384 1.189 148 1.888 1.888 1.888 1.888 1.888 0 1.888	52	MAR DEXTOR	
008.0 0.802 008.0 0.803 008.0 0.803	1.140	308 380 1.103 1.008 1.00	65	MAR DEXTOR	
202 088.0 088.0 525 088.0 981	1.140	2008 2008 1 1 1 200 2008 2008 2008 2008 2008 2008 2008	52	10,5	
008.0 0.802 008.0 0.803 008.0 0.803	1.140	2008 2008 1 1 1 200 2008 2008 2008 2008 2008 2008 2008	52	DONAIG MAR DEXTON	
202 088.0 088.0 525 088.0 981	1.140	308 380 1.103 1.008 1.00	52	DONAIG MAR DEXTON	
202 088.0 088.0 525 088.0 981	1.140	2008 2008 1 1 1 200 2008 2008 2008 2008 2008 2008 2008	52	DONAIG MAR DEXTON	
202 088.0 088.0 525 088.0 981	1.140	2008 2008 1 1 1 200 2008 2008 2008 2008 2008 2008 2008	52	DONAIG MAR DEXTON	
202 088.0 088.0 525 088.0 981	1.140	2008 2008 1 1 1 200 2008 2008 2008 2008 2008 2008 2008	52	DONAIG MAR DEXTON	
202 088.0 088.0 525 088.0 981	1.140	2008 2008 1 1 1 200 2008 2008 2008 2008 2008 2008 2008	52	DONAIG MAR DEXTON	
202 088.0 088.0 525 088.0 981	1.140	2008 2008 1 1 1 200 2008 2008 2008 2008 2008 2008 2008	52	MAR DEXTOR	
202 088.0 088.0 525 088.0 981	1.140	2008 2008 1 1 1 200 2008 2008 2008 2008 2008 2008 2008	52	DONAIG MAR DEXTON	

Table - A.11 (contd.)

1	63	8	41	2	9	2
	0					
	92	0.715	1.890	9.	46	
	26			-	54	W .
0.1.	105			0.753	0.5898	
1:110	136			0	61	
	211		-	0	77	
	272			S	86	4
	293			w	85	0.5679
	0			37.50		
	74			- 4		0
	140		l m	2	. 1	100
1:140	215	0.487	1.860	0.941	0.5891	300
	286		-			4
	338		-		0.8811	0.4438

	mmount oncount !	
	0.3839 0.3839 0.3839 0.3839 0.3838 0.3838	
	1120001 000001	41
-0.5		
	00000 000000	
	0.0000 0.	
	tonger canage	
	0000010010000001	00
	00000 0000000	
	20000 2000	
	malhana - ia ah aimin ta	
	85 - 85 F F F F F F F F F F F F F F F F F F	
	000001:0000000001	
	11.033 1.033	
	8888 8888 8888 8888 8888 8888 8888 8888 8888	
	60 00 00 00 00 00 00 00 00 00 00 00 00 0	
	hibbish bhbbbbbb	
	393258 8623636B	
	\$ F F 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6	(0)
	A STATE OF S	
	.000000.0000000	
	200010 221220 200010	10
	3338 3338 333 344 355 353 353 353 353 353 353 353	10
	338 388 388 388 388 388 388 388 388 388	to
	338 338 338 340 340 340 340 340 340 340 340 340 340	10
	338 338 338 340 340 340 340 340 340 340 340 340 340	10
	SSS SSS SSS SSS SSS SSS SSS SSS SSS SS	10
	338 338 338 343 343 343 343 343 343 343	10
	338 338 338 343 343 343 343 343 343 343	10
		10
		10
	140	10
		to
	110	to
		to
		to

Experimental data for catalyst - 4 at 400°C.

Pwx102	7	11.35 5409 6113 7107 9021 0246 1734 2456 6579 8329 9108 0025 1671 2586 3381 4033
-	1	าศศาสต์ผู้ผู้ อังอักล์กล่ำลำ
Pcx102	9	2.4751 2.6004 2.9473 3.937 3.9473 3.9473 3.5756 1.2827 1.5454 1.8037 2.0487 2.0487
P <sub>M</sub> x10 <sup>3</sup>	13	2.586 3.736 4.784 4.784 4.784 1.915 1.915 2.298 2.652 2.652 3.136
Pox101	4	1.8593 1.6579 1.5553 1.5592 1.5163 1.4693 1.4026 1.3846 1.7207 1.602 1.602 1.6198
PBx102	m	1.8318 1.3743 1.3743 1.1702 1.1247 1.0549 0.9974 0.9479 0.9305 0.8824 0.8824 0.8115 0.7422 0.6755 0.6343 0.6025
WF	S	68 116 127 180 231 294 318 88 88 88 205 205 318
benzene: air	1	1:50

Table - A.12 (contd.)

Head and the state of the state

8	00	000	183 216 221 221 294 0.46	70 0.65 109 0.47 139 0.42 222 0.36 267 0.34 326 0.33
4	riri	HHH	4888 1.7507 4659 1.7369 4662 1.7391 4358 1.7222	.6579 1.9480 .5080 1.8621 .4276 1.8184 .3623 1.7802 .3423 1.7608 .3302 1.7608
ß	1.109	1.821	2.122 2.132 2.139	0.882 1.136 1.434 1.888 1.950 1.951
9			1.3128	0.5466 0.6469 0.8076 1.0598 1.1383 1.1862
-			0.8574 0.9148 0.9074 0.9791	

	, agains	SANG.	
BORTAN BO		STATE OF STA	
200000 200000 2000000 2000000000000000	5 222	00000	
19-11 to 10-10-10	o the		

Experimental data for catalyst - 5 at 400°C.

benzene: air	W/F	pBx102	Pox101	PMx103	Pcx102	Pwx102
1	co.	8	4	23	9	
	0	1.8318	1.9234			
	64	1,3645	1,6459	2,432	1.8307	1 1502
	102	1,1818	1,5375	3,383	2.5462	7.6114
C III	136	1.1027	1,4882	3.720	2.8861	1.818.1
Octo	177	1,0098	1,4145	4.284	3.4276	2.0373
	222	0.9364	1,3889	4,445	3.5566	2.2476
74.3	250	0.9228	1,3913	4.396	3.5171	2.2872
	302	0.8761	1.4156	4.150	3.3206	2,2686
	0	1.1677	3.9379			
	64	0.8756	7.7690	7. 404	1000	
	103	0.7737	1.7010	1.00F	10.1401	0.7176
	140	0.7205	1.6698	2.267	1.7544	2000
7:80	183	0.6588	1.6346	2.636	1.9797	1 9474
	254	0.5911	1.5916	2.896	2.2729	1,4994
	262	0.5900	1.5919	2.932	2.2648	1.4220
	20 00 00 00 00 00 00 00 00 00 00 00 00 0	0.5808	1.5853	2.944	2,3144	1.4480
	279	0.5641	1.5714	808	OLCI C	1000

	-6	- 8
	20	- 8
		F 8
	•	- 10
100		-8
- 2		
	-	
- 40	•	
- 600	30	
<b>Print</b>	= 1	
-	ari i	
-	w 1	
- 64		
100	-	
-		
Bernel	80	

ELECTRONIC STREET

STREET BEEN SEE

SOCIOLOS STATES STATES TO A WORK

his billing the hand had been

62	0 0.8416 64 0.6377 103 0.5635 140 0.5100 194 0.4606 240 0.4399 250 0.4358 310 0.4176	0 0.6579 64 0.5067 98 0.4511 135 0.4136 175 0.3790 272 0.3283 272 0.3262 305 0.3169	
4	1.9441 1.8235 1.7763 1.7763 1.7141 1.6936 1.6936	1.9480 1.8590 1.8259 1.8043 1.7521 1.7521 1.7534	
5	1.077 1.361 1.645 1.920 2.037 2.106	0.782 1.098 1.316 1.495 1.710 1.801	
9	0.7921 1.1237 1.3163 1.5364 1.6301 1.6852	0.5878 0.9394 1.0751 1.2934 1.2691	
1	0.5038 0.6980 0.9509 1.0013	0.3688 0.5104 0.6014 0.6871 0.8147 0.8403	

Table - A.14 . Experimental conversions to maleic anhydride  $(x_M)$  and carbon dioxide  $(x_C)$  for catalyst - 1 at  $400^{\circ}C$ .

hhhikhhiti kithhih

nzene:air	W/F	× <sub>M</sub>	*c
	0 60 93	0.0665 0.0925	0.0835 0.1235
1:50	132 162	0.0960	0.1680
	190 228	0.1180	0.1980
	280	0.1102	0.2498
	0 <b>62</b>	0.0750	0.0690
1:80	90 132 160	0.0900	0.1020
2.00	192 204	0.1275 0.1350 0.1380	0.1529 0.1730 0.1760
	250 310	0.1450 0.1420	0.1700
	0		
	107	0.0645 0.0962	0.0756
1:110	154 183	0.1180 0.1250	0.1340
	212	0.1320 0.1360	0.1775
	321	0.1410	0.2000
	61 98	0.0610	0.0725
1:140	124 155	0.0980	0.1021 0.1250 0.1422
	180	0.1240	0.1510
	242 337	0.1362	0.1718 0.1858

bus (pr) salanging states to enstangues Leinspireum control (pr) and control of the design and (pr) shizelb and and control of the design and the control of the control of

		4/M	The repeated
	er commence de la servició de la decada co	An an arthur the American St. a. A.	Add of the first of the second of the second
The state of the s			
0.0333	0.000.0		
· · · · · · · · · · · · · · · · · · ·	0.0980	58	
0.001.0	0.0960	132	
MARKET U	0.22509	162	
0.1890 0.1880 0.3170 0.0498	0.1186	Yee	
OVER S	0.110g	988	
2001.0	SOLL O		
		ō	
The state of the s	Allen S		
0.0000	0.07500	88	
William .	100 May 1 - 17	08	
September - A	The state of	SSI	
0.1830 0.1939 0.1730 0.1780	0.1278 0.1278 0.1278 0.1278	051	
DOXL .U	1964.0		
24001	0.1880#	965	
0.1760	06.1.0		
		ore	
0.1940 0.1940 0.1940 0.1940			
	STATE A	7.7	
BOAT A	0.845 0.0850 0.1180 0.180	107	
A STATE OF	ADEC O	5.00	
OF 65 . O	APPL A	158	
VALUE OF	Other Co.		1,110
THE REAL PROPERTY.	AND A		
0.1779	0.1820 0.1800 0.1410		
Supple - U	- United and		
0.0725			
0.1081	1580.0		
	APOS		
0001.0	0257 75		
0.1423 0.1520 0.1718 0.1718	Daniel All		
Goze	NOW A PLANT		
DESCRIPTION OF THE PARTY OF THE	00000		
0,107	0.1290 0.1380 0.1360 0.1402	YEE	
	A Print and	100	
	and the second second second second		

Experimental conversions to maleic anhydride  $(x_M)$  and carbon dioxide  $(x_C)$  for catalyst - 2 at 310°C.

enzene:air	W/F	× <sub>M</sub>	×c
1:50	0 70 107 149 185 230	0.0280 0.0376 0.0469 0.0523 0.0492	0.0191 0.0293 0.0307 0.0340 0.0413
1:80	0 75 118 164 197 240	0.0213 0.0391 0.0408 0.0483 0.0488	0.0156 0.0252 0.0340 0.0388 0.0414
1:110	0 69 107 154 190 238	0.0179 0.0255 0.0343 0.0397 0.0447	0.0131 0.0167 0.0216 0.0254 0.0358

01.4 - 01012

Experimental conversions to walsic animalist  $(x_0)$  and  $(x_0)$  and  $(x_0)$  for satisfies -2 at  $310^{\circ}0$ .

a particular construction	with a real memory and all of the original way		
O <sub>E</sub>		3/8	Dengenoraly
	A STATE OF THE PARTY OF THE PAR		
Tern.o	0.0250		
\$950.0	0.0076	507	
V020.0	9040.0		
D480.0	6550.0	103	
616613	0.0498	088	
6.03.6	8130.0	57	
6.0353	1080.0		
0.000	CONT.O	401	1.500
9900.0	\$880.0	461	
Arbo.o	0.0403	0.00	
	The state of the same of the s		
1010.0	0.0179		
V61019	- 6880.0	701	
0.50.0	0.0343	AUL	
202010	7980.0	300	
Been.h	14240.0	988	
EGGU-U	11000	6.60	

xperimental conversions to maleic anhydride  $(x_M)$  and carbon dioxide  $(x_C)$  for catalyst - 2 at 330°C.

enzene:air	W/F	<b>x</b> M	x <sub>C</sub>
	0	0.0415	0.0267
1.50	104	0.0562	0.0379
1:50	149 194	0.0679	0.0611
	228	0.0862	0.0764
	0		6-1100
	72	0_0398	0.0263
1:80	113 155	0.0580	0.0389
1.00	209	0.0732	0.0594
	250	0.0862	0.0808
	0		100
	68	0.0352	0.0248
1:110	111	0.0520	0.0381
4.410	195	0.0633 0.0740	0.0564
	235	0.0804	0.0720

Experimental conversions to maleic anhydride (x<sub>M</sub>) and carbon dioxide (x<sub>C</sub>) for catalyst - 2 at 350°C.

enzene:air	W/F	× <sub>M</sub>	× <sub>C</sub>
1:50	0 61 99 131 173 199 230 313	0.0740 0.1019 0.1200 0.1477 0.1562 0.1690 0.1901	0.0542 0.0847 0.1041 0.1161 0.1238 0.1232 0.1402
1:80	0 65 107 150 178 219 244 319	0.0711 0.0977 0.1200 0.1313 0.1478 0.1516	0.0540 0.0920 0.1102 0.1187 0.1315 0.1422 0.1535
1:110	0 68 104 149 187 222 267 322	0.0692 0.0938 0.1170 0.1282 0.1377 0.1482 0.1533	0.0538 0.0813 0.1077 0.1276 0.1283 0.1420 0.1522
1:140	0 64 102 138 178 215 252 334	0.0620 0.0837 0.1088 0.1270 0.1403 0.1530 0.1682	0.0552 0.0818 0.0915 0.1028 0.1119 0.1190 0.1296

Table - A.16

Experimental conversions to maleic embydetas (x.) and
carbon diexide (xg.) for catelyst - 2 at asque.

Tre-selder

bee (30) ablessede ereter at east-selves to community and

common atomics (30) los ellesses - 2 &t 50000.

0			Thirdearns
The same of the sa	A STATE OF THE PARTY OF THE PAR	The second second second	
		0	
Si-60:0 76:50:0	0.0790	LO	
A COLUMN TO THE PARTY OF THE PA	0.1019 0.1000 0.1200 0.1503	131	
1401.0	0.1200	IGA	
0.1301	1777.0	173 199 200	
5552.0	ENGI.O	661	
STATE OF	0.1890	230	
0.1808 0.1808 0.1808	1001.0		
	The same of the sa	319 107 107 108 178 178 244 244	
0.0540	2570.0	65	
0.0020	TERM OF	107	
2011.0	OOSE.O		
YELL.O	GISI.O	1778	1:80
CLOL.O	0.0977 0.1200 0.1812 0.1878		
QRML C	0.1828		
0.1935	0.1822		
-			
8680.0	0.0692		
0.0913 0.1876 0.1888 0.1888			
6, 1977	0777		
0.1276	2201 6	187	11110
anni-o	0.1170 0.1877 0.1877 0.1877	939	NAME OF THE OWNER, OWNE
0,1480	020.5 0	267	
egar.o	0.1833	292	
Name of the last o	CHORDE ATA		
	The state of the s	AM p = V	
200.0	0.0020		
SIEO.	YESO, 0		
0.1139	0.0030 0.0037 0.1080		
8501.0	0.1870		
erir 6	EOMI.O		Offic
DELLO	DESCRIPTION OF THE PERSON OF T	arg see	
0.1206	0.1330		
The second second	SECT.		

Table - A.18 Experimental conversions to maleic anhydride  $(x_M)$  and carbon dioxide (xc) for catalyst - 2 at 375°C.

benzene:air	W/F	<b>*</b> M	*c
1:50	0 62 96 144 182 219 245 301	0.0807 0.1065 0.1445 0.1640 0.1791 0.1888 0.2010	0.0595 0.0877 0.1095 0.1339 0.1339 0.1415 0.1511
1:80	0 65 103 140 187 222 250 322	0.0777 0.1003 0.1258 0.1467 0.1612 0.1666 0.1771	0.0605 0.0917 0.1062 0.1300 0.1326 0.1415 0.1609
1:110	0 62 107 139 181 212 258 322	0.0750 0.1009 0.1240 0.1371 0.1489 0.1590 0.1648	0.0590 0.0912 0.1083 0.1295 0.1434 0.1490 0.1610
1:140	0 61 100 140 177 208 250 319	0.0727 0.0972 0.1161 0.1322 0.1352 0.1467 0.1560	0.0571 0.0878 0.1040 0.1311 0.1418 0.1497 0.1636

SF.A - sidsi

a (<sub>N</sub>x) substitutes states of emphasization institutions.

