

HOMOGENEOUS - HETEROGENEOUS
INTERACTION IN CATALYSIS

BY

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I should like to dedicate this work to my parents
for their constant beliefs in the value of learning, and
for continuous encouragement in all aspects of my work.

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Abstract

The presence of a homogeneous component in the oxidation of benzene to maleic anhydride and carbon dioxide over vanadia/molybdena catalysts has been identified. The homogeneous component has been shown to consist of a catalytically formed intermediate, designated as a benzene-oxygen adduct which undergoes subsequent reaction in the gas phase with molecular oxygen to give maleic anhydride. Semi-quantitative calculations show that effectively all of the anhydride is produced via this reaction route. This reaction, however, is influenced by free volume present both in and after the catalyst bed, and to a more marked degree by the nature and extent of surface present. Decomposition of the adduct on inert surface gives benzene and oxygen as products, whilst the presence of active (catalytic) surface leads to products of complete oxidation. It is concluded that the benzene-oxygen adduct is the basis of a homogeneous-heterogeneous interaction, in the sense that the nature of the homogeneous reaction may, under certain conditions, fundamentally affect further heterogeneous reaction of benzene.

Studies of the kinetics of the oxidation show that the reaction network can only be satisfactorily explained by taking this homogeneous contribution into account. Over-oxidation of maleic anhydride has not been found to be significant, either in the gas phase or over the catalyst. Initial measurements of kinetics have been completed in tubular reactors of various design. The identification of the homogeneous components of the reaction was aided by the development of reactors with free volume after the catalyst

bed: this space could be packed with varying amounts of active or inactive material as required. Using results obtained it was possible to calculate the kinetics of the homogeneous decomposition reaction of adduct to maleic anhydride, carbon dioxide, and to benzene and oxygen.

The results obtained were confirmed and extended by measurements made with the catalyst suspended in a stirred gas-solid reactor. This system minimised diffusional effects and allowed further study of the interaction between heterogeneous and homogeneous reactions. Combination of results obtained in all these systems was self-consistent, and allowed estimates of the kinetic parameters of individual reactions.

Using a mixed homogeneous-heterogeneous model as a basis, a preliminary reactor design has been formulated from an appropriate theoretical analysis. Combination of experimental results with equations derived have led to some interesting predictions, which give a basis to future experimental work.

CONTENTS

ACKNOWLEDGEMENTS	PAGE	3
ABSTRACT	PAGE	4
INTRODUCTION	PAGE	7
EXPERIMENTAL	PAGE	55
RESULTS	PAGE	93
DISCUSSION	PAGE	191
IMPLICATIONS OF ADDUCT THEORY TOWARD A REACTOR DESIGN	PAGE	234
APPENDICES	PAGE	276
REFERENCES	PAGE	285

INTRODUCTION

- 1 General: Gas and Gas-solid Reactions;
 - 1A Gas and Gas-solid Reactions in Combustion Systems
 - 1B Gas and Gas-solid Reactions in Heterogeneous Catalysis
- 2 Homogeneous-Heterogeneous Contributions in Catalyst Beds
- 3 Choice of a System for Study
- 4 Techniques for the Study of Homogeneous-Heterogeneous Reactions;
 - 4A Previous methods of study
 - 4B Present techniques

1 General: Gas and Gas-solid Reactions

The products of some chemical reactions have long been recognized to depend markedly on the nature and extent of a surface present in the reaction vessel. Two general effects have been recognized, one involving effectively any surface by which the product spectrum obtained from e.g. a combustion reaction is modified in rather an unselective fashion, and the other involving specific catalytic surfaces which direct the course of a reaction towards a more selective product spectrum. In both cases, the thermodynamic requirements of the systems must be met, but the rates of particular reactions are accelerated or decelerated by the surface. Of these two, by far the most attention has been paid to catalytic processes as a result of the considerable economic interest in obtaining desired products selectively by the reactions of a given fuel.

It has been possible to recognise a general pattern of behaviour for all catalytic reactions, involving five individual steps.

- (1) Diffusion of reactants to the surface
- (2) Adsorption of reactants at the surface
- (3) Chemical reaction on the surface
- (4) Desorption of products from the surface
- (5) Diffusion of products away from the surface

Of these, steps (1) and (5) are governed by relationships which describe mass and heat transfer quite generally, and which depend on the physical characteristics of the system, such as the porosity of the catalyst, fluid flow etc. Steps 2, 3 and 4, on the other hand, are general processes

which depend on the chemistry of the individual system for their particular application. It is possible, however, to show that some general rules apply.

Thus, for example, potential energy curves associated with homogeneous and heterogeneous reactions illustrate the advantages that may accrue from the use of a catalyst. Plots of potential energy vs a suitable reaction coordinate (see Figure 1.1) show that the overall energy released by the reaction must be the same but that the energy of activation (E_A) for the heterogeneous reaction may be considerably less than that for the homogeneous reaction. The reason for this lies in the existence of adsorbed reactants and products.

It is possible to calculate the order of magnitude of the difference in activation energies in the two cases by utilising the theory of absolute reaction rates. If two substances, A and B, can react homogeneously in the gas phase at a rate of reaction, v_{hom} , or, in the presence of a suitable catalyst, the molecules A and B can both be adsorbed at adjacent surface sites and reaction proceeds heterogeneously (v_{het}), then, from the theory of absolute reaction rates,

$$v_{\text{hom}} = c_A c_B \left(\frac{kT}{h} \right) \cdot \frac{F}{F_A F_B} \cdot \exp \left[- \frac{(\Delta E)_{\text{hom}}}{RT} \right]$$

where c_A and c_B are the respective gas phase concentrations and F is the respective partition function per unit volume. If c_{S_2} refers to the concentration of bare but adjacent surface sites, then the rate of the heterogeneous reaction

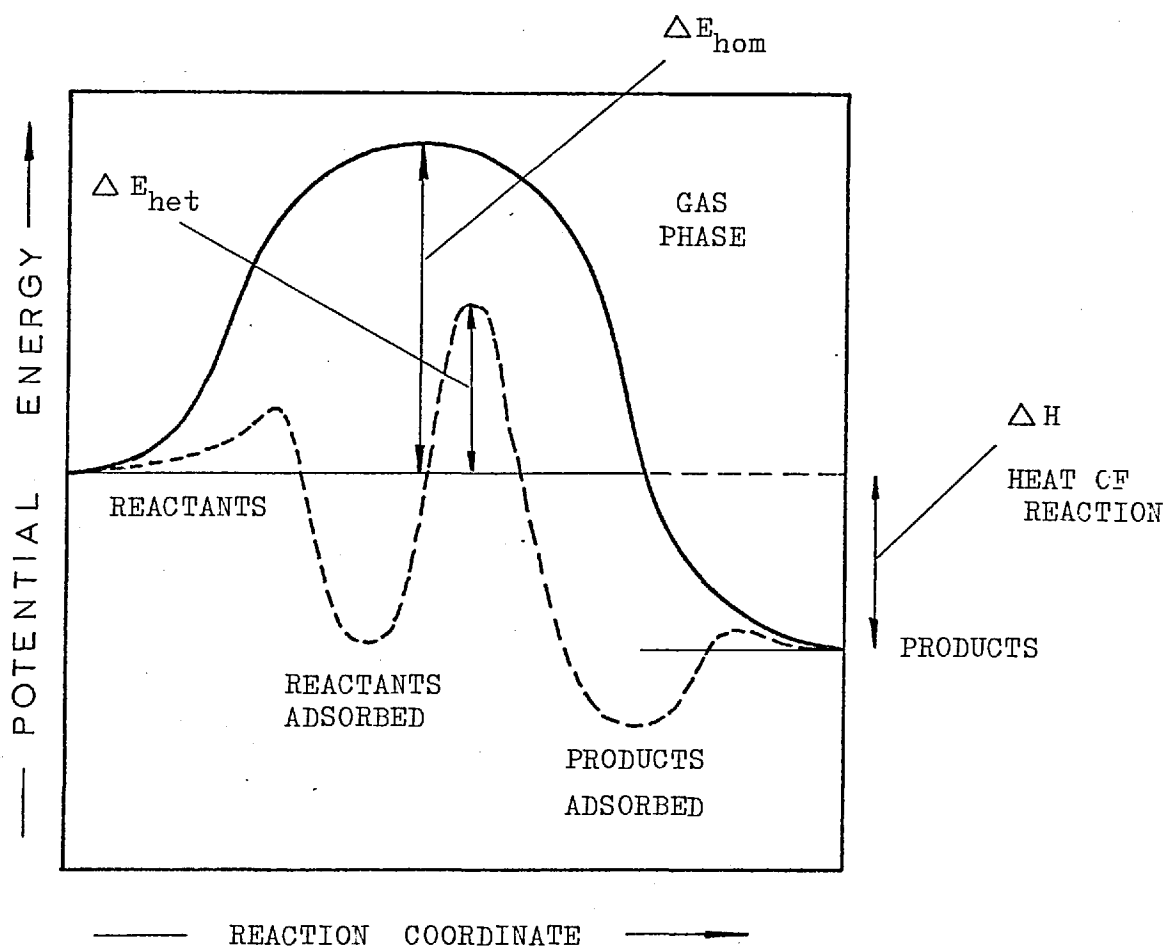


FIGURE 1.1 : COMPARISON OF POTENTIAL ENERGY CURVES
FOR HOMOGENEOUS AND HETEROGENEOUS
REACTION PATHS.

is

$$v_{\text{het}} = c_A c_B c_{S_2} \left(\frac{kT}{h} \right) \frac{1}{F_A F_B} \exp \left[- \frac{(\Delta E)_{\text{het}}}{RT} \right]$$

(the partition function is approximately equal to unity for an immobile transition complex and for a vacant surface site).

From the above,

$$\frac{v_{\text{het}}}{v_{\text{hom}}} = \frac{c_{S_2}}{F_A} \exp \left(\frac{(\Delta E)_1}{RT} \right)$$

$(\Delta E)_1$ referring to the amount by which the activation energy of the homogeneous reaction exceeds that of the heterogeneous case.

For an essentially smooth surface, most solids have a value of c_{S_2} close to 10^{15} per cm^2 . The value of F_A ranges from 10^{24} to 10^{30} , so

$$\frac{v_{\text{het}}}{v_{\text{hom}}} = 10^{-12 \pm 3} \exp \left[\frac{(\Delta E)_1}{RT} \right]$$

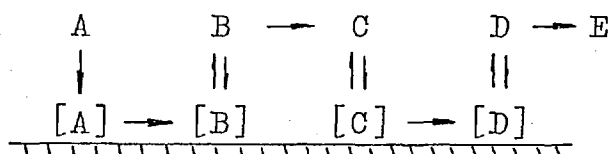
Thus, the heterogeneous reaction would be very much slower if the activation energies for the two reactions were the same. Clearly, the heterogeneous reaction will tend to become more significant when $(\Delta E)_{\text{het}}$ is less than $(\Delta E)_{\text{hom}}$, and the activation energy difference must be 16-17 Kcal.mole⁻¹ for the rates of heterogeneous and homogeneous reactions to be equal at room temperature. Obviously, as the reaction temperature increases, the disparity in activation energy must increase in order to maintain parity of rate. Experimental evidence bears out these conclusions.

In some cases, however, the difference in E_A for the two routes is insufficient for one to be completely favoured over the other. Alternatively, even if $E_{A_{het}}$ is $\gg E_{A_{hom}}$ for $A \rightarrow B$, alternative reactions such as $A \rightarrow C$ may exist and have an $E_{A_{hom}}$ low enough such that $A \rightarrow B$ (het) and $A \rightarrow C$ (hom) can both occur in the reactor. Thus, for example, the oxidation of o-xylene over MoO_3 leads both to benzoic acid produced heterogeneously, and to o-tolualdehyde and phthalic anhydride produced homogeneously by a different route (1). Such concurrent reactions complicate the overall product spectrum.

Further complications arise if a heterogeneous reaction leads to products which can react further in the gas phase. Perhaps the best recognised of these is over-oxidation, as for example, when methane is oxidised to $HCHO$ over palladium oxide, the formaldehyde being rapidly further oxidised to CO_2 in the gas phase (2). Consecutive reactions of this type may occasionally be advantageous, as for example in the oxidation of propene (3), where acetaldehyde produced heterogeneously reacts further in the gas phase to produce propene oxide, which can be a desired product (see on).

A further type of homogeneous-heterogeneous reaction has proved to be of particular theoretical interest, since this involves interaction. Considering concurrent and consecutive reactions, similar effects can be obtained using two reactors in series - one packed with catalyst and the other empty. In an interacting system this is not possible, as can be illustrated with reference to the oxidation of methane (4). The initial catalytic reaction produces formal-

dehyde which oxidises in the gas phase to give CO_2 by a radical reaction. As will be discussed below, radical reactions of this type can be quenched by surface, the final products depending on the nature and extent of the surface. Introduction of any surface - including that of the original catalyst - leads either to the isolation of formaldehyde or of products derived from formaldehyde. For example, a surface catalysed polymerisation may lead to the production of para-formaldehyde from the reaction. To summarise, a sequence of reactions such as



occurs in which it is not possible to go from A to D without a heterogeneous reaction ($\text{A} \rightarrow \text{B}$, $\text{C} \rightarrow \text{D}$) or a homogeneous reaction, $\text{B} \rightarrow \text{C}$.

Before considering interaction between homogeneous and heterogeneous reactions, it is necessary to review briefly evidence that has been obtained from combustion systems.

1A Gas and Gas-solid Reactions in Combustion Systems

In many gas-phase free radical reactions, wall processes play a significant part, either by removing free radical species or by generating them from stable molecular species. In many respects, wall initiation of free radicals (to maintain or increase the overall rate of reaction), falls into the category of heterogeneous catalysis, as for example, where Agudo et al (5) have shown the rate of oxidation of hexane to be enhanced in the presence of Zeolite X - it is

proposed that non-heterogeneous processes are initiated at the zeolite surface. It is more usual, however, to read of investigations into the effect of various surfaces on free radical chain reactions (6, 7, 8) and particularly, since it offers a convenient reference point, on systems at the explosion boundary (9, 10).

Quantitative description of the effect of surface on free radical reactions is complicated by the fact that surface can both catalyse and inhibit the reaction. It has been suggested that inhibition occurs in the early stages of oxidation reactions and in the ignition stage while promotion occurs in the intervening stages (11).

Most of the investigations completed to date follow a general pattern of recording pressure change and product spectra from a combustion reaction at low and high surface to volume ratios. Studies reported by Hay, Knox and Turner (12) are perhaps typical and illustrate the difficulties involved in quantitative estimation of importance of reactions. Results from the oxidation of isobutane and isobutene between 250° and 350°C. revealed that the initial distribution of minor products was highly sensitive to the nature of the reaction vessel wall. It was concluded that, contrary to general combustion theory, a considerable part of the minor products were formed by heterogeneous reactions. General considerations, however, demanded that the heterogeneous processes were not independent but were consequent on primary homogeneous processes involving free radicals.

The relative importance of homogeneous and heterogeneous reactions in gas phase kinetics has been investigated from a more theoretical viewpoint by Hudson and Heicklen (13).

The treatment was for static rather than flow systems and use of experimental data from other sources (14) led to the successful testing of the equations developed. The analysis included terms for the homogeneous production of an active species which maintained the overall reaction; first order termination at the walls and removal in the gas phase was assumed. The ratio of gas phase reaction to reaction at the walls was developed for both spherical and cylindrical reaction vessels - this ratio being dependent on only two dimensionless groups K_v and K_w ; where K_v was the rate constant for gas phase reaction $\times$ (radius of vessel)² $\div$ the diffusion coefficient, and K_w was defined by the rate constant for wall reaction $\times$ (vessel radius) $\div$ diffusion coefficient.

Wise et al (15) have extended the above treatment in a more sophisticated fashion to deal with similar problems in flow systems.

There has been very little work done on a theoretical basis to investigate the effects of wall-initiation of free radicals on continuing gas phase reactions. However, such a phenomena offers an informative example as to what is meant by homogeneous-heterogeneous interaction. If a particular system requires a certain free radical, produced at the wall, for reaction to occur, then formation and desorption into the gas phase will cause further reaction with other reactants to form either products and/or more free radicals. These radicals may either react further in the gas phase or may diffuse back to the wall where deactivation or further reaction may take place. The interaction between gas and

gas-solid reactions is clearly seen - the gas phase (homogeneous) reaction is dependent upon species formed at the wall (heterogeneously), and further surface reactions will be dependent on the results of the initiated gas phase reaction.

Such problems have been studied in liquid phase oxidation reactions (16, 17) but only in a limited sense for gas phase reactions, although one interesting study as to the effects of surface:volume ratio on the gas phase cracking of hydrocarbons has been completed by Levich (18).

1B Gas and Gas-solid Reactions in Heterogeneous Catalysis

During the heterogeneous oxidation of hydrocarbons it is well established that gas phase reactions consecutive and concurrent to (but independent of) the catalytic reactions can be important (see above).

Such reactions are not strictly examples of homogeneous-heterogeneous interaction, and it is important in any study of a particular reaction system to make this differentiation. A commonly used method for studying concurrent gas phase reactions is to compare results obtained with the reactor charged with catalyst with those obtained with the reactor empty. If no reaction occurs in the empty reactor it is concluded that the reaction being studied is wholly catalytic. This conclusion is not always justified since combined homogeneous-heterogeneous reactions may occur. Work reported on the oxidation of propene (3) illustrates this particularly well.

Over a catalyst consisting of bismuth, phosphorus and molybdenum oxides on silica, acrolein is the principal

FIGURE 1.2 : Effect of residence time in the post - catalyst zone of the reactor on the product distribution.

Moles of reactants $\times 10^6$; propene 224 , oxygen 299. Temperature : 445°C .

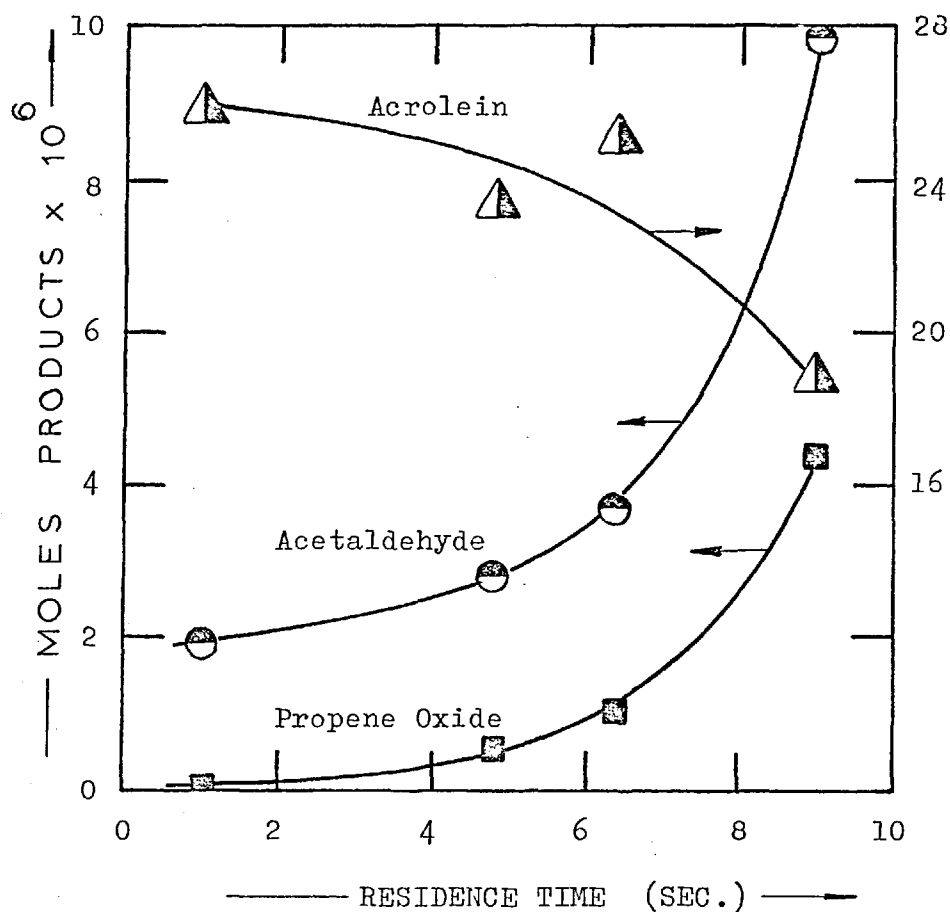


TABLE 1.1 : OXIDATIONS AT 445°C . IN ABSENCE OF CATALYST

Moles reactants $\times 10^6$			Residence Time (sec.)	Moles products $\times 10^6$		
Propene	Acrolein	Oxygen		Acrolein	Acetaldehyde	Propene Oxide
227	—	304	9.2	—	0.2	—
—	26.0	303	8.6	18.1	0.9	—
227	26.8	305	8.4	20.9	2.3	0.7

product of the oxidation at 450°C , acetaldehyde and propene oxide also being formed in lesser amounts. Using a glass reactor with a variable free volume after the catalyst bed, a series of runs was carried out with a constant propene-oxygen reaction mixture and a constant catalyst contact time, while the residence time in the empty zone of the reactor was varied from 1 to 9 sec. The results plotted in Figure 1.2 show that increased residence time in the post-catalyst zone cause a marked increase in the yields of acetaldehyde and propene oxide. It is evident that propene oxide is formed only in this after-zone; extrapolation to zero time indicates that acetaldehyde is formed in the catalyst bed as well as in the post-catalyst zone.

Table 1.1 shows the results obtained at similar propene, oxygen and acrolein partial pressures with the reactor empty. The propene-oxygen mixture gave virtually no reaction, while a mixture of acrolein and oxygen led to the formation of a small amount of acetaldehyde, but no propene oxide. Both propene oxide and an increased amount of acetaldehyde were formed, however, when the reaction mixture contained propene, acrolein and oxygen. The yields of propene oxide and acetaldehyde were not so large as would have been obtained in a corresponding catalyst run at the same residence time. The difference was attributed to the absence of acetaldehyde formed in the catalyst zone which was suggested to function as an additional initiator for the homogeneous reaction. In agreement with this, acetaldehyde is a more effective chain-branching agent than acrolein in the homogeneous oxidation of propene (19).

The results suggest that propene oxide is formed by a homogeneous reaction of propene and oxygen initiated by the aldehydes formed in the catalytic reaction. Acetaldehyde is formed in part by the catalytic reaction and in part by the homogeneous oxidations of acrolein and propene.

Another interesting example of interacting homogeneous and heterogeneous reactions has been observed during the oxidation of n-butenes and methyl acetylene over copper catalysts (20). Homogeneous oxidation of n-butene to oxygenated products occurs readily from 290°-400°C (21). In a reactor without catalyst, at a temperature below 300°C and a reactant pressure of 300-400 mm, the oxidation reaction did not take place. On introduction of the copper oxide catalyst to the reactor, the temperature and the pressure limit at which the reaction was initiated was significantly decreased and the liberation of large amounts of heat indicated that homogeneous reactions were important. Surface initiated homogeneous oxidation was also found to occur in the void volume between catalyst particles. This reaction could not be prevented even when the reactor was filled with glass capillaries (the catalyst being deposited on the reactor wall). Figure 1.3 shows the temperature rise of the reaction mixture using filled and unfilled reaction vessels. The temperature rise (a direct measure of the reaction rate) was found to decrease significantly in the presence of a high surface to volume ratio, but the reaction preserved its heterogeneous-homogeneous character.

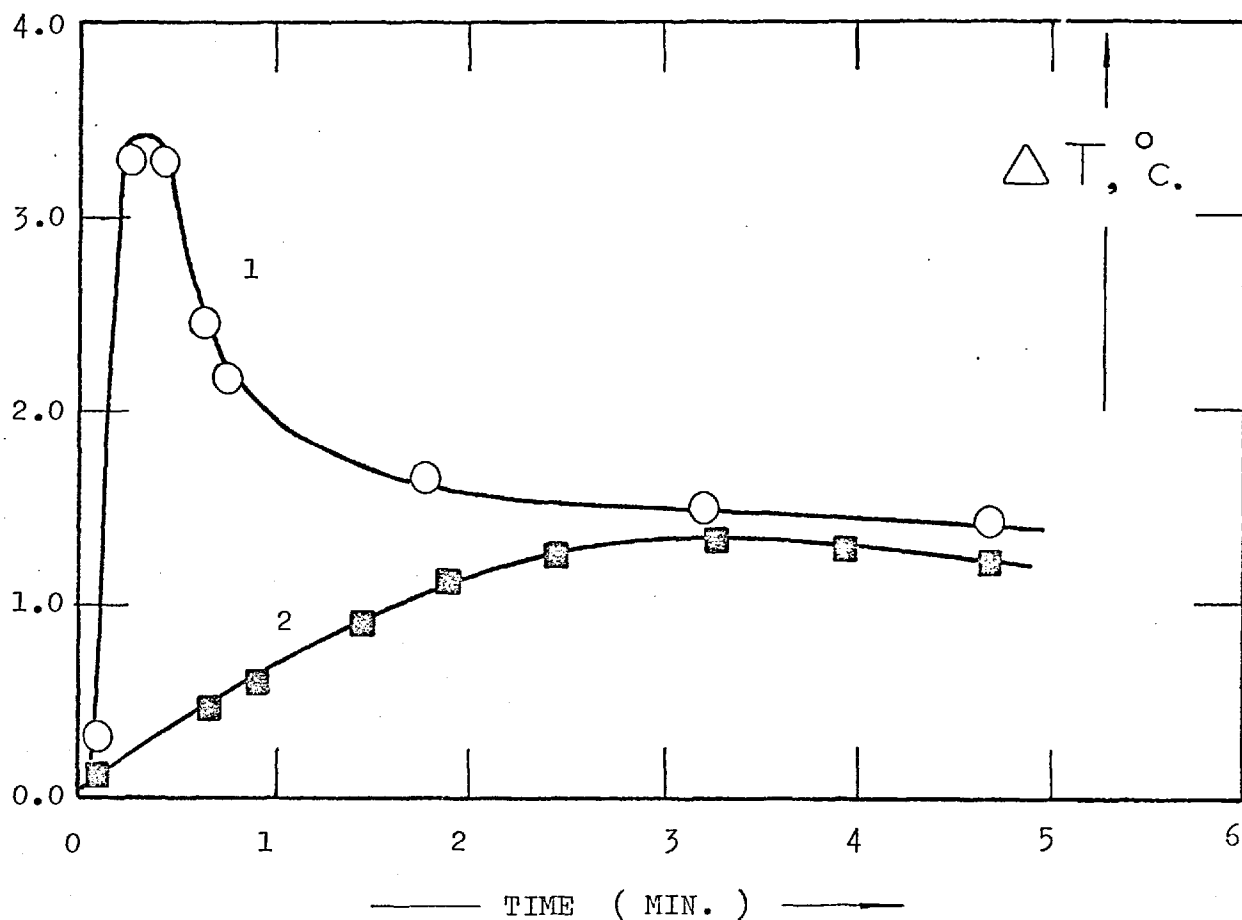


FIGURE 1.3 : Oxidation of n - butenes on copper oxide catalyst. Temperature : 374°C . ; n-butene : 44 mm. Hg.

Catalyst placed on the reactor wall.

1 : reactor not filled with glass capillaries

2 : reactor filled with glass capillaries.

(the temperature rise is directly proportional to the reaction rate)

2 Homogeneous-Heterogeneous Contributions in Catalyst Beds

In the conventional design of catalytic reactors the sizing of the catalyst pellets is usually discussed in terms of pressure drop considerations, and in terms of improving effectiveness factors and selectivity (22, 23, 24): the implicit assumption of chemical reaction proceeding only on the catalyst is generally held. To a certain extent, gas phase reactions, such as product over-oxidation, are allowed for by choosing catalyst pellets of low surface area, thereby decreasing the chances of over-oxidation in pores - but the influence of void volume on the overall reaction rate is usually neglected.

When a reaction is proceeding via a homogeneous-heterogeneous interacting mechanism such considerations are seen to be very important indeed. The most common situation involves production of the desired compound via a surface reaction, with subsequent reactions, such as over-oxidation, occurring in the gas phase. In such a case, the pellet/bed design should allow for the production of primary product by using a high specific surface area catalyst, and should minimise homogeneous reaction by reducing the pore and void volumes. More complex reaction schemes, such as the inter-related heterogeneous-homogeneous oxidation of propylene to acrolein or to acetaldehyde (3), involves a more sophisticated solution.

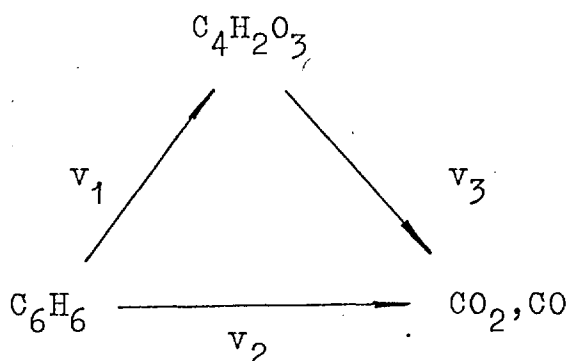
Additional problems can also arise from heat or mass transfer effects. In practice, oxidation reactions are rarely isothermal. Heat transfer gradients in catalyst beds are commonplace, and catalyst surface temperatures are often greatly in excess of the temperature of the surrounding fluid

phase. Such considerations will have a marked effect on the relative sizes of homogeneous and heterogeneous contributions to the overall reaction. As homogeneous rates are usually more temperature sensitive than catalytic rates it would be expected that homogeneous contributions to the reaction as a whole would vary with radial temperature gradients in a more marked fashion than any heterogeneous contributions. In cases where minimisation of homogeneous reaction is necessary, temperature gradients in the bed may seriously affect the selectivity of the overall reaction.

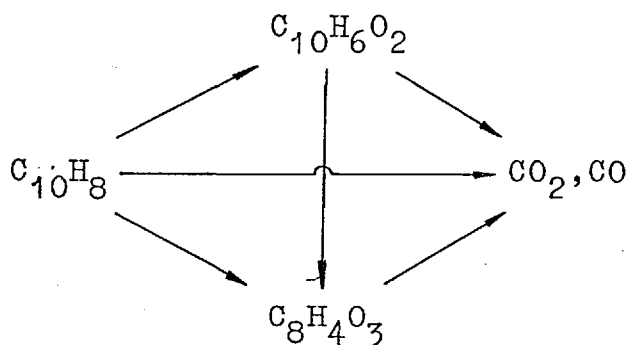
3 Choice of a System for Study

In the past, homogeneous reactions occurring in the presence of heterogeneous catalytic reactions have been identified during studies of the oxidation of hydrocarbons (2, 25, 26). These effects are seen most clearly in systems which involve consecutive reactions (3), either as over-oxidation or as inter-related reactions. It is perhaps significant that these effects are most marked during the oxidation of aromatic hydrocarbons, where the mechanism of the oxidation reaction is not well understood. Satterfield and Sherwood, in their investigations into the catalytic oxidation of o-xylene (25), gave strong indications of the presence of interacting gas and gas-solid reactions, and results on the oxidation of toluene over a molybdena catalyst (26) showed similar effects.

Gas phase interacting processes have also been suggested to occur during the oxidation of benzene and n-butenes to maleic anhydride over a vanadia-molybdena catalyst (27, 28). Over-oxidation of the product is presumed to take place catalytically giving products of complete oxidation, and the general reaction network for the oxidation of the hydrocarbon can be drawn:-



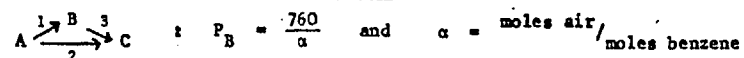
Naphthalene and o-xylene give both phthalic and maleic anhydrides as principal products, and although the reaction scheme for their oxidation is a little more complicated, there is a similar pattern of parallel and consecutive reactions (29)



These mechanisms may be too simplistic as it has also been suggested that, during the oxidation of butenes over a vanadia catalyst, maleic anhydride is removed by interacting gas-phase and catalytic reactions (30). As a result, it was decided that the oxidation of benzene to maleic anhydride would be suitable for the study of interacting homogeneous and heterogeneous reactions.

To date, the system has been generally considered to involve the reaction sequence shown above, and previous studies of the kinetics of the reaction are summarised in Table 1.2 (31, 32, 33, 34, 35, 36, 37, 38). It has been suggested that the oxidation passes through various intermediates such as phenol (39,40), hydroquinone (39, 41), and quinone (39, 41, 42). Dixon and Longfield (27) suggested that only about 10% of the benzene is oxidised via such a route, most of the fuel being oxidised by simultaneous reaction paths to maleic anhydride and to carbon dioxide.