13° ove in 8 - included not (gx) abtracts modical

		. a/h	Theremenad
	The second secon	care for a strain.	
Bud"		2	
cicass	C10807		
7730:0	780110		
C.IOSO	0.1440		
TTODIO CONTO	0.1145 0.1510 0.1701 0.1858	193	1:00
0111339	T071.0	SIS	
dist.o	0.1888		
IIGI.0	0.2010	ros	
6080.0	7770.0	0.0	
	0.1003	EOL	
SADELY	8881.0	531	
5000	X21.6 19		
0.1000 0.1320 0.1320	0.1467 0.1612 0.1666		
Walter and	20000	- ozs	
6001.0	COOL VI	000	
Table .	0.1771	838	
200.0	Davo.	29	
2110.0	- ROOL.O	107	
CHOIL O	OFST.O	cet	
0.000.0 0.100.0 0.100.0 0.100.0 0.100.0 0.000.0	0.0780 0.1840 0.1871 0.1871 0.1890 0.1890	181	
ACRI.O	CENT.O	ELE	
Dell's	0691.0		
orer.e	8/51.0		
The state of the s	The second of		
ITYOO.O	PETO.O		
0.0373	5,000.0		
0.0373 0.1040 0.1040 0.1407 0.1497 0.1497	0.0727 0.0872 0:1161 0:1803		
fier.	fical to		11110
STATE OF	97.07	NYI 809	
700000	0.1359 0.1467 0.1660		
DOME OF	0.355.0	350	
7 15 95 50 7 2			
A THE DESCRIPTION OF THE PARTY	The state of the s		

Table - A.19

Experimental conversions to maleic anhydride  $(x_M)$  and carbon dioxide  $(x_C)$  for catalyst - 2 at  $400^{\circ}C$ .

enzene:air	W/F	× <sub>M</sub>	*c
	0	0.0700	0.0379
	53	0.0750	0.0550
	107 135	0.1150	0.0961
1:50	189	0.1740	0.1363
	226 240	0.1852	0.1470
	305	0.2080	0.1522
	346	0.2040	0.1700
	0	0.790	0.0450
	53 119	0.780	0.0459
1.00	147	0.1298	0.1023
1:80	177 238	0.1425 0.1592	0.1275
29,120	268	0.1715	0.1520
	322	0.1820	0.1650
	70	0.0710	0.0730
	117	0.0980	0.1025
1:110	175 190	0.1325 0.1440	0.1170
1:110	240.	0.1541	0.1420
	266 322	0.1642 0.1740	0.1500
		0.1110	0.2000
	60	0.0715	0.0630
	98	0.0950	0.0892
1:140	140 222	0.0930	0.1372
	234	0.1485	0.1480
	272 346	0.1590 0.1722	0.1573

Of .A - a.ldaT

Experimental conversions to maleic enlydride  $(x_0)$  and .000. The makelyst - 2 at  $100^{\circ}$ C.

Andrew Co.			
O <sub>X</sub>	10	3/8	Tia:sneshed
		0	
0.0379	0.070.0		
0.000.0	0.070.0	500	
1000.0	0.1150		
0.1193	SERE D	661	
0.1383	0.1820		
07.1.1	STREET,	000 000 000	
0.3580	0.1900	170.00	
0.2582	9808.0		
0.1700	0.8040		
0,6459	6.230	58	
7900	ordi o		
SECT.0	2002.0		
0.1275	0.1325	VAI VVI 8ES	1460
0.1173	seaf.		
0.1520	arti.	865	
O. Idao	0801.0	SEE	
0.1028	OTTO TO		
STORY OF	08981.0		
OVIII.O	TOOT A		
1881.0	0.1295		1:110
			MARKA
05.34.0	0.1511	240. 255	
0.2683	0.1642		
0000.0	0.1740		
0.0830	0.0735		
9980.0	0.0000		
0.1379	0.0930		
0.1006	PART.0		
0.1420	Open - G		
CYCL A	near.a	575	
0.1008	1271.0		

Table - A.20

Experimental conversions to maleic anhydride  $(x_M)$  and carbon dioxide  $(x_C)$  for catalyst - 3 at  $310^{\circ}C$ .

benzene:air	W/F	× <sub>M</sub>	×c
1:50	0 58 100 130 169 235	0.0282 0.0373 0.0418 0.0452 0.0566	0.0189 0.0230 0.0279 0.0338 0.0356
1:80	0 64 107 132 194 236	0.0224 0.0376 0.0442 0.0523 0.0571	0.0158 0.0249 0.0298 0.0375 0.0440
1:110	0 70 110 140 190 248	0.0191 0.0256 0.0322 0.0381 0.0407	0.0141 0.0212 0.0235 0.0294 0.0349

Ni. L aldal

mertweetel conversions to salete embydeles (mg) em

6.7		5/4	vla:emeand
9810.0 0.0980 0.0990 0.0890 0.0890	9890.0 0.0373 0.0413 0.0566	O D D D D D D D D D D D D D D D D D D D	OF:I
0.0188	2000.0 6400.0 6400.0 6400.0 04000	0 40 701 723 194 194	
0.023.0	0.029	70 70 110 140	

Table - A.21

Experimental conversions to maleic anhydride  $(x_M)$  and carbon dioxide  $(x_C)$  for catalyst - 3 at 330°C.

benzene:air	W/F	x <sub>M</sub>	×c
1:50	0 63 104 130 168 220	0.0445 0.0660 0.0696 0.0782 0.0917	0.0253 0.0517 0.0576 0.0598 0.0718
1:80	0 70 107 132 187 237	0.0415 0.0621 0.0708 0.0852 0.0901	0.0235 0.0352 0.0417 0.0670 0.0736
1:110	0 68 112 138 193 244	0.0346 0.0551 0.0694 0.0741 0.0882	0.0277 0.0451 0.0576 0.0630 0.0715

IS.A.T. aLiaY

Experimental conversions to salate amphitics ( $_{\rm H}$ ) and earlies to a large ( $_{\rm SC}$ ) and earlies that the carries of the conversion along the conversion and the conversion and the conversion of the conve

green the second second		and the broke transport of the last	the transport of the state of t
9 <sup>x</sup>		2/4	nanionietai.r
Matthews are as the contractor		CARAMATA A CAMADA A CAMADA	the state of the state of the state of
8880.0	0.040	80	
0,0027	3030.0	104	
0.0576	0.0696	130	1150
0.6548	0.6788	Leg	
0.0712	0.0917		
6683.0	ha later in		
CRET NO		0	
6688	CLAO.	0.5	
ECEP.O	1880.0	107	
VII-0.0	0.0708	SEL	1:20
0.0070	\$520.0		
0.0788	0.0901	Y68	
	- 200		
S. Special Company		O.	
3720.0	0.0340	88	
1820.0	1000.0	1112	
0780.0	4880.0	SEL	DETal
0.0830	1990.0	193	
0.0713	5880.7		
Control of the Contro		N. There's a substitute of the same of the	Miles and all absences and a contract that we
CARL AT			
100			
	. 1014.5.55		
	HUM		
	·		

carbon dioxide (x<sub>C</sub>) for catalyst - 3 at 350°C.

benzene:air	W/F	× <sub>M</sub>	x <sub>C</sub>
1:50	0 75 90 120 139 162 200 244 310	0.0881 0.0920 0.1283 0.1343 0.1419 0.1585 0.1710 0.1597	0.0700 0.0813 0.0922 0.1056 0.1128 0.1280 0.1311 0.1397
1:30	0 81 103 128 177 203 255 318	0.0900 0.0983 0.1125 0.1313 0.1476 0.1645 0.1612	0.0711 0.0882 0.0945 0.1172 0.1191 0.1267 0.1308
1:110	0 75 102 150 211 270 294 338	0.0841 0.1082 0.1208 0.1303 0.1366 0.1451 0.1408	0.0707 0.0823 0.0993 0.1192 0.1231 0.1222 0.1286
1:140	0 79 96 147 168 215 280 346	0.0780 0.0925 0.1143 0.1267 0.1369 0.1421 0.1481	0.0690 0.0881 0.0907 0.0956 0.0945 0.115 0.1210

Table - A.23

0.0831 0.1843 0.1843 0.1816 0.1917 0.1917 0.0900 0.0903

0.1333

0.1545

0.1000

FUNDE .O

BOAL . G

0.0780 0.0863 0.0148

0.0700 0.0818 0.1034 0.1034 0.1036 0.1030

0.0949 0.1173 0.1189 0.1289

sost.0

6.0707

8380.0

DEEL . O

Experimental conversions to maleic anhydride  $(x_M)$  and carbon dioxide  $(x_C)$  for catalyst - 3 at  $375^{\circ}C$ .

enzene:air	W/F	M	×c
1:50	0 65 75 129 211 282 352	0.0903 0.1015 0.1365 0.1664 0.1767 0.1582	0.0695 0.0811 0.1177 0.1363 0.1410 0.1558
1:80	0 76 92 124 202 246 322	0.0953 0.1001 0.1395 0.1550 0.1683 0.1642	0.0753 0.0698 0.0877 0.1238 0.1251 0.1382
1:110	0 77 116 135 202 270 360	0.0875 0.1122 0.1235 0.1314 0.1473 0.1527	0.0692 0.0804 0.1119 0.1190 0.1235 0.1305
1:140	0 73 92 141 183 283 312	0.0752 0.0857 0.1145 0.1366 0.1485 0.1510	0.0655 0.0808 0.0916 0.0897 0.1003 0.1105

Experimental conversions to malaic anightide (sg.) acres of states anight of the states of the state

	a Farmer Living		
			then sense alor
34			
medical selection date		STATE OF THE PARTY OF	
0.0895	6,090.0	35	
0.0311	ovacas	65	
OFFEE OF	desivo	129	1:50
east.o	lesi.o	IIS	
OLDI.O	C. 1787	929	
0.1552	6, 1988	935	
*		- 0	
BEYO.O	8690.0		
0.0898	1001.0		
6.0377	0.1388	ARI	1170
0.1238	0.1830	808	
resi.o	0.1683		
0.1882	0.1642		
	Vanna a	97	
0.0092	6780.0	17	
10.50.0	0.1180	ari	
0.1139	0.1283	802	
CEST.O	0:1873	296	
0.1360	6.1387	038	
100.00	7,01544, 407		
6680.0	0.6708	88	
5000.0	7080.0		
ULGG.O	0.1130		Obl:I
798010	0.1386		
500E10	CBAL.O	285	
6.1105	0.3520	are -	

 $\frac{\text{Table - A.24}}{\text{Experimental conversions to maleic anhydride }(x_{\text{M}}) \text{ and }}$  carbon dioxide  $(x_{\text{C}})$  for catalyst - 3 at  $400^{\circ}\text{C}$ .

benzene:air	W/F	× <sub>M</sub>	xc
1:50	0 74 123 143 224 280 308	0.108 0.142 0.154 0.188 0.191 0.185	0.096 0.099 0.112 0.133 0.148 0.155
1:80	0 95 128 185 224 280 306	0.107 0.128 0.156 0.169 0.175 0.172	0.095 0.093 0.102 0.110 0.137 0.134
1:110	0 76 97 105 136 211 272 293	0.079 0.089 0.083 0.117 0.128 0.146 0.158	0.066 0.078 0.087 0.088 0.116 0.123 0.117
1:340	0 74 140 215 286 338	0.077 0.132 0.145 0.154 0.159	0.055 0.070 0.103 0.108 0.120

## 10.4 - alder

two (ix) oblymous stellar to receive the farming of the (ix) oblymous to a - Jugister tol (ix) oblymous carbon distribution (ix)

		6/2	camene: ir
STATE OF STREET		A STATE OF THE PARTY OF THE PAR	
S	The state of the s	0	
1500.0	3901.0	24	
3000	0.1.0	3.23	
COPP IN	0.189		I so
Allog their college	-201 0	600	
DC14 * /	TOTAL ST	982	
Della All	2007	202	
0.000.0	607.0		
	-	2	
0.093 0.093 0.102 0.103 0.130 0.134	0.199	36	
880.0	0.199		
Carlo	0.175 0.175 0.175	188 294 206 206	08:1
	OUT	500	
MAA: • ·	SUF O	000	
YOU.	Wilder A		
- ASI . 0	817.0		
***			
0.088	0.079	7.5	
200.0	980.0	40	
- 6000-0	0.000	76	
0.000	NAME AND ADDRESS OF THE PARTY O	120	10110
	0.188	1.00	
OLL VI		278	
Edit .	0.138	808	
WEE'S	501.0		
	*	9	
0.055	570.0	1.4	
0.108 0.108 0.108	DOL. O	1.60	
ONT A	def.0		11110
100 E 10	0.131		
The state of the s	10 Sept. 10		
002.0	0.359		

Table - A.25

Experimental conversions to maleic anhydride  $(x_M)$  and carbon dioxide  $(x_C)$  for catalyst - 3A at 350°C.

benzene:air	W/F	× <sub>M</sub>	x <sub>C</sub>
1:50	0 62.5 102 130 175 217	0.0792 0.1211 0.1368 0.1676 0.1800	0.0763 0.0862 0.1175 0.1363 0.1502
1:80	0 69 106 130 188 230	0.0871 0.1115 0.1263 0.1552 0.1715	0.0803 0.0946 0.1675 0.1328 0.1382
1:140	0 63 97 126 175 221	0.0771 0.0983 0.1158 0.1382 0.1400	0.0654 0.0884 0.0985 0.1106 0.1231

ES.A. \_ sida!

but (gr) obtubules of the convergence Industrial and convergence of the state of the convergence of the conv

*	i.	NV.	bosemerale
AND THE RESERVE OF THE PERSON NAMED IN		6	
8870.0	0.0792	0.00	
2690.0	1181.0 0.1288		
CILITY	C. 1288	130	
SEEL.	SYSELO		
0.1502	008170		
4150			
208919	0.0871		
20,00,00	0.007T		
878110	8321.0		1.60
0:1353	0.1100		
200210	CITI D		
-			
2000.0	0.0771		
N. 038%	ERRO.O	69	
\$550.0 5560.0	0.1888	288	
901110	SERE!		
ISSE 10	003400	100	
		THE REAL PROPERTY OF THE PERSON NAMED IN COLUMN TWO IS NOT THE PERSON NAMED IN COLUMN TWO IS NAME	

Experimental conversions to maleic anhydride  $(x_M)$  and carbon dioxide  $(x_C)$  for catalyst - 3B at 350°C.

benzene:air	W/F	x <sub>M</sub>	× <sub>C</sub>
1:50	0 64 98 122 181 222	0.0690 0.1029 0.1381 0.1682 0.1718	0.0669 0.0968 0.1217 0.1521 0.1726
1:80	0 62 65 95 120 190 212	0.0720 0.0755 0.0982 0.1273 0.1661 0.1730	0.0650 0.0623 0.0906 0.1124 0.1388 0.1475
1:140	0 68 99 126 190 220 225	0.0671 0.0901 0.1133 0.1398 0.1449 0.1471	0.0512 0.0895 0.1128 0.1309 0.1340 0.1331

has (my) shirbying nieins to enlare (my) and enlare (my) and careen aloying (my) for untalyst " is at south.

		The state of the s	The second secon
			There was no
9050.0 8890.0 VISI'0 INGL'0	0.0000 0.1029 0.1381 0.1381	0 20 30 222 181 181 882	
0,1720	0.070.0		8841
SSOC.0 BONG.0 ASLI.0 BEEL.0 BYEL.0	Control of Control	200 100 200 200 200 200 200 200 200 200	
COLL.	0.0901 0.1203 0.1203 0.1203 0.1203 0.1400 0.1400		

 $\frac{\text{Table - A.27}}{\text{Experimental conversions to maleic anhydride }(x_{\text{M}}) \text{ and }}$  carbon dioxide  $(x_{\text{C}})$  for catalyst - 3C at 350°C.

benzene:air	W/F	<b>*</b> M	x <sub>C</sub>
1:50	0 60 93 125 180 221	0.0728 0.1197 0.1488 0.1822 0.1927	0.0797 0.1025 0.1242 0.1475 0.1678
1:80	0 54 94 133 169 250	0.0701 0.1092 0.1408 0.1583 0.1896	0.0536 0.0936 0.1153 0.1304 0.1581
1:140	0 51 93 125 178 222	0.0592 0.1070 0.1255 0.1497 0.1611	0.0497 0.0913 0.1015 0.1214 0.1262

Table - A.28

Experimental conversions to maleic anhydride  $(x_M)$  and carbon dioxide  $(x_C)$  for catalyst - 4 at 400°C.

0:1949 0:1849 0:1849 0:1849 0:1849 0:1849 0:01949

0.0722 0.1197 0.1322 0.1322

0.0701 0.1092 0.1408 0.1552 0.1320

enzene:air	W/F	× <sub>M</sub>	x <sub>C</sub>
1:50	0 68 116 127 152 180 231 294 318	0.1412 0.1878 0.2040 0.2241 0.2339 0.2612 0.2580 0.2500	0.1085 0.1552 0.1572 0.1619 0.1902 0.1943 0.2245 0.2426
1:80	0 60 88 93 122 161 205 250 318	0.1333 0.1661 0.1702 0.1993 0.2300 0.2551 0.2720 0.2751	0.1013 0.1300 0.1498 0.1569 0.1840 0.1947 0.2054 0.2222
1:110	0 62 73 124 144 183 216 221 294	0.1318 0.1451 0.1962 0.2180 0.2388 0.2522 0.2601 0.2832	0.0983 0.1151 0.1513 0.1520 0.1804 0.1942 0.1860 0.1990
1:140	0 70 109 139 222 267 304 326	0.1380 0.1803 0.2181 0.2712 0.2870 0.2964 0.3011	0.0998 0.1038 0.1319 0.1781 0.1927 0.2017 0.1989

 $\frac{\text{Table - A.29}}{\text{Experimental conversions to maleic anhydride }(x_{\text{M}}) \text{ and }}$  carbon dioxide  $(x_{\text{C}})$  for catalyst - 5 at 400°C.

benzene:air	W/F	<b>x</b> <sub>M</sub>	xc
1:50	0 64 102 136 177 222 250 302	0.1328 0.1847 0.2031 0.2339 0.2427 0.2400 0.2266	0.1223 0.1701 0.1949 0.2148 0.2461 0.2562 0.2951
1:80	0 64 103 140 183 254 262 282 318	0.1280 0.1700 0.1942 0.2258 0.2511 0.2480 0.2522 0.2482	0.1221 0.1677 0.1888 0.2100 0.2436 0.2458 0.2504 0.2687
1:110	0 64 103 140 194 240 250 310	0.1200 0.1618 0.1955 0.2282 0.2421 0.2503 0.2586	0.1142 0.1686 0.1984 0.2245 0.2352 0.2319 0.2452
1:140	0 64 98 135 175 257 272 305	0.1188 0.1670 0.2001 0.2273 0.2600 0.2739 0.2777	0.1110 0.1473 0.1713 0.1966 0.2410 0.2302 0.2406

bes (pr) substance clother of materies of substance community of the deviation of the community of the deviation of the community of the commu

SISTING TARS O ONL ONL SISTEMAN OF THE STORY OF THE STORY

0.1293 0.0245 0.0245 0.0245 0.025 0. 

Table - A.30

Comparison of the rates (r) calculated by the modified Hinshelwood model for total benzene disappearance and the rates (r1) calculated by the Hougen-Watson model for maleic anhydride formation with the corresponding experimental rates Temperature - 330°C.

03

Catalyst -

benzene:air	WF	rx104 Exptl.	rx104 Calc.	Error,	rlx104 Expt1.	rlx104 Cale.	Error,
1:50	69 104 149	7.70	11.62 8.07 6.61 5.79	1 1 + 1 + 0 + 0 0 m 0 0 0 0 0 0 0 0 0 0 0 0 0 0	5.77	11.37 6.00 5.07 4.43	130.7
	228	3.00	2.79	+ 7.0		3.70	+10.0
1,80	113 155 209 250	7.20 8.41 2.63 2.88	2.32 4.77 2.20 5.56	1 + 1 - 1 - 1 - 1 - 2 - 2 - 2 - 2 - 2 - 2 -	5.40 3.45 2.70	4 . u. u	+ 115.2 - 19.4 - 24.0
1:110	68 111 149 195 235	8.000 800 8	2.4.6. 2.9.86 2.91 6.29 6.29	1+1+1 140 140 140 140 140 140 140 140 140 14	2.35 3.92 1.96 1.96	2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	+29.0 +28.4 +25.5 n11
	Average error:			5.8			198

the second property of the second	1 7	
e Faths . Picted . 1964		
一位 "百万万万" "这个有效		
1 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4		
· · · · · · · · · · · · · · · · · · ·		
· · · · · · · · · · · · · · · · · · ·	1 9 1	
日本語を開発を開発を開発を発展し、対象を表現を 日本語を表現し、対象を表現を表現といる。 日本語を表現といる。	1925	
	40.00	
	A THE REAL PROPERTY.	
	4 - 1 - 17	
	1	
· 医性性免疫的 经存出的 经现代证明	1 4 9	
	Participation of the participa	5
historia historia interiore	1 7 1	
	1 10 4	
	A STATE OF	
	1	1
	1 0	1
	A COUNTY	1
	1 9	
		1
10110 111010 001011		
	1	
	6 . 10	
SCHEER RESERVED	100	1
	1 50	1
labilitation intribution indications	100	1
		1
		1
L women accept of the	1 1	
1 一位 自然自然的 的复数形态 自然的对象		
delicate apparate apparate		
	1 10 10	1
A STATE OF THE RESERVE THE STATE OF THE STAT		
		1
	the same	
		3 -
I worked organic operation		
A HERRO SERVICE STREET	1 2	
The state of the s		1
	1 3 6 3	
		1
	1 - N N-	
	The Party of	1
	The same	
	A DESCRIPTION OF THE PERSON OF	1
	1020	
		A 163
	Sire Sire	
	45	
	1 6 3	
	THE PROPERTY.	

Table - A.31

0

Comparison of the rates (r) calculated by the modified Hinshelwood model for total benzene disappearance and the rates (r1) calculated by the Hougen-Watson model for maleic anhydride formation with the corresponding experimental rates

3

Catalyst -

Temperature - 310°C,

Error, ++++1 971478 7.00018 +221-51-2 15-15-1 15-61-1 rlx104 22.22.11 3,31 1,62 1,48 1,41 rlx104 Exptl. 2,52 1,44 1,43 1,24 0,39 Error, nil -16.0 +16.6 +18.6 20000 100000 100000 rx104 6.75 2.59 1.81 1.47 6.10 8.50 8.50 8.43 1.34 rx104 25.00 20.00 22.80 2.00 0 107 132 194 236 W/F 130 benzene: air 1:80

199

14.7

12.5

Average error:

+25,9 +18,1 - 1,1 - 8,7 -19,3

20.5 -32.0 -32.0 -19.7

70 110 140 190 248

1:110

THE PARTY OF THE P SA SEE RESERVE SALLAL Control destate destate and THE SAME ARESES FOREIGN

APPENDIX - B

Figures

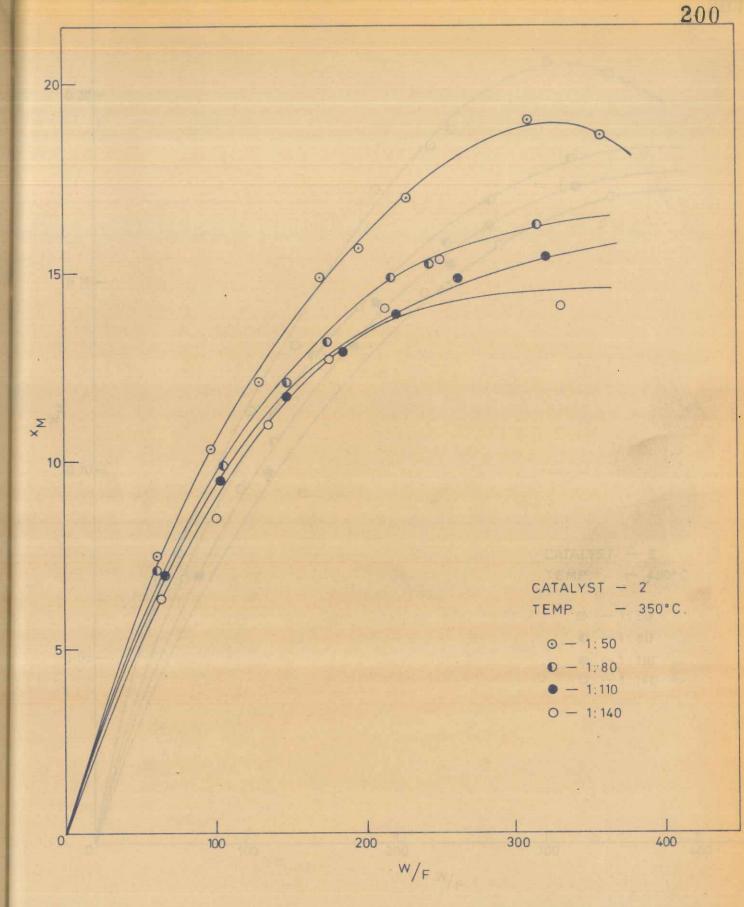
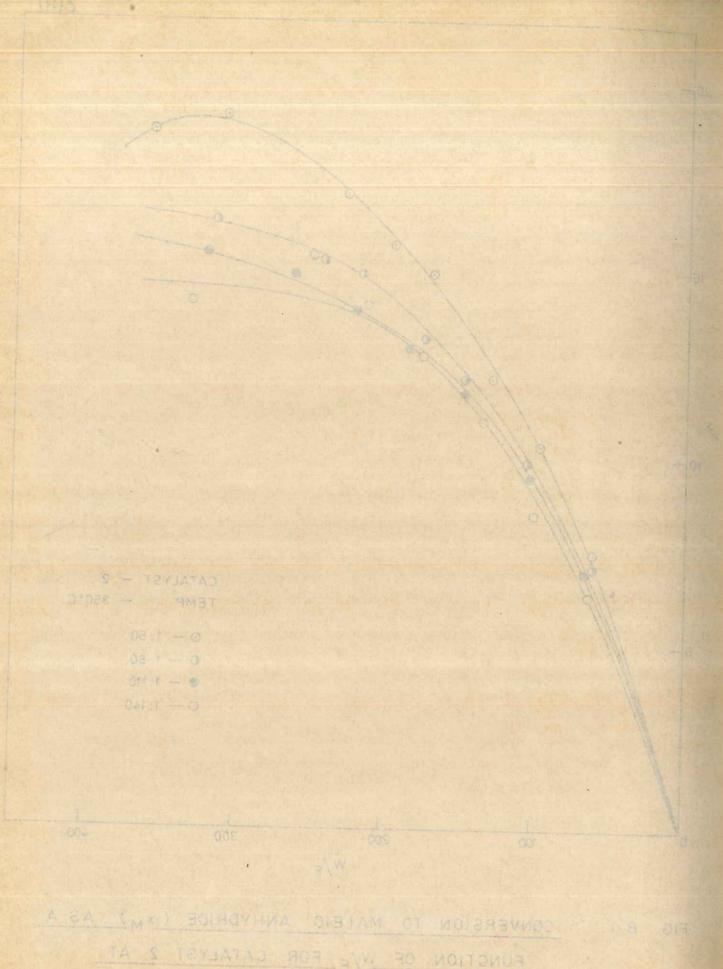
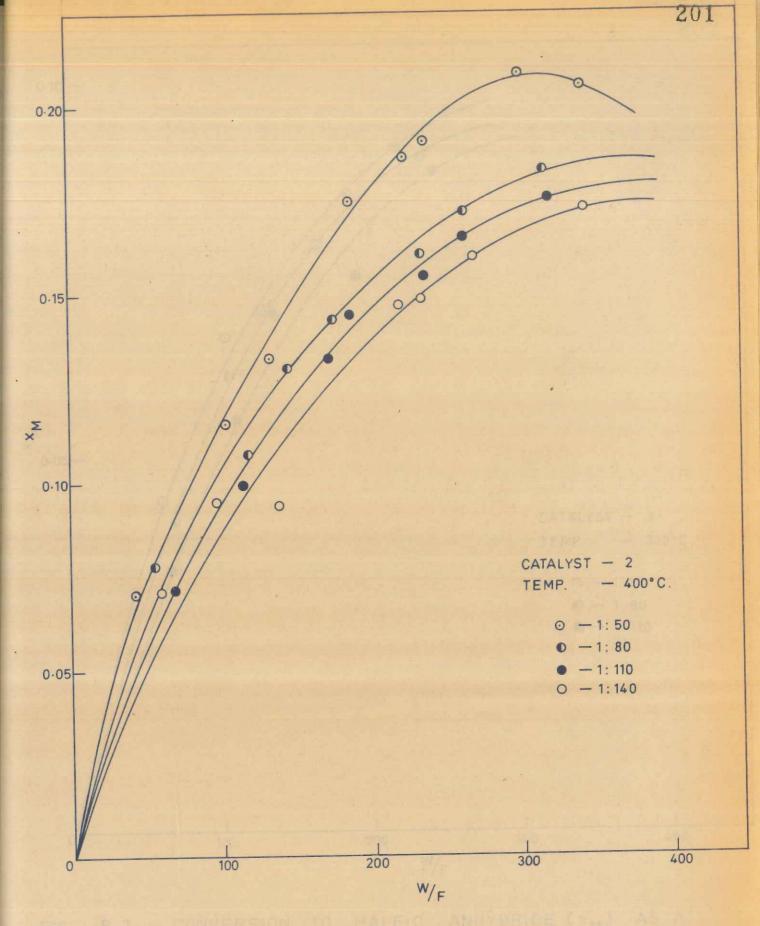


FIG. B.1. CONVERSION TO MALEIC ANHYDRIDE (x<sub>M</sub>) AS A

FUNCTION OF W/F FOR CATALYST 2 AT

TEMPERATURE 350°C





CONVERSION TO MALEIC ANHYDRIDE (XM) AS A FIG. B.2. FUNCTION OF W/F FOR CATALYST 2 AT TEMPERATURE 400°C.

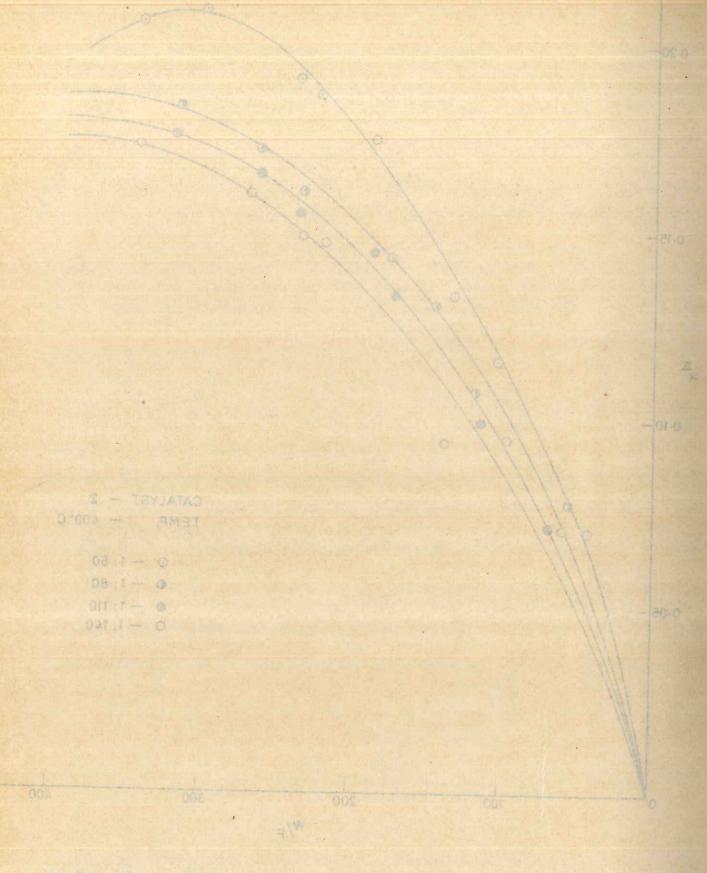


FIG. B. 2. CONVERSION TO MALEIG AMHYDRADE (XM) AS A FUNCTION OF W/F FOR CATALYST 2 AT TEMPERATURE 400° 6.