TABLE 1



Authors	Catalyst	Temperature Range °C	Reaction	Order w.r.t. benzene		Order w.r.t. maleic anhydride		Order w.r.t. oxygen		Energy of Activation K cal/mole °K
				P. in mm Hg	Order	P. in mm Hg	Order	P. in mm Hg	Order	
Hammar, 1952	$V_2O_5 - MoO_3/Al_2O_3$	375 - 400	1 and 2	$2.5 < P_B < 5$ for $P_O = 150$	1	---	-	$P_O = 150$	0	28 ± 4 for 1, 2, and 3
			3	---	-	$0 < P_{maa} < 20$	1	?	?	
Holsen, 1954	V_2O_5/Al_2O_3	325 - 450	1 and 2	$7 < P_B < 14$ for $P_O = 150$	1	---	-	$P_O = 150$	?	19 - 20 for 1 & 2 $325^\circ - 375^\circ$; 8-9 $375^\circ - 450^\circ$; 13-14 for 3
			3	---	-	$0 < P_{maa} < 20$	1 (above 375°)	---	-	
Mars, 1958	$V_2O_5 - K_2SO_4/SiO_2$	285 - 377	1 and 2 only	$P_B < 70$ for $P_O = 175$	1 + 0	---	-	$100 < P_O < 800$ $P_B = 14.5$	> 0	---
Ioffe, et al. 1962 1963	$V_2O_5 - MoO_3/Al_2O_3$	380 - 440	1	$0 < P_B < 38$ for all P_O	0.78	---	-	$0 < P_O < 120$	2	22.6 for 1
			2	$0 < P_B < 38$ for all P_O	0.71	---	-	$120 < P_O$ --- for all P_B	0	37.0 for 2
			3	---	-	$0.2 < P_{maa} < 20$	1	$120 < P_O$	0	12.5 for 3
Hayashi, et al. 1963 & 1969	$V_2O_5 ;$ K_2SO_4 / SiO_2	320 - 400	1 and 2	$0 < P_B < 25$ for all P_O	> 0	---	-	$0 < P_O < 25$ for $P_B = 3.5$ $0 < P_O < 50$ for $P_B = 5.5$ $0 < P_O < 67$ for $P_B = 4.7$	1 + 0 1 + 0 > 0	---
			3	---	-	?	?			
Germain et al. 1965 1966 1969	$V_2O_5 - MoO_3/Al_2O_3$	380 - 500	1 and 2 only	$5 < P_B < 15$ $P_O = 155$	1 + 0	---	-	$0 < P_O < 160$ $P_B = 9.5$	1 + 0	1 & 2 same E_A : at $380^\circ C$ 22 at $500^\circ C$ 10
Dmuchovsky, et al. 1965	$V_2O_5 - MoO_3/SiO_2$	320 - 380	1	$0 < P_B < 10$ for $P_O = 155$	1	---	-	$P_O = 155$	0	25 ± 2 for 1
			2	$0 < P_B < 10$ for $P_O = 155$	1	---	-	$P_O = 155$	0	26 ± 2 for 2
			3	---	-	$0 < P_{maa} < 10$	1	$P_O = 155$	0	4.9 ± 0.5 for 3

It is interesting to note that during studies of the homogeneous oxidation of benzene, (which is not significant below 550°C) phenol, quinone and maleic acid were all observed as products of reaction (43). However, the introduction of catalyst surface would seem to make the reaction much more specific to the production of maleic anhydride and carbon dioxide, although detectable amounts of quinone can be isolated at low conversions (37).

An excellent review of work completed in the heterogeneous oxidation of benzene to maleic anhydride has been presented by Dixon and Longfield (27). Germain (44) and Margolis (45) have also presented detailed reviews of the subject. High yields of maleic anhydride (70%) can be obtained at 350°-450°C (46) and detectable amounts of quinone have also been found at low conversions (37), but there is general agreement that the triangular formal scheme is sufficient. Exact values of the kinetic constants are less easily recognised, a variety of results being obtained by different workers (Table 1.2). The rate of benzene consumption ($v=v_1+v_2$) is zero order for both reactants at higher pressures and first order at low pressures (31, 34, 38), indicating that benzene and oxygen are not competing for sites. Limiting values are about 15 mm Hg for C_6H_6 (=Bz) and 160 mm Hg for oxygen (=O₂) (36). Similar results were obtained for other V_2O_5 based catalysts: pure V_2O_5 (32, 35), $V_2O_5-K_2SO_4$ (33) and $V_2O_5-MoO_3-Ag_2O$ (28). The apparent activation energies decrease in the higher temperature region owing to diffusional limitations. Among the products, Ioffe (34) found that maleic anhydride (=maa) has a strong inhibiting effect,

as shown in the kinetic expressions:-

$$v_1 = k_1 \frac{[Bz]^{0.78}[O_2]^2}{[Maa]^{0.74}}, E_1 = 22.6 \text{ Kcal/mole}$$

$$v_2 = k_2 \frac{[Bz]^{0.71}[O_2]^2}{[Maa]^{0.74}}, E_2 = 37 \text{ Kcal/mole}$$

which are valid within a limited range of concentrations.

The initial selectivity ie. the yield of maa at low conversions, changes very little with partial pressures or temperatures, being about 70% for a molar ratio $MoO_3/V_2O_5 = 1/3$. This indicates very similar kinetics for v_1 and v_2 , in good agreement with Ioffe's equations. The selectivity, however, changes sharply with the Mo/V ratio, going through a maximum at the above mentioned composition (47, 48): overall activity follows the same trend. This maximum coincides with the maximum of magnetic susceptibility (48), and of V^{4+} cation concentration, and with the limit of solubility of MoO_3 in V_2O_5 . Similar trends were noted for the oxidation of butene (49).

A large improvement in selectivity is observed when small amounts of P_2O_5 are added to the above catalyst. Yields of maa of up to 80% are obtained, and these decreased only slowly with the conversion, showing that both ratios v_1/v_2 and v_1/v_3 are increased (50, 51).

Direct oxidation of benzene to phenol has not been successful to date, partly owing to the high rate of phenol oxidation to maa. At $500^\circ C$, with a $Cu_3(PO_4)_2$ catalyst, a yield of 63% of phenol was reported for a 2.5% conversion (52),

but the homogeneous reaction gives similar results at a slightly higher temperature (53).

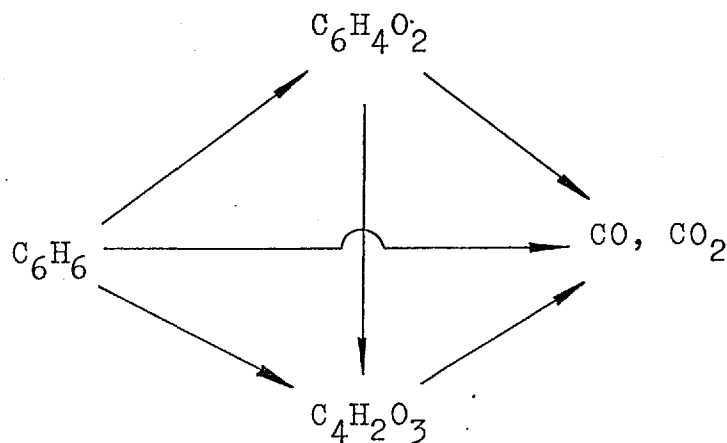
Benzoquinone is formed at low conversions in the benzene reaction with V-Mo-O catalysts. Below 2% conversion, the selectivities summarised below have been found (37)

Table 1.3

Concentration of MoO ₃ in catalyst %	Yield of anhydride %	Yield of quinone %
100	10	0
81.5 ^I	21.5	4
24.3	62	5
14.5	56	5
0	27	5

(I : MoO₃/V₂O₅ molar ratio = 1)

Taking the case of the best catalyst (24.3% MoO₃) for the production of maleic anhydride (maa), the "initial selectivity" of 70% previously mentioned is observed for conversions higher than 10% and the following kinetic scheme is probably more representative:



It is interesting to note that Darby (54) and Germain (55) have both claimed that yields of maa from the oxidation of benzene may be improved by treating the steel equipment with ammonia or ammonium carbonate at 400° to 600°C. The pre-treatment is reported to reduce the oxidation or destruction of the maa formed by the catalytic oxidation of benzene.

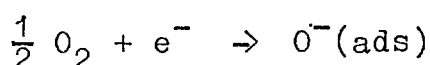
There has been some controversy concerning the role which the catalyst takes during the oxidation of aromatic hydrocarbons. Under normal conditions of oxidation, it has been reported that the catalyst is reduced from V_2O_5 to a mixture of V_2O_4 and V_2O_3 (56, 57). On the other hand, the rate of oxygen exchange has been compared with the rate of catalytic oxidation of various hydrocarbons, and it appears that exchange takes place at temperatures higher than the temperature at which catalytic oxidation proceeds (58). Rates of oxygen exchange on V_2O_5 and V_2O_4 have been studied and compared with the activity of the catalyst for xylene oxidation (59) but no clear relationship was developed.

Some evidence which suggests that hydrocarbons act as electron donors to oxidation catalysts such as V_2O_5 , NiO , Cr_2O_3 and Cu_2O is provided by electrical conductivity and work function measurements (60). Conductivity and thermoelectric power measurements have been used to follow changes occurring in the catalyst during the oxidation of o-xylene (61). At room temperature it was shown that although the electronic energy levels within the solid were unaffected, the chemisorbed xylene acts as an electron donor to the solid. At temperatures at which the oxidation occurs, both

the conductivity and the thermoelectric power increased to a marked extent, indicating that the Fermi level of the quasi-free electrons in the catalyst had been reduced to a considerable level below that of the conduction band. Thus both the surface and interior of the catalyst are affected by the reaction. It is suggested that, as an adsorbed o-xylene molecule is oxidised, an oxygen-deficient region containing defects is formed. These defects are mobile at temperatures at which the reaction proceeds and migrate throughout the reduced oxide. Chemisorption of oxygen at such a defect would then regenerate the pentoxide. The adsorption of oxygen is believed to be the rate determining step in the overall oxidation, since kinetic studies (61) showed that the reaction is zero order w.r.t. o-xylene and half order w.r.t. oxygen. However, just as for benzene oxidation (31), mass transfer effects can seriously affect the observed kinetics.

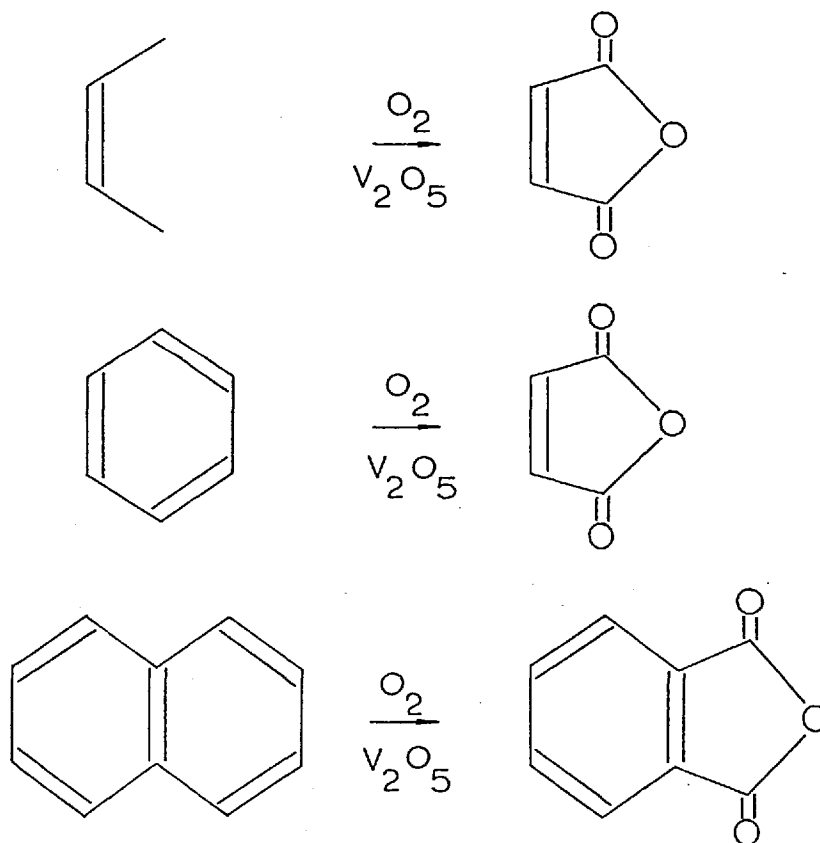
The overall picture obtained from such experiments, together with kinetic and product distribution data, is that the hydrocarbon oxidation proceeds through the following sequence of events:

(1) the hydrocarbon is chemisorbed, donating an electron to the catalyst, which is an n-type semiconductor containing anion vacancies, (2) the adsorbed hydrocarbon reacts with oxygen ions of the lattice, (3) the products of oxidation are desorbed, (4) oxygen from the gas phase replenishes the lattice oxygen lost during interaction in step (2). As indicated, this last step

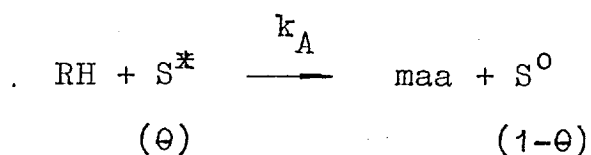


probably determines the observed overall kinetics.

A perfunctory glance at the oxidation of butenes, benzene and naphthalene and their respective oxidation products on vanadium pentoxide based catalysts, apparently confirms this common mechanism on the surface, e.g.

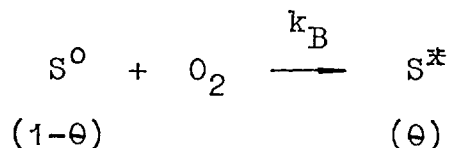


Mars and Van Krevelin (62) interpreted their results for benzene and naphthalene oxidation in terms of this general 'redox' mechanism, the hydrocarbon being first oxidised on an active site



where θ is the fraction of the total surface containing active sites S^* . The rate at which the active sites were reoxidised was assumed to be proportional to some power n of the oxygen pressure, and the fraction of surface not

containing active sites $(1-\theta)$.



The rate of hydrocarbon reaction is then given by

$$-\frac{dp_{RH}}{dt} = k_A \cdot p_{RH} \cdot \theta \quad (1)$$

where p_{RH} is the partial pressure of hydrocarbon at a time corresponding to t , and the rate of oxidation of the surface to the active state is equal to

$$k_B \cdot p_{O_2}^n \cdot (1-\theta) \quad (2)$$

If v molecules of oxygen are required for the oxidation of one molecule of hydrocarbon, then, in the steady state,

$$v k_A \cdot p_{RH} \cdot \theta = k_B \cdot p_{O_2}^n (1-\theta) \quad (3)$$

The rate of oxidation of the hydrocarbon is therefore of the form:

$$-\frac{dp_{RH}}{dt} = \frac{k_A p_{RH} \cdot k_B p_{O_2}^n}{k_B p_{O_2}^n + v \cdot k_A p_{RH}} \quad (4)$$

or,

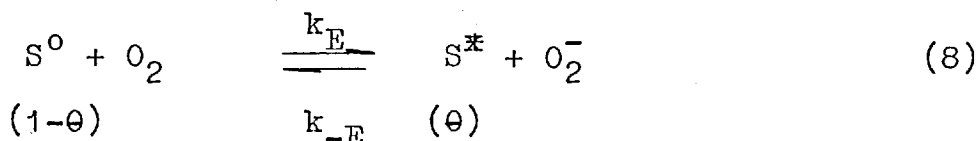
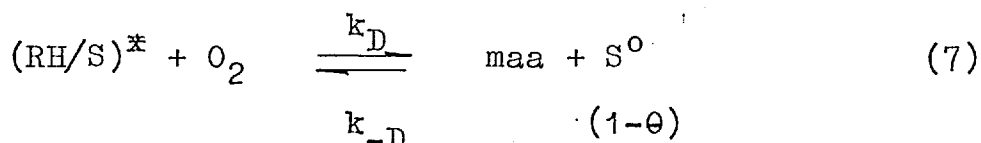
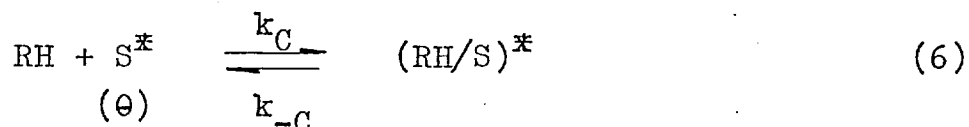
$$-\frac{dp_{RH}}{dt} = \frac{1}{\frac{1}{k_A p_{RH}} + \frac{v}{k_B p_{O_2}^n}} \quad (5)$$

In most experiments excess oxygen is used, so that $p_{O_2}^n$ is constant. This equation therefore shows that, for small values of p_{RH} , the rate is first order w.r.t. the

partial pressure of the hydrocarbon, whereas for large values of p_{RH} the rate is zero order. These conclusions are in good agreement with measured reaction kinetics. Experiments also show that when p_{RH} is constant and p_{O_2} is varied, the reaction is first order w.r.t. oxygen, so that the exponent n is unity. The basic assumption of active sites regenerated by oxidation would therefore seem to be fairly sound.

It is an obvious step to try to sophisticate the Mars and Van Krevelin approach by setting out a reaction scheme including an additional elementary reaction for the reaction of the hydrocarbon with oxygen on the surface.

Such a mechanism would be:-



Using similar expressions for the rate of oxidation of the hydrocarbon and for the rate of oxidation of the surface, use of the steady state approximation

$$\frac{\partial (RH/S)^*}{\partial t} = 0 \quad (9)$$

gives the following complicated expression for θ ,

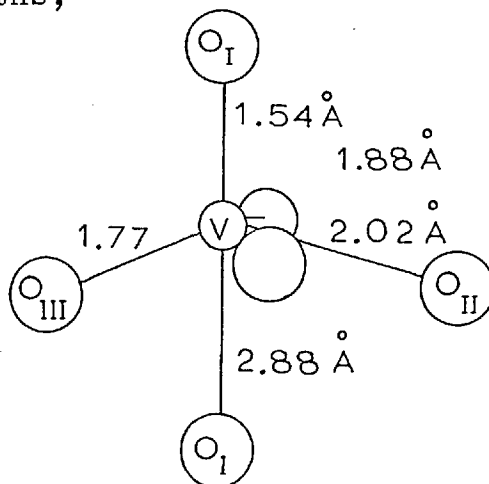
$$\theta = \frac{\frac{k_{-C}k_{-D} p_{maa}}{k_{-C} + k_D p_{O_2}} + k_E p_{O_2}}{k_C p_{RH} + k_E p_{O_2} - \frac{k_{-C}(k_C p_{RH} - k_{-D} p_{maa})}{k_{-C} + k_D p_{O_2}}} \quad (10)$$

which leads to a rate of hydrocarbon consumption given by

$$-\frac{dp_{RH}}{dt} = \frac{k_C p_{RH} \cdot k_E p_{O_2} - k_{-C} k_C p_{RH} + \frac{k_{-C}^2 k_C p_{RH}}{k_D p_{O_2}}}{k_C p_{RH} + k_E p_{O_2} - \frac{k_{-C} k_C p_{RH}}{k_D p_{O_2}}} \quad (11)$$

Neglecting the last two terms on the right in the numerator and the last term on the right of the denominator, the Mars and Van Krevelin rate expression is obtained. Interpretations of the overall rate expression (11) ideally requires values for six rate constants, failing which qualitative arguments may be used to give some idea of the relative rates of hydrocarbon adsorption, oxidation on the surface and re-oxidation of the surface itself.

Further to the approach of a general reduction-oxidation mechanism, it is useful to look at the configuration of the vanadia surface in a little more detail. The crystal structure of V_2O_5 (63) consists of vanadium to oxygen bonds of variable lengths;



$V-O_I = (a) 1.54 \text{ \AA} \text{ and } (b) 2.88 \text{ \AA} ; V-O_{II} 2.02 \text{ \AA} ;$
 $V-O_{III} = 1.77 \text{ \AA} \text{ and } 1.88 \text{ \AA} .$

The longest $V-O$ bond (the $V-O_I$ (b) bond) is the weakest and V_2O_5 has a tendency to cleave along the (001) face exposing the shortest $V-O_I$ (a) bond on the surface.

Splitting of the $V-O_I$ (b) bond could lead to the formation of the V^{4+} state, tetrahedrally coordinated. Tamura (48) explains the increased activity of the vanadia/molybdena catalyst by suggesting that splitting along the (001) face is increased due to the presence of MoO_3 , and that the exposed $V-O_I$ (a) bond, which is weakened by the increase in V^{4+} , is the controlling factor in catalytic activity. The evidence for the weakening of the bond lies in the fact that the I.R. spectrum shifts from 1025 cm^{-1} to 1015 cm^{-1} .

Kasansky et al (64) have shown, by E.S.R. studies that adsorption of oxygen on V_2O_5 occurs at tetrahedrally coordinated V^{4+} ions; the g values indicate that the oxygen is held as O_2^- while the hyperfine splitting shows the electron to be partially shared. This may well be the route by which the V^{4+} surface is oxidised and may account for half of the redox mechanism. The oxygen chemisorbed at V^{4+} , reacts to form O_2^- leaving a tetrahedrally coordinated V^{5+} as a site for hydrocarbon adsorption. As previously mentioned, work function measurements of V_2O_5 surfaces on which oxygen has been adsorbed show an increase, while hydrocarbon adsorption produces a decrease (65). It would indeed seem that the oxygen and the hydrocarbon are adsorbed by an opposite mechanism; the oxygen is an electron acceptor from V^{4+} while the hydrocarbon is an electron donor as was suggested in the basic Mars and Van Krevelin approach.

4 Techniques for the Study of Homogeneous-Heterogeneous Reactions

4A Previous methods of study

Studies of mixed homogeneous and heterogeneous effects have been carried out in the context of combustion and of catalysis. In addition to the conventional method of using reactors coated with different substances (12), more quantitative work in the context of combustion has been based on differential calorimetry. This method, first developed by Kovalskii (66), determines to what extent the reaction occurs in the volume and on the surface by comparing temperatures measured within the reaction vessel with those calculated from the rate and heat yield of the reaction, assuming some mode of heat liberation. Differential thermocouples are used to make experimental measurements, one junction being at the centre of the vessel and the other at the wall, the couples being insulated with fine capillaries of the reaction vessel material. The temperature difference ΔT is proportional to the heat of reaction and gives a measure of the reaction rate.

ΔT depends on the mode of heat liberation and on the vessel geometry. If the heat is liberated uniformly throughout the vessel, ie. the reaction is purely homogeneous, then, with a cylindrical vessel and steady conditions,

$$\Delta T_1 = \frac{q_1}{4\pi\lambda} \quad (1)$$

where λ is the thermal conductivity of the reaction mixture and q_1 is the amount of heat liberated per unit time per unit volume.

If the heat is liberated purely heterogeneously, ie only at the surfaces (- including the surface of the central capillary)

$$\Delta T_2 = \frac{q_2}{4\pi\lambda} \cdot \frac{2r}{R+r} \cdot \ln(R/r) \quad (2)$$

where r is the radius of the central capillary, R that of the vessel and q_2 is the heat liberated at the surface. If the rate is measured independently and q is known, ΔT can be calculated easily from (1) and (2). The reaction type is then determined by comparing computed and experimental values. Similar expressions may be developed for reactions of mixed homogeneous-heterogeneous nature. Catalysts may be studied by presenting them as thin coatings on the central capillary or reaction vessel.

This method has been used successfully by many workers to investigate wall effects on gas phase reactions. Markevich (67) has shown the reduction of SO_2 to proceed in the gas phase via a catalytic initiating reaction, and Polyakov et al (68) have observed interesting effects, which can only be explained on the basis of homogeneous-heterogeneous reactions, during the oxidation of methane in the presence of oxides of nitrogen. More quantitative results have been obtained using the method to study the oxidation of n-butenes over a copper oxide catalyst (see section (1) of the Introduction). Calculations showed that only 4.8% of the total heat generated was evolved on the surface of the catalyst. It was concluded that the oxidation of n-butenes takes place mainly in the free volume, and the probable role of the catalyst is merely the formation of an intermediate

active allyl radical which is desorbed into the reaction volume and is there further oxidised to other compounds.

It was not possible in this investigation, and indeed, it is not possible by the method of differential calorimetry, to investigate the further effect of surface once the reaction in the gas phase has been initiated. The method is ideally suited for the study of over-oxidation problems and of homogeneous reactions initiated by surface, but the study of further catalytic effects on products of gas phase reactions is rather more complex. The method would seem to be effective only in static systems, or in those systems with small Reynolds number (69) and this is a serious drawback to its possible use in the study of benzene oxidation.

An alternative method for studying interacting homogeneous-heterogeneous processes has been put forward by Gorokhovatskii (70), based on the fact that homogeneous reactions may occur in the unoccupied volume between catalyst granules which changes in size when the dimensions of the granules are changed. The method is only suitable for branched radical reactions, as the reaction rate is independent of the vessel size and the distance between granules for unbranched reactions (71)

If radical chains are nucleated at the external surfaces of the granules, the reaction rate W is ,

$$W = S \cdot n_0 \cdot \frac{ad}{1 - \delta ad}$$

where S is the external surface area of the catalyst, n_0 is the number of primary centres nucleated per unit surface area, and δ is the probability of branching of a

chain on a given granule of diameter d .

When the granule size is changed by a factor of i ,

$$W_n = S_n \cdot n_o \cdot \frac{ad}{1-\delta ad} ; \quad W_N = S_N \cdot n_o \cdot \frac{aD}{1-\delta aD}$$

where the subscripts n and N denote small and large granules, respectively. If $S_n/S_N = i$, then $d/D = 1/i$, then

$$\frac{W_n}{W_N} = \frac{1-\delta aD}{1-\delta ad} \text{ which is } < 1$$

When there is a decrease in the granule size, the rate of a homogeneous-heterogeneous reaction per unit external surface area of the catalyst should decrease. With a small extent of branching, this decrease is slight, and W_n/W_N is close to unity. Thus, the method of varying granule size may not be very sensitive.

Using the rate per unit total surface area S_{Total} , rather than the rate per unit external surface area, the equations become

$$\frac{W_n}{W_N} = \frac{d}{D} \cdot \frac{1-\delta aD}{1-\delta ad} = \frac{1}{i} \cdot \frac{1-\delta aD}{1-\delta ad}$$

since for such catalysts, $S_{\text{total}}^n \cong S_{\text{total}}^N$. The decrease in rate should then be more evident.

Since the surface area of the catalyst changes with granule size, the reaction rate (or yield) must be referred to unit surface area. The authors used the following technique in order to maintain the same active surface area. A large-granule carrier was impregnated with the active catalyst and the yield of catalyst determined. This catalyst

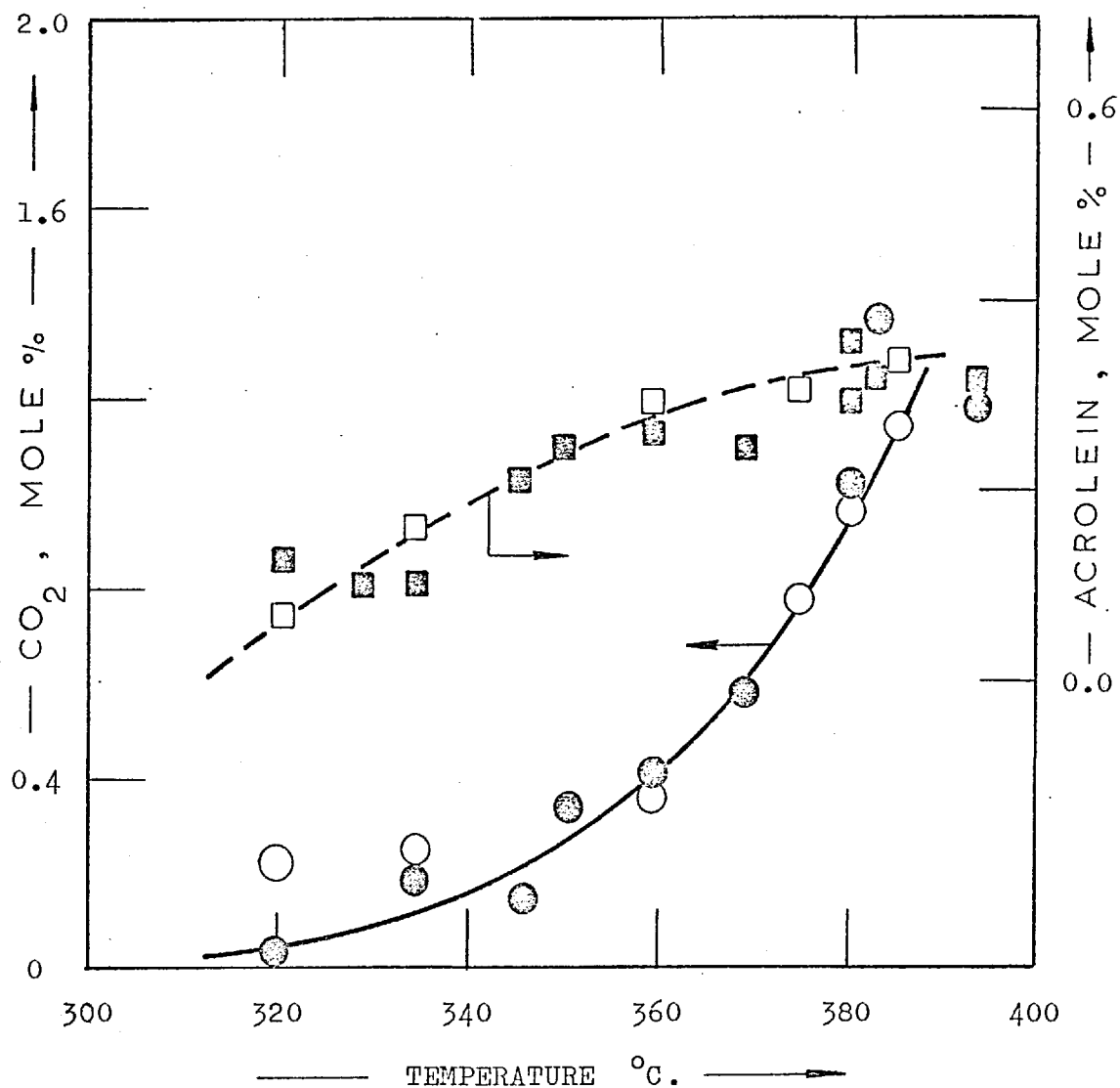


FIGURE 1.4 : Dependence of the amount of propylene oxidation products formed on temperature, for Cu_2O catalysts on a non-porous carrier with various granule sizes:

7 - 8 mm. for the $\bullet$, $\blacksquare$ symbols

2 - 3 mm. for the $\circ$, $\square$ symbols

was then broken into successively smaller granules and the yield again determined at each size. For an equal charge of catalyst, the changes in granule size does not affect the magnitude of the surface area of the active substance (only the carrier is broken down), and the latter need not be known.

This method was used to study the oxidation of propene over a cuprous oxide catalyst deposited on non-porous carborundum. The results, shown in Figure 1.4, show that product concentrations from 320^o-365^oC are independent of catalyst granule size (or the distance between particles) and hence that homogeneous reactions are not important. The data was apparently in agreement with other studies on propene oxidation where vessels with variable free volume above and below the catalyst were used (72). Other reaction systems were studied by this method, although it is perhaps significant that no homogeneous reactions were detected in any case. The oxidation of ethylene to ethylene oxide over a silver catalyst, propylene to acrolein over a copper oxide catalyst, and acetylene over active manganese dioxide were all studied and no homogeneous effects were detected.

It was also interesting to note that gas-phase reactions were not detected in the oxidation of naphthalene to phthalic anhydride over a vanadia based catalyst.

A major criticism of this technique for studying the importance of volume reactions lies in the fact that it is not possible to change the effective surface:volume ratio by a large degree, and the chances of detecting gas phase reactions must be small. It is unfortunate that the authors

did not use a bismuth molybdate catalyst for their work on propene oxidation, as McCain and Godin (3) have demonstrated clearly that homogeneous reaction does occur over that particular catalyst.

It was decided not to use the above procedure to study the oxidation of benzene, for two reasons. Firstly, there are more convenient methods of studying free volume effects in the catalyst bed, by which it is possible to vary the surface to volume ratio in a much more marked fashion than is possible with the method above. Secondly, changing of the catalyst particle size does not allow the easy calculation of homogeneous kinetics, which would be necessary for inclusion into a general model of homogeneous-heterogeneous interaction.

4B Present techniques

It was decided that new and more exact techniques must be developed for the study of interacting gas and gas-solid reactions. To this end, preliminary experiments on the oxidation of benzene over a suitable vanadia based catalyst were completed in a reactor much the same as the one used by McCain (3). The volume after the catalyst bed was varied under a variety of reacting conditions and resulting inconsistencies obtained in product yields indicated that this free space was influencing the rate of the overall reaction. It was not possible to differentiate between over-oxidation and other possible homogeneous effects, but the results gave strong indication that it is not possible to explain fully the reaction kinetics of the oxidation of benzene to maa on a solely heterogeneous basis.

The basis of the present work is the investigation, identification and subsequent quantification of such gas phase reactions that occur during the heterogeneous oxidation of benzene. The measurement of the reaction kinetics subject to the influence of free volume effects seemed the ideal approach, but the choice of reactor in which to perform the studies was not so obvious.

Since the preliminary studies had shown that free volume in the reactor had an effect on product yield (see above), further experiments to test the importance of homogeneous reactions was completed using a reactor of the same general type, in which the free volume after the catalyst bed was packed with varying amounts of inert solid. As discussed in part 1 of this chapter, inert surface has a marked effect on the course of a homogeneous gas-phase reaction and it was hoped to ascertain semi-quantitatively the importance of the gas reactions in the system.

There are problems, however: the difficulties of establishing quantitative kinetic data with the aid of such integral tubular reactors are well established (73), particularly with respect to maintaining isothermality in the system. Alternatively, the differential tubular reactor with a short catalyst bed operating at low conversion is commonly employed in an attempt to measure point reaction rates. However, this requires very accurate multi-component analyses in order to be able to specify not only average concentrations but also the complete mass balance over the reactor. Furthermore, if the reactor is to be operated isothermally, the temperature rise across the bed normally

should not exceed one to two degrees, which implies that the gas concentration should be measured to the same precision as the temperature - usually not an easy task. As in the integral reactor, heat and mass transfer are entirely dependent on inlet gas flow-rate, and with the small catalyst charge, there is always the danger of non-uniform packing and poorly defined gas-solid contacting.