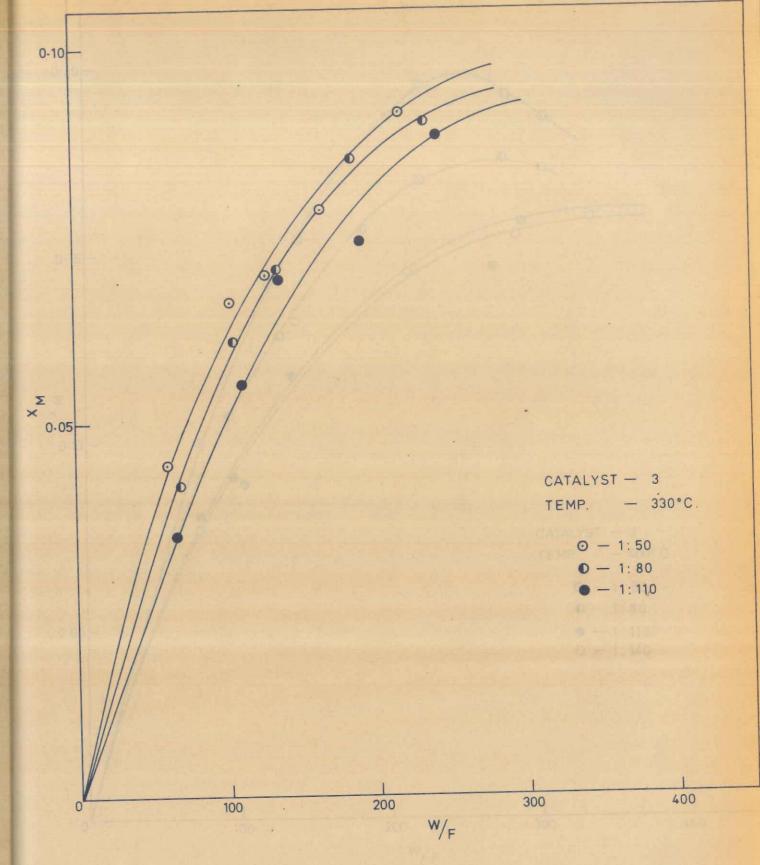
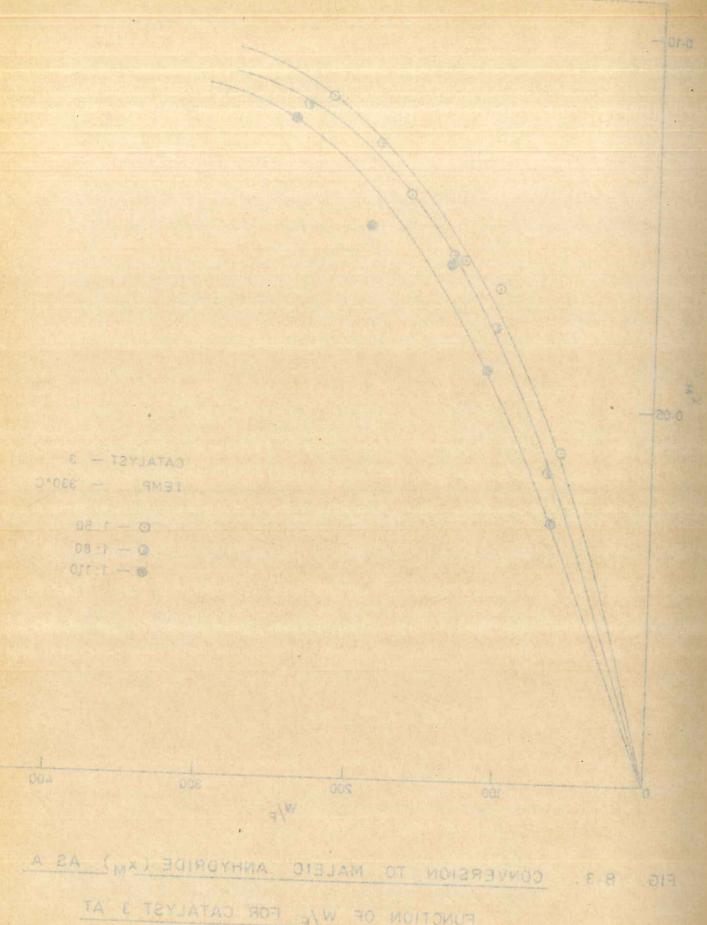


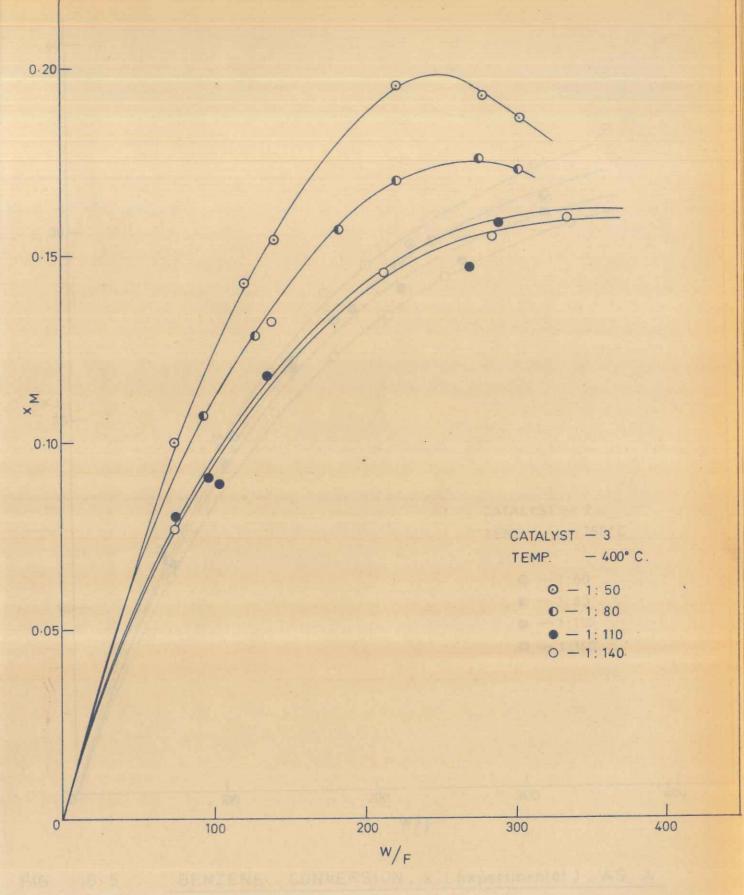
FIG. B.3. CONVERSION TO MALEIC ANHYDRIDE (xM) AS A

FUNCTION OF W/F FOR CATALYST 3 AT

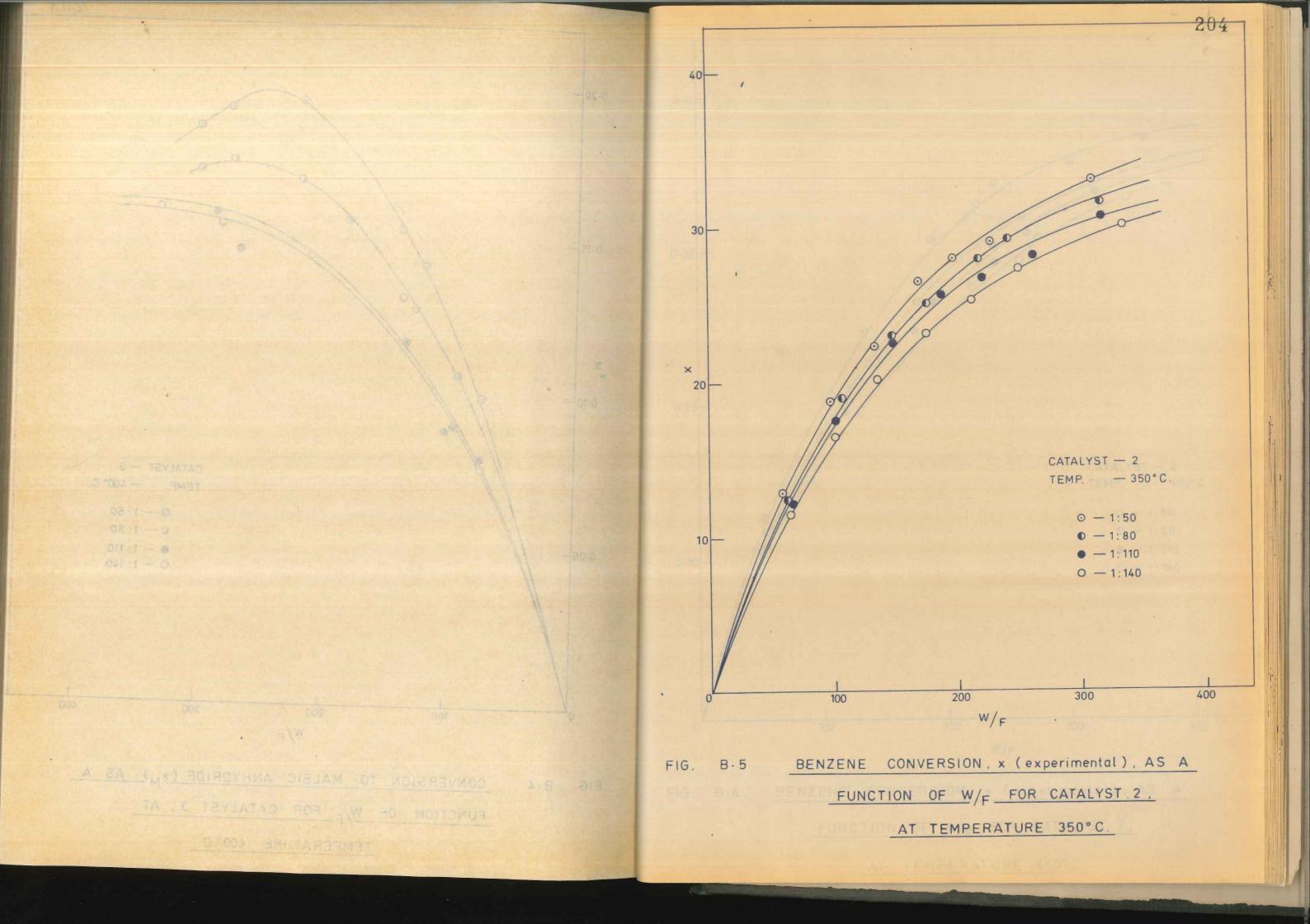
TEMPERATURE 330°C.

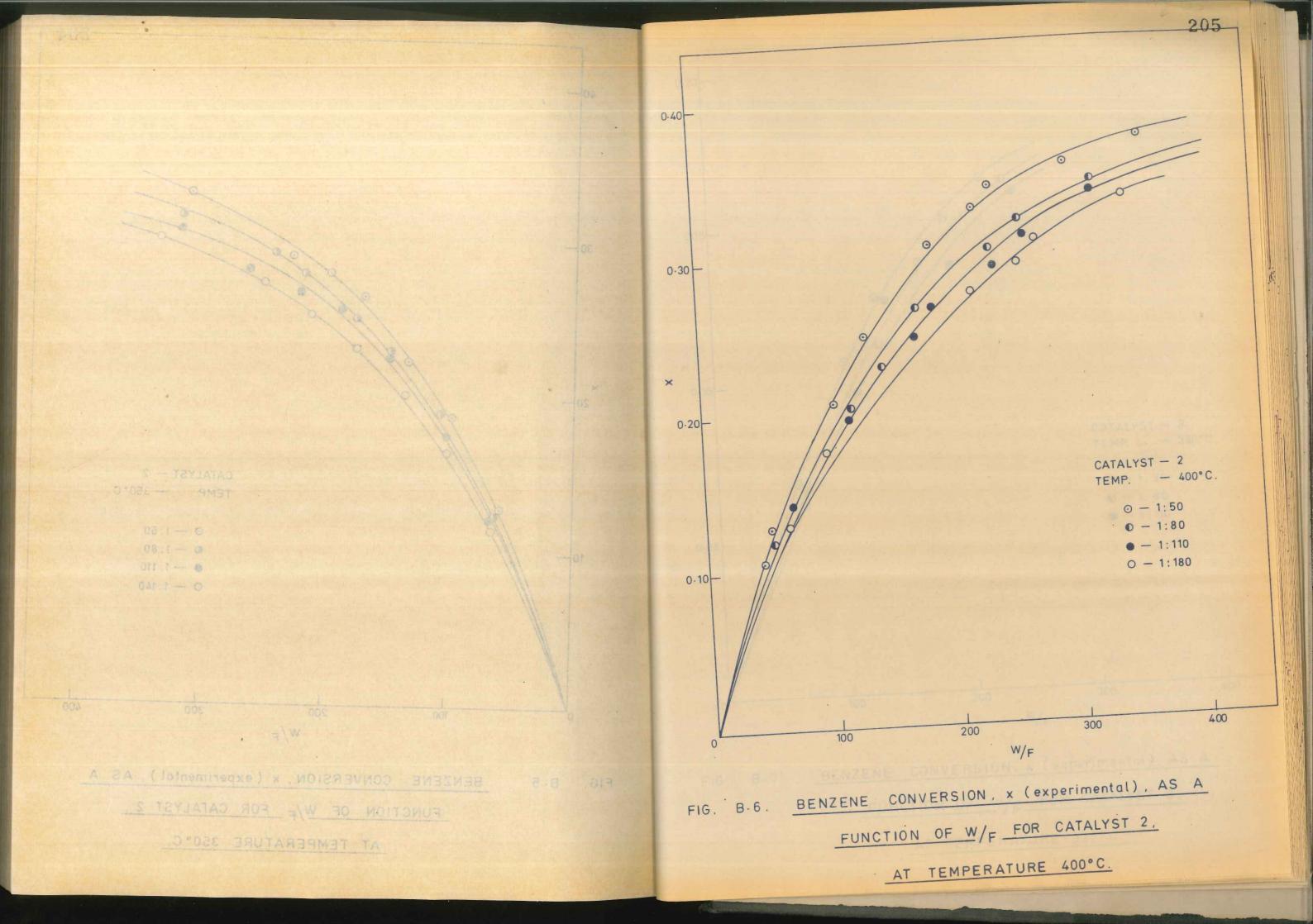


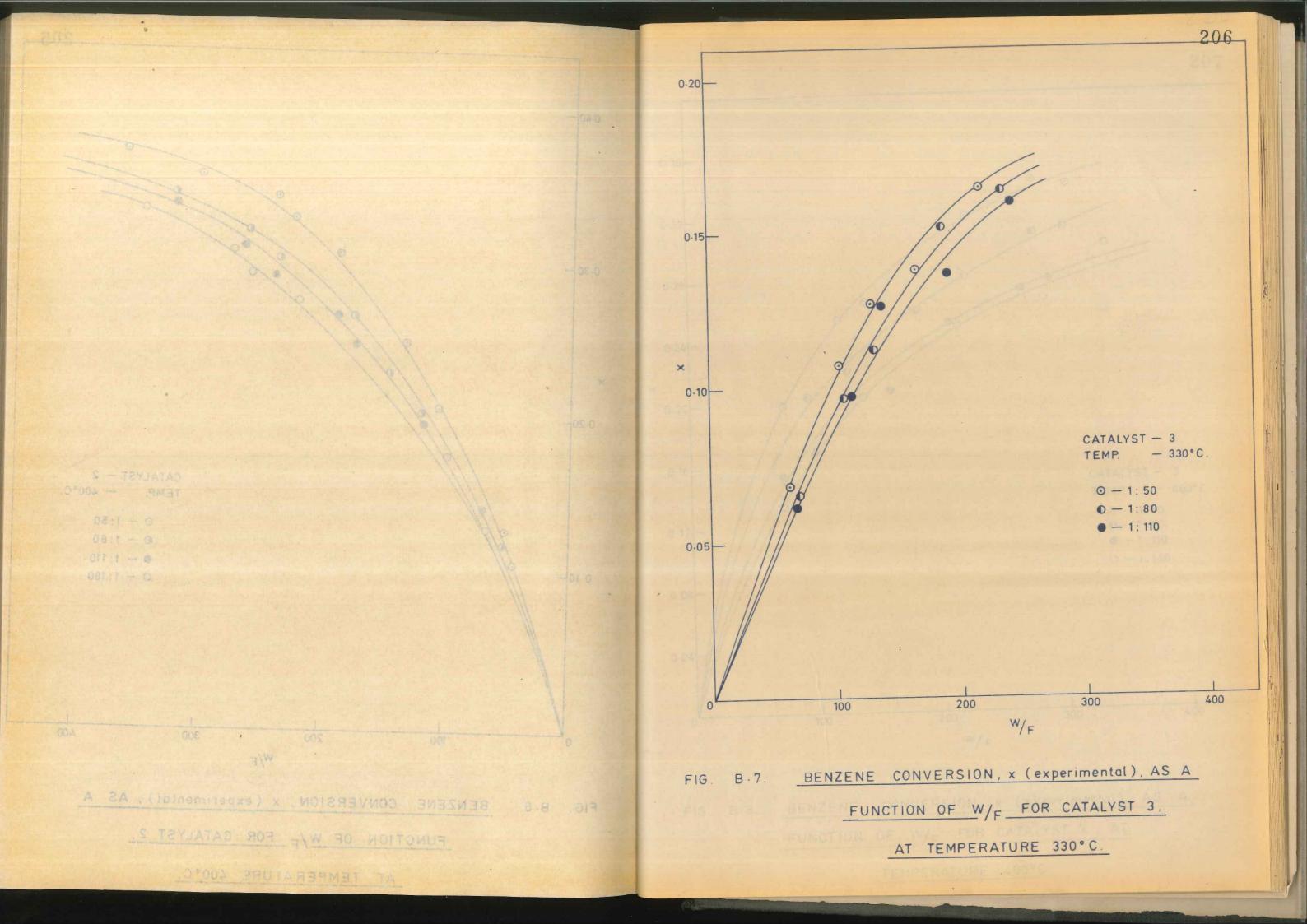
FUNCTION OF W/F FOR CATALYST 3 AT



CONVERSION TO MALEIC ANHYDRIDE ( \*M) AS A FIG. B.4 FUNCTION OF W/F FOR CATALYST 3, AT TEMPERATURE 400°C.







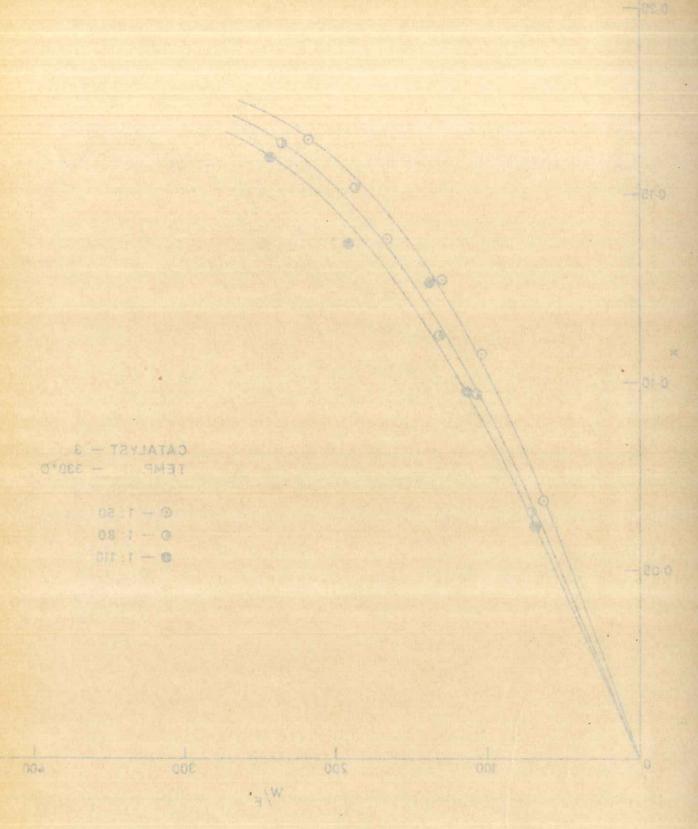


FIG. 8-7. BENZENE CONVERSION X (experimental), AS A FUNCTION OF W/F FOR CATALYST 3.

AT TEMPERATURE 330°C

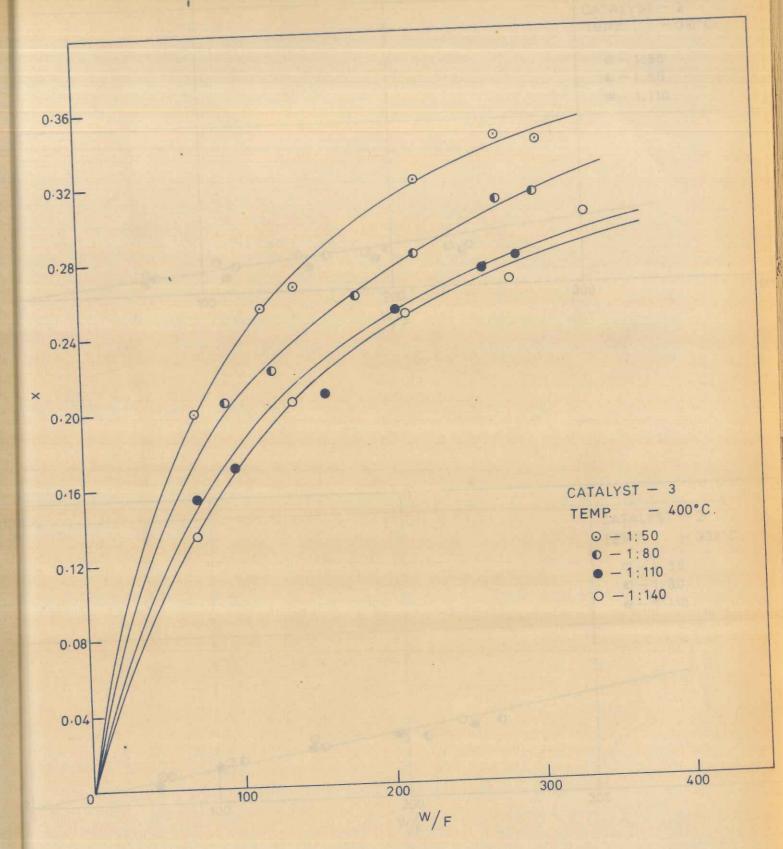
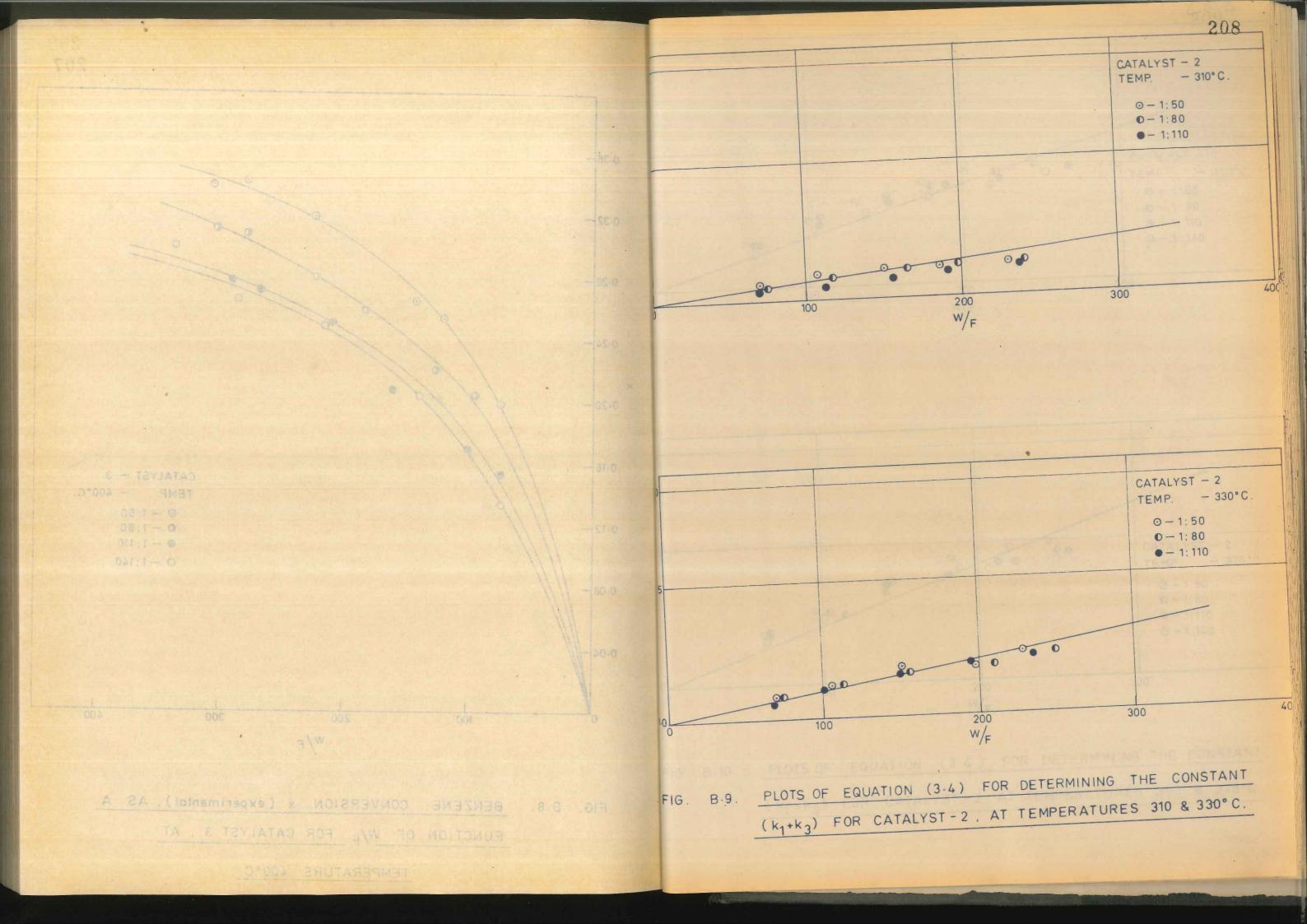
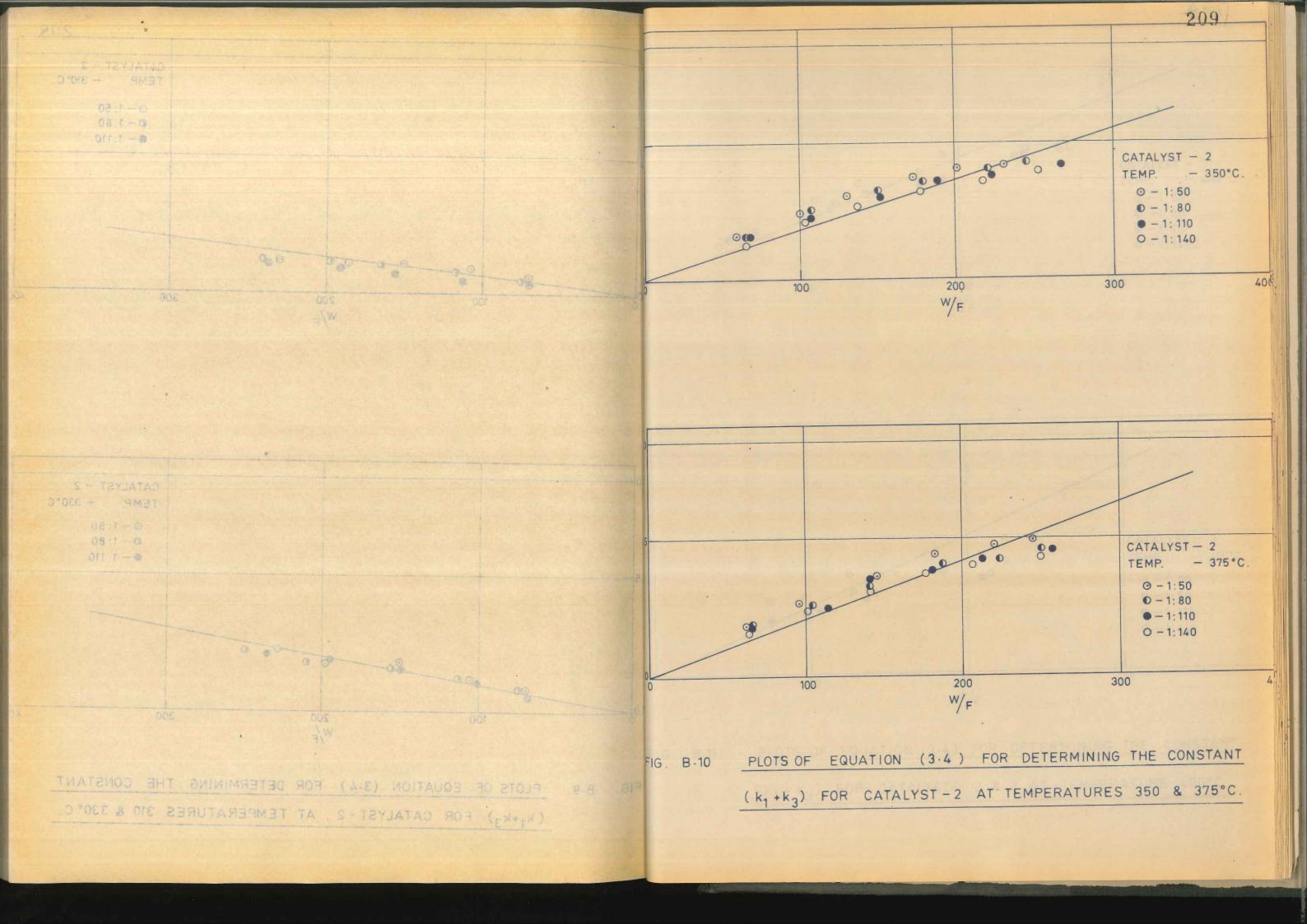


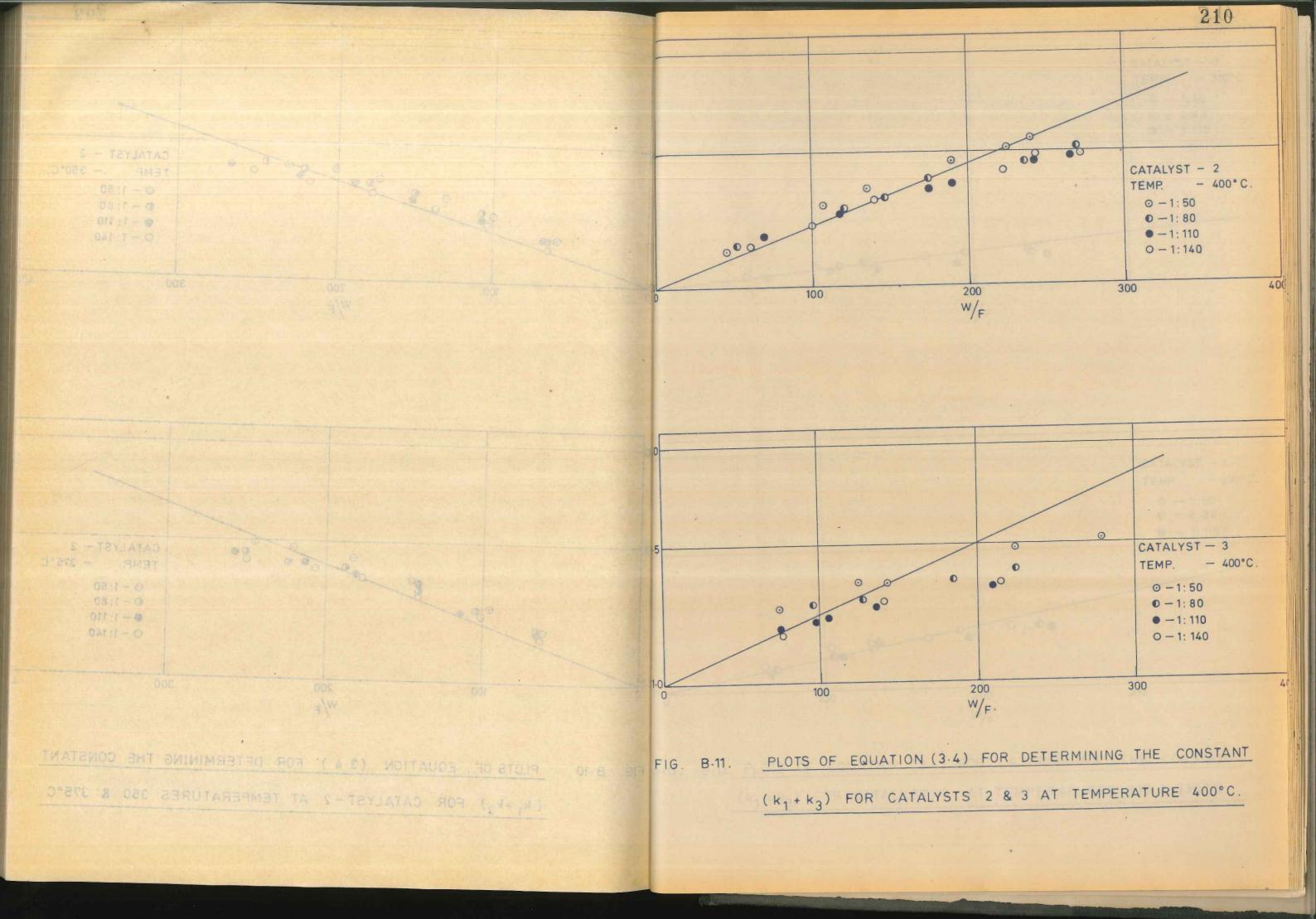
FIG. B.8. BENZENE CONVERSION, x (experimental), AS A