The recycle reactor, with continuous feed and product streams and with a recirculating flow (74, 75) is an attempt to combine the desirable features of both integral and differential reactors. The chief advantage is that variable (and high) degrees of overall conversion can be obtained with essentially differential conversion per pass through the catalyst bed, at known conditions of temperature and concentration. Although the concentration in the bed is still strictly an average value, as in a true differential reactor, when operated at high values of recycle ratio (greater than 20) it approaches the measured exit concentration (see on). Another important feature at high recycle rates is that changes in throughput will not alter the flow regime in the catalyst bed. It is thus possible to avoid mass transfer limitations, provided non-uniform packing does not cause channelling in the bed. However, there are mechanical difficulties with recycle reactors since they need a positive displacement pumping device, which may be required to operate under hot, corrosive conditions, possibly at high pressures. Very rapid heating and cooling of the gas stream on either side of the catalyst bed may be necessary to protect the pump, but this also minimises any concurrent homogeneous reaction of feed or product. The difficulty of defining

Table 1.4 - Comparison of Stirred Reactors, employed for Gas-solid Catalytic Reactions

Authors	Reaction Studied	Temp. °C	Pressure (atm)	Residence Time (sec)	Stirrer Speed rev/min	Catalyst Arrangement	Remarks
Trotter and Wilhelm (76)	Hydrogen oxida- tion over platinum catalyst	10-75	1.1	1-11	400-1100	40-100 micron particle size catalyst, solid paddle used to stir partially fluidised cata- lyst and gas	Analysis of first order kinetic data to provide evidence for adequate gas mixing
Ford and Perlmutter (77)	Dehydrogenation of 2-butanol over brass catalyst	290-370	1		2000	Metal catalyst filter as liner to inner walls	Large free catalyst vol- ume. Virtually little more than a single phase stirred gas reactor
Relyea (78)	Hydrogenation of C_2H_4 over nickel alumina catalyst	45-200	1	10-140	Stirrer speed quoted as motor volts only	Alumina annu- lus 5 in long; o.d. 4½ in; i.d. 3 in.	5 in. deep, 3 in. diam. space with four bladed impeller, stationary catalyst liner

(contd./over)

Authors	Reaction Studied	Temp. °C	Pressure (atm)	Residence Time (sec)	Stirrer Speed rev/min	Catalyst Arrangement	Remarks
Carberry (79)	Carbon Monoxide oxidation over supported palla- dia catalysts	200-234	1	25 (minimum)	1600	Array of $\frac{3}{16}$ in diam.spherical pellets in four bladed paddle shape, blade thickness equals single sphere	Catalyst adsorbed on to sphere as a thin layer to prevent pore diffu- sion. Additional impellers added to pro- vide additio- al agitation Large free volume
Brisk et al (80) (I.C.I./C.I.R.L.)	Hydrocarbon oxidation over supported catalysts	300-475	1-10	0.5-12	3000-6000	(a)Circular Basket (b)Cruciform Basket Random pack- ing for particle sizes from $\frac{1}{16}$ in. to $\frac{1}{4}$ in.	

the homogeneous residence time under these conditions makes this reactor unsuitable for study of non-catalytic side reactions.

The construction of a reactor with internal, rather than external recycle is an obvious means of removing the mechanical and physical drawbacks of the recirculating reactor. A number of approaches to the design of stirred gas-solid reactors (S.G.S.R.) has been made, as is shown in Table 1.4. Of these, the reactor developed by I.C.I./C.I.R.L. (80) is probably the most sophisticated version. The design is very similar to that of Carberry, although the latter has a very much larger free volume to catalyst volume ratio.

One of the S.G.S. reactors developed by I.C.I./C.I.R.L. has been used in the present work to study the presence of concurrent gas phase reactions during the catalytic oxidation of benzene. The study has been facilitated by the use of differing reactor internals, whereby the contact time over the catalyst may be kept constant whilst the gas phase residence time is varied, giving, in theory, a direct indication as to the importance of gas phase reactions.

Besides the more common advantages of perfectly-mixed reactors, the S.G.S.R. has the following additional benefits. Firstly, high gas circulation rates past the catalyst surface reduces interfacial resistances to give high rates of heat and mass transfer, allowing the reaction to be carried out under conditions of chemical and not physical control. Secondly, good gas to wall heat transfer enables the reactor to be operated under isothermal conditions. Thirdly, the overall conversion can be varied over a very wide range

whilst still maintaining differential conversion in each pass of the internal recycle system. This allows the reaction rate to be calculated directly from the conversion data. Finally, it is possible to vary the catalyst particle size over a moderate range without causing any alteration in the gas transport characteristics.

Characterisation of the S.G.S.R., to determine the approach of the system to an ideal perfectly-mixed reactor, has been completed by Brisk et al (80). Use was made of appropriate heat and mass transfer correlations to calculate the maximum differences in temperature between the gas and the catalyst surface. Predicted curves of temperature difference versus stirrer speed are shown in Figure 1.5. Comparison of conditions in the stirred reactor with corresponding conditions that could exist in a tubular reactor show a difference in temperature of 5.5°C between the gas and the catalyst surface in the S.G.S.R. against a temperature difference of 30°C or more in the tubular reactor.

Mixing characteristics for circular and cruciform baskets in the S.G.S.R. reactor are shown in Figure 1.6. "Mixing" refers to macroscopic mixing in the gas, and implies uniformity of gas composition and temperature at all points in the reactor and outlet stream. The results in Figure 1.6 were obtained for the catalyst basket charged with $1/8''$ catalyst - the mixing curves may differ for smaller particles.

Calculation of reaction rates from data on reactor conversion:

A fundamental similarity between recycle and stirred catalytic reactors is that they both give a direct measure of the rate of reaction from the measured difference between

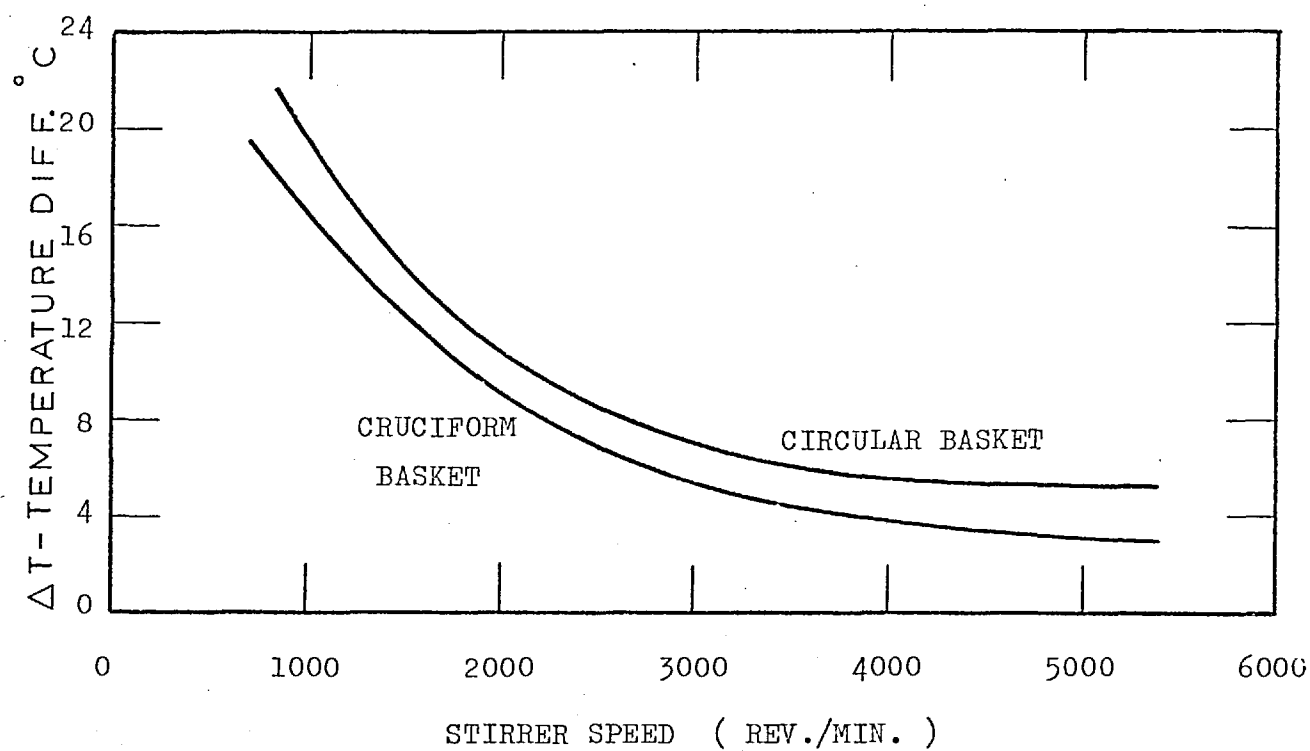


FIGURE 1.5 : Predicted Temperature Difference between Gas and Catalyst.

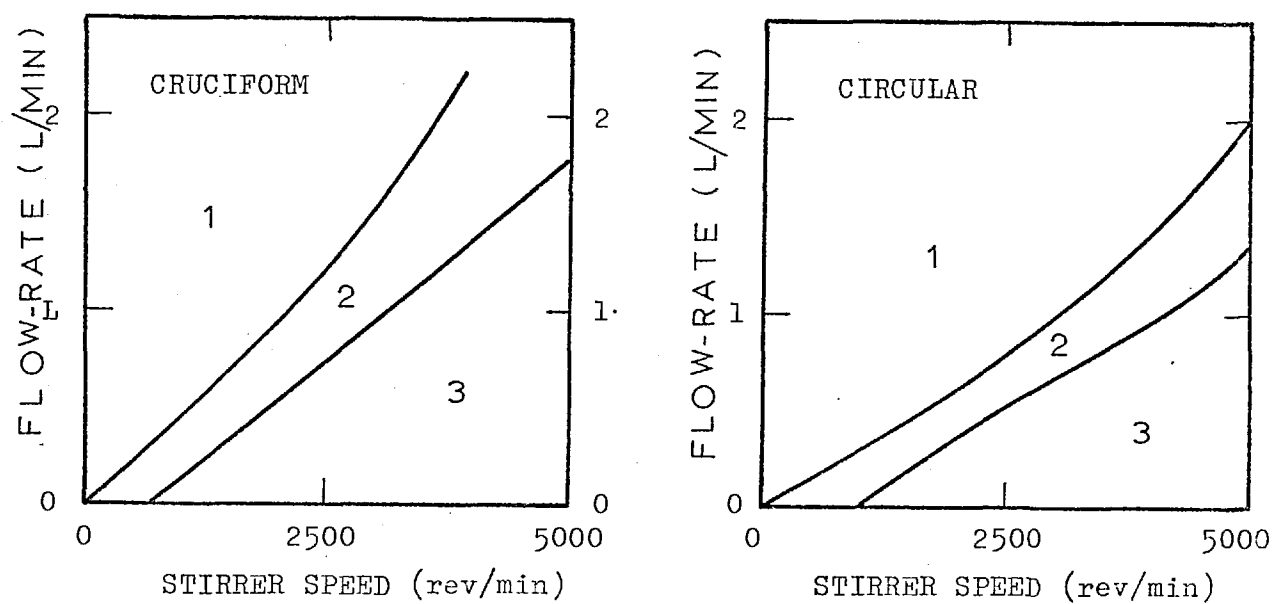


FIGURE 1.6 : Mixing Characteristics.

1 : Badly mixed region, 2 : Partly mixed region 3 : Well mixed region

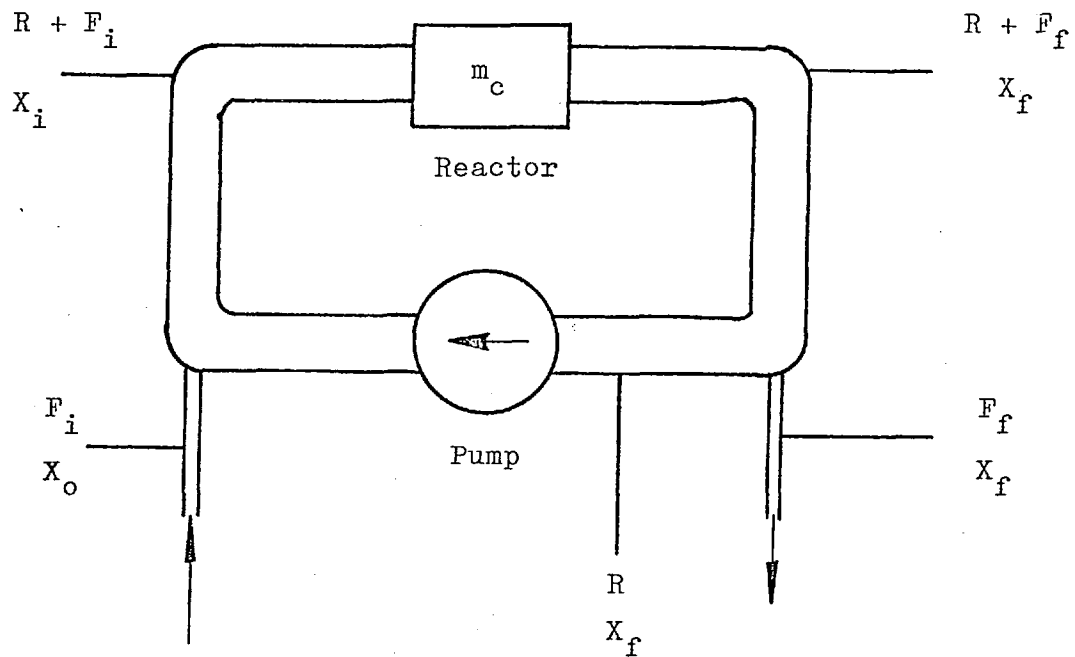


FIGURE 1.7 : RECYCLE REACTOR

Symbols Used :

- F = flow-rate (mol/unit time)
- m_c = mass of catalyst (gm.)
- R = recycle flow-rate (mol/unit time)
- r_A = reaction rate of a component per
unit mass of catalyst (mol/gm.unit time)
- X = mole fraction

Subscripts :

- f = final or exit value
- i = initial or inlet value
- o = feed value

inlet and outlet concentrations. For this condition to be satisfied, the mass balances obtained in the recycle loop must be examined. Using the nomenclature of Figure 1.7

Balance over reactor section:

$$r_A \cdot m_C = (R+F_f)X_f - (R+F_i)X_i \quad (1)$$

Balance over inlet section:

$$F_i X_o + R X_f = (R+F_i)X_i \quad (2)$$

Hence, from (1) and (2)

$$r_A = \frac{1}{m_C} (F_f X_f - F_i X_o) \quad (3)$$

If there is no molar change due to reaction ie. $F_f = F_i = F$,

$$r_A = \frac{F}{m_C} (X_f - X_o) \quad (4)$$

$$\text{From (2) ,} \quad X_i = \frac{1}{R/F_i + 1} \cdot X_o + \frac{R/F_i}{R/F_i + 1} \cdot X_f \quad (5)$$

and, for $R/F_i \geq 1$, $X_i \approx X_f$.

Therefore the degree of approach to a perfectly mixed system depends on the extent to which R exceeds F_i . When $R \geq F_i$, the conversion per pass is still small as $X_i \approx X_f$ (differential operation), but the overall conversion may be very much larger (X_o can be much larger than X_f). For example, with an overall conversion of 10%, and R/F_i equal to 20, the error arising from the assumption that $X_i \approx X_f$ is only 1%.

It is a relatively easy matter, therefore, to calculate the overall rate of catalytic reaction in the S.G.S.R. Knowledge of the total volumetric flowrate through the reactor,

the active mass of catalyst, and the inlet and outlet concentrations of the reactants will give, by use of equation (4), an exact value of the rate of removal or production of the reactant.

It is useful, at this stage, to examine some of the features which need to be taken into account when considering the application of the stirred gas-solid reactor.

(a) Since the reactor uses a rotating catalyst basket, temperature measurement in the direct vicinity of the catalyst is not an easy task and predicted catalyst temperatures must usually be used.

(b) If a particular study requires any alteration in design which affects the reactor internals, this may modify the mixing and mass transfer behaviour. Fresh characterisation studies would then be necessary if this modification is at all extensive.

(c) Experimental designs need to be formulated in terms of outlet rather than inlet conditions, since the directly measured rate is dependent on the actual reactor concentration, which is identical with the outlet value. Since the experiments are set up in terms of inlet values, some iteration may be necessary. However, the use of many of the recently developed statistical design techniques (81) is greatly simplified because the solution of differential equations is not required to describe the data generated by the reactor.

(d) The measured yield and conversion data from the S.G.S.R. cannot be compared directly with tubular reactor results. In the simplest case the data must be integrated by use of a plug-flow reactor model in order to arrive at a

valid comparison.

Although these constraints may appear to outweigh any advantages gained from a system specifically designed to measure point reaction data, the decision to employ the reactor to measure catalytic conversion rates depends heavily on the end use to which the data is to be put. The S.G.S.R. appears to be an ideal tool for the study of gas phase reactions concurrent to the catalysed reaction. The large inherent free volume and the necessarily longer catalyst contact/reactor residence times will promote secondary reactions in any system in which they occur, and use of the cruciform and circular catalyst baskets will give a direct measure of the influence of free space on reactions occurring in the reactor.

Once the presence of homogeneous reaction during the oxidation of benzene to maleic anhydride has been identified, further studies must be undertaken to investigate homogeneous-heterogeneous interaction. The primary requirement of the identification of interaction is the distinction of over-oxidation effects, which cannot be completed in a simple fashion in the S.G.S.R. system alone as the catalyst surface is still able to influence any homogeneous process. Integral tubular reactors must be used for this purpose. This will allow the study of volume effects on any gas phase reaction occurring (a) without the presence of catalyst surface or (b) in the presence of inert surface. Thus, it is not intended, primarily, to use integral tubular reactors for the measurement of rate data, but rather to investigate the effect of free volume and surface:volume ratio on product yield.

In summary, it is intended to investigate the oxidation of benzene over a vanadia-molybdena catalyst with particular reference to the identification of homogeneous reactions. It is hoped that use of tubular reactors with variable free volume and surface after the catalyst bed will elucidate the possible gas-phase reactions occurring, and that subsequent use of the S.G.S.R. will facilitate the calculation of the combined heterogeneous/homogeneous kinetics.

EXPERIMENTAL.

1 Materials

2 Catalyst Preparation

3 Apparatus

3A Reactant delivery and measurement

3B Reactors and Furnace:

3B(a) Description of the S.G.S.R. and ancillary equipment

3B(b) Tubular reactors

3B(c) Reactor Furnace and controls

3C Analysis of reactants and products:

3C(a) The flame ionisation detector

3C(b) The katharometer chromatograph

3C(c) Identification of products

3C(d) Calibration

4 Procedure

5 Catalyst Stability and Life

1 Materials

The purity and source of all materials which have been used are reported in Tables 2.1,2.2. Table 2.1 lists the organic materials and gases used as reactants, and for identification and analysis. Chemicals used in the catalyst preparation, described in the following section, are tabulated in Table 2.2 .

2 Catalyst Preparation

Sufficient catalyst was prepared, using the specifications of Dmuchovsky et al (38), so that material from the same batch could be used for all experiments. 3/16" aluminium oxide 'Alundum' cylinders were impregnated with a solution containing known amounts of ammonium metavanadate (6.42%), ammonium molybdate (3.17%), sodium phosphate (.365%) and nickel nitrate (.281%), all dissolved in concentrated hydrochloric acid. The mixture was concentrated at 100°C and the coated pellets dried and fired in air at 400°C for one hour. The resulting catalyst was very dusty and was centrifuged before use. This final catalyst, catalyst 1, contained 9% of active coating by weight, and the surface area was found to be less than $1\text{m}^2\text{g}^{-1}$.

A second catalyst used only in later experimental work was prepared in the same way but with 1% Lithium sulphate added to the coating (catalyst 2).

Table 2.2

Organic Materials and Gases

<u>Name</u>	<u>Purity %</u>	<u>Use</u>	<u>Source</u>
Acetaldehyde	99	Identification	B.D.H.
Acetone	S.L.R.	Identification/Calibration	Fisons
Acrylic Acid	99	Product	B.D.H.
Benzene	ANALAR Reagent	Product-Reactant	Hopkins Williams
p-Benzoquinone	99	Identification	Hopkins Williams
Formaldehyde	ANALAR Reagent	Product	B.D.H.
Fumaric Acid	99	Identification	B.D.H.
Maleic Acid	99.5	Identification	
Maleic Anhydride	99.5	Product-Reactant	B.D.H.
Phenol	99.5	Product	B.D.H.
Air		F.I.D.	B.O.C.
Carbon Dioxide	99	Product	Distillers Ltd.
Carbon Monoxide	99.9	Identification	Air Products
Hydrogen	99	Chromatographs	B.O.C.
Oxygen	99	Reactant	B.O.C.
Nitrogen	99	Diluent	B.O.C.

Table 2.2

Catalyst Materials

<u>Formula</u>	<u>Amount in catalyst 1; wt. % of total</u>	<u>Source</u>
NH_4VO_3	6.42	B.D.H.
$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$	3.17	B.D.H.
$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$	0.365	B.D.H.
$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	0.281	B.D.H.
Concn. Hydrochloric Acid (1.16.S.G.)	44.8*	B.D.H.
Al_2O_3 Fused 'Alundum' (Type SA 101)	45.0 [†]	Norton Catalyst Carriers
$\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ (used for catalyst 2)	1.0	B.D.H.

*In absolute terms 42.9 ml. of acid were used, and using the specific gravity shown, the weight % was calculated to be 44.8.

[†]50 gms. (45.0 wt.%) of type SA 101 ($\frac{3}{16}$ " cylindrical pellets) alumina were used as support for the active material.

3 Apparatus

A standard flow apparatus with special provision for feeding in maleic anhydride was used in conjunction with specially designed reactors in all cases, (see Figure 2.1). The system was designed to allow the study of both heterogeneous catalytic reactions and homogeneous gas-phase reactions involving gaseous and liquid reactants under isothermal plug-flow or well mixed conditions. Basically, the system is comprised of three parts; the reagents delivery and measurement system, the reactors and furnace, and the analytical system.

3A Reactant Delivery and Measurement

Gases flowing to the reactor were metered at constant pressure (measured by open-ended manometers) through rotameters at a flow rate (5cc/min upwards) which was controlled by fine needle valves (Hoke-Milli-Mite Series). The flowmeters were calibrated for each gas using the soap bubble flow meters shown in Figure 2.1 . By maintaining the identical pressure on the manometer during both calibration and normal use, there was no need to apply pressure correction factors to rotameter readings. Constant and accurately known flow rates were obtained by using high quality needle valves and rotameters, and by careful calibration.

The system used for the vaporisation of the liquid reactant, benzene, was developed in order to satisfy the two criteria of constancy and accuracy. It involved a series of bubblers designed to saturate a measured gas stream,

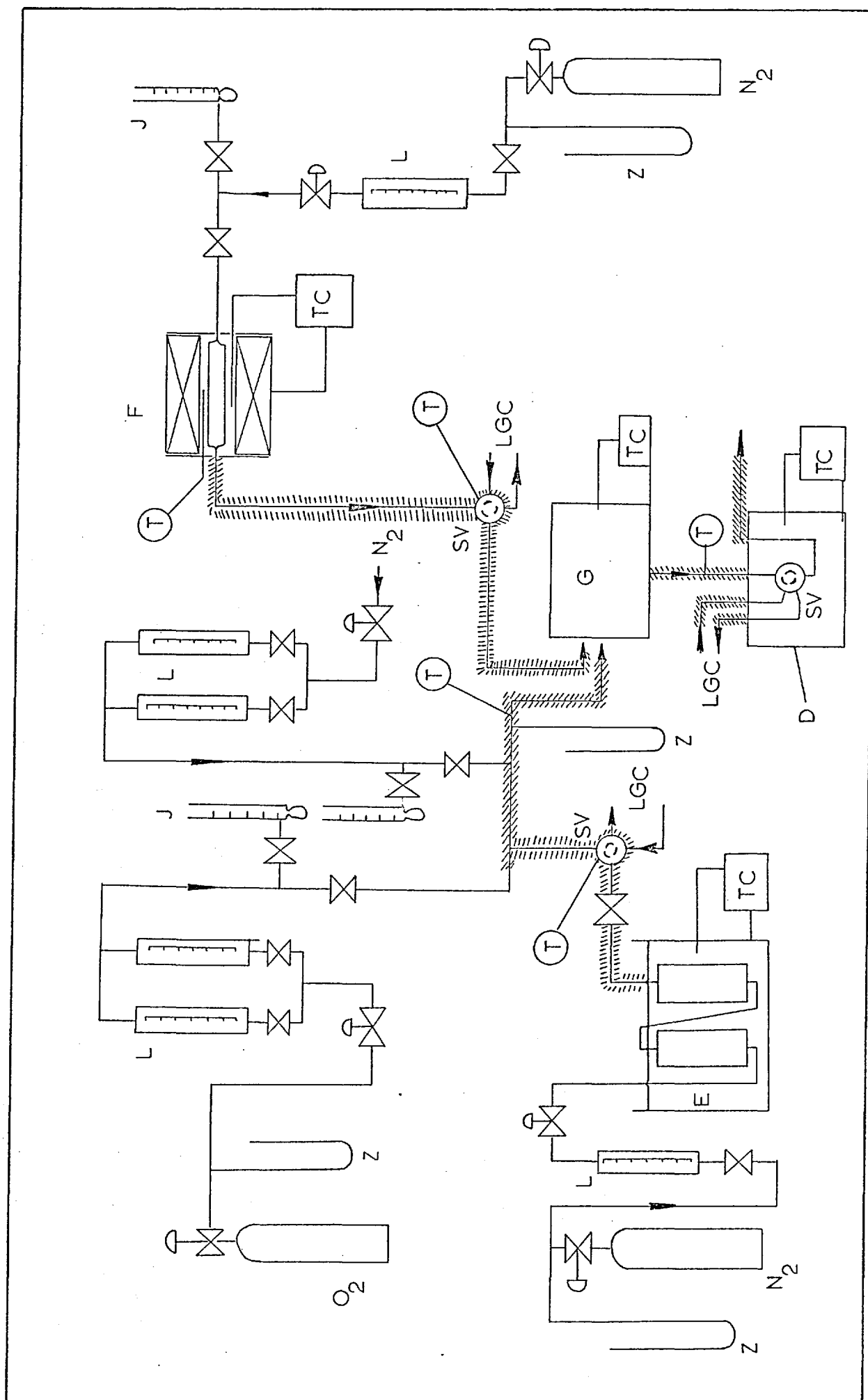


Figure 2.1 : General Flow Diagram.

LEGEND FOR FIGURE 2.1

Ⓣ	Thermocouple Point
TC	Temperature Controller
Z	Pressure Tapping (open ended Hg manometer)
LGC	Line to appropriate detector in the gas chromatograph
SV	Gas Sampling Valve
D	Temperature controlled Air Oven
E	Benzene Saturator System
F	Maleic Anhydride Feed System
G	Reactor Assembly, housed in temperature controlled Air Furnace
J	Soap - Bubble Meters
L	Rotameters

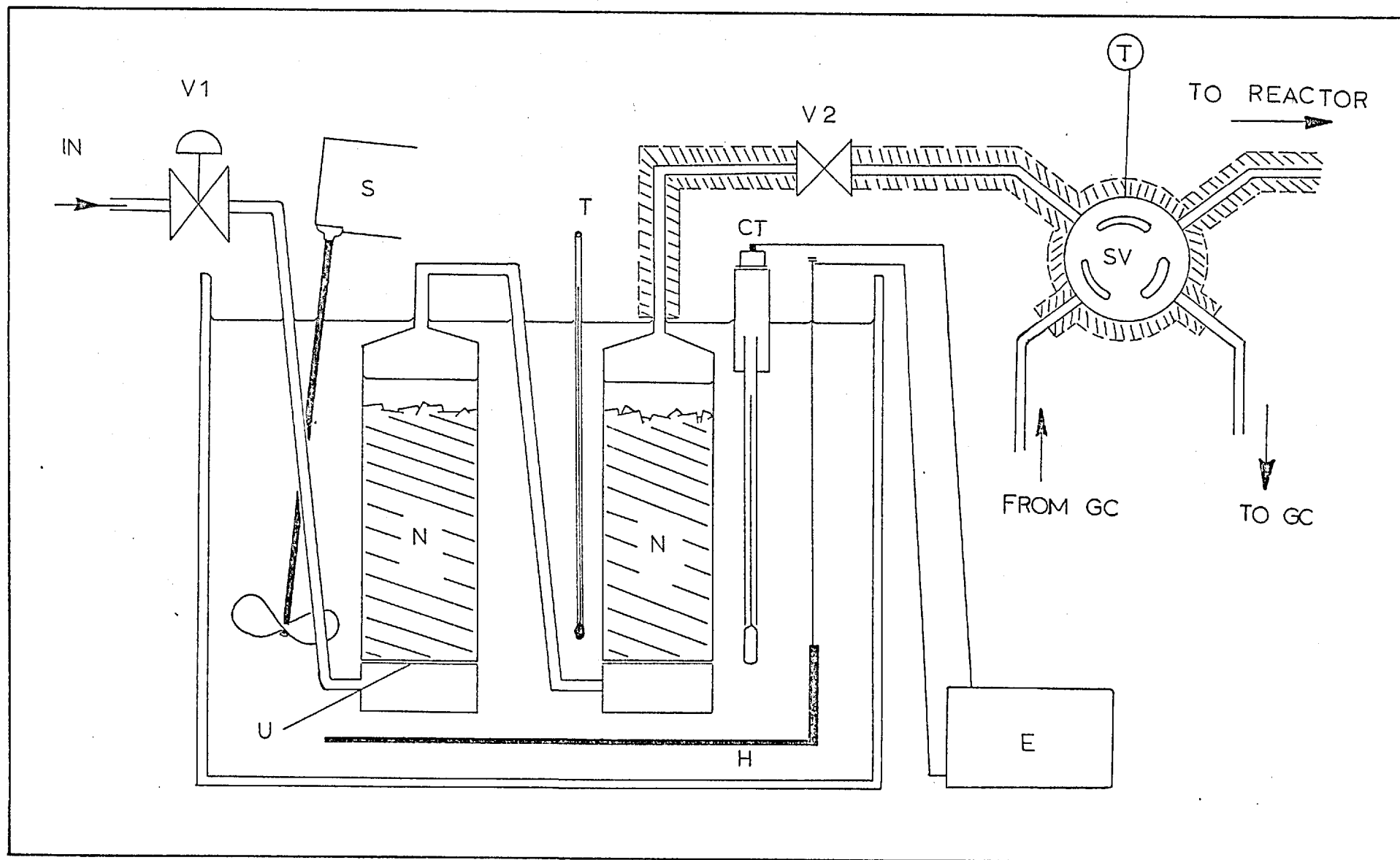
LEGEND FOR FIGURE 2.2

Ⓣ	Thermocouple Point
SV	Gas Sampling Valve
E	Electronic Relay
CT	Contact Thermometer
H	Heater Element
T	Thermometer (Hg in glass, 0 to 110°C.)
S	Variable Speed Stirrer
N	Drechsel Bottles containing Benzene
U	Glass Sintered Plate
V1	Fine Needle Valve
V2	ON/OFF Valve



Indicates heated line

Figure 2.2 : Saturator for Benzene Feed.



as shown in Figure 2.2 . The liquid benzene was contained in two modified Drechsel bottles, (capacity 500mls. each), connected in series and suspended in a water bath ($\pm 0.2^{\circ}\text{C}$) at a constant temperature controlled by a contact thermometer and an electronic relay. Gas passing through the bottles was dispersed efficiently at the glass sinter in the base of each bottle - the bubbles being prevented from reforming by filling the Drechsel bottles with glass raschig rings. The exit gas was passed via a heated line to an on-line sampling valve (Perkin Elmer Type 451) where regular analyses showed that the composition of the exit stream was constant and reproducible. The heated line was continued to a premixer where metered streams of oxygen and nitrogen were introduced, the resulting stream going to the reactor.

Preliminary experiments were performed on the 'pick-up' assembly to ascertain the best temperature at which to operate the water bath. It was thought that reproducibility of pick-up would be best achieved by approaching saturation of the gas stream. The theoretical amount of benzene which should saturate a known flow of gas was calculated using the formula:

$$\frac{P_0}{(P-P_0)} = \frac{\text{weight of benzene (gm/min)/molecular weight of benzene}}{\text{Total flow rate (moles/min)}}$$

where P_0 is the vapour pressure of benzene at any temperature T , and P is the total pressure in similar units.