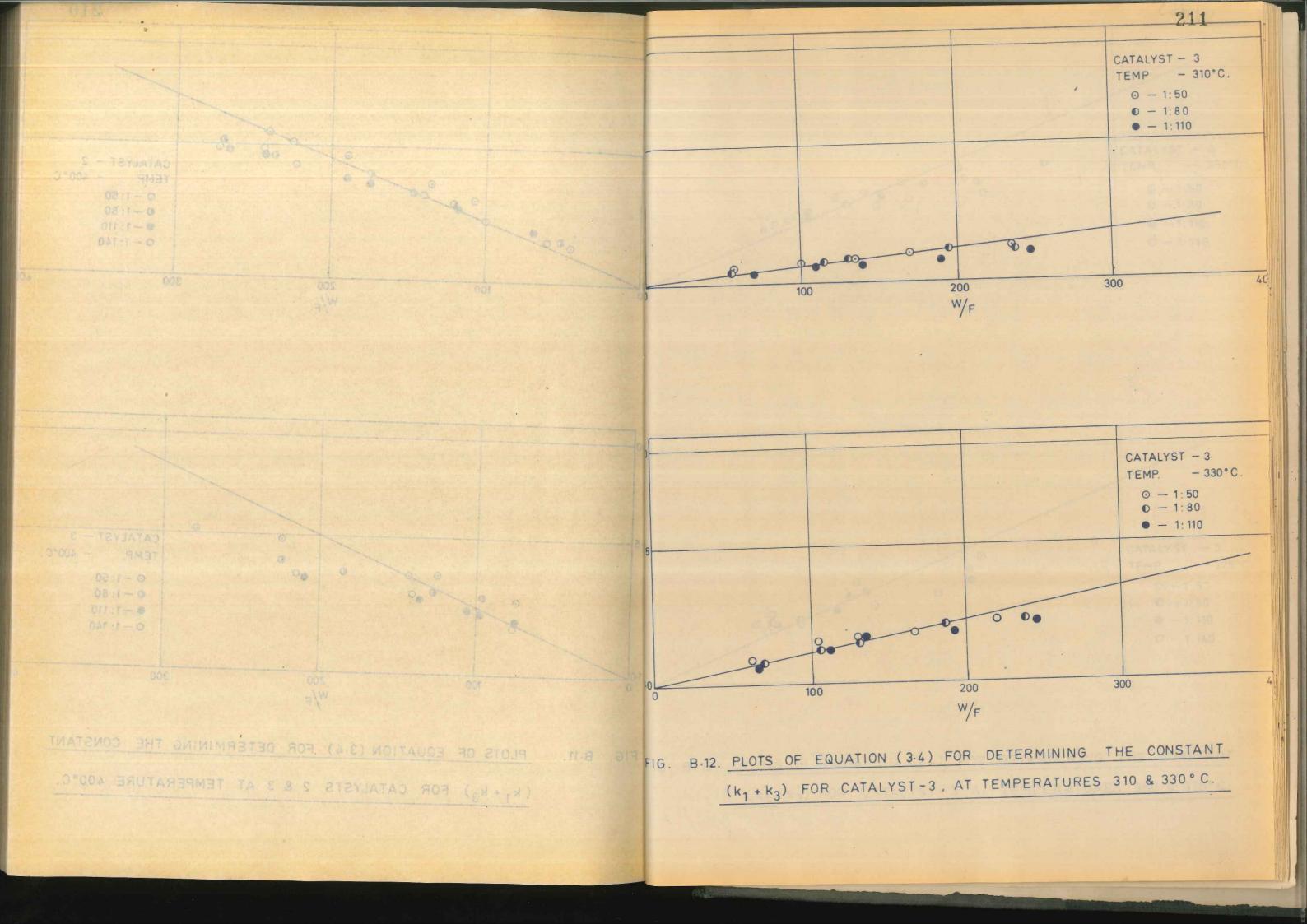
FUNCTION OF W/F FOR CATALYST 3, AT

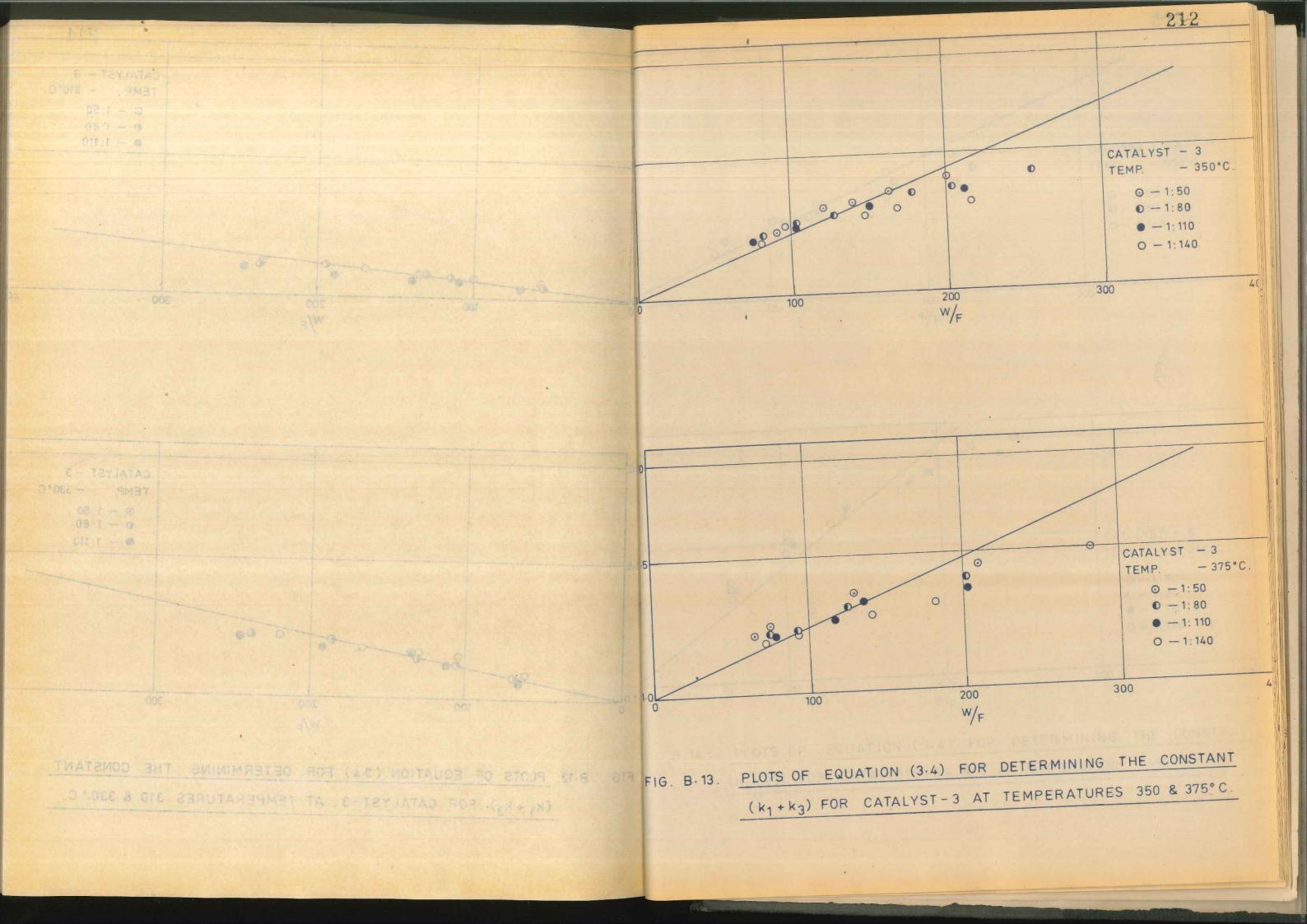
TEMPERATURE 400°C.

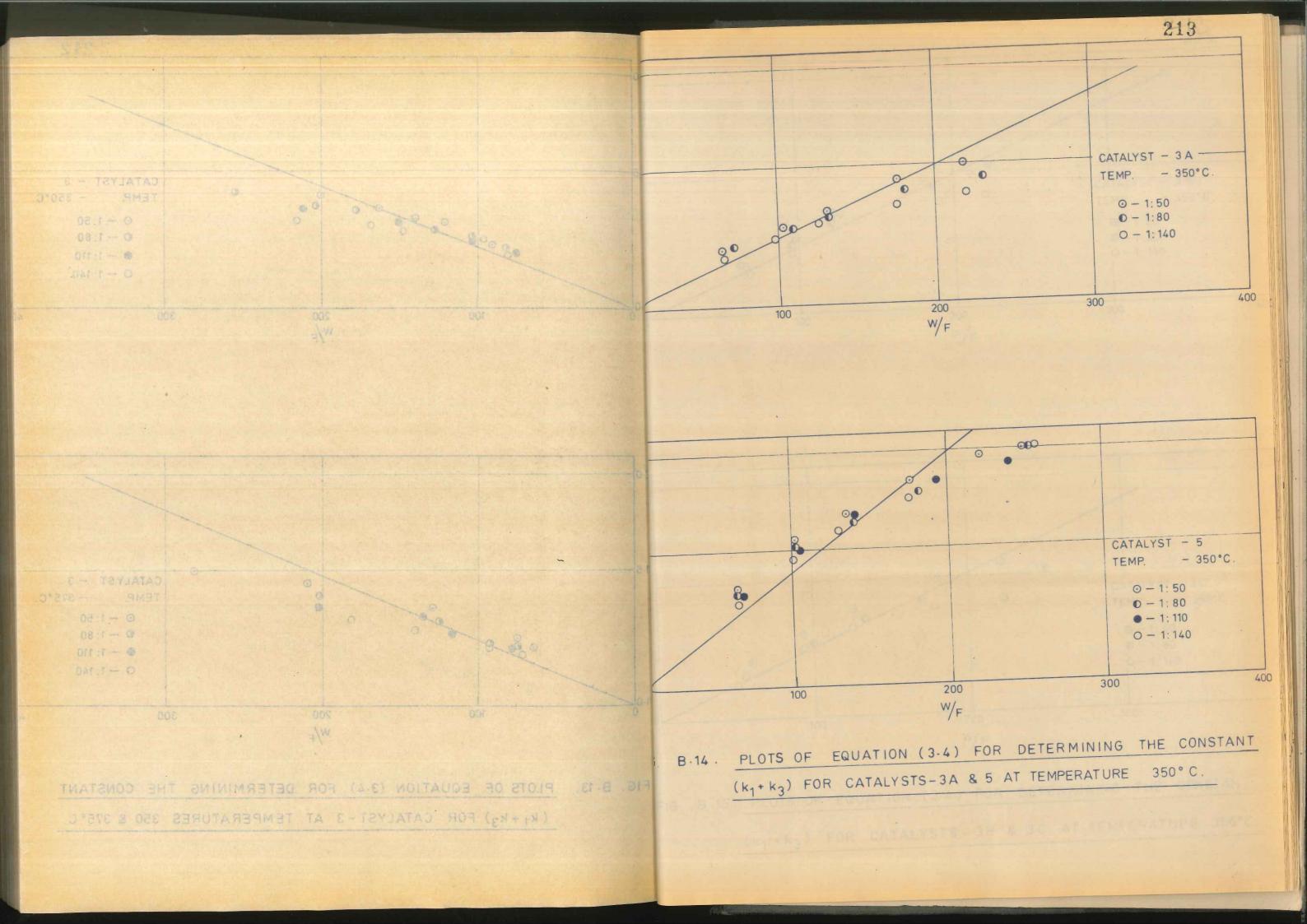


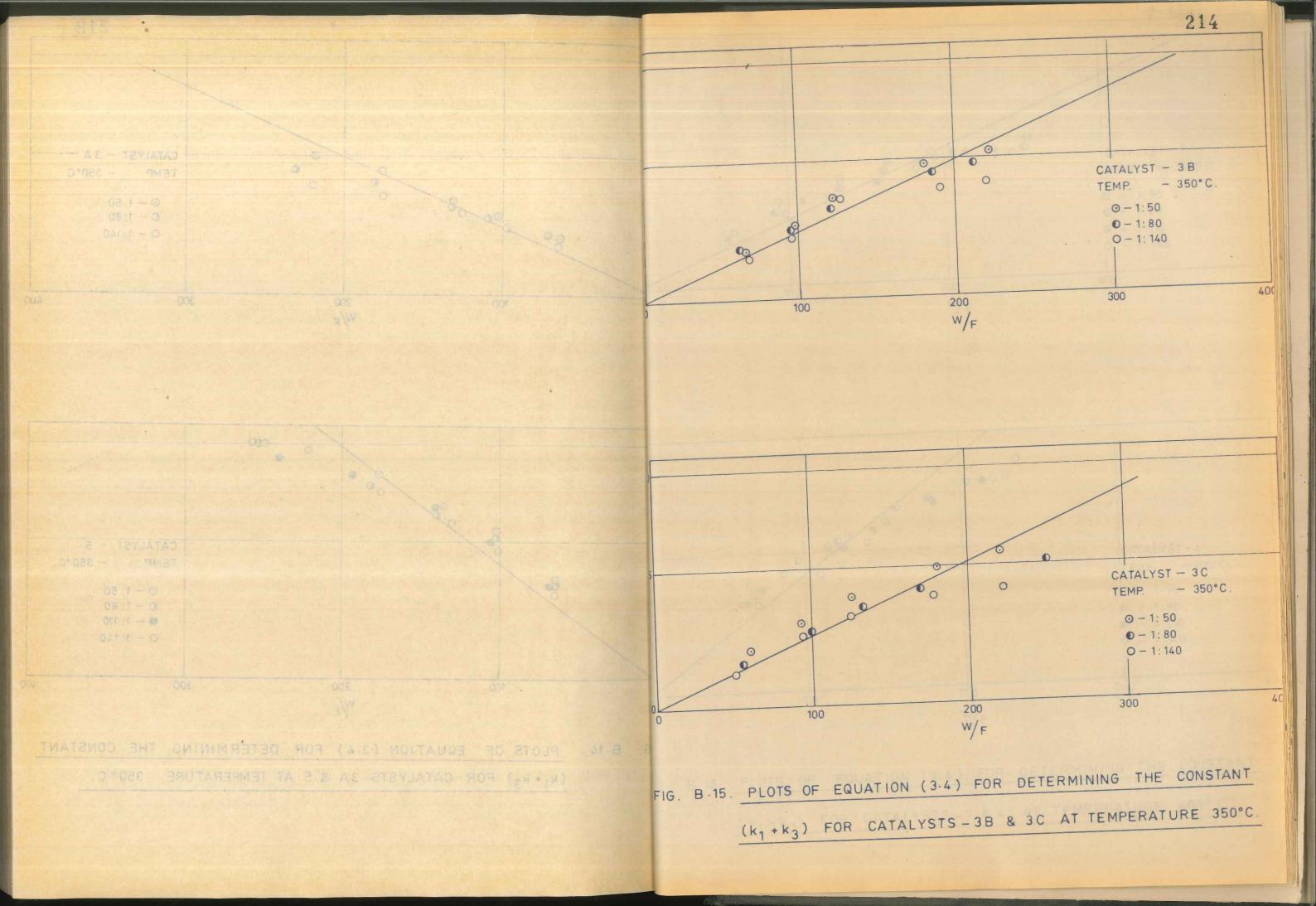


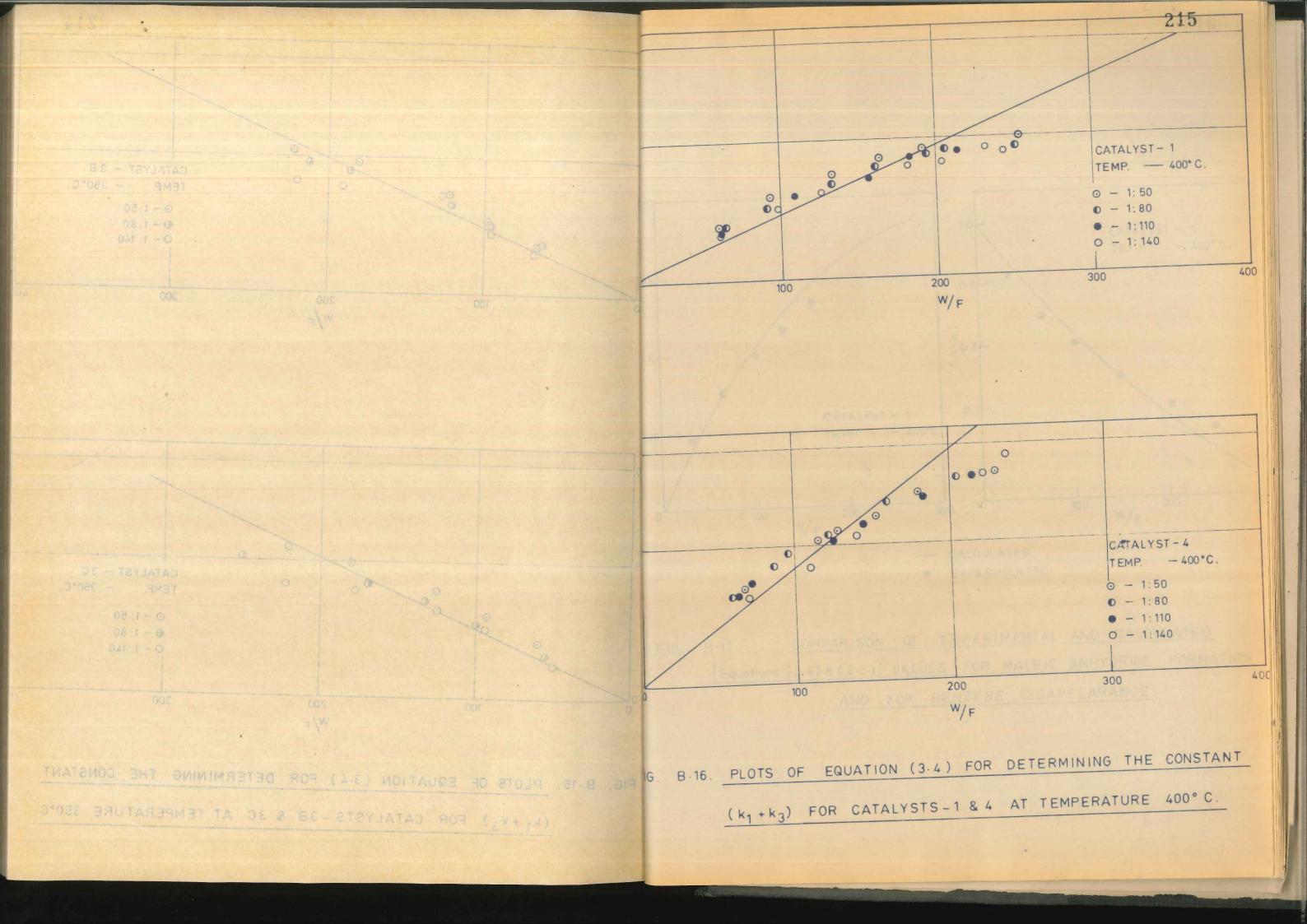


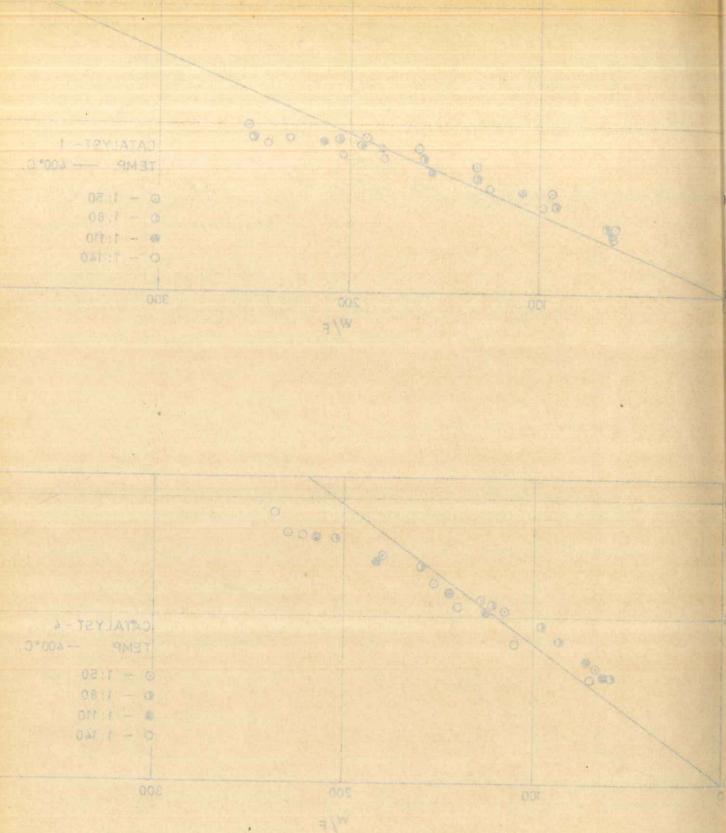












TIG BITS PLOTS OF EQUATION (3:4) FOR DETERMINING THE CONSTANT (KT + kg) FOR DATALYSTS - 1 & 4 AT TEMPERATURE 400°C

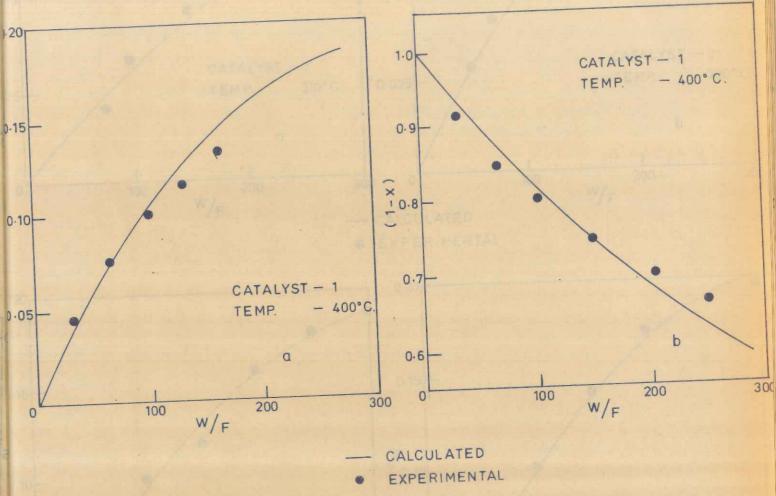


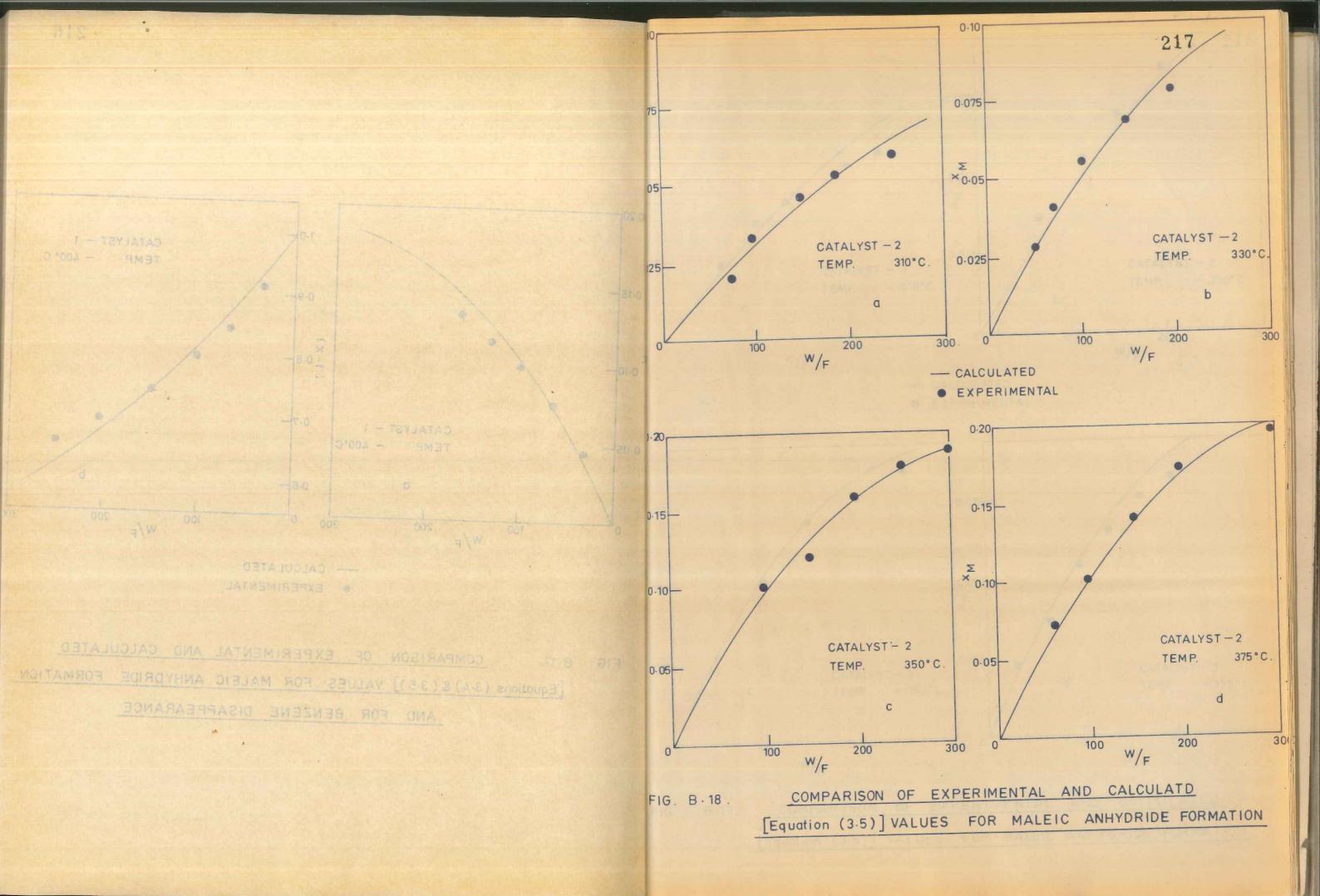
FIG. B.17. COMPARISON OF EXPERIMENTAL AND CALCULATED

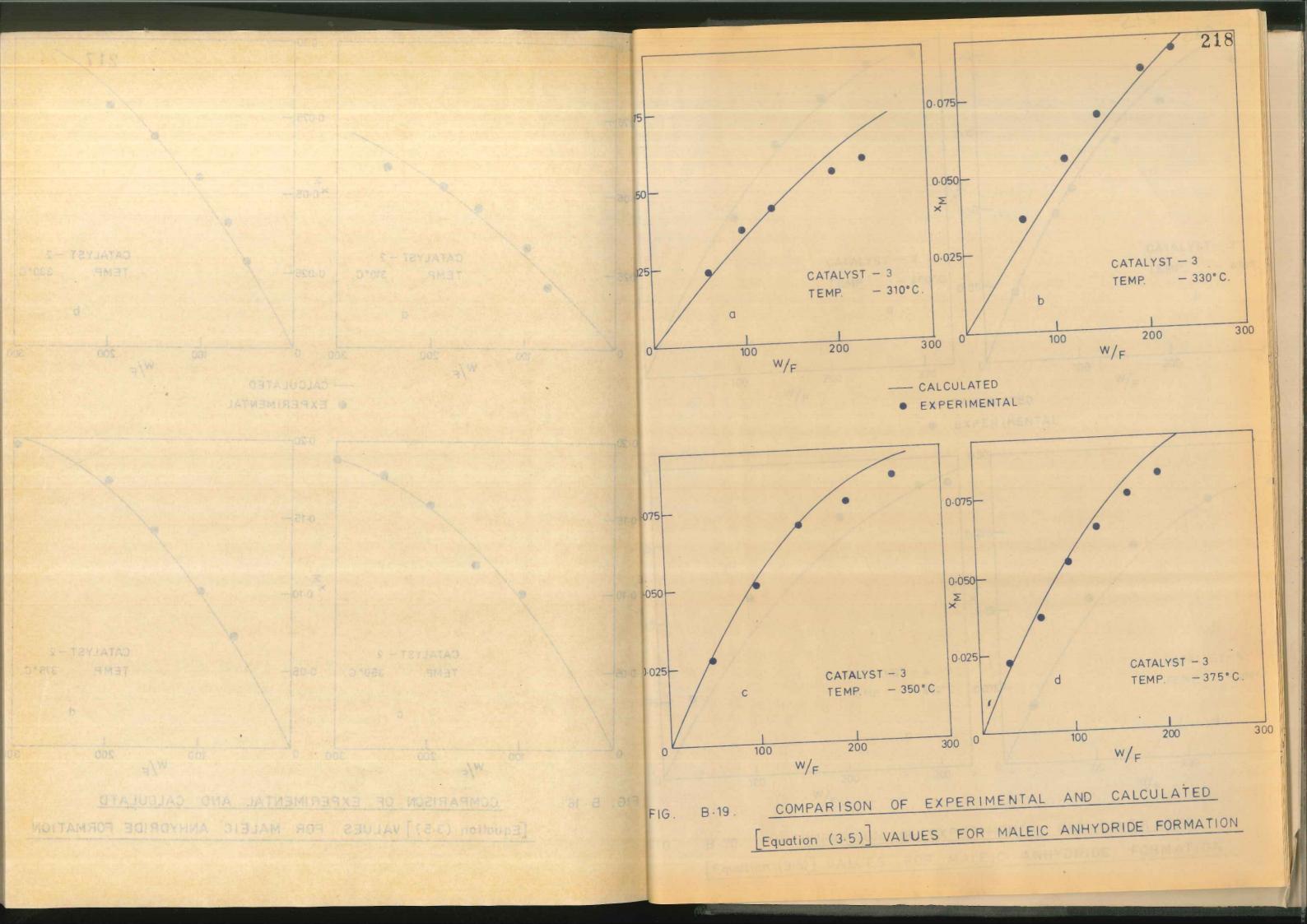
[Equations (3.4) & (3.5)] VALUES FOR MALEIC ANHYDRIDE FORMATION