For any gas flow rate the amount of benzene picked-up can be plotted as a function of temperature. The actual amount of benzene removed from the bottles by the gas was determined at various flow rates and temperatures by using

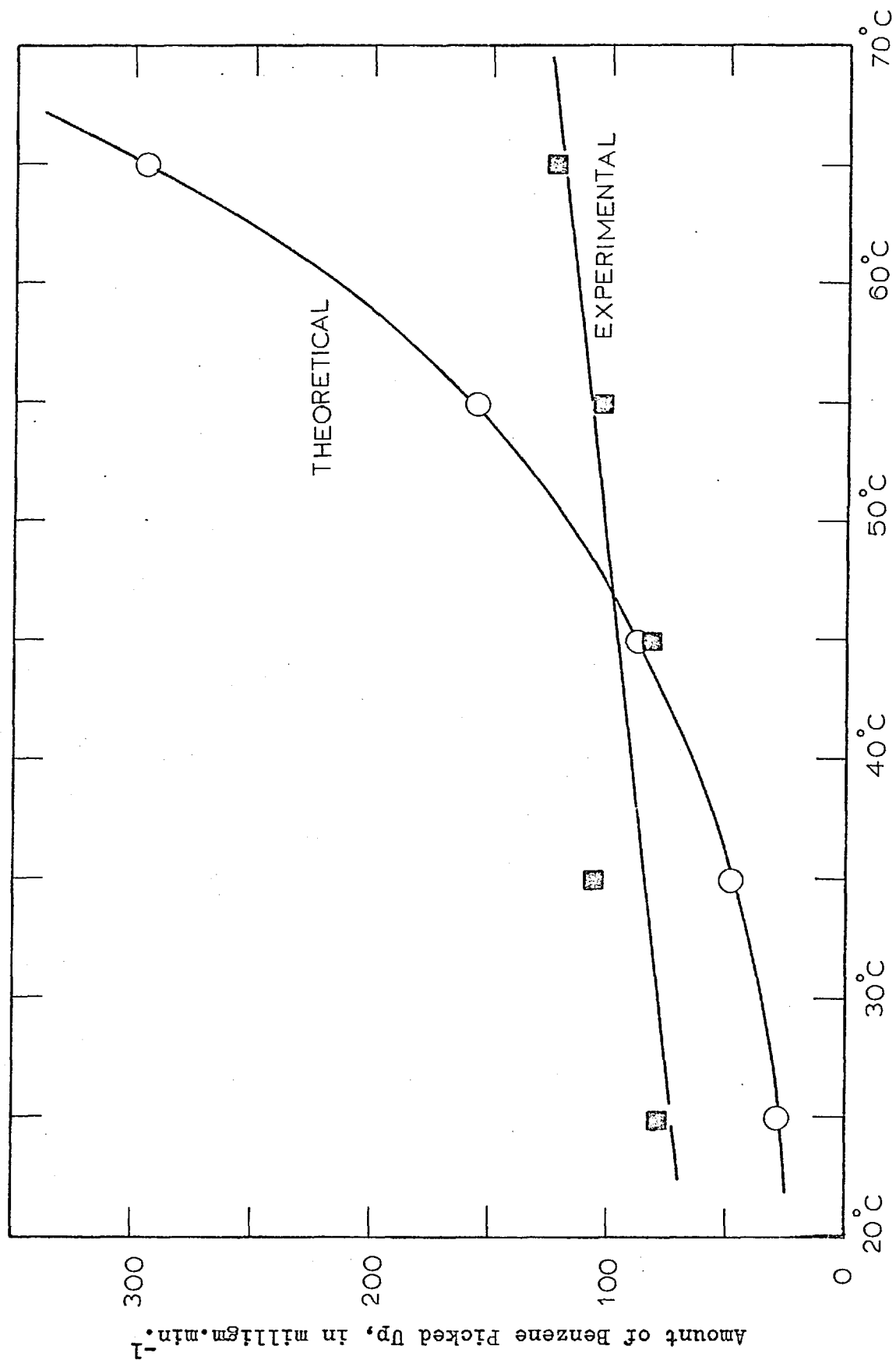


Figure 2.3 : Data from Benzene Saturator ; Amount of Benzene picked up vs. Temperature of operation. Theoretical and Experimental Results shown, for a constant N_2 Flowrate of $57 \text{ ml} \cdot \text{min}^{-1}$

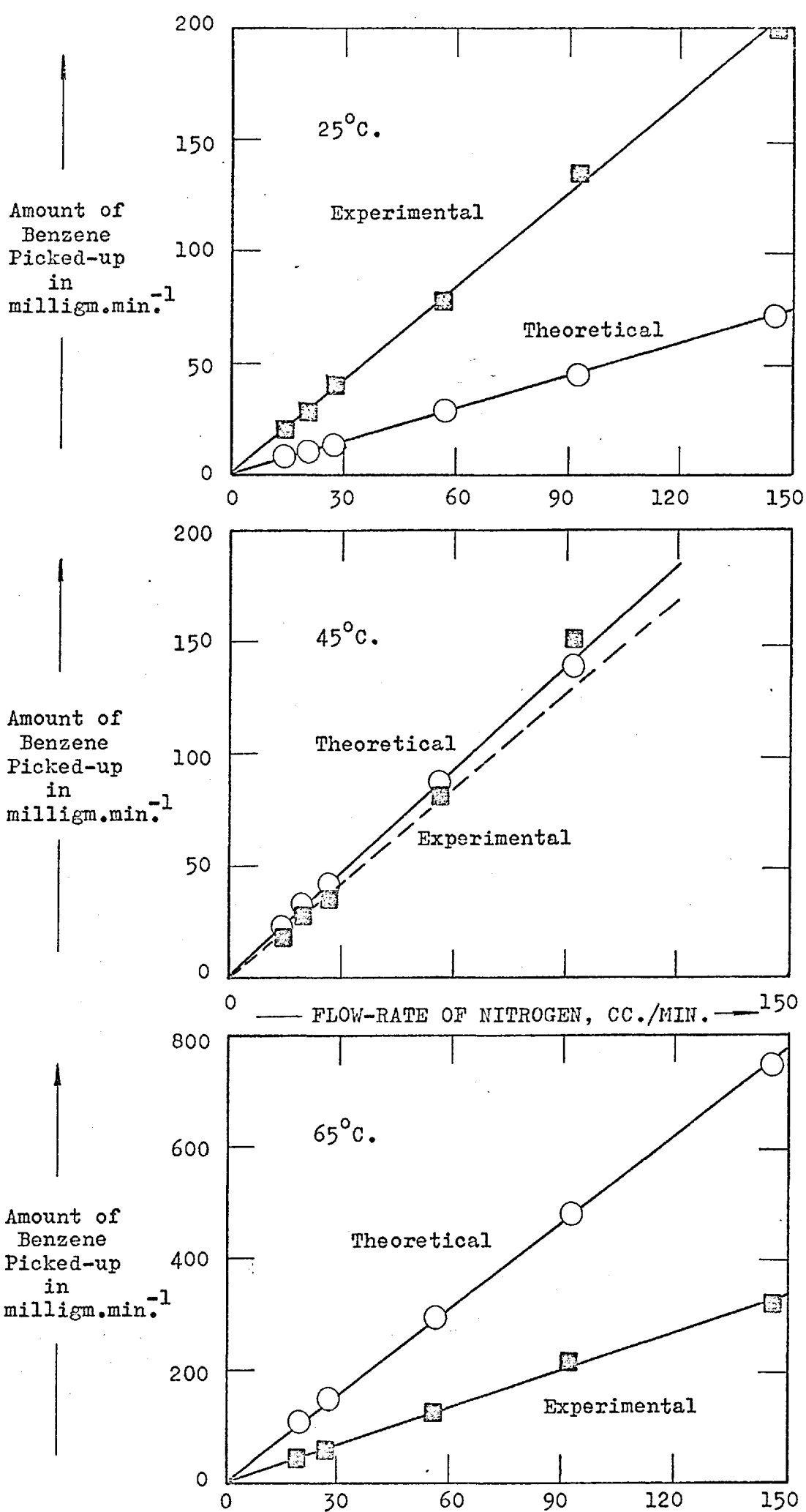


FIGURE 2.4 : Data from Benzene Saturator ; Variation of Amount of Benzene picked up with gas flowrate at constant Temperature.

glass helical coil traps immersed in ice. Figures 2.3, 2.4 show the relation between theoretical and actual pick-up of benzene in a stream of nitrogen for a variety of temperatures and flow rates. It can be seen that the closest approach to saturation is achieved in practice at 45°C. Operation of the bath at higher temperatures than 45°C meant larger amounts of benzene vapourised, (and it was necessary, when working with high benzene feed concentrations, to do this), but the approach to saturation was smaller. However, in practice it was found that saturation was not necessary for reproducibility of pick-up, even at high bath temperatures, the input of benzene as feed remained at a constant value over a wide range of flow rates.

In later experiments it was necessary to add maleic anhydride to the feed as a vapour stream. This was achieved by operating a fixed bed adsorber in reverse - as a fixed bed desorber. The apparatus is shown diagrammatically in Figure 2.5. A concentrated solution of maleic anhydride in acetone was used to saturate 1/8" alumina pellets and the acetone was evaporated from the solid by heating to 40°C. The resulting pellets were then placed inside a glass tubular vessel of 1" I.D. and at least 20" in length, which could be heated to and controlled at temperatures between 100°C and 170°C ($\pm 1^\circ\text{C}$) by use of a variac. An accurately metered stream of nitrogen was then passed through the bed, the flow rate of the gas and the temperature of the bed determining the exact amount of maleic anhydride picked up by the gas.

Analysis of the exit gases using a heated on-line Pye Sample Valve connected to the appropriate analytical devices showed that a continuous stream of gas containing constant

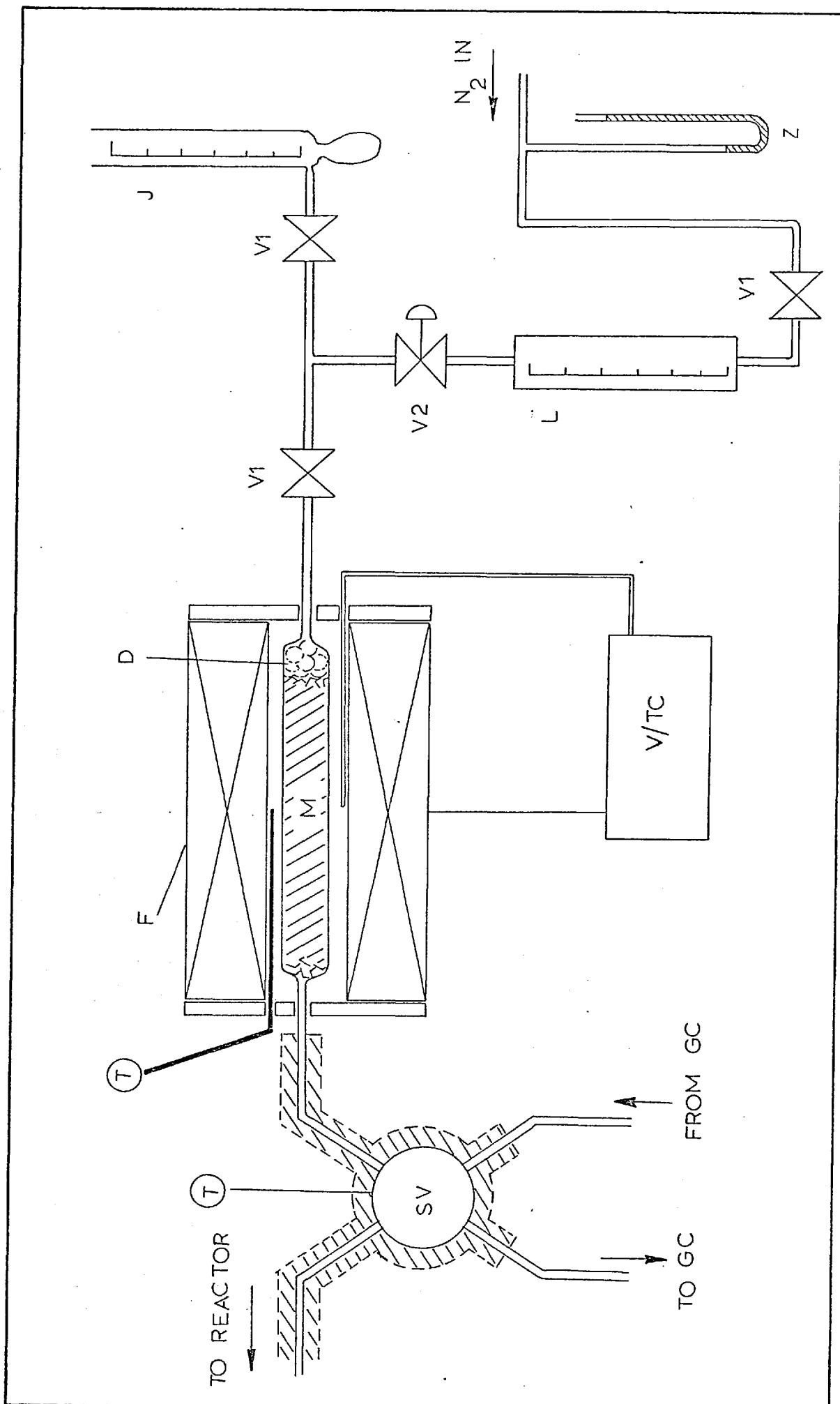


Figure 2.5 : Apparatus for Maleic Anhydride Feed.

LEGEND FOR FIGURE 2.5

Ⓣ	Thermocouple Point
V/TC	Temperature control by Variac
SV	Gas Sampling Valve
F	Air Oven
M	Alumina pellets coated with maleic anhydride
D	Premixing section - 6 mm. diam. glass spheres
L	Rotameter
J	Soap - Bubble Meter
Z	Pressure Tapping (open ended Hg manometer)
V1	ON/OFF Valve
V2	Fine Needle Valve
////	Indicates Heated Line

LEGEND FOR FIGURE 2.7

1 : Belt Drive Groove	9 : Thermocouple Entries
2 : Outer Magnet Bearings	10 : Pressure Tapping
3 : Upper Bearing	11 : Inlet Port (showing Purge)
4 : O ring Seals	12 : Catalyst Basket
5 : Outer Magnet	13 : Reactor Pot
6 : Inner Magnet	14 : Baffles
7 : Reed Relay	15 : Outlet Port
8 : Lower Bearing	

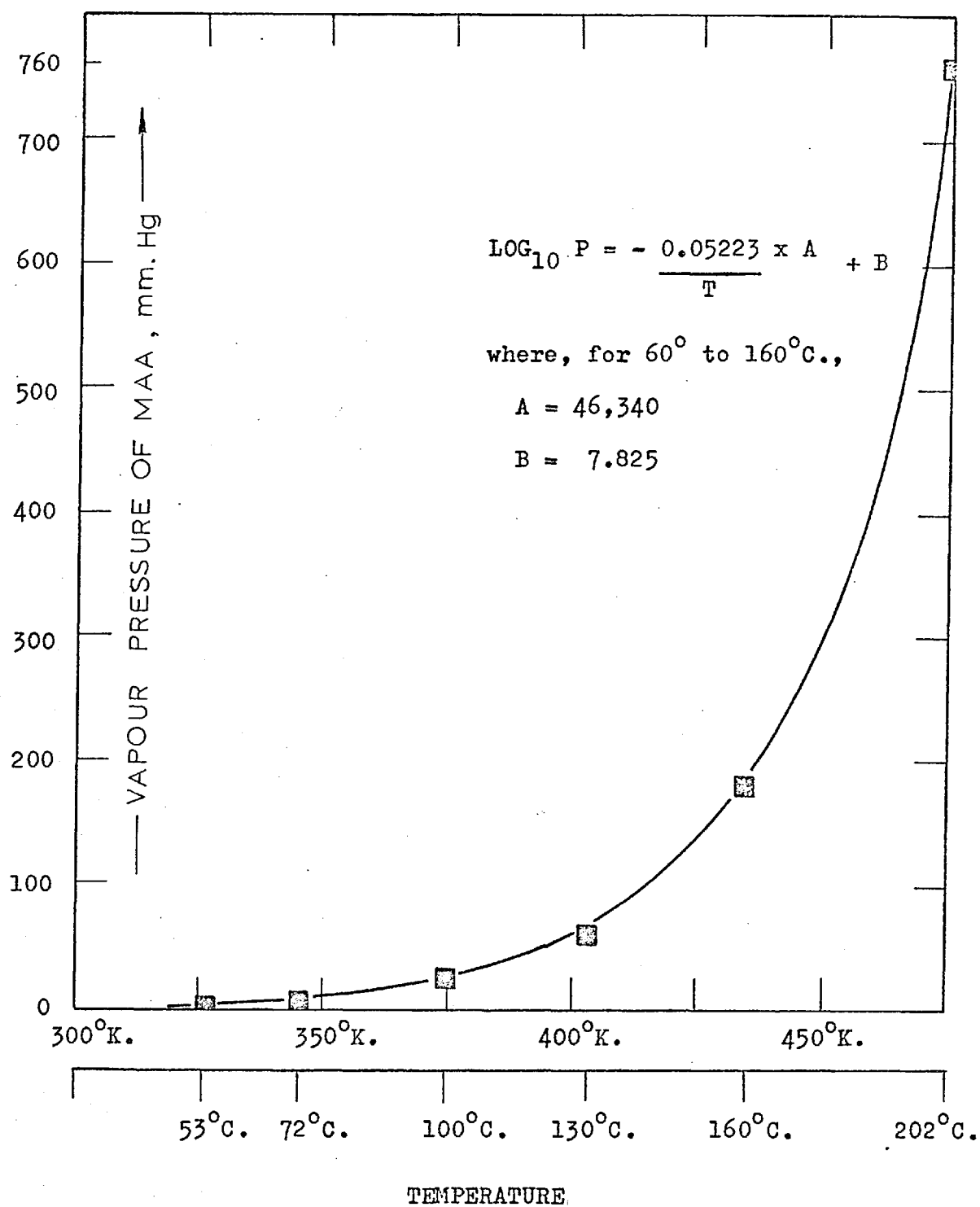


Figure 2.6 : Vapour Pressure Data for Maleic Anhydride

(reprinted from data by WEISS and DOWNS (82))

amounts of anhydride could be produced, although pick-up was very sensitive to the bed temperature. This was to be expected from looking at the vapour pressure temperature curve for maleic anhydride. (Figure 2.6 (82))

3B Reactors and Furnace

(a) Description of the S.G.S.R. and ancillary equipment

The reactor is conceived as a catalyst basket doubling as a stirrer paddle rotating in a small reaction vessel. It has been argued (79,80) that rotation of the basket at high enough speeds would cause the gas phase to be perfectly mixed and the concentration of the gas would be identical not only in every part of the free gas space but also over the surface of every catalyst particle. This means that under steady state operation the inflowing gas would be almost instantaneously mixed with the recirculating gases in the reactor. The out-flowing gas concentration would be identical with the bulk gas concentration in the reactor, and the reaction rate would be dependant, not on input concentrations, but on the bulk reacting gas concentrations. The theory behind the operation and the additional benefits accruing from this situation have been discussed more fully in the Introduction.

The components of the reactor assembly are a stirrer drive unit with stirrer shaft, the reactor vessel, and the catalyst basket, (Figures 2.7, 2.8). The whole of the assembly was supported on a frame constructed in heavy angle iron.

The Drive Unit:

A completely sealed, magnetically coupled drive is used to rotate the catalyst basket with no vibration at speeds up

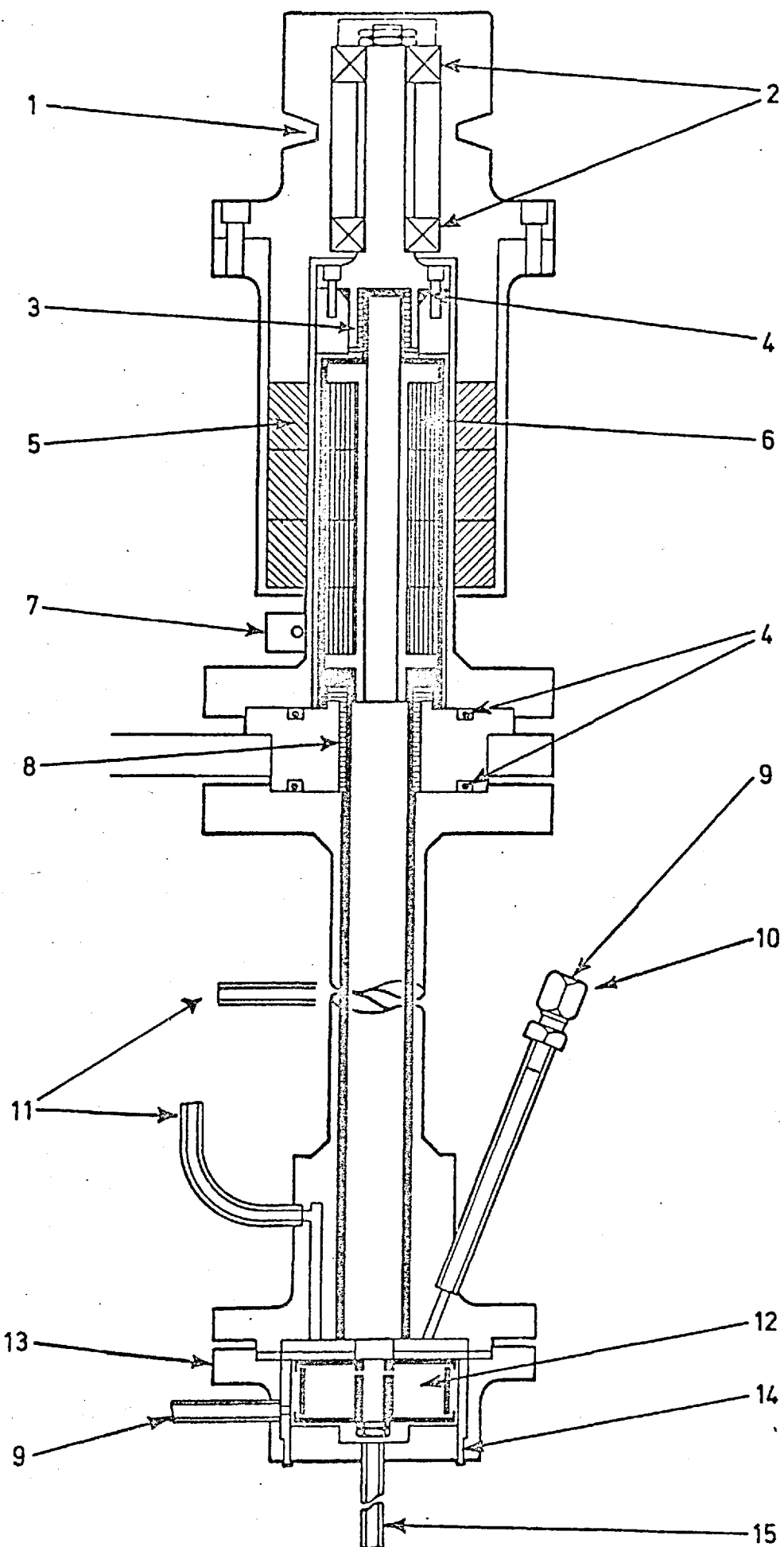


FIGURE 2.7 : THE STIRRED GAS SOLID REACTOR (S.G.S.R.)

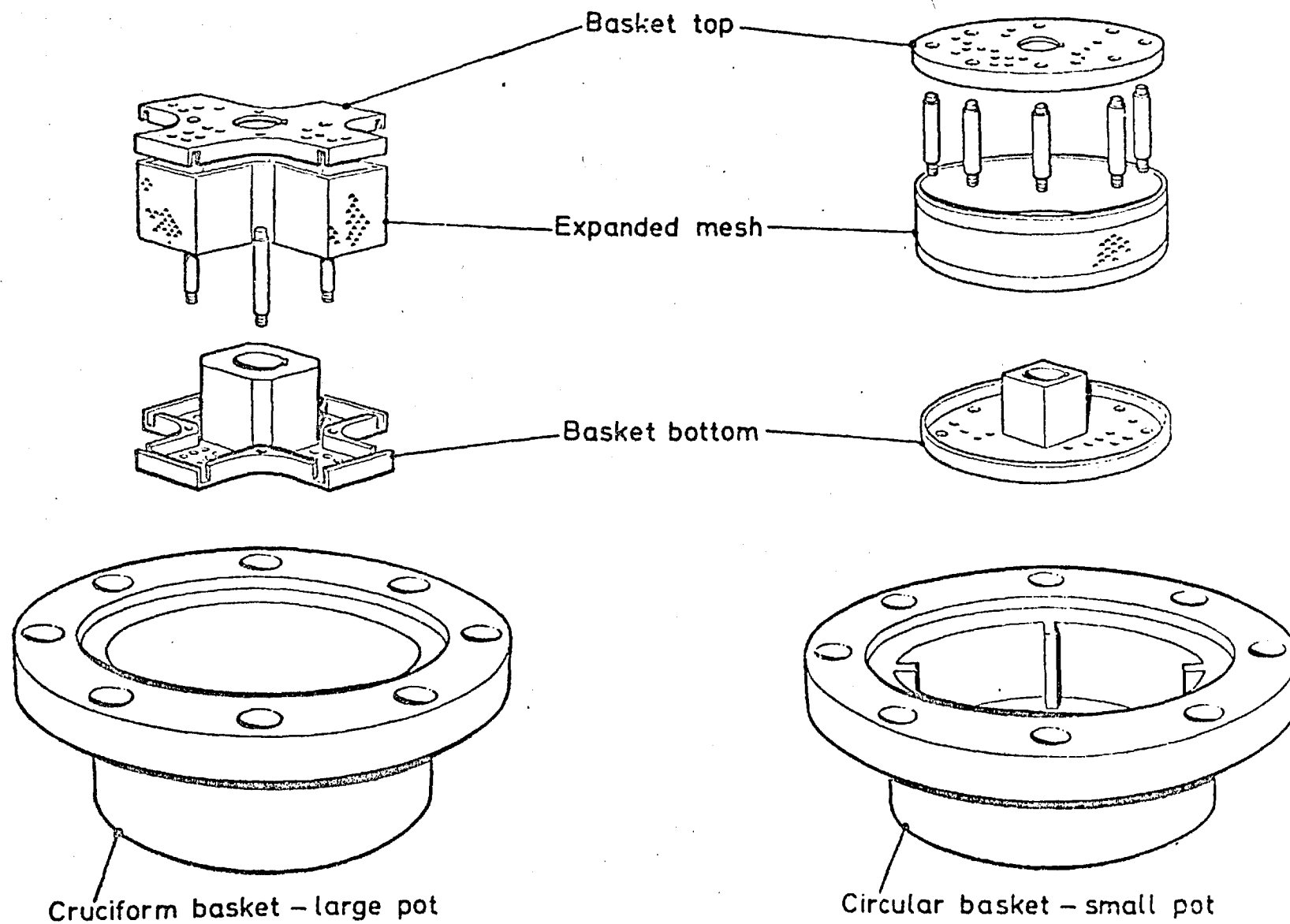
to 6000 rev/min. under reactor conditions extending to 500°C and 300 lbf/in²g. No leakage of gas past the drive shaft and no contamination of gas or catalyst by bearing lubricants occurred. The drive consists of two concentric rings of cermet magnets, the outer ring being rotated by a belt drive from a $\frac{1}{3}$ h.p. motor, whilst the encased inner ring (magnetically driven by the outer ring) is attached to the drive shaft. Unless the torque limit is exceeded, a direct drive with no slip is obtained.

Maximum speed of rotation was limited by the combined weight of shaft, basket and catalyst charge, and for high speeds it was essential to balance all rotating parts dynamically and to ensure that an evenly loaded catalyst basket was used.

The Reactor Vessel:

The flow of feed gas, normally premixed before entering the reactor (Figure 2.1), is split into three streams prior to entering the two inlet ports in the reactor top plate, adjacent to the periphery of the rotating basket, and the third inlet port situated approximately two-thirds of the way up the stirrer shaft housing. As experiments necessitate the use of a dusty V₂O₅ catalyst, which in use could cause damage to the lower bearing of the drive unit, it was necessary to have the latter inlet port so that a portion of feed could be purged down the shaft housing to prevent upward flow of material. For premixed feed a maximum of 20% of the total flow can be introduced in this way. The purge was restricted to 5% of total flow when the feed was not premixed, (as in the case of maleic anhydride feed),

FIGURE 2.8 : REACTOR POTS AND CATALYST BASKETS



and in this case it was convenient to purge nitrogen (as diluent) instead of feed. The reactor top plate also carried two thermocouple points which were fitted with 1/16" O.D. Chromel/Alumel thermocouples. The bottom section of the reactor vessel, which carried the exit line and a thermocouple point, was flanged and bolted to the top plate using a suitable gasket of non-corrosive material. This section includes vertical baffles and gives a total reactor volume of 30cm^3 (see Figure 2.8).

The Catalyst Basket:

Two interchangeable types of catalyst basket can be used to hold randomly packed charges of catalyst pellets from 1/4" to 1/32": a circular disc shape and a cruciform shape (Figure 2.8). They are constructed of perforated stainless steel top and base plates with stainless mesh side walls. The ratios of catalyst volume to free volume (including volume of catalyst voidage) available with the two types of basket are:

Cruciform 1 : 3.8

Circular 1 : 1.2

The volumes available for catalyst charge in the two baskets are

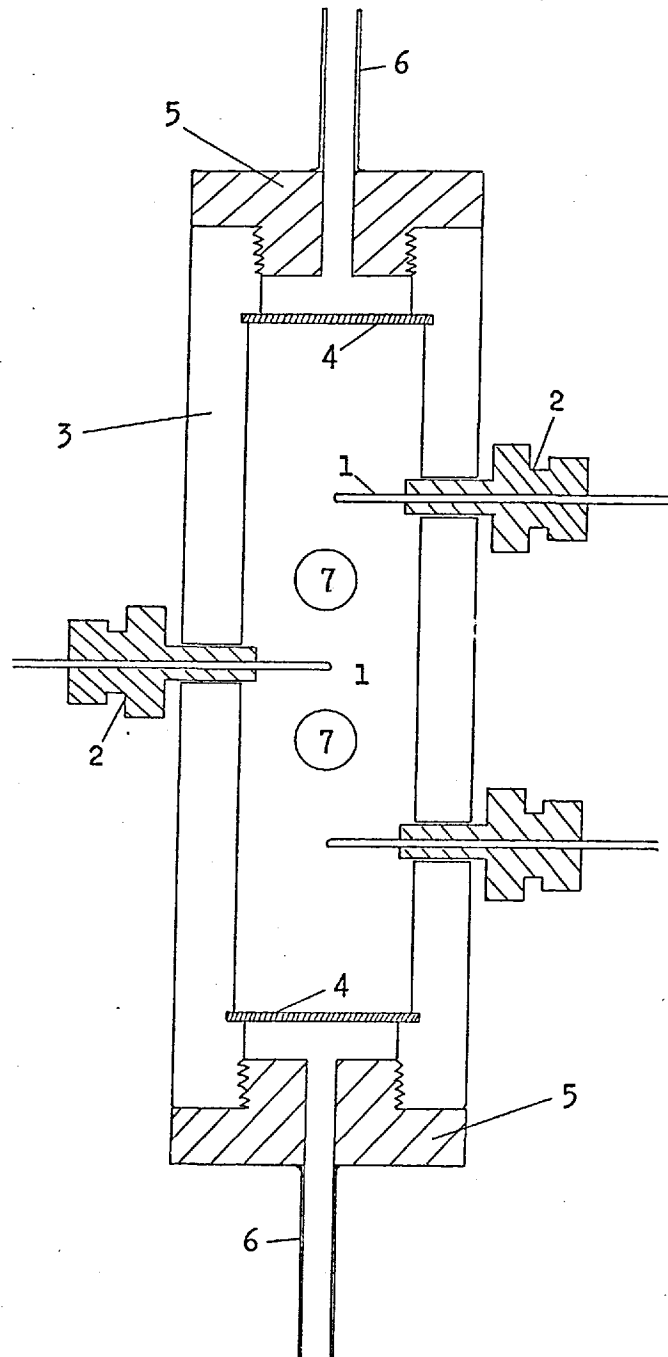
Cruciform : 10.4 cm^3 (2.6cm^3 per arm)

Circular : 22.3 cm^3

(b) Tubular reactors

In some experiments, catalyst was held in conventional tubular reactors fabricated in either glass or in 316 stainless steel. The steel reactor used, with an internal volume

FIGURE 2.9 : Tubular Reactor Fabricated from 316 Stainless Steel



LEGEND :

- 1 : Chromel - Alumel Thermocouples
- 2 : S./ Steel Connector , $\frac{1}{16}$ "
- 3 : S./ Steel Tube
- 4 : S./ Steel Sintered Discs
- 5 : S./ Steel End Plugs
- 6 : S./Steel Tubing , $\frac{1}{8}$ " O.D.
- 7 : Internal Volume (5 ml.) : Catalyst / Empty

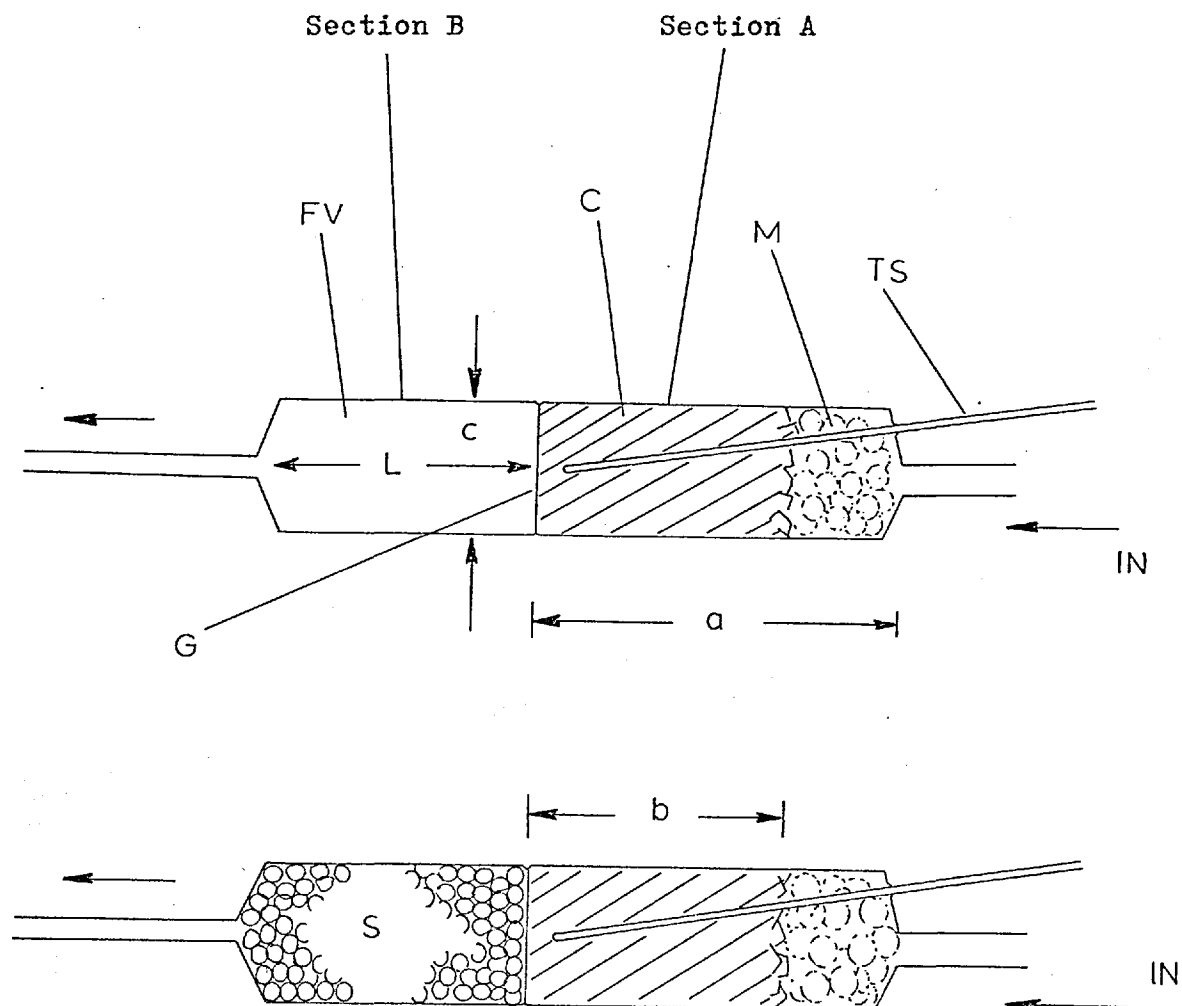
of 5ml, is shown in Figure 2.9 . Sintered metal discs were used to support the catalyst and to distribute the gases. Three $1/16''$ O.D. Chromel-Alumel thermocouples were inserted along the reactor length to measure the temperature profile. Because of extensive homogeneous oxidation the steel reactor was not used for catalytic experiments with maleic anhydride as feed, reactors fabricated in ''Pyrex'' glass being preferred. Experiments were also carried out with the catalyst suspended in a glass reactor, the general design and dimensions of which are shown in Figure 2.10 . The catalyst was located in the right hand chamber of the vessel, separated by a glass sintered plate from a second chamber. This was either empty, or filled with various solids to give different surface:volume ratios. Details of the reactors used are given in Table 2.3 .