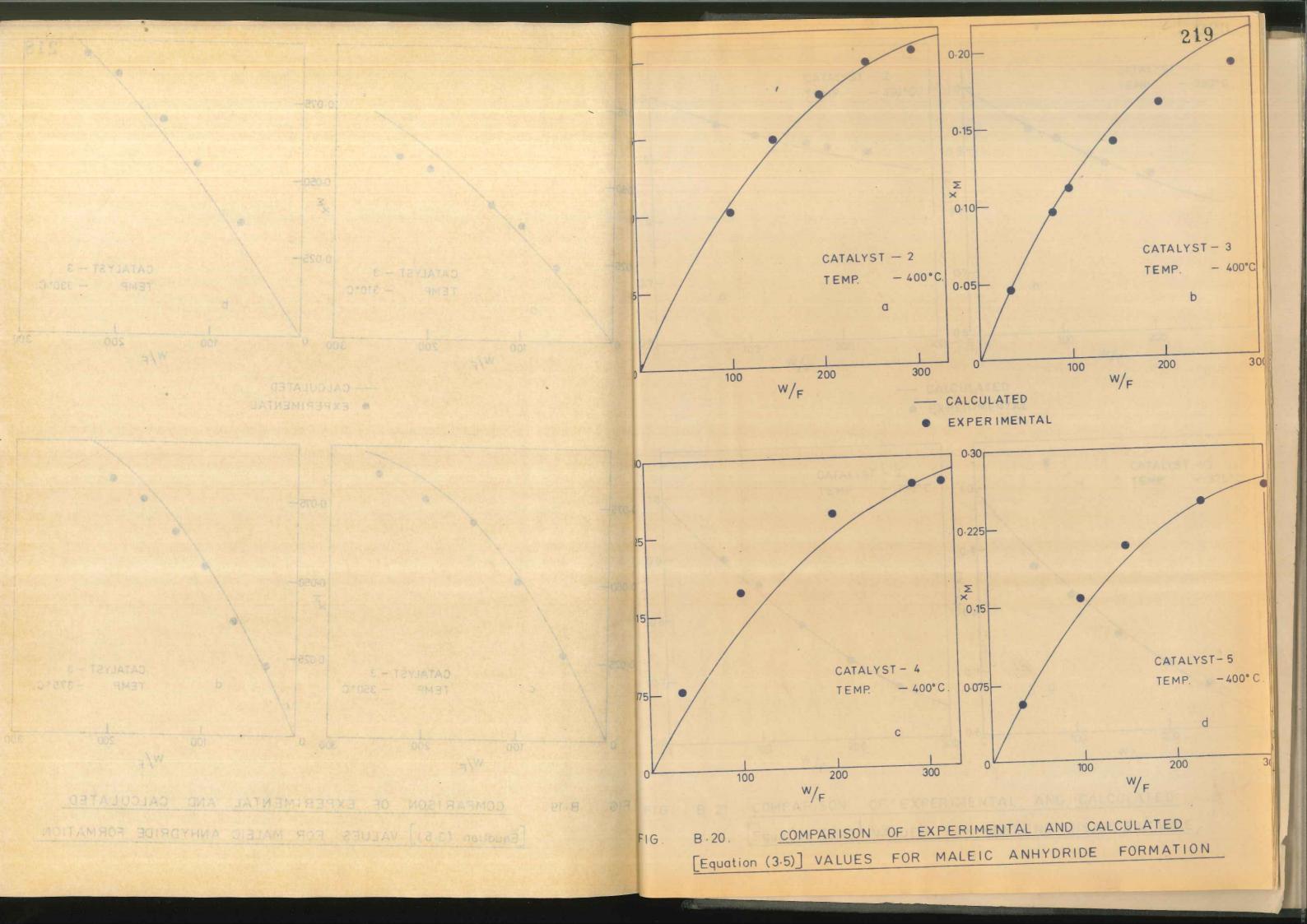
AND FOR BENZENE DISAPPEARANCE

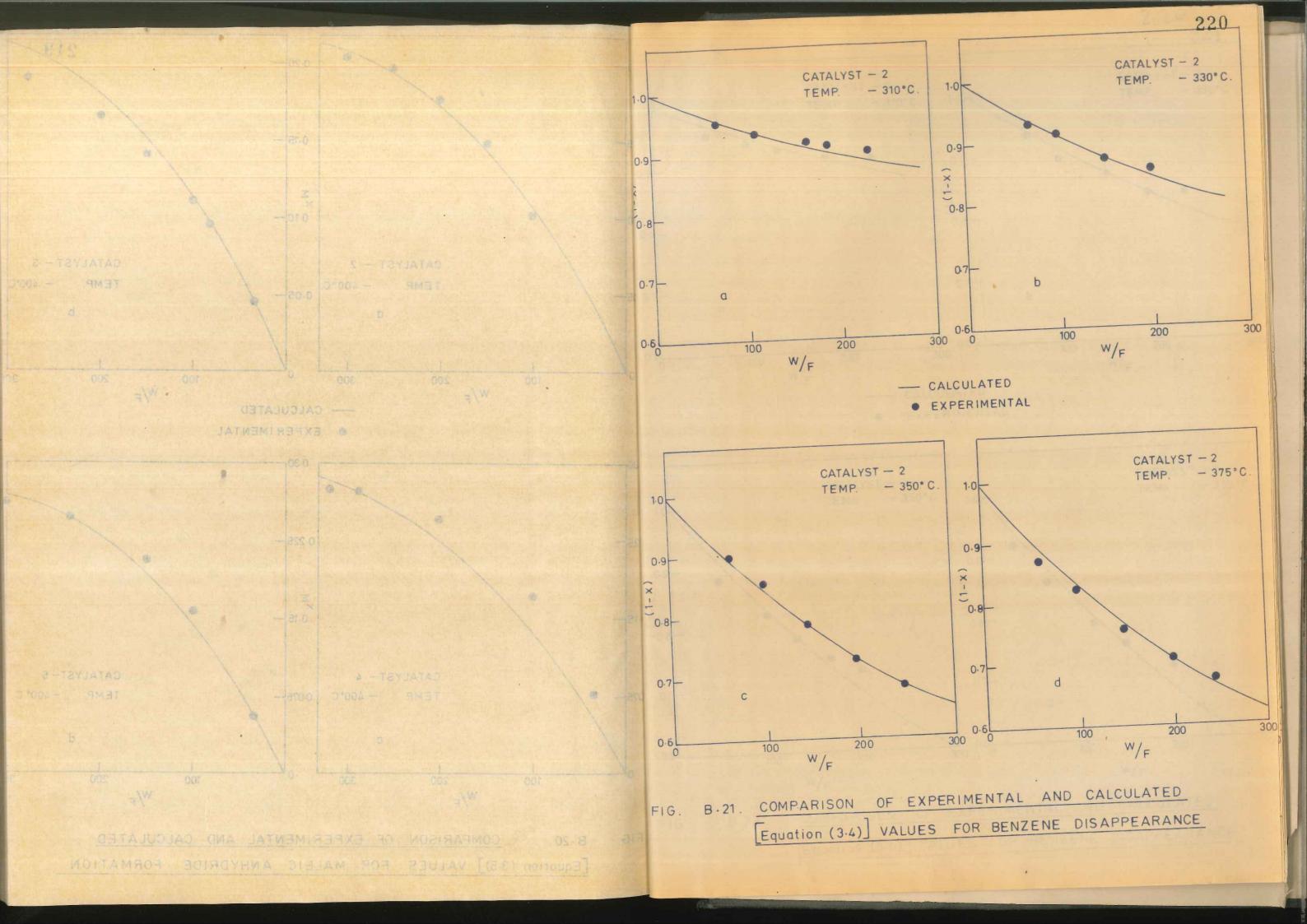
COMPARISON OF EXPERIMENTAL AND LAUGHASE

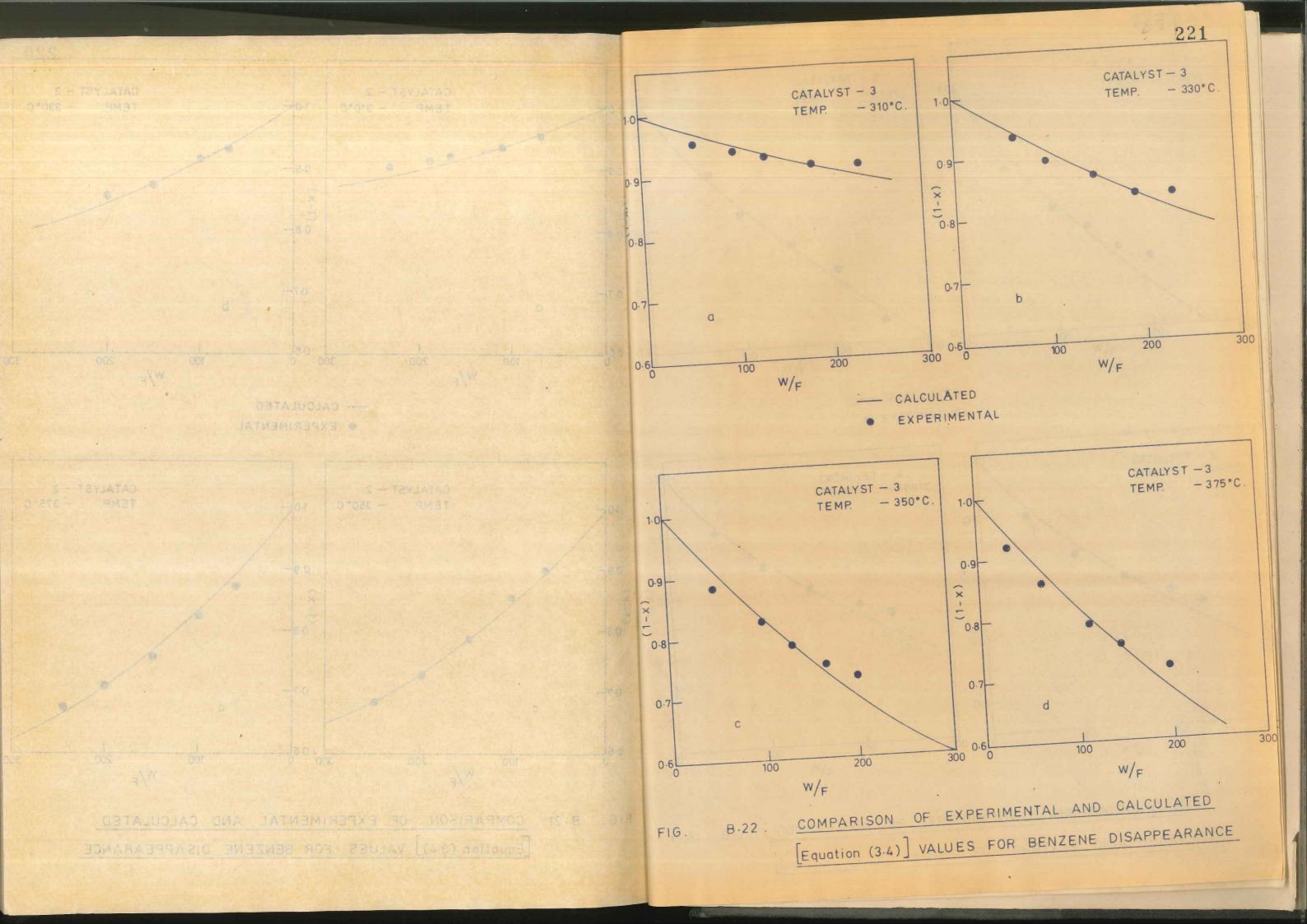
Transfer (3.5) VALUES FOR MALEIC AMITT

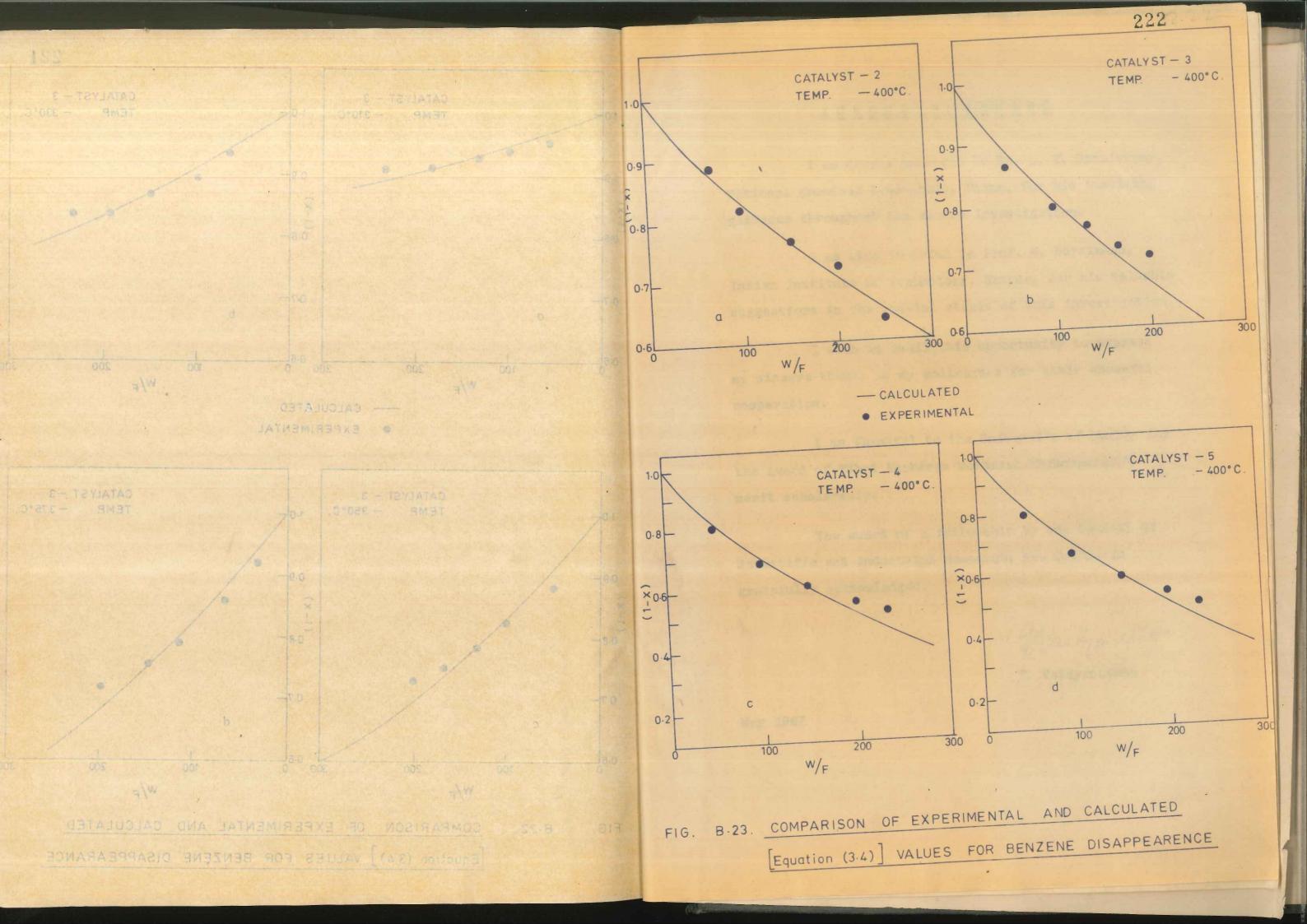


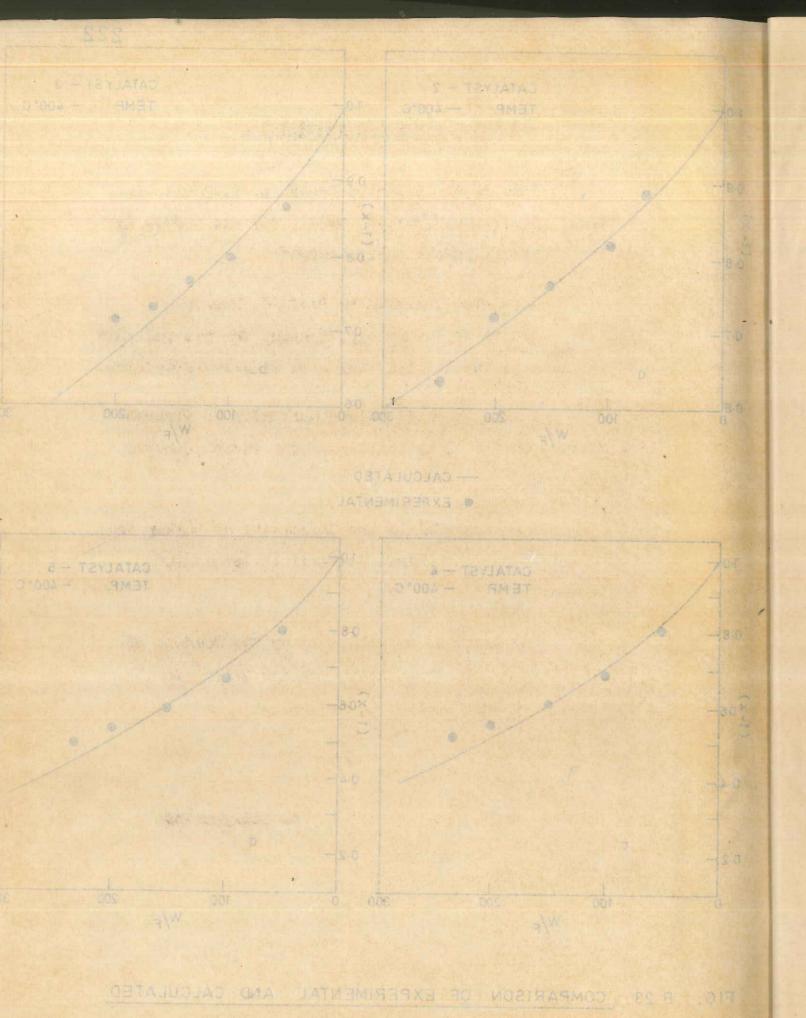












## ACKNOWLEDGEMENT

I am deeply indebted to Dr. L. K. Doraiswamy, National Chemical Laboratory, Poona, for his inspiring guidance throughout the entire investigation.

I am also thankful to Prof. G. Narsimhan, Indian Institute of Technology, Kanpur, for his valuable suggestions in the initial stages of this investigation.

I wish to avail, this opportunity to express my sincere thanks to my colleagues for their cheerful cooperation.

I am thankful to the University of Bombay for the award of "Shri Kushiram Wadhumal Khubchandani" merit scholarship.

The award of a fellowship by the Council of Scientific and Industrial Research, New Delhi, is gratefully acknowledged.

Mar Ganathan

K. Vaidyanathan

May 1967

TH-435

14-435