Provision was made to measure the temperature of the bed in all cases.

(c) Reactor Furnace and controls

Both the S.G.S.R. and tubular reactors were supported in an electrically heated air oven, the temperature of which could be controlled to within $\pm 0.5^{\circ}\text{C}$ by an A.E.I. R.T.5 Proportional temperature controller used in conjunction with a platinum resistance thermometer probe located inside the furnace tube wall. The furnace tube was a 4'' diameter Asbestos cylinder, 10'' in length. A $1/4''$ diameter hole was drilled vertically down through the wall, parallel to the axis of the cylinder, to receive the probe. Careful winding of the furnace tube with nichrome wire and insulation by

Figure 2.10 : Glass Tubular Reactor - General Design



C	Catalyst Charge
G	Glass Sintered Plate
M	Premixing Section , 4mm. Pyrex spheres
TS	Thermocouple Sheath
FV	Free Volume , which could be varied for other reactors by changing L
S	Solid Packing

General Dimensions :

$$a = 10.5 \text{ cm.}$$

$$b = 7.8 \text{ cm.}$$

$$c = 20 \text{ mm.}$$

TABLE 2:3

REACTOR NO.	SECTION A	DETAILS OF SECTION B
1	IDENTICAL CATALYST CHARGE (15.11 gm.)	No Sintered Glass Plate ; MINIMAL - " 0 ml." - Free Space
2		16.32 ml. Free Space after the Catalyst Bed ; MINIMAL Surface
3		8.16 ml. Free Space after the Catalyst Bed ; MINIMAL Surface
4		8.16 ml. Free Space ; 105.9 cm ² of ALUMINA Surface. (7 mm. diam. spheres)
5		8.16 ml. Free Space ; 156 cm ² of GLASS Surface. (6.5 mm. diam. spheres)
6		8.16 ml. Free Space ; 437 cm ² of STONE Surface. (2.2 mm. diam. spheres)
7		8.16 ml. Free Space ; 475 cm ² of 316 Stainless Steel Surface. (specific area = 26.5 cm ² .gm. ⁻¹)

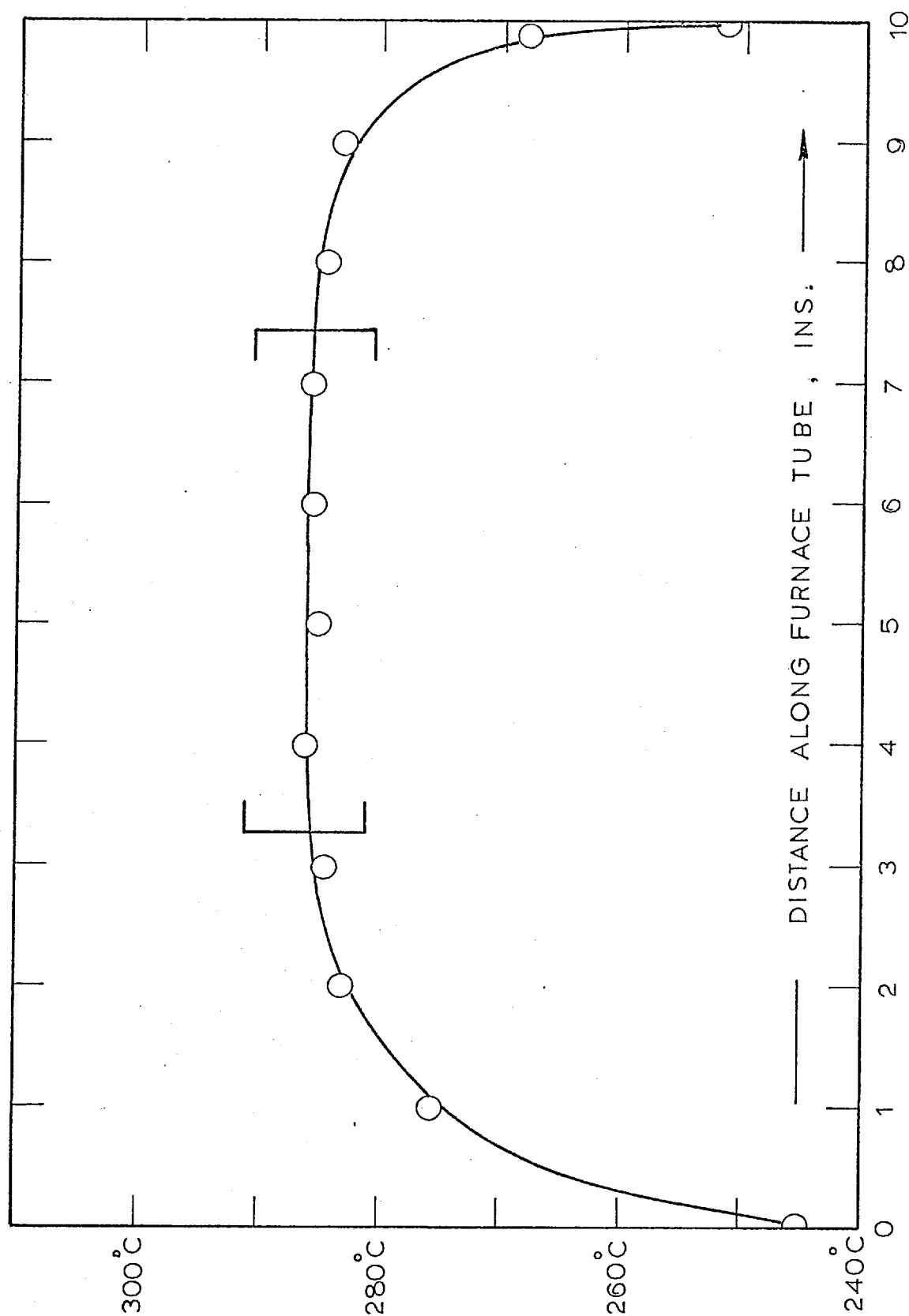


Figure 2.11 : Temperature Profile along the axis of the Reactor Furnace. (Total Length of Furnace Tube is 10 ins.)

Reactor Situation shown between brackets.

layers of asbestos cement with vermiculite surrounds avoided electrical short circuits and gave a flat temperature profile down the tube axis (see Figure 2.11). Both the reactor pot of the S.G.S.R. and the tubular reactors used for experimental work were situated in the central region of the tube. The inlet and outlet capillary arms of the glass reactors extended out of the furnace, and connections to heated lines were made with small pieces of silicone rubber tubing capable of withstanding 200°C.

3C Analysis of Reactants and products

In addition to the reactants, benzene, maleic anhydride, oxygen and nitrogen, possible products may involve any C_6 , C_4 , C_3 and C_2 oxygenated compounds. Furan groups and maleic acid isomers may also be present. Products of complete oxidation such as carbon dioxide, carbon monoxide, water and formaldehyde could also be produced.

(a) The flame ionisation detector

The flame ionisation detector (F.I.D.) was chosen for detection of the organic products due to its high sensitivity. As the organic was already diluted by oxygen and nitrogen, experiments at low conversions resulted in very low concentrations of products. The detection limit of a normal katharometer detector is 10^{-7} gm.mole of sample (83 and 84) but the F.I.D. is able to detect concentrations as low as 0.001 ppm. (83 and 84), although compounds such as oxygen, nitrogen and water are not detectable. The F.I.D. chromatograph shared with the katharometer a sampling system comprising an injection port and a

Servomex pneumatically operated (Type 234) gas sampling valve. The valve has ten ports and can be arranged to take two known sample volumes alternately from the product stream and send them via hydrogen carrier streams either to the F.I.D. chromatograph or to the Katharometer chromatograph (Figure 2.12).

Operation of the valve with the slide at position A meant that a known volume of product stream was swept by hydrogen carrier gas to the F.I.D. chromatograph column housed in a temperature controlled air-oven at 150°C. Analysis was completed using a Reoplex 400/ celite column (8ft:150°C), the column temperature being controlled to $\pm 0.5^{\circ}\text{C}$ by an A.E.I. R.T.3 proportional temperature controller. The compounds were eluted directly into the detector, where a small current proportional to the concentration was generated. This current was amplified and attenuated by a Pye Ionisation Amplifier and recorded by a Honeywell one millivolt recorder. The detector normally required 30 - 50 ml/min. of hydrogen and 500 ml/min. of air to support combustion and to remove the heat produced. As the F.I.D. is insensitive to temperature, flowrate and fluctuation it is an ideal research chromatograph with its high sensitivity.

For purposes of identification and calibration, an injection point was placed very near to the sample valve. The design of the injector port (DOERR , (95)) allowed the sample to be injected into a hot, fast moving stream of carrier gas, thereby producing sharp narrow injection peaks. The injector and all tubing in contact with a liquid sample were heated by glass cloth sheathed nichrome wire electrically heated to a temperature controlled by a variac (ca 125°C).

LEGEND FOR FIGURE 2.12

C ₁	Hydrogen Carrier Gas for Katharometer
C ₂	Hydrogen Carrier Gas for F.I.D.
S	Effluent Line from the Reactor
L ₁	Sample Loop for Katharometer Detector
L ₂	Sample Loop for F.I.D.
SV	SERVOMEX TYPE 234 Gas Sampling Valve
D	Diaphragm, attached to valve slide
LSD	Air Lines to valve switching device
HT	High Tension (170 v.) lead to F.I.D. Jet
Z	Chromatographic Column for the F.I.D.
	Indicates Heated Line

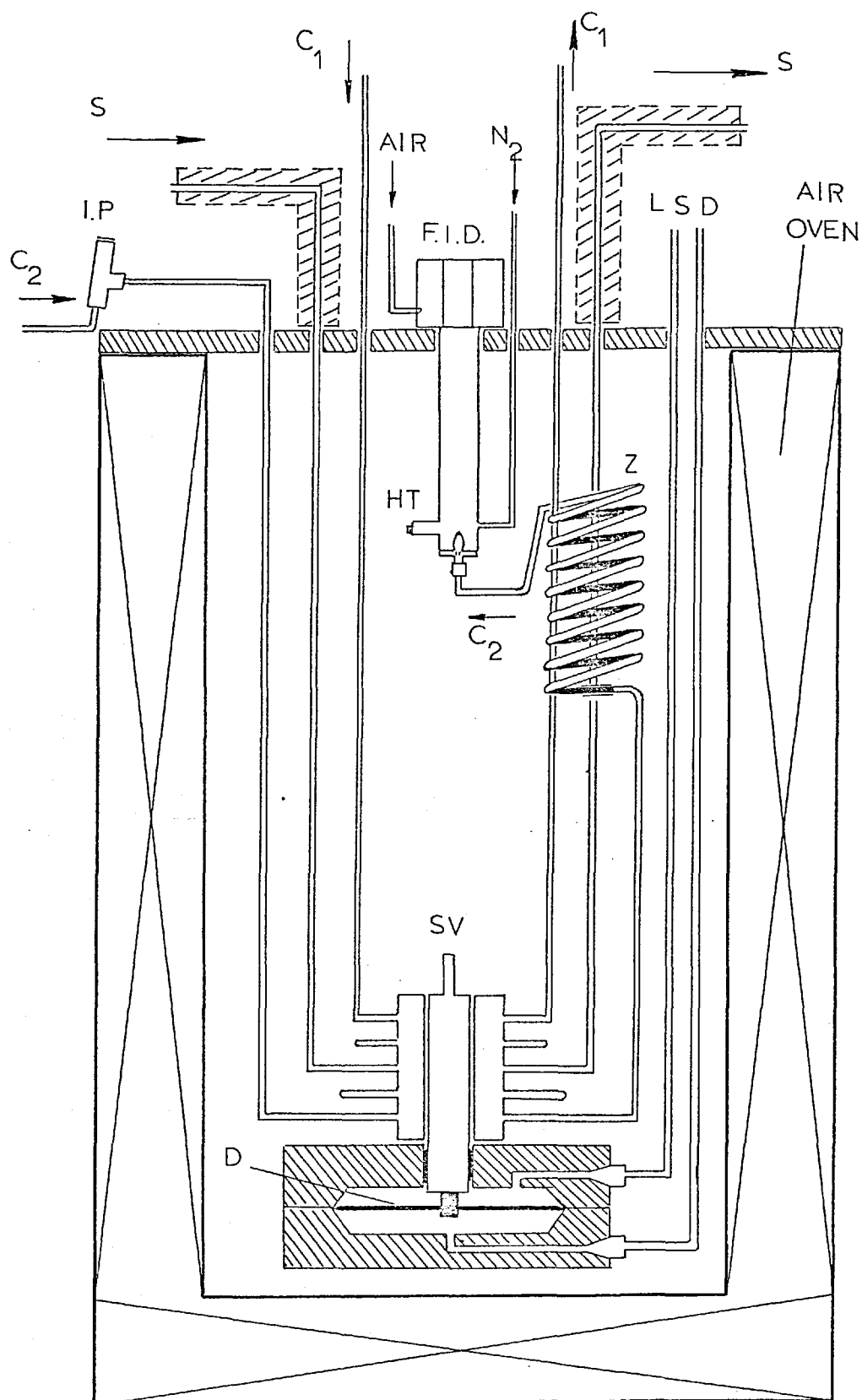


Figure 2.12 : Arrangement for Sampling of the Reactor Exit Stream , showing the F.I.D.

(contd./over)

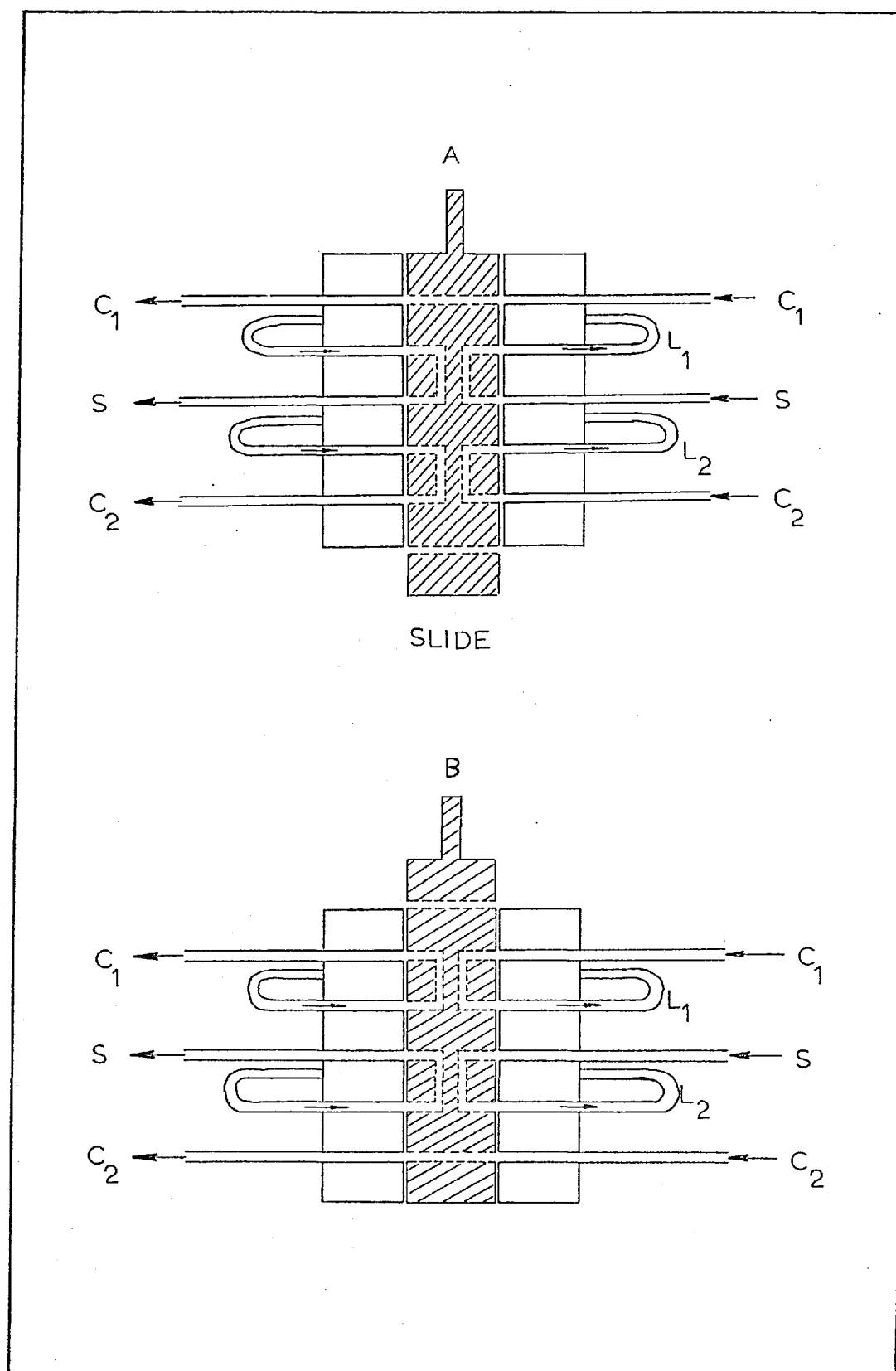


Figure 2.12 (contd.) : Slide Positions of the Sampling Valve

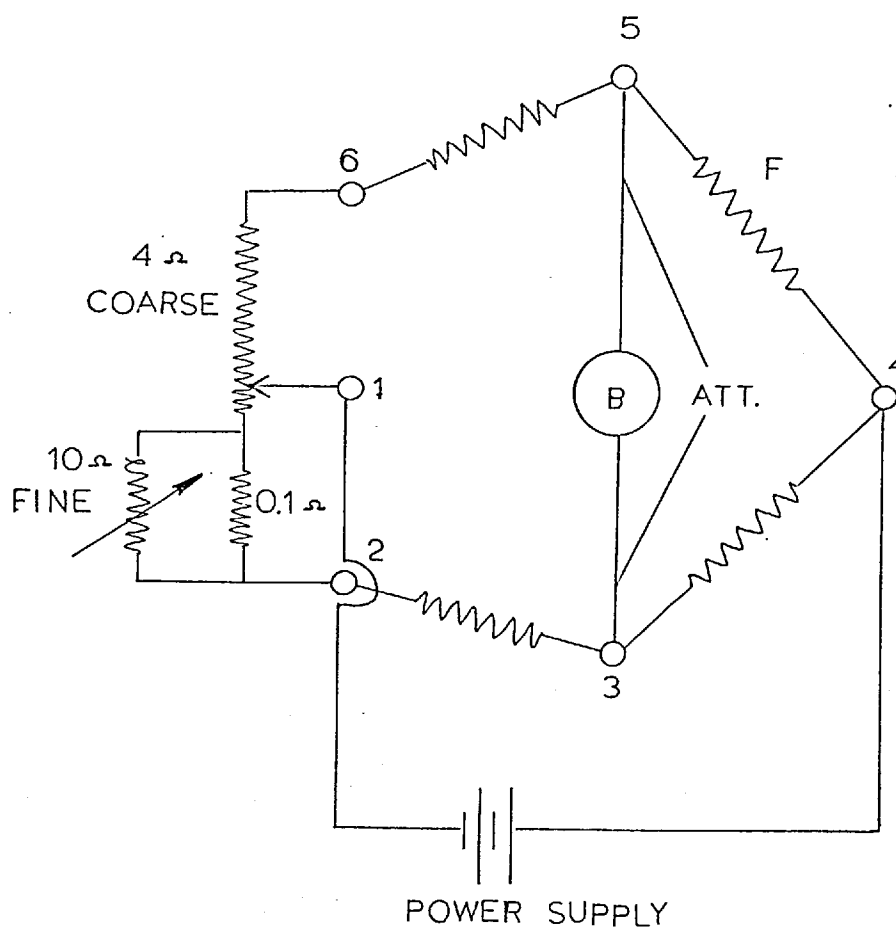
Regular samples of feed material, benzene and/or maleic anhydride, taken using the appropriate on-line gas sampling valve were also analysed in the same chromatograph, making use of a common hydrogen carrier gas. All lines were kept heated as before.

(b) The katharometer chromatograph

The detection of non-combustible compounds is not possible with a flame ionisation detector and these compounds are normally detected by use of a katharometer, designed around the necessary column separation. This required two columns placed in parallel and connected to a Servomex MK 158 katharometer used in conjunction with a MICROREG Type 300 Power Supply and the 234 gas sampling valve. Hydrogen carrier gas passed over the reference filaments and through the sample valve where a known volume of the product stream was picked up when the valve slide was in position B, (Figure 2.12). The carrier gas and sample returned to the columns where the flow was directed through either a molecular sieve 5A column (6ft:25°C) or a silica gel column (6ins:25°C) by a simple switching device. In the molecular sieve column, carbon monoxide and the permanent gases were separated and analysis was completed in the silica gel column for carbon dioxide.

The peaks were eluted from the column into the sampling side of the katharometer, where a voltage change was generated across the bridge. The detector output was attenuated by a system designed and fabricated in this department (Figure 2.13), subsequent to being recorded on a one millivolt Vitatron recorder. The katharometer filaments were normally operated

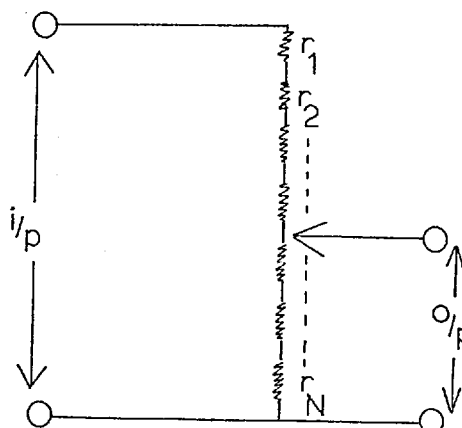
Figure 2.13 : Attenuation system for Signal from Katharometer Detector.



$r_1, r_2 \dots r_N$ have the following values,

(all in ohms.)

10,10,20,40,80,160,
320,640,1280,2560,
and 5120.



LEGEND :

F Katharometer Filament, approx. 20 ohm.

B Balance for Bridge Circuit

ATT i/p to Attenuation Circuit

1,2,3,4,5 and 6 are the relevant Bridge Terminals

1 is the Bridge Supply + ve.

4 is the Bridge Supply - ve.

at 300 milliamps. with a flowrate of 50 cc/min of hydrogen.

(c) Identification of products

Typical chromatograms for the F.I.D. column and the Katharometer columns are shown in Figure 2.14 .

The products were separated on the appropriate column and the retention times were compared with retention times of known compounds. Before an identification was accepted, the retention times had to match on any particular column under differing conditions (change in column temperature or carrier flowrate). A sample of the pure compound was then added to the product mixture and the appropriate peak was checked to increase in the product chromatograph.

A mass spectrogram of the product stream was also recorded to check that no major product was overlooked.

(d) Calibration

The gaseous products were calibrated by measuring the peak area and peak height obtained from injecting samples of the pure gas into the heated injection port, using Hamilton gas-tight syringes (0-0.1ml. and 0-1.0 ml. range). This calibration was checked using an appropriate flow method. Two or more streams of different gases, whose flowrates are known, are mixed and introduced to the sample valve at a known temperature and pressure. The calculated number of moles may then be checked against detector response.

For the calibration of liquid products, a 0-1.0 ml. standard syringe and a 0-1.0 microlitre S.G.E. High Pressure syringe were used to inject a measured volume of liquid into the heated injection port. Dilution of the pure liquid was

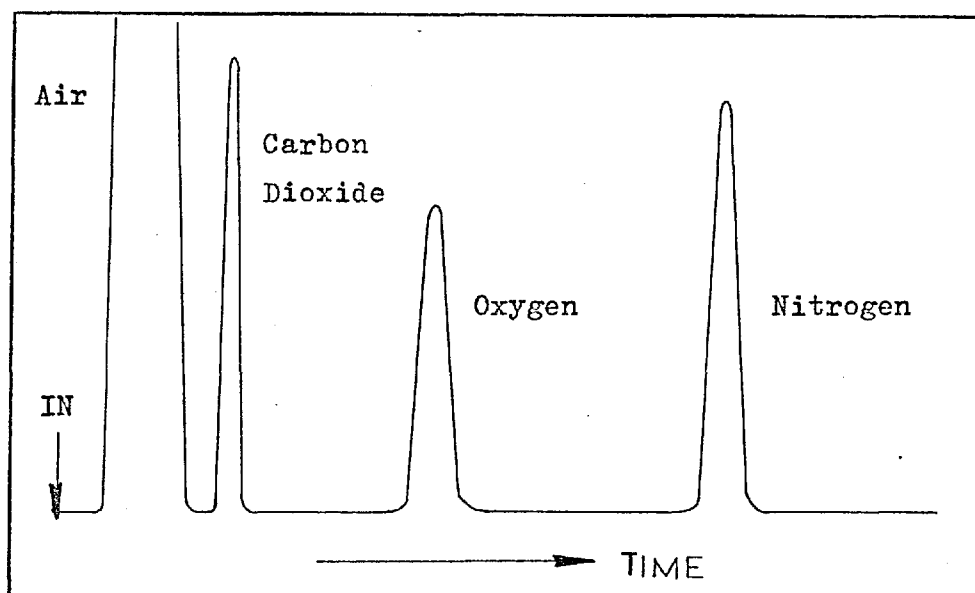
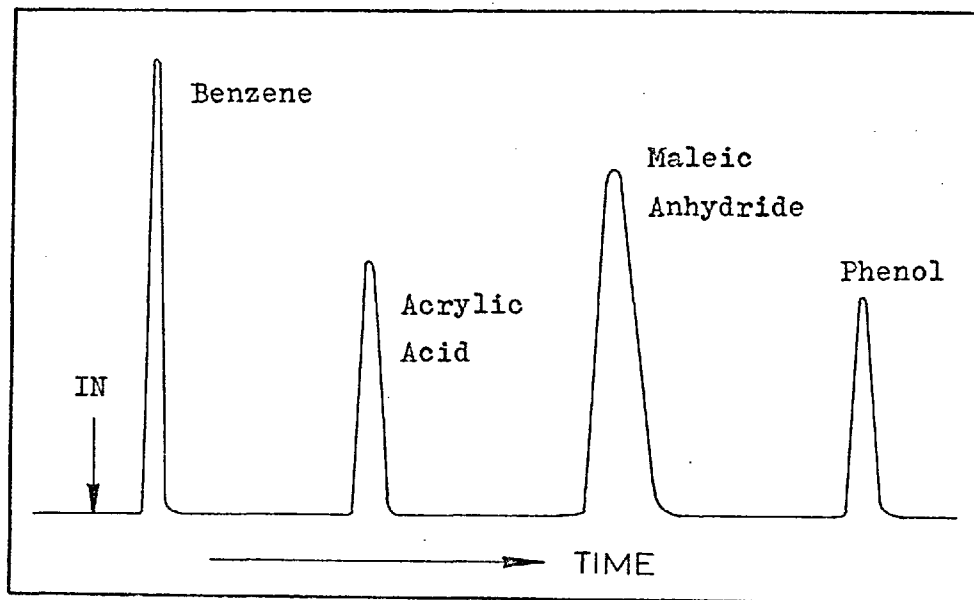


Figure 2.14 : Typical Chromatograms for F.I.D.
and Katharometer.

often necessary to increase the calibration range, and the liquid was then mixed with a solvent that would vapourise quickly and not interfere with the desired peak. Knowledge of the liquid density and molecular weight allowed plots of gm. moles versus detector response to be constructed.

In all cases the plots of peak height versus amount in gm. moles was found to be satisfactory as compared with plots of peak area versus amount. Calibration curves were checked at regular intervals, normally monthly, unless the system was altered in any way which could affect the calibration.

4 Procedure

The rotameters (Figure 2.1) were first calibrated with soap bubble meters at a constant up-stream pressure of 44 cm. of Hg. If benzene was to be used as feed material the water bath was allowed to reach the set value for operation. Similarly, when maleic anhydride was used as a reactant the adsorber furnace temperature was carefully preset using the variac.

All lines, including the sample valves, that could come into contact with condensable products were heated to approximately 125°C.

The required weight of sized catalyst, normally 3/16" cylindrical pellets, was placed in the appropriate section of one of the tubular reactors, (or cruciform/circular basket in the S.G.S.R.), and the catalyst was held in position by 5 mm. soda-glass spheres which also acted as a secondary premixing section. The reactor was then placed

carefully inside the furnace and the furnace top and bottom plates were screwed tightly down. Asbestos wool was used to keep the parts of the reactor just outside the furnace hot, thereby preheating the reactants and preventing condensation of the products. The furnace was switched on and time was allowed for the temperature to reach the desired value.

With the reactor-furnace system at reaction temperature, a stream of nitrogen, and then oxygen plus nitrogen was passed over the catalyst for at least an hour. If the required concentrations of oxygen and fuel were below the explosive limit, the oxygen and nitrogen flow rates were adjusted to the required value before the fuel was slowly introduced. If the reaction mixture was above the explosive limit, the flow of nitrogen and fuel were set before the oxygen was brought on stream. The flows to both chromatographs were set, and after a period of time the instruments were turned on. For experiments in the S.G.S.R. system the stirrer speed was set to the desired value (normally 3000 r.p.m.) by means of a tachometer used with a variac.

The temperature of the catalyst bed was measured periodically during the run by pre-calibrated Chromel-Alumel thermocouples connected to a Pye potentiometer.

After all systems were equilibrated, samples were taken for analysis as described above. Sampling was repeated until constant results were obtained. The amounts of products in any sample were obtained from calibration curves and a carbon balance was completed for each analysis.

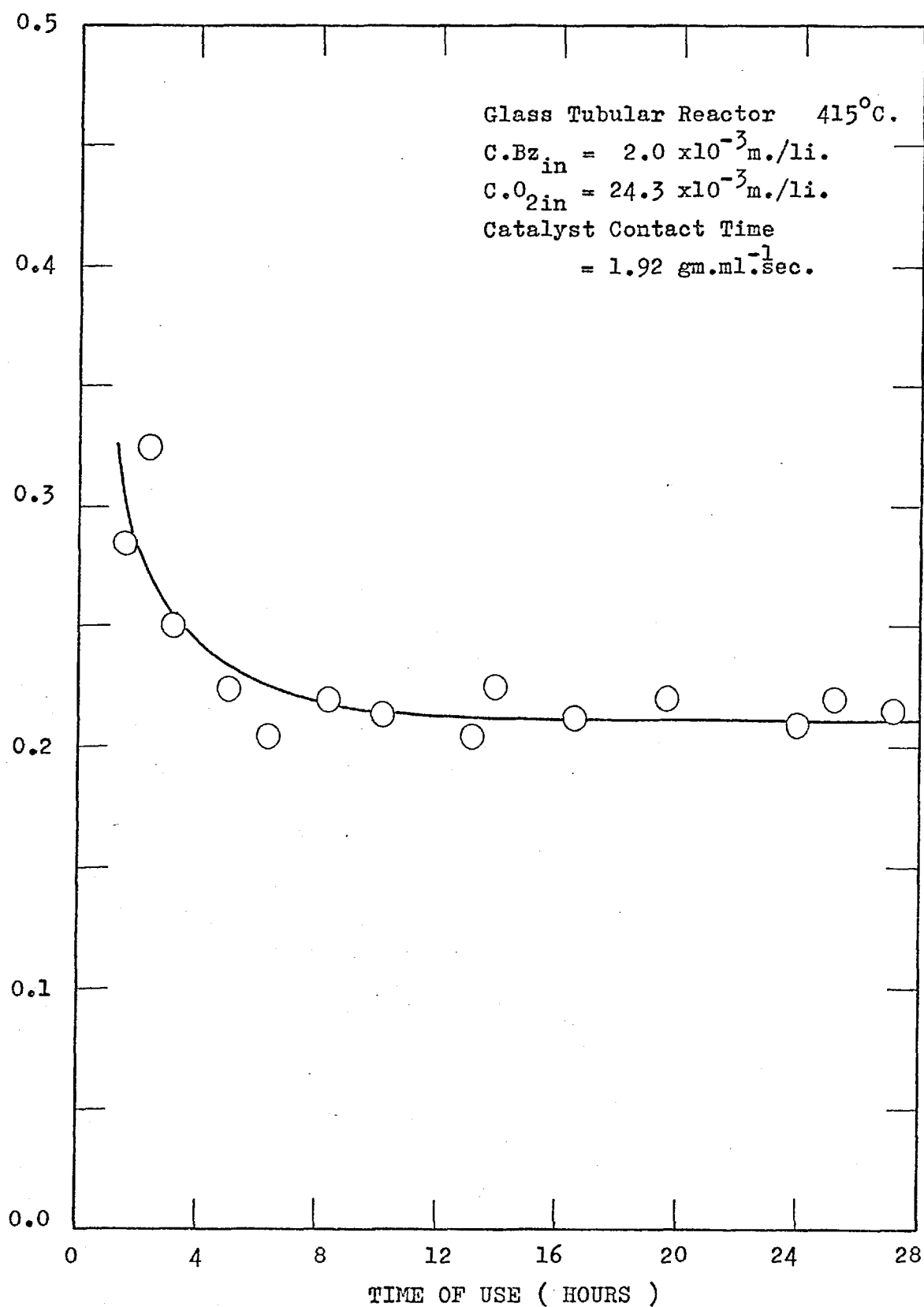


Figure 2.15 : Catalyst Activity as a function of Time of Use
 Conversion to MAA, variation with Time.

After the run was completed the flows of reactants were cut off in the reverse sequence to the start-up. This prevented an explosive reaction mixture from entering the reactor. The catalyst was left overnight under a stream of oxygen and nitrogen at the appropriate reaction temperature.

5 Catalyst Stability and Life

Studies were carried out to investigate the stability and life of the vanadium pentoxide - molybdenum oxide catalysts. The reactor system was set up to allow a known oxygen : benzene mixture to pass over the catalyst under carefully controlled conditions. Analysis of products was completed at intervals of up to ca 300 hours. After an initial short term deactivation (ca 5 hours) no change in activity of the catalyst could be observed throughout the investigation. The yield of maleic anhydride as a function of time, which was typical of all the oxidation products, is shown in Figure 2.15 for the first thirty hours of reaction.

RESULTS

1 Definitions

- 1A Catalyst Contact time
- 1B Reactor Residence time
- 1C Conversion
- 1D Selective Yield
- 1E Carbon Yield

2 Evidence of Homogeneous-Heterogeneous Interaction

- 2A Introduction
- 2B Effects of reactor free volume on product conversion
- 2C Influence of temperature on the effects of free volume

3 The Homogeneous Contribution to the Overall Reaction

- 3A Introduction
- 3B Reaction in the absence of catalyst
- 3C Reaction in the presence of catalyst
 - 3C1 - The oxidation of maleic anhydride with air
 - 3C2 - The oxidation of benzene with air
 - 3C2(i) - The effect of free volume after the catalyst bed
 - 3C2(ii) - The effect of surface:volume ratio after the catalyst bed
- 3D Reaction using a feed of benzene and maleic anhydride
- 3E Carbon Balances

4 Kinetics of the Oxidation of Maleic Anhydride

- 4A Introduction
- 4B Oxidation in the presence of catalyst
 - 4B1 - Effects of temperature on rates of reaction
 - 4B2 - Energy of Activation for maa oxidation
- 4C Oxidation in the absence of catalyst

5 Kinetics of the overall oxidation of Benzene to
Maleic Anhydride in the S.G.S.R. system

5A Introduction

5B Influence of temperature on product conversion and
reaction rate

5C Incorporation of maleic oxidation data in the
S.G.S.R results

5C1 - Distinction between total and net rates
of production of maa

5C2 - Distinction between total and net rates
of production of carbon dioxide

5D Evaluation of benzene oxidation rate

1 Definitions

1A Catalyst Contact time (C.T.) : The time for which the reactants were in contact with the catalyst was calculated using the following equation:

$$\text{Contact Time} = \frac{M T_1}{F T_2} \text{ gm.ml.}^{-1} \text{ sec.}$$

where T_1 = room temperature ($^{\circ}\text{K}$)
 T_2 = temperature of catalyst bed ($^{\circ}\text{K}$)
 F = Flowrate of gases at room temperature (ml/sec)
 M = mass of catalyst (gm.)

In order that all contact times should be strictly comparable, the same catalyst sizing was used throughout the kinetic studies ($3/16''$ cylinders).

1B Reactor Residence time (R.T.) : The time for which the reactants were in the reactor free space was calculated using

$$\text{Residence Time} = \frac{V T_1}{F T_2} \text{ sec.}$$

where T_1 , T_2 and F have the above values and V is the free space volume in ml. present in the bed.

1C Conversion is defined by : $\frac{\text{moles of product}}{\text{moles of initial feed}}$

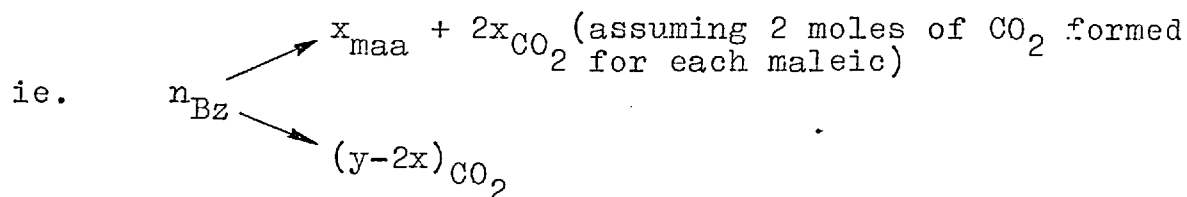
1D Yield (selectivity) is defined by : $\frac{\text{moles of product}}{\text{moles of feed consumed}}$

1E Carbon Yield is defined by : $\frac{\text{moles of product}}{\text{moles of feed consumed}} \times \text{Appropriate Carbon Ratio}$

The interrelationship between 1C , 1D and 1E may be shown by the following:

Consider 1 litre of total mixture, containing m moles of

benzene initially. After a time t , if n moles are converted to x moles of maleic anhydride and y moles of CO_2



We know that from carbon balances,

$$6n = 4x + 2x + (y-2x)$$

$$\therefore 6n = 4x + y$$

or ,

$$\boxed{\frac{n}{m} = \frac{2}{3} \frac{x}{m} + \frac{y}{6m}} \text{ used for 'Conversion'}$$

and ,

$$\boxed{1 = \frac{2}{3} \frac{x}{n} + \frac{y}{6n}} \text{ used for 'Carbon Yield'}$$

2 Evidence of Homogeneous-Heterogeneous Interaction

2A Introduction

As any gas phase reaction that could occur would be promoted to a larger extent in any reactor with an inherent large free volume than in a reactor with a small amount of free space, it was decided to investigate possible homogeneous reactions occurring during benzene oxidation by use of the S.G.S.R. Use of cruciform and circular baskets would enable a study of the effect of reactor free volume on the yields and rates of reaction. Conventionally, the cruciform basket is used to study the catalytic reaction at low contact times, and assuming no homogeneous reactions (Brisk et al 80).

Catalyst which had reached constant activity (Chapter 2, section 5) was used in all experiments described in this section.

2B Effects of reactor free volume on product conversion

The influence of free volume present in the reactor was effectively studied by repeating a series of standard runs, firstly using the circular basket and then the cruciform basket to hold the catalyst charge.

Benzene feed concentrations were varied from 1.5 to 20 mole % and the total throughput was varied for each fixed benzene input concentration, using total flows of 100, 150 and 250 ml.min⁻¹ (measured at room temperature). The circular basket held a catalyst charge of 15.11 gm., the cruciform basket holding almost exactly half of this (7.61 gm.).

A stirrer speed of 3000 r.p.m. was employed in both cases, the bed temperature was maintained at 376°C and the total pressure at ca 1 atmosphere.

Results using both baskets are given in Tables 3.1 and 3.3. Reactant and product conversion as a function of catalyst contact time are shown graphically in Figures 3.1, 3.2, 3.3. The amount of benzene converted and the conversion to maleic anhydride at the same contact time are seen to be markedly reduced when using the cruciform as opposed to the circular basket. Constant catalyst contact times means different gas space residence times for the two baskets and differences in maleic anhydride conversion could be accounted for in terms of overoxidation. However it is not possible to explain the variation in the conversion of benzene in such a manner. Unless homogeneous oxidation of benzene is important, it would appear that some gas phase reaction involving benzene

C.Bz _{in}	C.O _{2in}	Contact Time	C.Bz _{out}	C.O _{2out}	C.Maa	C.CO ₂	Carbon Balance
m./li. (x10 ⁻³)	m./li. (x10 ⁻³)	gm.ml. ⁻¹ sec.	m./li. (x10 ⁻³)	m./li. (x10 ⁻³)	m./li. (x10 ⁻³)	m./li. (x10 ⁻³)	%

CRUCIFORM BASKET : 7.606 gm. of Catalyst 1 ; 376°C.

.606	26.1	.835	.536	25.4	.023	.315	99.5
1.76	24.5	.835	1.66	23.1	.023	.511	100.
3.38	20.8	.85	3.25	19.8	.024	.677	100.5
6.76	11.05	.87	6.69	10.00	Trace	.406	99.
.653	26.1	1.39	.538	25.0	.038	.55	101.
1.575	24.5	1.39	1.41	22.6	.0355	.819	100.
3.11	20.9	1.43	2.91	19.3	.038	1.08	101.
6.17	10.58	1.475	6.06	9.6	Trace	.542	98.5
.609	26.1	2.09	.451	25.0	.056	.752	100.5
1.575	24.5	2.09	1.34	22.4	.058	1.20	100.5
3.02	21.0	2.15	2.70	19.8	.060	1.625	99.
6.49	11.5	2.19	6.28	10.05	.008	.974	99.

CIRCULAR BASKET : 15.11 gm. of Catalyst 1 ; 376°C.

.584	27.0	1.67	.444	26.15	.059	.609	100.5
1.87	25.3	1.66	1.57	23.8	.106	1.36	100.
3.73	22.8	1.68	3.28	19.8	.136	2.55	101.5
7.98	11.95	1.68	7.60	8.7	.09	1.715	99.5
.628	27.0	2.77	.405	25.8	.095	1.055	102.5
1.60	25.3	2.77	1.21	23.6	.146	1.80	100.
3.29	22.8	2.83	2.63	20.7	.238	2.75	99.
6.28	11.2	2.93	5.76	8.66	.125	2.44	99.5
.629	27.2	4.16	.30	26.2	.124	1.292	95.5
1.82	26.0	4.16	1.20	24.0	.254	2.69	100.
3.12	23.2	4.27	2.35	20.3	.295	3.57	100.5
6.48	13.1	4.38	5.57	8.58	.19	3.565	97.

TABLE 3.1 : The Oxidation of Benzene at 376°C.

Effects of Free Volume on Results from the S.G.S.R.

CRUCIFORM : 376°C.

CIRCULAR : 376°C.

CONV. OF BZ %	BENZENE OXD. RATE -1 -1 m.gm.sec.	CONV. TO MAA %	CONV. TO CO ₂ %	CONV. OF BZ %	BENZENE OXD. RATE -1 -1 m.gm.sec.	CONV. TO MAA %	CONV. TO CO ₂ %
11.5	.839 x10 ⁻⁷	3.80	51.9	24.0	.842 x10 ⁻⁷	10.00	104.5
5.68	1.200	1.31	29.0	16.05	1.810	5.77	72.7
3.85	1.530	.71	20.0	12.05	2.680	3.65	68.4
1.035	.805	—	6.0	4.8	2.270	1.13	21.5
17.6	.827	5.82	84.2	35.5	.806	15.10	168.0
10.5	1.190	2.25	52.0	24.4	1.410	9.13	112.5
6.43	1.400	1.22	34.7	20.0	2.330	7.25	83.6
1.78	.746	—	8.8	8.3	1.785	1.99	38.8
25.9	.756	9.20	123.5	52.0	.790	19.75	205.0
14.9	1.125	3.65	76.2	34.0	1.490	13.95	148.0
10.6	1.480	1.99	53.9	24.7	1.800	9.46	114.5
3.23	.959	.12	15.0	14.0	2.070	2.93	55.0

CRUCIFORM : 453°C.

CIRCULAR : 453°C.

CONV. OF BZ %	BENZENE OXD. RATE -1 -1 m.gm.sec.	CONV. TO MAA %	CONV. TO CO ₂ %	CONV. OF BZ %	BENZENE OXD. RATE -1 -1 m.gm.sec.	CONV. TO MAA %	CONV. TO CO ₂ %
26.6	2.16 x10 ⁻⁷	5.95	167.0	47.1	1.94 x10 ⁻⁷	17.5	213.0
18.4	4.66	4.24	93.9	38.2	4.87	14.0	173.0
16.1	8.27	2.73	81.0	33.0	7.83	13.5	145.5
9.5	9.35	2.03	72.7	20.4	9.49	7.5	86.0
41.8	2.12	9.05	215.0	63.0	1.67	22.1	299.0
32.4	3.97	5.60	174.0	50.7	3.43	19.75	244.0
27.7	6.92	4.10	145.0	44.6	5.97	16.3	195.0
12.75	6.80	3.05	96.0	26.5	7.38	9.2	121.5
57.3	1.86	11.00	300.0	73.5	1.25	25.2	360.0
44.1	3.46	8.42	237.0	62.0	2.82	19.0	300.0
34.7	5.38	6.15	196.0	53.9	4.45	17.8	252.0
20.9	6.08	3.77	109.5	33.9	5.86	9.6	165.0

TABLE 3.3

S.G.S.R. ; Temperature : 376°C.

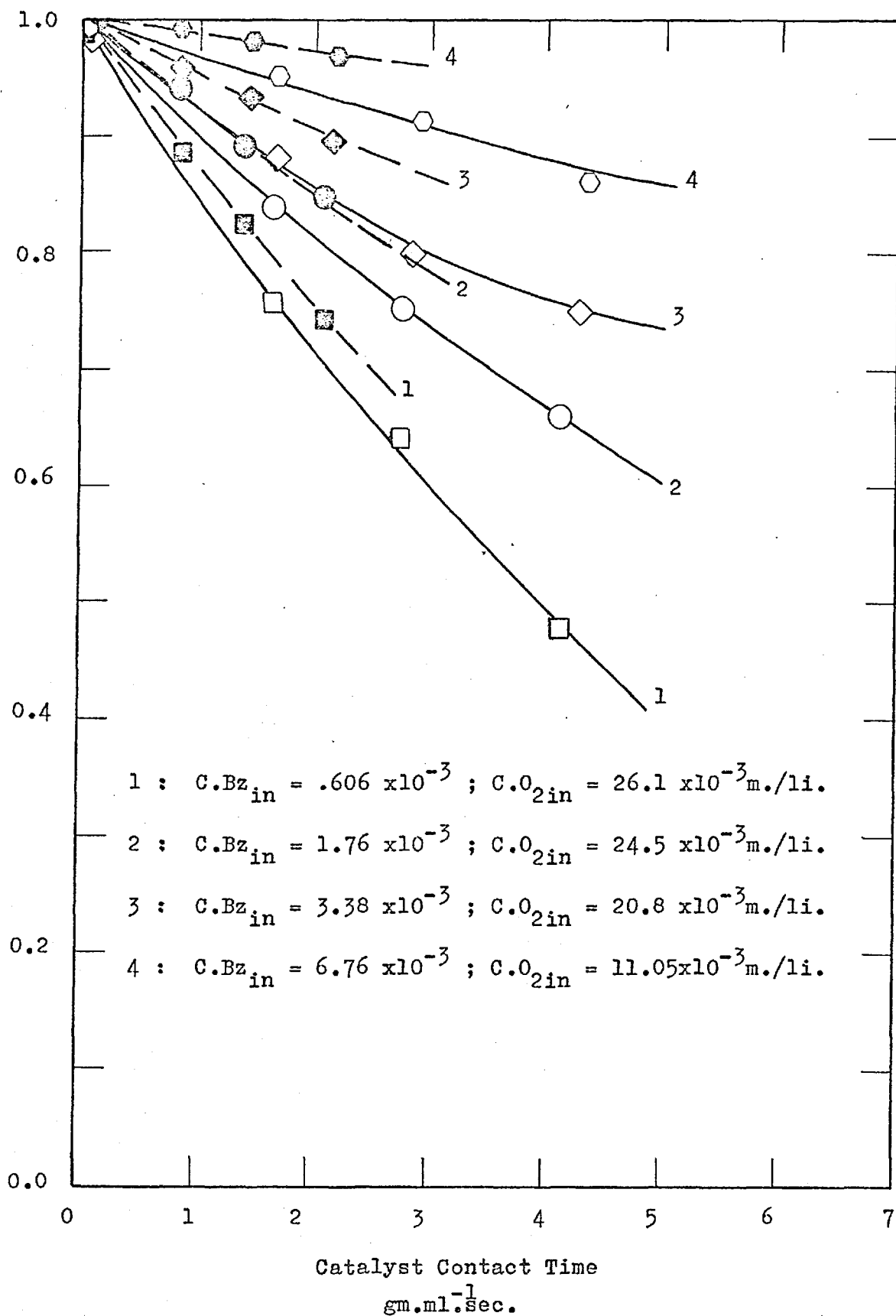


FIGURE 3.1 : Benzene Conversion vs. Catalyst Contact Time

○, □, △, ◇ : Results using CIRCULAR Basket
 ●, ■, ▲, ◆ : Results using CRUCIFORM Basket

S.G.S.R. ; Temperature : 376°C.

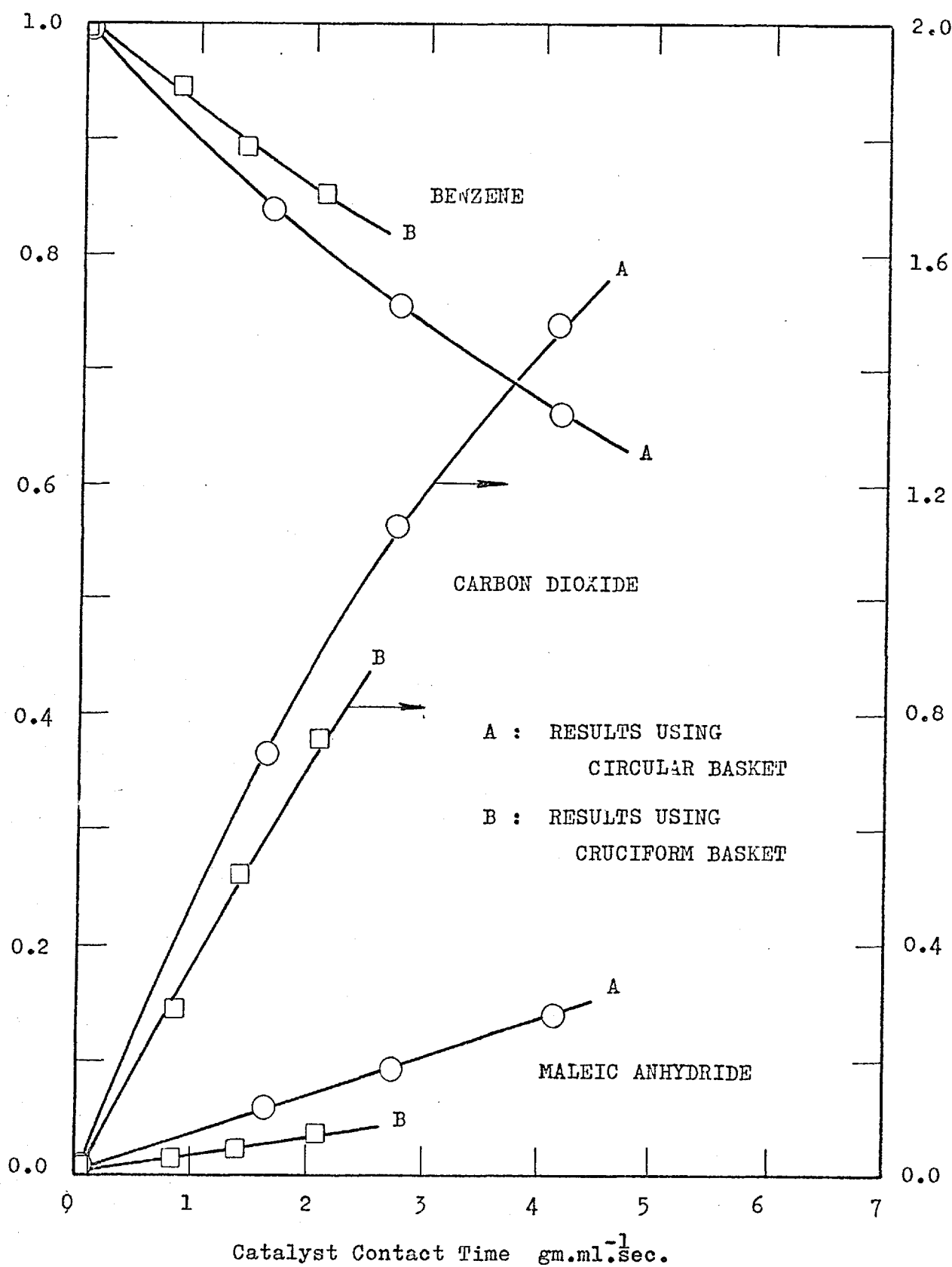


FIGURE 3.2 : Product Conversion vs. Catalyst Contact Time

Feed Conditions : $C_{Bz_{in}} = 1.76 \times 10^{-3} \text{ m./li.}$ $C_{O_{2in}} = 24.5 \times 10^{-3} \text{ m./li.}$

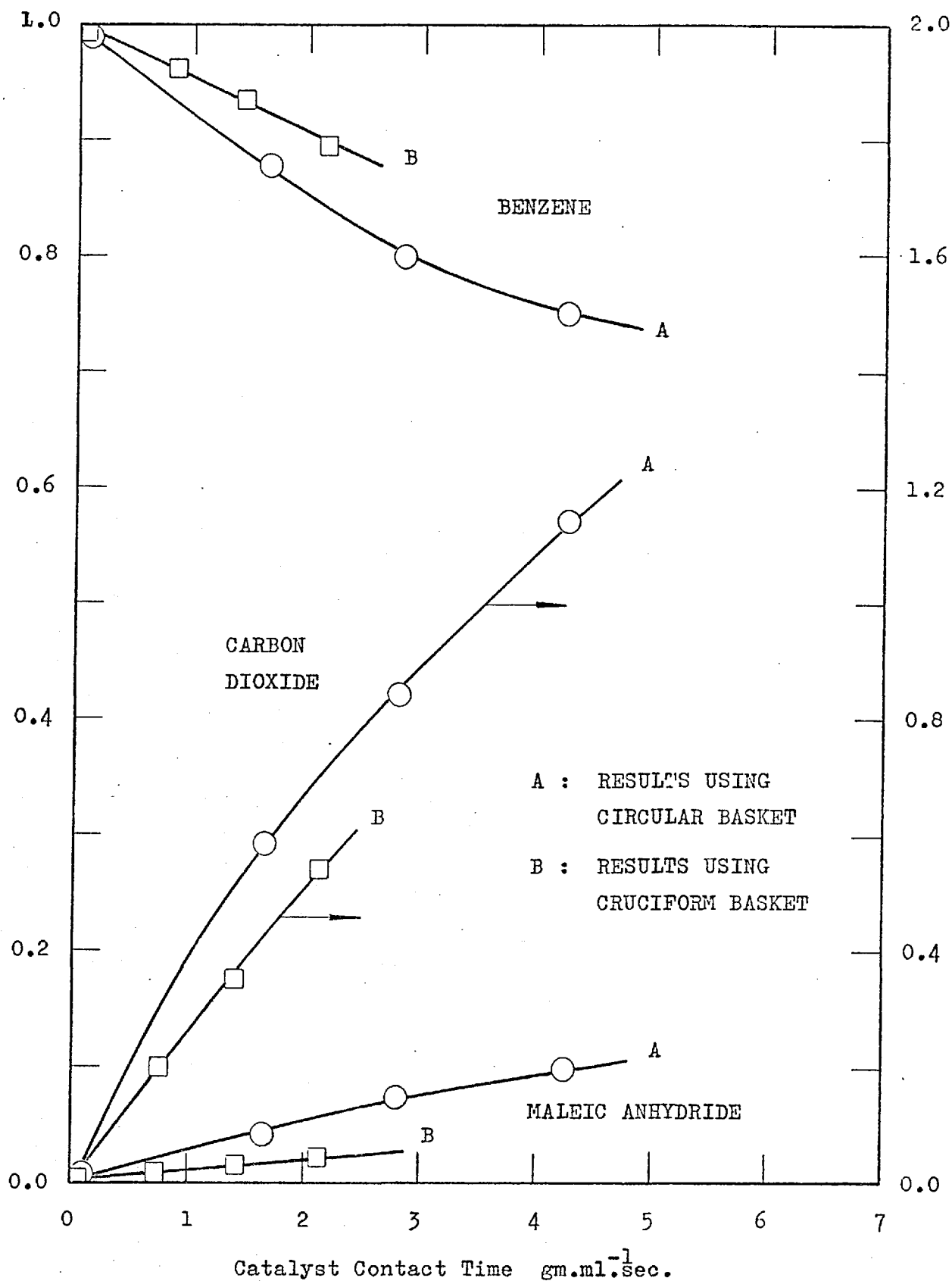


FIGURE 3.3 : Product Conversion vs. Catalyst Contact Time

Feed Conditions : $C_{Bz_{in}} = 3.38 \times 10^{-3} \text{ m./li.}$
 $C_{O_{2in}} = 20.8 \times 10^{-3} \text{ m./li.}$

is occurring which is linked to the catalytic process.

2C Influence of temperature on the effects of free volume

The apparent differences seen in the product-time curves for circular and cruciform baskets at 376°C were studied under identical conditions at 453°C. At this temperature any differences due to gas-phase reactions should show an increasingly marked effect, as homogeneous rates of reaction are usually more temperature sensitive than catalytic rates (85).

Results are given in Tables 3.2 , 3.3 , and conversion-time curves shown in Figures 3.4,3.5,3.6 . Similar effects to those at 376°C were observed; benzene conversion in the cruciform basket being smaller than in the circular at constant catalyst contact time - although differences were apparently smaller than at 376°C. The drop in conversion to maleic anhydride is again very marked.

3 The Homogeneous Contribution to the Overall Reaction

3A Introduction

In view of the observation that homogeneous effects were involved in the reaction, experiments were completed to quantify the effects. As discussed in the Introduction, homogeneous effects can involve three general reactions

- 1 Consecutive 'over-oxidation' reactions.
- 2 A homogeneous reaction which is concurrent but independent of the catalytic reaction.
- 3 A homogeneous reaction which is concurrent to and linked with the catalytic reaction.

C.Bz _{in}	C.O _{2in}	Contact Time	C.Bz _{out}	C.O _{2out}	C.Maa	C.CO ₂	Carbon Balance
m./li. (x10 ⁻³)	m./li. (x10 ⁻³)	gm.ml. ⁻¹ sec.	m./li. (x10 ⁻³)	m./li. (x10 ⁻³)	m./li. (x10 ⁻³)	m./li. (x10 ⁻³)	%

CRUCIFORM BASKET : 7.606 gm. of Catalyst 1 ; 453°C.

.606	26.1	.745	.445	25.2	.036	1.014	105.
1.875	24.8	.74	1.53	23.2	.08	1.76	100.5
3.85	20.6	.75	3.23	18.8	.105	3.12	99.
7.45	13.95	.76	6.74	8.35	.151	5.42	104.
.629	27.7	1.24	.366	26.2	.057	1.35	100.
1.52	24.8	1.24	1.03	23.9	.085	2.65	101.5
3.17	21.9	1.27	2.29	18.8	.13	4.61	99.
6.20	13.95	1.31	5.31	8.66	.189	5.95	104.
.602	26.7	1.86	.257	25.4	.066	1.806	100.
1.46	24.95	1.86	.817	23.4	.123	3.46	101.
2.97	21.9	1.92	1.94	18.0	.1825	5.65	101.
5.81	14.05	1.99	4.60	8.75	.219	6.37	100.

CIRCULAR BASKET : 15.11 gm. of Catalyst 1 ; 453°C.

.606	27.6	1.475	.32	25.9	.106	1.29	99.
1.875	26.0	1.465	1.16	23.9	.26	3.25	100.
3.56	23.2	1.495	2.39	18.8	.48	5.175	100.
7.06	14.4	1.525	5.62	8.45	.522	6.07	99.
.653	27.5	2.47	.242	25.2	.144	1.95	102;
1.662	25.6	2.47	.82	23.0	.329	4.06	103.
3.44	23.4	2.50	1.95	17.3	.56	6.71	100.
7.07	14.75	2.54	5.20	8.45	.648	8.61	99.
.63	28.0	3.69	.168	26.5	.159	2.27	103.5
1.67	26.05	3.69	.634	21.3	.317	5.02	101.
3.12	23.1	3.78	1.44	16.1	.555	7.86	100.
6.68	14.4	3.86	4.42	8.40	.642	11.00	101.

TABLE 3.2 : Oxidation of Benzene at 453°C.

Effects of Free Volume on Results from S.G.S.R.

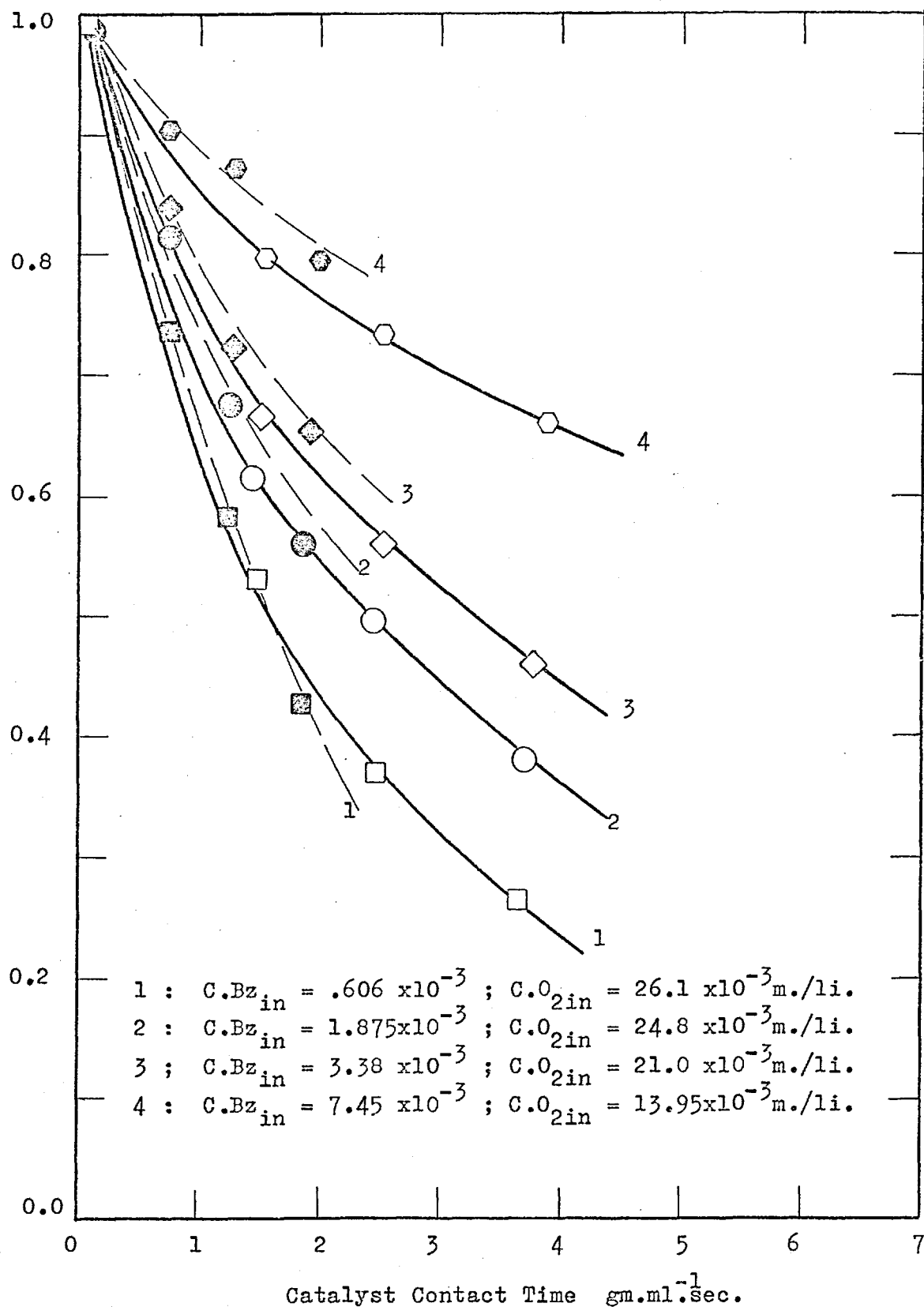


FIGURE 3.4 : Benzene Conversion vs. Catalyst Contact Time

□, ○, ◇, ☆ : Results using CIRCULAR BASKET
 ■, ●, ◆, ⊗ : Results using CRUCIFORM BASKET

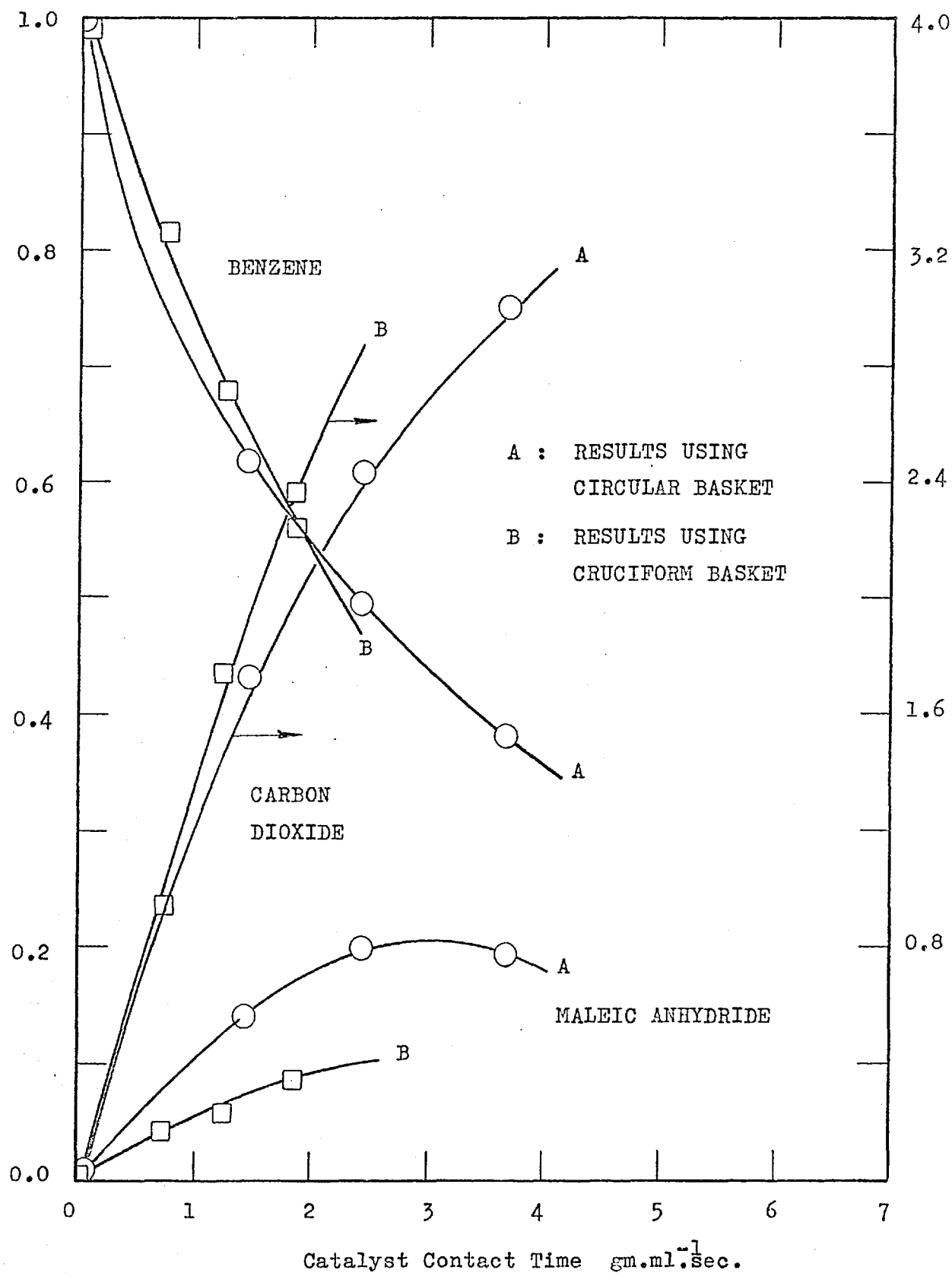
S.G.S.R. ; Temperature : 455°C .

FIGURE 3.5 : Product Conversion vs. Catalyst Contact Time
 Feed Conditions : $C_{Bz_{in}} = 1.875 \times 10^{-3} \text{ m./li.}$
 $C_{O_{2in}} = 24.8 \times 10^{-3} \text{ m./li.}$

S.G.S.R. ; Temperature : 453°C.

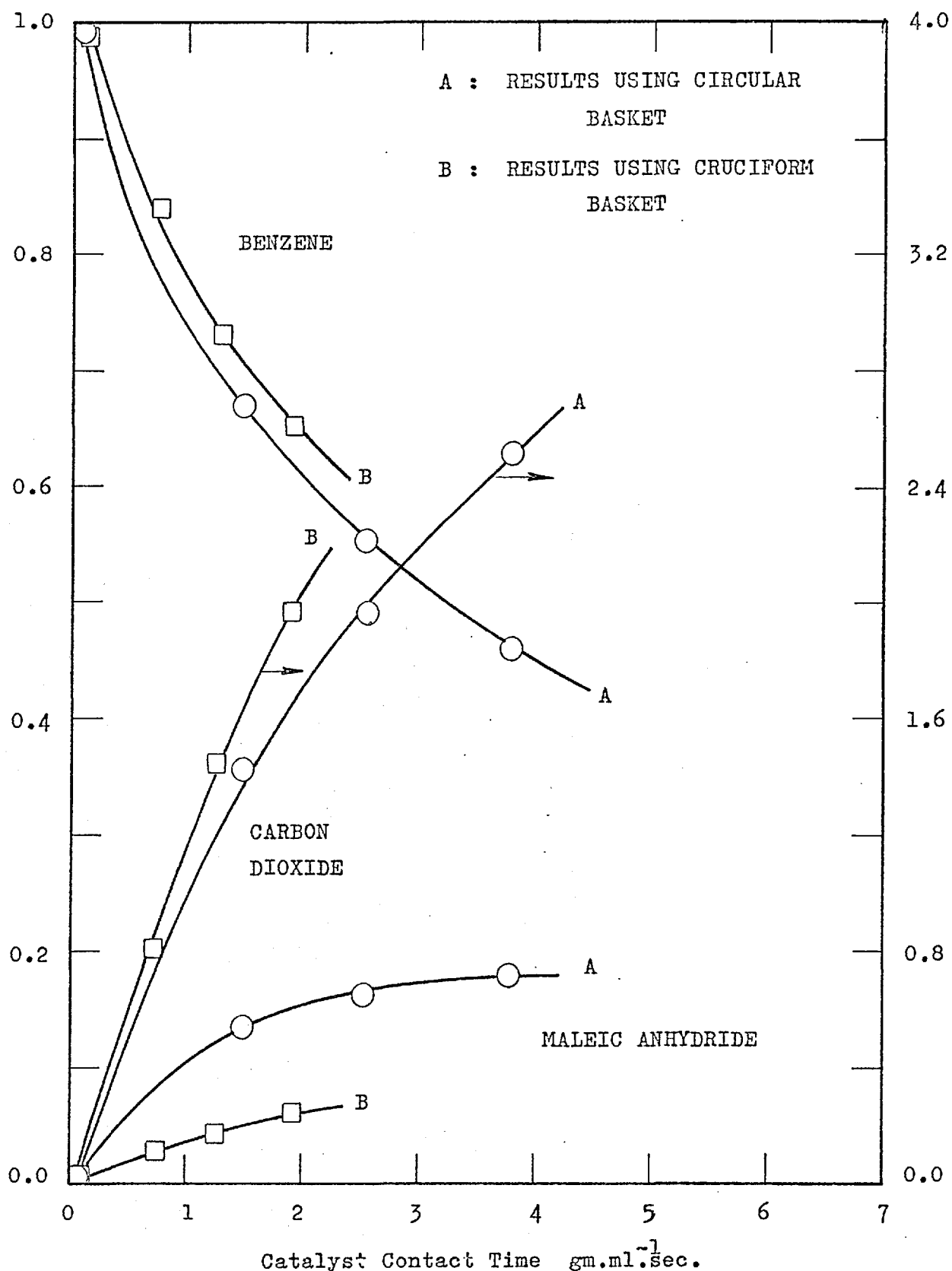


FIGURE 3.6 : Product Conversion vs. Catalyst Contact Time

Feed Conditions : $C_{Bz_{in}} = 3.38 \times 10^{-3} \text{ m./li.}$
 $C_{O_{2in}} = 21.0 \times 10^{-3} \text{ m./li.}$

The primary requirement for the identification and quantification of interaction is the distinction of over-oxidation and concurrent, independent effects. This cannot be completed in the S.G.S.R. system alone, as the catalyst surface is still able to influence any homogeneous process.

In order to ascertain the importance of all of these reactions, glass tubular reactors of various design were used. Three of these had differing unfilled free volumes after the catalyst bed (Figure 2.10), and several others had this same free space filled with materials to increase the amount of surface exposed to the reacting gases. For the latter reactors the voidage gas space in the filled section after the catalyst bed was kept at 8.16 cc. which was the same as one of the unfilled reactors. This allowed comparison of results where the contact time over the active catalyst and the residence time in the reactor were the same, but the amount of surface exposed to the reacting gases could be varied. Homogeneous and concurrent independent reactions were examined in reactors of the same general type, facilitating studies at constant gas residence time.

Where necessary the same catalyst was used in these reactors as was employed in the S.G.S.R. work (the same 15.11 gm. charge being used). Regular repeat experiments were completed to show that the activity of the catalyst had not changed (see Chapter 2, section 5). The temperature of operation was 415°C and identical input conditions and O₂/fuel ratios were employed for all experiments.

Preliminary results showed that maa and carbon dioxide were by far the major products of the oxidation of benzene

over the catalyst, only very minor quantities of other organic molecules being present under special conditions.

3B Reaction in the absence of catalyst

In agreement with the findings reported in the literature (6, 27, 36 and 43) no significant attack on benzene in the gas phase was observed at the fuel:oxygen ratios and temperatures used in this study in a glass reactor, and "'homogeneous"' oxidation was minimal in the stainless steel reactor - even at residence times of approx. 2.6 secs. benzene conversion was never greater than 1.4%. Similar experiments were carried out, at the same temperature of 415°C, for the oxidation of maleic anhydride (maa) in a glass reactor and no carbon dioxide could be detected. Extensive oxidation was observed, however, when the maa experiments were repeated in the stainless steel reactor. Even at relatively low residence times, (the order of 0.4 sec.), conversion of maleic anhydride approached 95%, producing mainly carbon dioxide and formaldehyde.

3C Reaction in the presence of catalyst

3C1 The oxidation of maleic anhydride with air:

The oxidation of maa over the catalyst, in the presence and absence of free space after the bed, was studied under a wide range of conditions. In a glass reactor, oxidation was negligible in all cases, amounts of carbon dioxide produced never exceeding 8% for catalyst contact times of 5 gm.cc⁻¹sec. Similar results were obtained using catalysts 1 and 2. Repetition of the experiments in the stainless steel reactor led to very high conversions of maa to carbon dioxide and water, even at contact times of less than 1 gm.cc⁻¹sec.

3C2 The oxidation of benzene with air:

(i) The effect of free volume after the catalyst bed:

The effect of free volume on the kinetics of the reaction was examined using exactly the same charge of catalyst in reactors containing the minimal free volume (designated "0ml"), and with 8.16 or 16.32 ml. free volume after the catalyst. The reactor with minimal free volume was used both first and last and no difference in results was observed. Results are presented in Tables 3.4, 3.5, 3.6, and some typical ones are shown graphically in Figures 3.7, 3.8, 3.9. It should be remembered that the reactor containing minimal free volume was not fitted with a sintered glass plate. As a result, experiments with this reactor are not strictly comparable to those using the other reaction vessels.

At relatively low concentrations of benzene, increasing the free volume from 8.16 ml. to 16.32 ml. results in an increased consumption of benzene (up to 9%) mainly to produce carbon dioxide (Figure 3.8). At higher concentrations of inlet benzene, the same effects are observed, although the concentration of maa among the products drops (Table 3.7). At relatively high concentrations of benzene (18.9 mole %) and low oxygen concentrations (18.9 mole %), the amount of maa produced per molecule of benzene oxidised passed through a maximum at ca 12% as the benzene conversion increased (Figure 3.10). Selectivity would appear to be independent of oxygen:fuel ratio; at low benzene:oxygen ratios (4.9 mole % : 60 mole %) the selectivity was effectively constant at 22% over all benzene conversions.

As stated above, these results are not affected by the catalytic oxidation of maa, nor by homogeneous over-oxidation

VOLUME AFTER THE CATALYST BED (NO SINTERED PLATE) = 0 ml.

15.11 gm. of Catalyst 1 ; Temperature : 415°C.

C.Bz _{out}	CONV.	C,Maa	CONV.	C.CO ₂	CONV.	Contact Time	Carbon
m./li.	of Bz		to Maa		to CO ₂		Balance
(x10 ⁻³)	%	m./li.	%	m./li.	%	gm.ml. ⁻¹ sec.	%
		(x10 ⁻³)		(x10 ⁻³)			

Concn. Bz_{in} = 2.0 x10⁻³ m./li. ; Concn. O_{2in} = 24.3 x10⁻³ m./li.
(4.95 mole %) (60. mole %)

.24	88.0	.61	30.5	8.26	413.	5.13	101.
.27	86.5	.54	27.0	8.10	405.	3.87	98.
.332	83.0	.457	22.8	7.68	384.	2.57	96.5
.442	77.5	.425	21.25	7.05	352.5	1.92	95.5
.63	68.5	.413	20.6	6.10	305.	1.54	100.
.724	63.0	.371	18.5	5.80	290.	1.28	97.

Concn. Bz_{in} = 4.08 x10⁻³ m./li. ; Concn. O_{2in} = 20.4 x10⁻³ m./li.
(10. mole %) (50. mole %)

.612	82.5	.925	22.7	16.40	401.	5.19	97.5
.97	76.3	.89	21.8	15.05	370.	3.89	100.
1.235	70.0	.89	21.8	13.35	327.	2.59	99.
1.63	60.0	.82	20.1	11.35	279.	1.95	100.
2.01	50.7	.795	19.4	9.80	241.	1.56	102.
2.32	43.1	.74	18.05	8.05	197.	1.30	103.

Concn. Bz_{in} = 8.0 x10⁻³ m./li. ; Concn. O_{2in} = 7.7 x10⁻³ m./li.
(19.5 mole %) (18.9 mole %)

5.36	32.9	1.695	21.2	8.25	103.	5.19	98.5
5.86	26.7	1.71	21.4	6.35	79.3	3.89	100.5
6.37	20.4	1.34	16.75	4.62	57.8	2.59	100.
6.82	14.7	1.13	14.1	2.83	35.4	1.95	100.5
7.10	11.3	.915	11.45	2.43	30.5	1.56	101.5
7.20	10.0	.733	9.17	2.13	26.6	1.30	100.5

TABLE 3.4 : Studies in Glass Tubular Reactors
Effect of Free Volume after the
Catalyst Bed.

VOLUME AFTER THE CATALYST BED = 8.16 ml.

15.11 gm. of Catalyst 1 ; Temperature : 415°C.

C.Bz _{out}	CONV.	C.Maa	CONV.	C.CO ₂	CONV.	Contact Time	Carbon
m./li.	of Bz	m./li.	to Maa	m./li.	to CO ₂	gm.ml. ⁻¹ sec.	Balance
(x10 ⁻³)	%	(x10 ⁻³)	%	(x10 ⁻³)	%		%

Concn. Bz_{in} = 2.0 x10⁻³ m./li. ; Concn. O_{2in} = 24.3 x10⁻³ m./li.
(4.95 mole %) (60.0 mole %)

.245	87.8	.589	29.5	8.10	405.	5.13	99.
.315	84.2	.528	26.4	7.86	393.	3.87	99.
.571	71.5	.453	22.7	6.46	323.	2.57	97.
.764	61.8	.421	21.0	5.75	287.5	1.92	100.
.905	54.75	.393	19.7	5.00	250.	1.54	100.
1.020	49.0	.360	18.0	4.30	215.	1.28	98.

Concn. Bz_{in} = 4.08 x10⁻³ m./li. ; Concn. O_{2in} = 20.4 x10⁻³ m./li.
(10. mole %) (50. mole %)

.605	85.5	.884	21.7	16.05	393.	5.19	95.5
.82	80.0	.857	21.0	15.0	368.	3.89	96.
1.48	63.7	.857	21.0	12.16	298.	2.59	100.
2.12	52.0	.813	19.9	9.4	230.	1.95	103.
2.35	42.3	.78	19.1	7.25	178.	1.56	100.
2.63	35.5	.725	17.8	5.7	140.	1.30	99.

Concn. Bz_{in} = 7.7 x10⁻³ m./li. ; Concn. O_{2in} = 7.7 x10⁻³ m./li.
(18.9 mole %) (18.9 mole %)

5.01	35.0	1.625	20.9	8.57	111.	5.25	98.
5.48	28.8	1.43	18.4	6.83	89.	3.93	98.5
5.99	22.2	1.29	16.6	4.7	61.	2.62	100.
6.8	11.75	.931	12.0	2.33	30.3	1.97	101.
6.93	10.1	.701	9.0	2.10	27.3	1.57	100.
7.0	9.1	.615	7.93	1.97	25.5	1.31	100.5

TABLE 3.5

VOLUME AFTER THE CATALYST BED = 16.32 ml.

15.11 gm. of Catalyst 1 ; Temperature : 415°C.

C.Bz _{out} m./li. (x10 ⁻³)	CONV. of Bz %	C.Mea m./li. (x10 ⁻³)	CONV. to Mea %	C.CO ₂ m./li. (x10 ⁻³)	CONV. to CO ₂ %	Contact Time gm.ml. ⁻¹ sec.	Carbon Balance %
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Concn. Bz_{in} = 1.94 x10⁻³ m./li. ; Concn. O_{2in} = 24.0 x10⁻³ m./li.
(4.75 mole %) (59.1 mole %)

.233	88.0	.567	29.2	8.35	430.	5.15	103.
.302	84.45	.504	26.0	7.81	409.	3.86	100.
.364	81.2	.417	21.5	7.23	373.	2.57	95.5
.61	68.5	.385	19.9	6.25	322.	1.93	98.
.705	63.0	.385	19.9	5.55	284.	1.53	96.5
.908	53.5	.355	18.3	4.85	250.	1.29	101.

Concn. Bz_{in} = 4.08 x10⁻³ m./li. ; Concn. O_{2in} = 20.2 x10⁻³ m./li.
(10. mole %) (49.5 mole %)

.58	86.0	.86	21.0	17.60	431.	5.19	100.
.65	84.0	.80	19.6	16.4	402.	3.89	95.5
1.21	70.4	.71	17.5	14.25	348.	2.59	100.
1.71	58.2	.67	16.5	11.55	283.	1.95	101.
2.12	48.0	.645	15.8	8.65	212.	1.56	97.5
2.49	39.1	.623	15.2	7.4	181.	1.30	102.

Concn. Bz_{in} = 7.7 x10⁻³ m./li. ; Concn. O_{2in} = 7.7 x10⁻³ m./li.
(18.9 mole %) (18.9 mole %)

4.93	36.0	1.135	14.75	9.25	120.	5.25	95.5
5.39	29.9	.921	12.0	7.67	99.7	3.93	95.5
5.83	24.3	.741	9.65	5.68	73.7	2.62	96.
6.67	13.25	.50	6.5	3.60	46.7	1.97	99.5
6.88	10.6	.40	5.15	2.73	35.3	1.57	99.5
6.93	10.0	.343	4.5	2.38	31.0	1.31	99.

TABLE 3.6

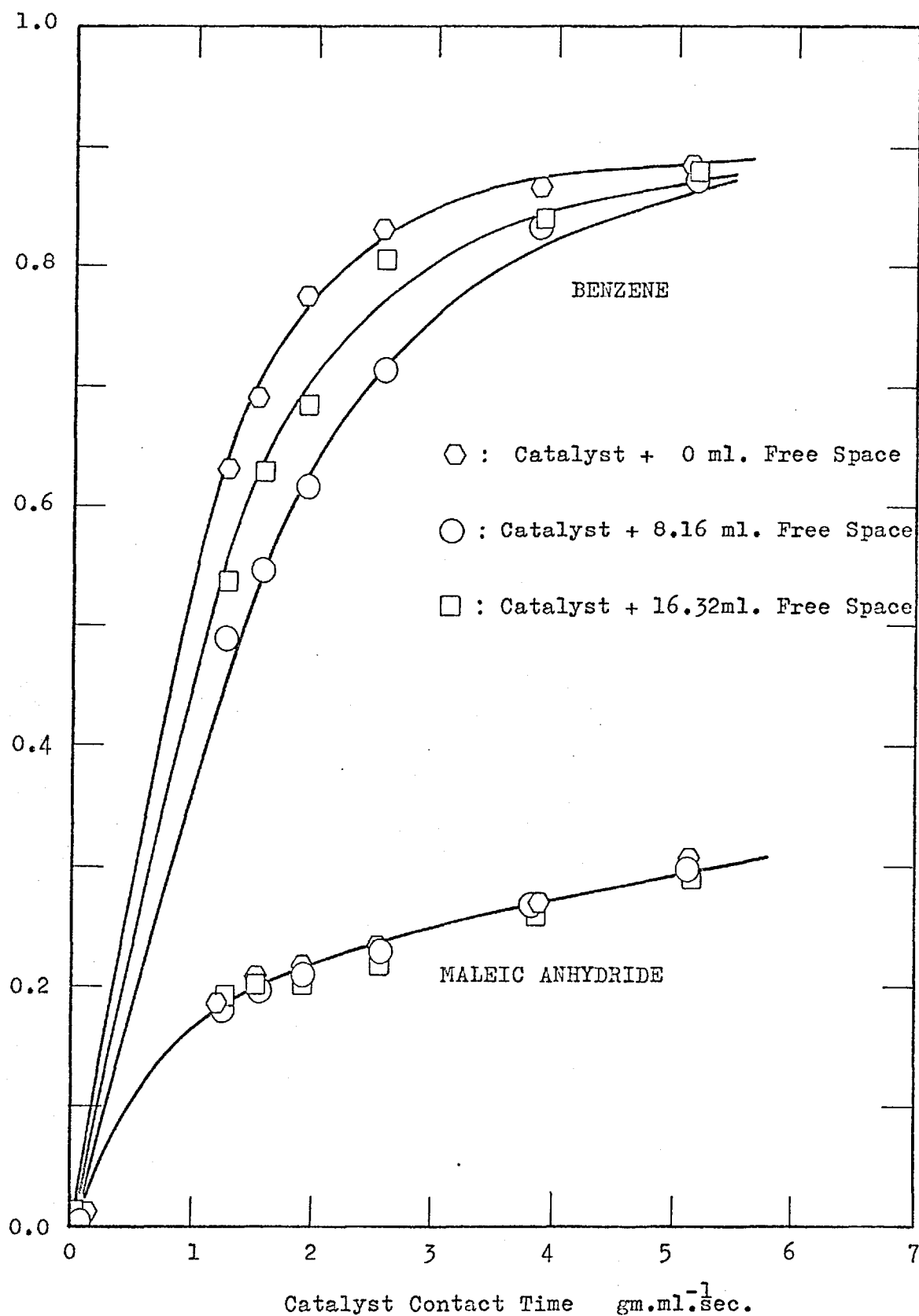


FIGURE 3.7 : The Effects of Free Volume after the Catalyst Bed ; Product Conversion vs. Contact Time.

(the CO_2 results are omitted for clarity)

Feed Conditions : $\text{C.Bz}_{\text{in}} = 4.9 \text{ mole\%}$

$\text{C.O}_{2\text{in}} = 60.0 \text{ mole\%}$

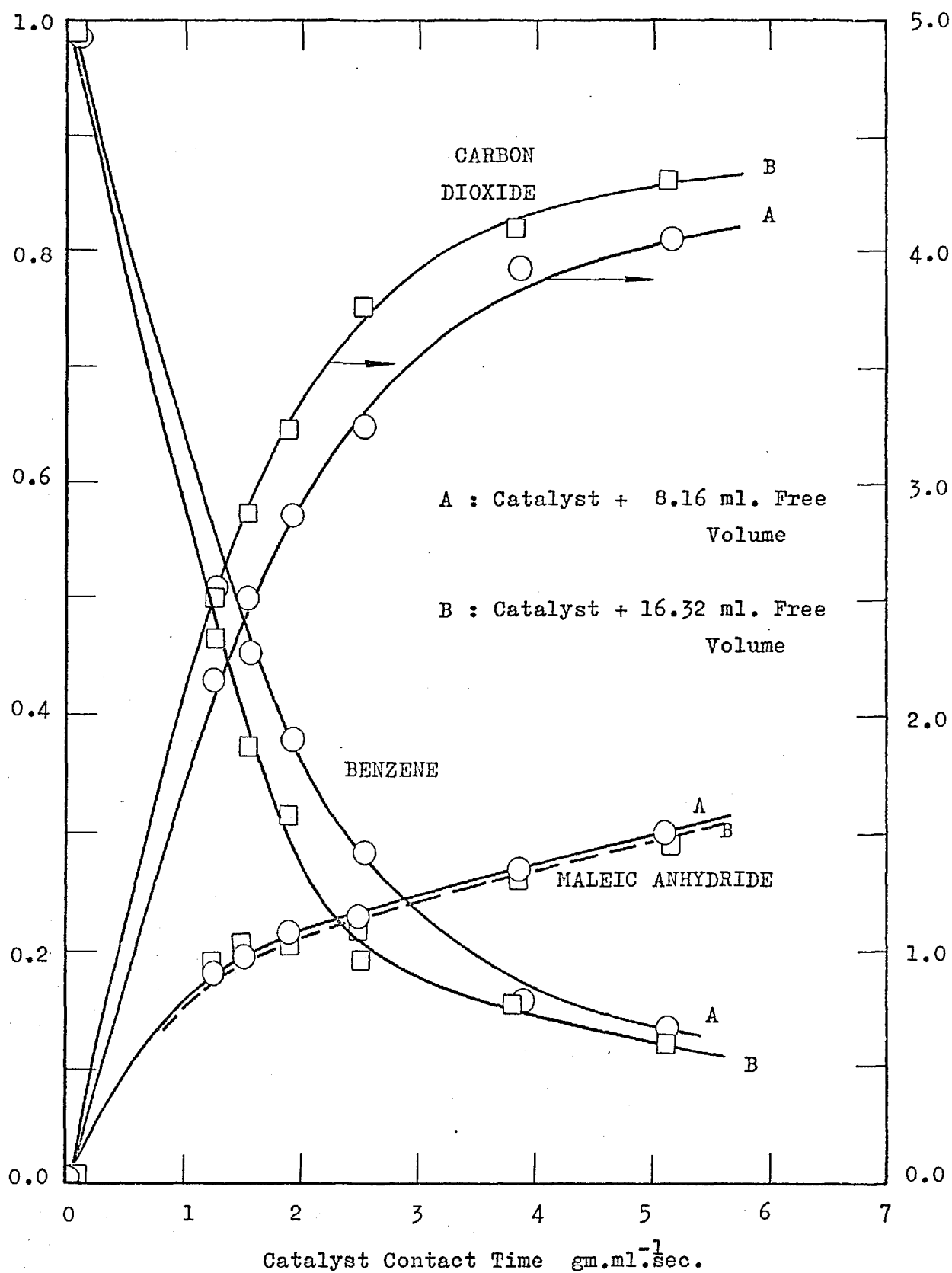


FIGURE 3.8 : The Effects of Free Volume on Product Conversion

Feed Conditions : $C_{Bz_{in}} = 4.9 \text{ mole\%}$
 $C_{O_{2in}} = 60.0 \text{ mole\%}$

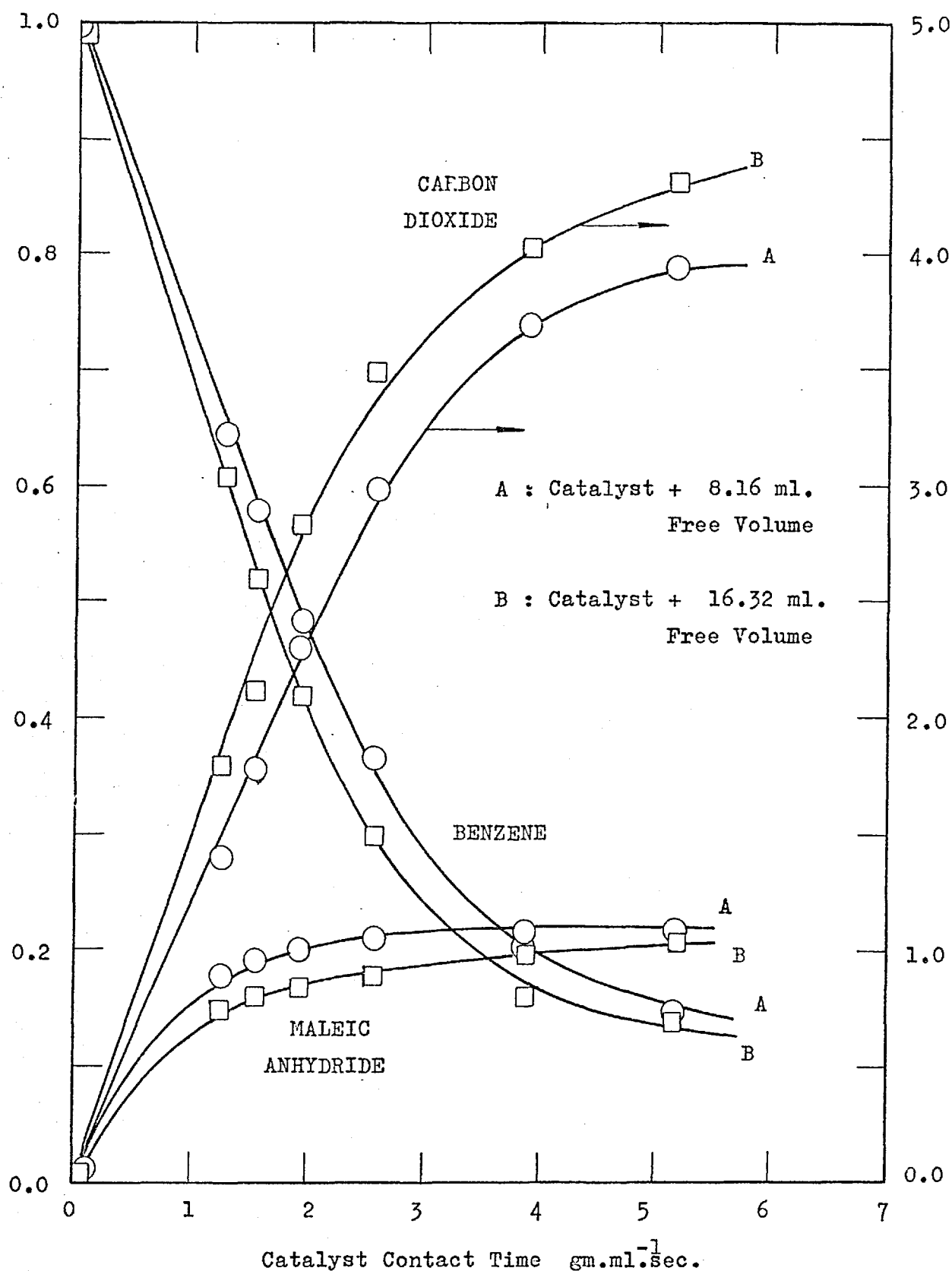


FIGURE 3.9 : The Effects of Free Volume on Product Conversion

Feed Conditions : $C_{Bz_{in}} = 10 \text{ mole\%}$
 $C_{O_{2in}} = 50 \text{ mole\%}$

TABLE 3.7

THE EFFECT OF FREE VOLUME ON THE KINETICS OF THE REACTION

Typical results , for various catalyst contact times, and at 415°C.

Catalyst Contact Time = 2.0 gm. ml.⁻¹sec.

Benzene Feed Conc'n. mole %	Oxygen Feed Conc'n. mole %	Benzene Converted		Conversion to Maa		Conversion to CO ₂	
		8.16ml	16.32ml	8.16ml	16.32ml	8.16ml	16.32ml
4.9	60.0	63.0%	72.5%	21.5%	21.0 %	292.%	330.%
10.0	50.0	52.5%	58.5%	20.0%	17.0%	232%	288%
18.9	18.9	13.0%	13.75%	12.5%	7.0%	31.5%	47.5%

Catalyst Contact Time = 4.0 gm.ml.⁻¹sec.

4.9	60.0	84.0%	86.5%	27.0%	26.5%	392%	414%
10.0	50.0	79.5%	81.5%	21.5%	19.5%	369%	403%
18.9	18.9	30.0%	31.5%	19.0%	12.5%	94%	100%

Tubular Reactor ; Temperature : 415°C.

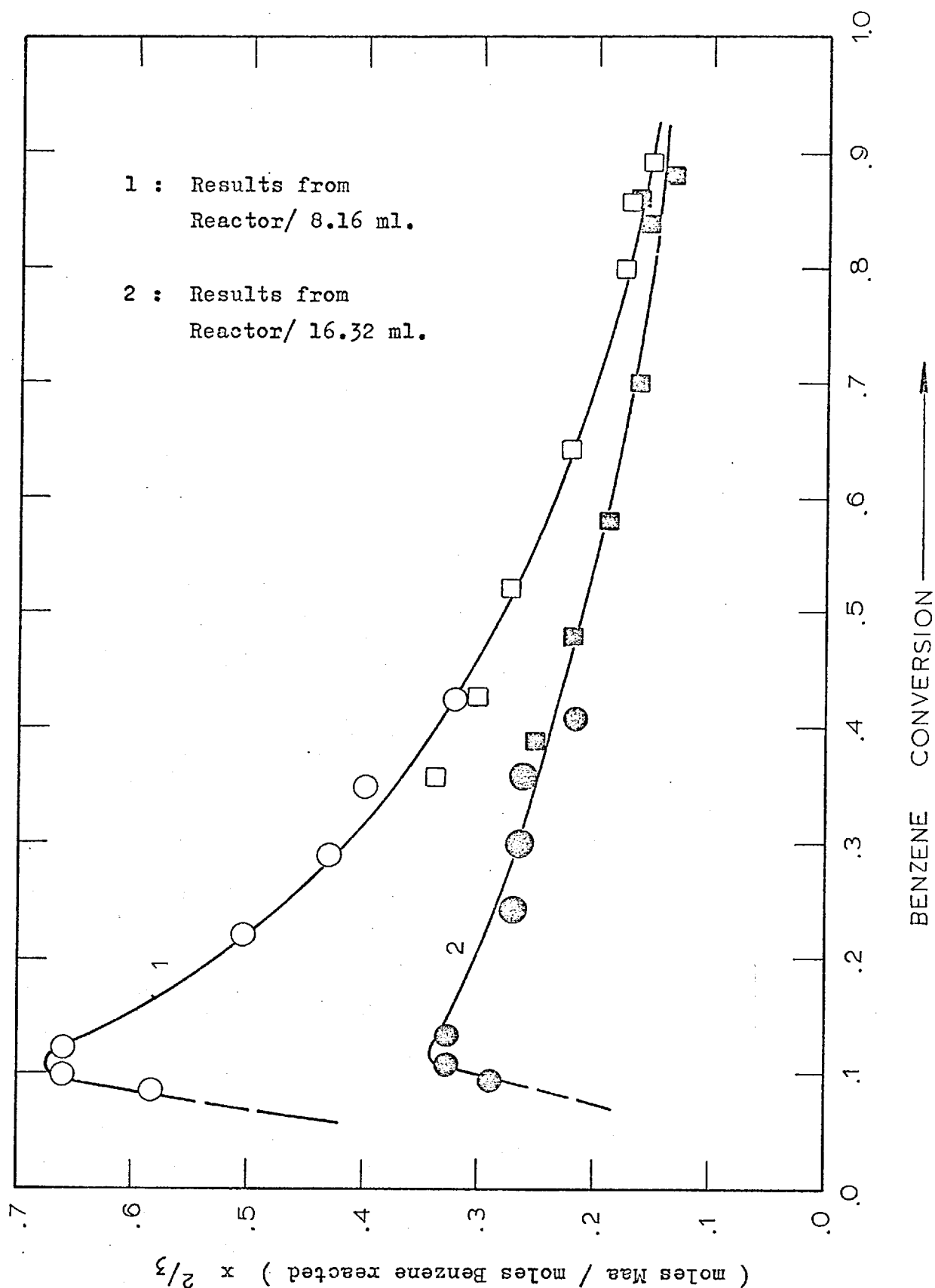


FIGURE 3.10 : The Effect of Free Volume on the Selective Carbon Yield of MAA for different O_2 /Fuel Ratios.

Feed Conditions : $\bigcirc, \bullet$ $C_{Bz_{in}} = 18.9 \text{ mole\%} = C_{O_{2in}}$
 $\square, \blacksquare$ $C_{Bz_{in}} = 10 \text{ mole\%} ; C_{O_{2in}} = 50 \text{ mole\%}$

of benzene or maa.

(ii) Effects of surface:volume ratio after the catalyst bed:

The effect of increasing the surface:volume ratio in the gas space after the bed is much more marked. As the amount of catalytically inert surface after the bed is increased, the benzene conversion and yield of maa drop at all oxygen:fuel ratios. A full list of results for all reactor configurations used is given in Tables 3.8, 3.9, 3.10, 3.11 and some typical results are shown in Figures 3.11, 3.12, 3.13, 3.14 and Table 3.12.

The selectivity of the oxidation to maleic anhydride is shown as a function of benzene conversion for results at oxygen:fuel ratios of 1:1 and 5:1 in Figure 3.15. Again, selectivity to maa would appear to be independent of oxygen:fuel ratios (the 12:1 results have been omitted for the sake of clarity but they give a reasonable fit to the curves). As previously, the curves pass through a maximum at ca 12% benzene conversion, but increases in surface after the catalyst bed decreases the maximum selective yield of maa.

Since the contact time and the amount of catalyst remains constant, as does the residence time in the free gas space in the reactor, it must be concluded that the changes in product spectra result from increases in the "inert" surface area after the bed.

At high inert surface area, traces of other compounds were observed amongst the products of reaction. At high concentrations of oxygen and high inert surface area, traces of phenol were observed in increasing quantities as the residence/contact time increased. Again, increases in the amount of surface led to the appearance in increasing quan-

TOTAL VOLUME AFTER THE CATALYST BED = 8.16 ml.
 TOTAL ALUMINA (Al_2O_3) SURFACE AFTER
 THE CATALYST BED = 105.9 cm^2

15.11 gm. of Catalyst 1 ; Temperature : 415°C.

C.AA = Concentration of Acrylic Acid

C.Ph = Concentration of Phenol

C.Bz _{out}	CONV.	C.Maa	CONV.	C.CO ₂	CONV.	C.AA	Contact	Carbon
m./li.	of Bz		to Maa		to CO ₂		Time	Balance
($\times 10^{-3}$)	%	m./li.	%	m./li.	%	m./li.	gm.ml. ⁻¹ sec.	%
($\times 10^{-3}$)		($\times 10^{-3}$)		($\times 10^{-3}$)		($\times 10^{-3}$)		

Concn. Bz_{in} = 2.1×10^{-3} m./li. ; Concn. O_{2in} = 24.5×10^{-3} m./li.
 (5.1 mole %) (60.1 mole %)

.25	88.0	.576	27.4	8.85	422.	.06	5.12	102.
.35	83.5	.484	23.1	8.50	405.	.04	3.85	101.
.755	64.0	.40	19.1	6.40	305.	.015	1.92	100.
1.04	50.5	.344	16.4	5.05	240.	—	1.28	101.

Concn. Bz_{in} = 3.85×10^{-3} m./li. ; Concn. O_{2in} = 19.9×10^{-3} m./li.
 (9.5 mole %) (48.8 mole %)

.62	84.0	.554	14.5	16.10	430.	.07	5.22	104.
.925	76.0	.71	18.4	14.95	390.	.05	3.91	102.
1.56	59.5	.681	17.6	11.55	300.	.018	2.61	102.5
2.11	45.25	.618	16.1	8.00	213.	.006	1.96	100.
2.43	36.9	.541	14.1	6.25	162.	—	1.57	99.

Concn. Bz_{in} = 8.41×10^{-3} m./li. ; Concn. O_{2in} = 7.77×10^{-3} m./li.
 (20.5 mole %) (19. mole %)

5.91	29.7	1.52	18.1	8.00	95.	.02	5.15	98.5
6.4	23.9	1.57	18.7	6.30	75.	.006	3.87	101.
6.91	17.8	1.375	16.4	4.25	50.5	—	2.57	101.5
7.4	11.9	1.265	15.1	2.70	32.1	—	1.93	104.
7.73	8.0	1.11	13.2	1.54	18.3	—	1.29	103.5

TABLE 3.8 : Results from Glass Tubular Reactors
 Effect of Surface after the Catalyst Bed.

TOTAL FREE VOLUME AFTER THE CATALYST BED = 8.16 ml.
 TOTAL GLASS SURFACE - " - - " - - " - = 156.0 cm²

15.11 gm. of Catalyst 1 ; Temperature : 415°C.

C.AA = Concentration of Acrylic Acid

C.Ph = Concentration of Phenol

(where relevant)

C.Bz _{in}	CONV. of Bz	C.Maa	CONV. to Maa	C.CO ₂	CONV. to CO ₂	Contact Time	Carbon Balance
m./li. (x10 ⁻³)	%	m./li. (x10 ⁻³)	%	m./li. (x10 ⁻³)	%	gm.ml. ⁻¹ sec.	%

Concn. Bz_{in} = 2.04 x10⁻³ m./li. ; Concn. O_{2in} = 24.5 x10⁻³ m./li.
 (5. mole %) (60.1 mole %)

.284	85.1	.309	15.2	9.0	441.	5.13	97.5
.388	81.0	.256	12.6	8.85	433.	3.85	100.
.61	70.1	.239	11.7	7.6	373.	2.57	100.
.81	60.3	.221	10.9	6.65	326.	1.93	102.
1.01	50.0	.203	10.0	5.3	260.	1.28	99.

Concn. Bz_{in} = 4.08 x10⁻³ m./li. ; Concn. O_{2in} = 20.4 x10⁻³ m./li.
 (10. mole %) (50. mole %)

.75	81.5	.554	13.6	17.7	433.	5.19	100.
1.065	74.0	.59	14.45	15.7	385.	3.89	101.
1.73	57.6	.73	17.9	11.16	273.	2.59	99.5
2.27	44.3	.722	17.6	8.0	196.	1.95	101.
2.96	28.1	.631	15.4	4.2	103.	1.30	99.5

Concn. Bz_{in} = 8.41 x10⁻³ m./li. ; Concn. O_{2in} = 8.01 x10⁻³ m./li.
 (20.5 mole %) (19.5 mole %)

6.06	27.9	1.34	16.0	7.33	87.0	5.16	99.5
6.47	23.0	1.33	15.9	6.0	71.0	3.87	99.5
7.11	15.5	1.10	13.1	3.75	44.7	2.57	100.5
7.64	9.15	.82	9.8	2.8	33.3	1.94	103.
7.85	6.17	.49	5.85	1.57	18.7	1.29	100.

TABLE 3.9

TOTAL VOLUME AFTER THE CATALYST BED = 8.16 ml.
 TOTAL INERTS (STONE) SURFACE AFTER
 THE CATALYST BED = 437. cm²

15.11 gm. of Catalyst 1 ; Temperature : 415°C.

C.AA = Concentration of Acrylic Acid

C.Ph = Concentration of Phenol

C.Bz _{out} m./li (x10 ⁻³)	CONV. of Bz %	C.Maa m./li. (x10 ⁻³)	CONV. to Maa %	C.CO ₂ m./li. (x10 ⁻³)	CONV. to CO ₂ %	C.AA m./li. (x10 ⁻³)	C.Ph m./li. (x10 ⁻³)	Contact Time gm.ml. ⁻¹ sec.	Carbon Balance %
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Concn. Bz_{in} = 2.0 x10⁻³m./li. ; Concn. O_{2in} = 24.3 x10⁻³m./li.
 (4.95 mole %) (60.0 mole %)

.775	61.2	.018	.9	6.53	326.	.018	.022	3.89	95.5
1.125	43.7	.052	2.6	4.55	228.	.009	.01	1.94	97.5
1.315	34.3	.065	3.25	3.82	191.	Trace	Trace	1.29	101.

Concn. Bz_{in} = 4.05 x10⁻³m./li. ; Concn. O_{2in} = 20.5 x10⁻³m./li.
 (9.92 mole %) (50.1 mole %)

2.25	44.5	.103	2.55	9.25	228.	.025	.012	3.89	96.5
3.00	26.0	.22	5.45	5.40	133.	.01	Trace	1.95	100.
3.24	20.0	.23	5.70	3.99	98.5	Trace	—	1.30	100.

Concn. Bz_{in} = 7.77 x10⁻³m./li. ; Concn. O_{2in} = 7.7 x10⁻³m./li.
 (19.0 mole %) (18.9 mole %)

6.57	15.35	.426	5.50	4.17	53.7	.025	Trace	3.95	100.
7.25	6.6	.337	4.35	2.34	30.2	.005	—	1.97	104.5
7.31	5.75	.28	3.6	1.76	22.7	—	—	1.31	102.

TABLE 3.10

TOTAL VOLUME AFTER THE CATALYST BED = 8.16 ml.
 TOTAL 316 S.STEEL (SHAVINGS) SURFACE
 AFTER THE BED = 475 (approx.) cm²

15.11 gm. of Catalyst 1 ; Temperature 415°C.

C.AA = Concentration of Acrylic Acid

C.Bz _{out}	CONV. of Bz	C.Maa	CONV. to Maa	C.CO ₂	CONV. to CO ₂	C.AA	Contact Time	Carbon Balance
m./li. (x10 ⁻³)	%	m./li. (x10 ⁻³)	%	m./li. (x10 ⁻³)	%	m./li. (x10 ⁻³)	gm.ml. ⁻¹ sec.	%

Concn. Bz_{in} = 2.04 x10⁻³ m./li. ; Concn. O_{2in} = 24.3 x10⁻³ m./li.
 (5.0 mole %) (60.0 mole %)

.61	70.2	Trace		8.56	420.	—	3.85	100.
1.13	44.6	Trace		5.65	277.	—	1.54	102.

Concn. Bz_{in} = 8.41 x10⁻³ m./li. ; Concn. O_{2in} = 8.0 x10⁻³ m./li.
 (20.5 mole %) (19.6 mole %)

6.93	17.5	.34	4.04	5.07	60.3	.11	3.87	96.
7.88	6.25	.186	2.2	1.43	17.0	Trace	1.55	97.5

TABLE 3.11

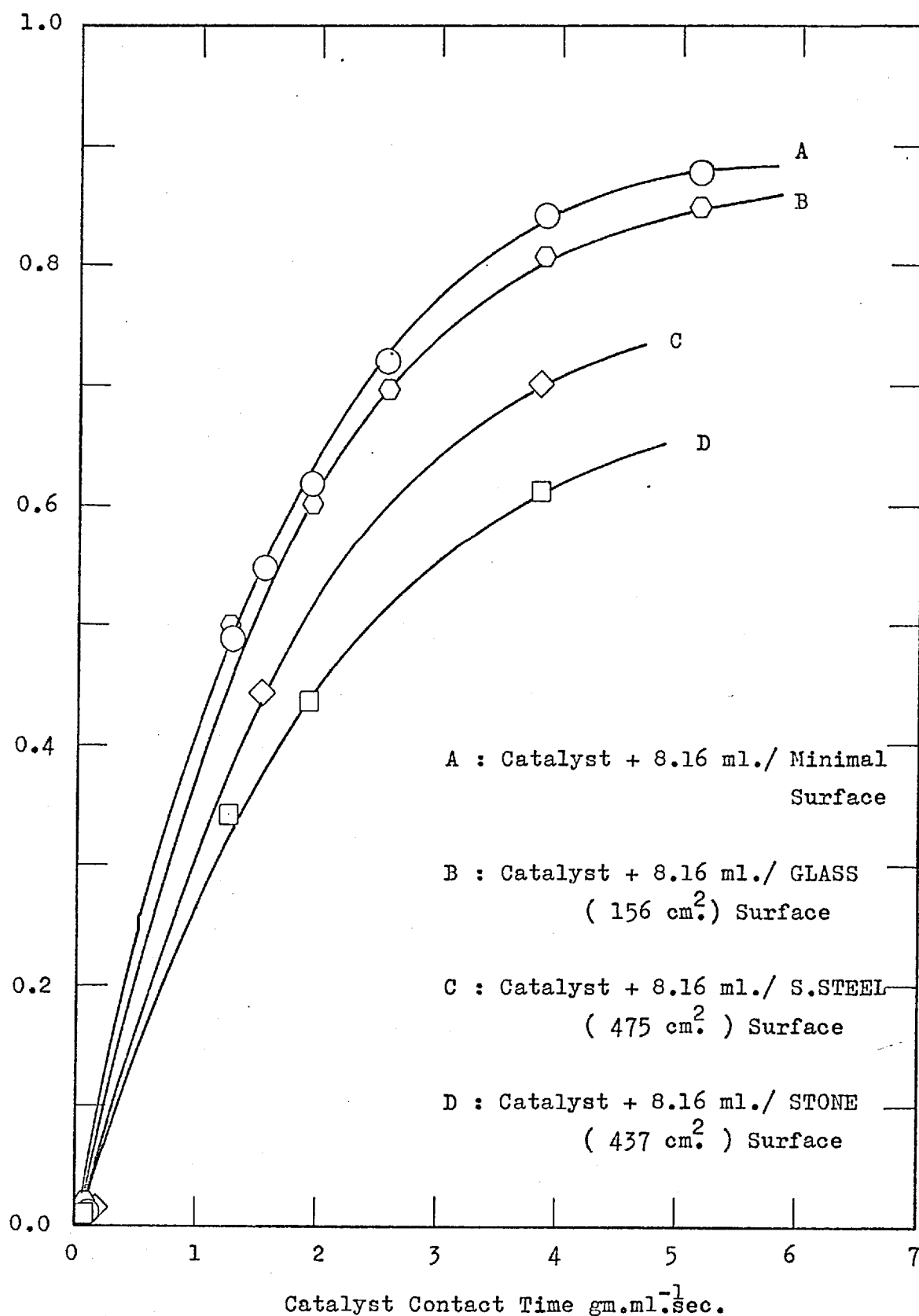


FIGURE 3.11 : The Effect of Surface:Volume Ratio after the catalyst bed on Benzene Conversion.

Feed Conditions : $\text{C.Bz}_{\text{in}} = 5 \text{ mole\%}$; $\text{C.O}_{2\text{in}} = 60 \text{ mole\%}$

Tubular Reactor ; Temperature : 415°C.

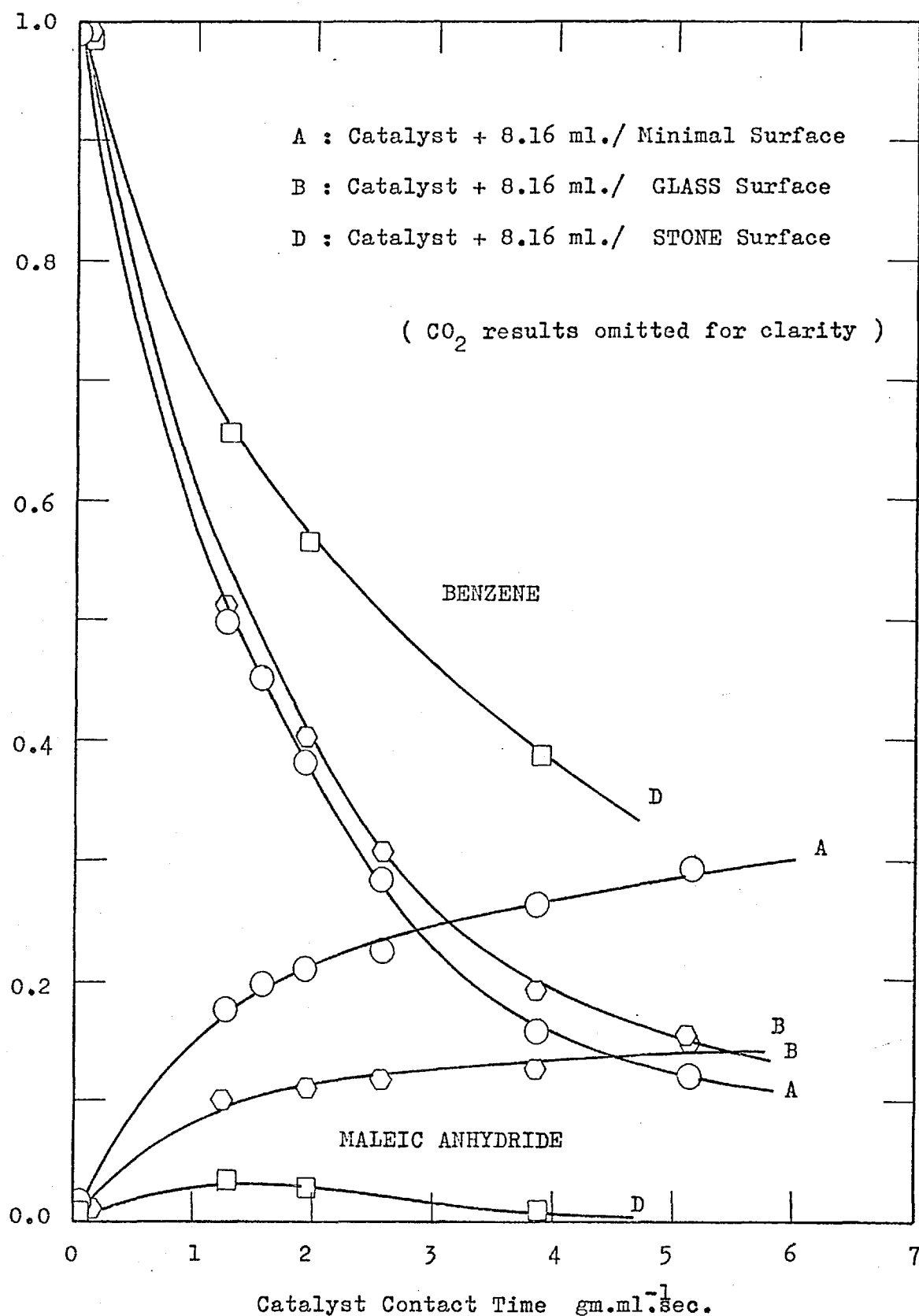


FIGURE 3.12 : The Effect of Surface:Volume Ratio on Product Conversion.

Feed Conditions : C.Bz_{in} = 5 mole%
C.O₂_{in} = 60 mole%

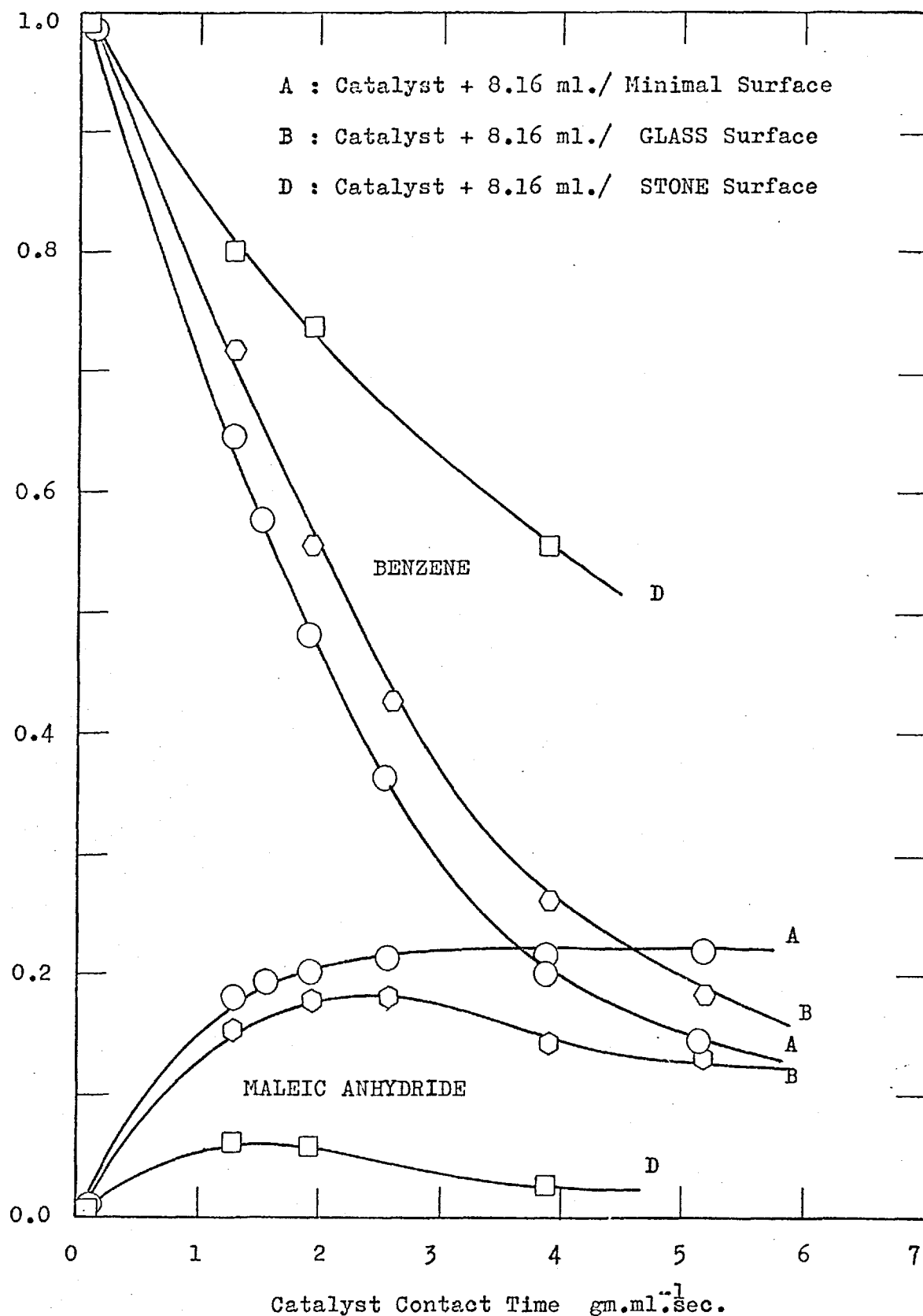


FIGURE 3.13 : The Effect of Surface:Volume Ratio on Product Conversion. (CO_2 results omitted)

Feed Conditions : $\text{C.Bz}_{\text{in}} = 10 \text{ mole\%}$
 $\text{C.O}_{2\text{in}} = 50 \text{ mole\%}$

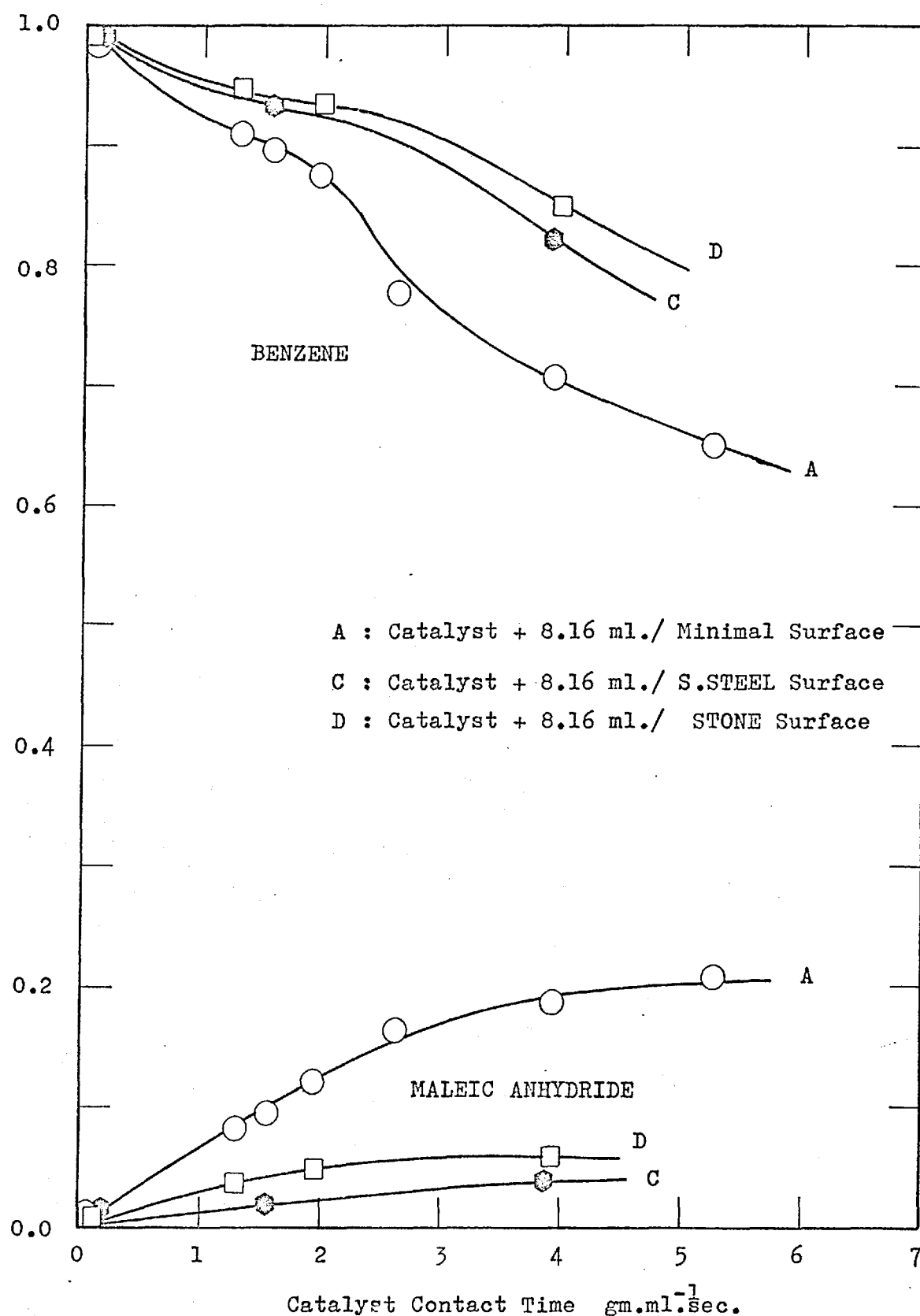


FIGURE 3.14 : The Effect of STAINLESS (316) STEEL Surface after the Catalyst Bed on Product Conversion. (CO₂ results omitted)

Feed Conditions : C.Bz_{in} = 18.9 mole% = C.O_{2in}

TABLE 3.12

THE EFFECT OF SURFACE:VOLUME RATIO AFTER THE CATALYST BED
ON THE KINETICS OF THE REACTION

Typical results , for various catalyst contact times , using
a fixed charge of Catalyst 1 (15.11 gm.), and at 415°C.

S/V = surface to volume ratio (cm^{-1})

Catalyst Contact Time = $2.0 \text{ gm.ml}^{-1} \text{ sec.}$

Benzene Feed	Oxygen Feed	Benzene Converted			Conversion to Maa			Conversion to CO_2		
		S/V			S/V			S/V		
mole %	mole %	2.0	19.3	53.5	2.0	19.3	53.5	2.0	19.3	53.5
4.9	60.0	63.%	60.%	44.%	21.5%	11%	2.5%	292%	330%	235%
10.0	50.0	52.5%	45.%	27.5	20.%	18%	5.5%	232%	205%	140%
18.9	18.9	13.%	10.%	7.%	12.5%	10%	4.5%	31.5%	33%	31%

Catalyst Contact Time = $4.0 \text{ gm.ml}^{-1} \text{ sec.}$

4.9	60.0	84.%	81.%	62.%	27.%	13.5%	1.%	392%	435%	330%
10.0	50.0	79.5%	74.5	45.%	21.5	15.%	2.5%	369%	390%	230%
18.9	18.9	30.%	23.5	15.5	19.%	16.%	5.5%	94%	75%	55%

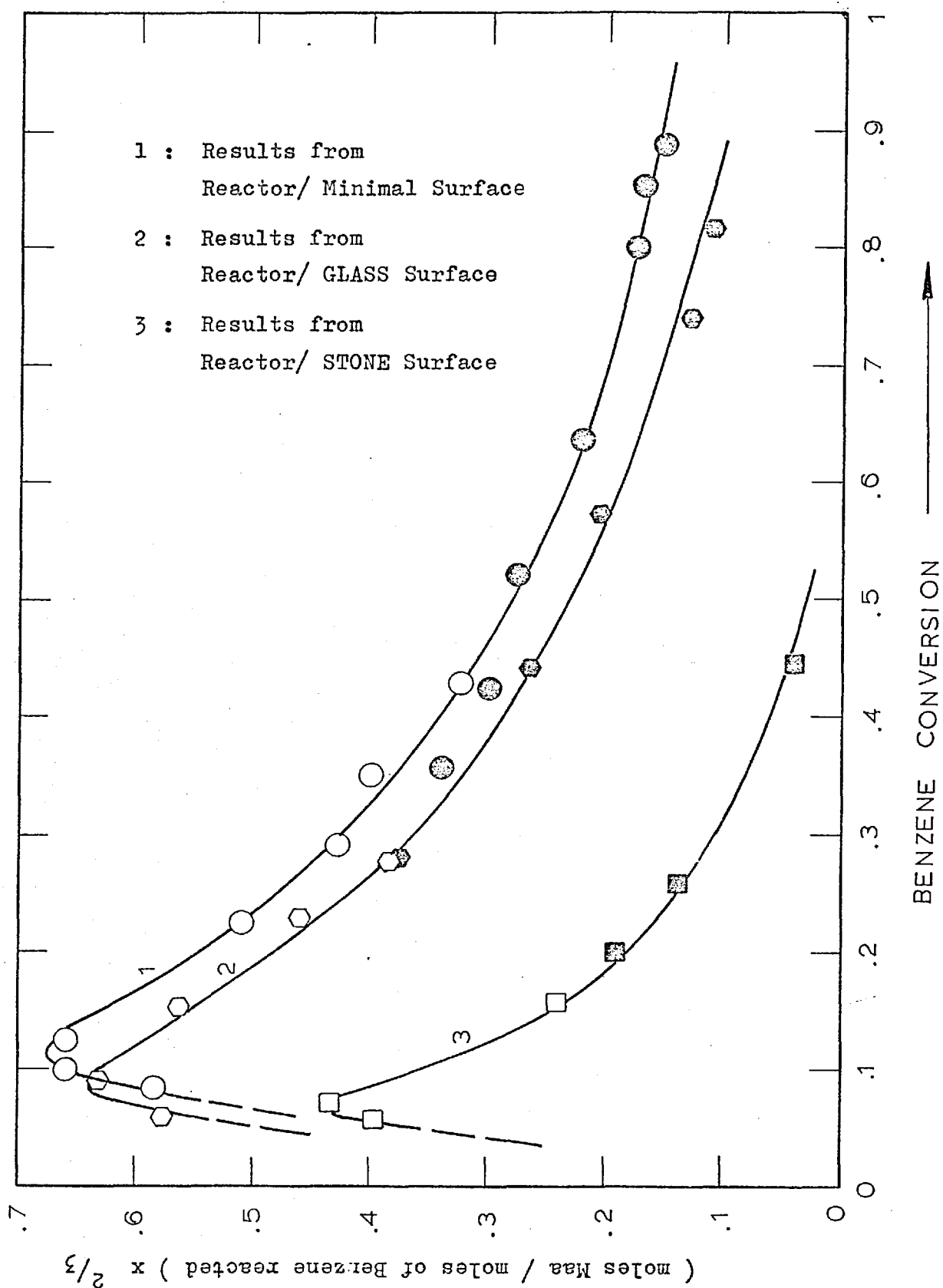


FIGURE 3.15 : The Effect of Surface:Volume Ratio on the Selective Carbon Yield of MAA for different O_2 /Fuel Ratios.

Feed Conditions : $\bigcirc, \square, \hexagon$ $C.Bz_{in} = 18.9 \text{ mole\%} = C.O_{2in}$

$\odot, \blacksquare, \hexagon$ $C.Bz_{in} = 10 \text{ mole\%} ; C.O_{2in} = 50 \text{ mole\%}$

ties of acrylic acid. The results obtained over both catalysts which were used are compared in Table 3.13 .

The importance of homogeneous effects was also studied using the more active catalyst 2 at a lower temperature of 378°C. The results, shown in Table 3.14 and Figure 3.16, present a similar pattern to those obtained over catalyst 1.

3D Reaction using a feed of benzene and maleic anhydride

Several experiments were completed in the absence of catalyst, using a feed of appropriate mixtures of benzene, maa and air at residence times between 0.4 and 13 secs. No measurable conversion of benzene or maleic anhydride was noted in the glass tubular reactors, even in the presence of inert packing.

Substitution of the glass reactor for the one fabricated from stainless steel led to extensive oxidation of maleic anhydride almost exclusively to carbon dioxide. It was not possible to detect any effect on benzene concentration, other than that due to removal of benzene ''homogeneously'' (see 3B).

3E Carbon Balances

When evaluating the effects of free volume and surface to volume ratio after the catalyst bed, it is essential to possess accurately known amounts of products and reactants. Carbon balances, completed for all experiments reported above and for the studies in the S.G.S.R., showed that the carbon could be accounted for within $\pm 5\%$ in all cases.

TABLE 3.13

VARIATION OF ACRYLIC ACID YIELD WITH CATALYST CONTACT
TIME — THE EFFECT OF INERT PACKING AFTER THE BED.

15.11 gm. of Catalyst 1 ; Temperature : 415°C.

Concn. Bz_{in} = 4.9 mole % ; Concn. O_{2in} = 60.0 mole %

Contact Time gm.ml. ⁻¹ sec.	S/V = 2.0 cm. ⁻¹ % YIELD	S/V = 53.5 cm. ⁻¹ % YIELD
1.29	—	Trace
1.94	—	1.03 %
3.89	Trace	1.47 %

15.1 gm. of Catalyst 2 ; Temperature : 378°C.

Concn. Bz_{in} = 1.96 mole % ; Concn. O_{2in} = 20.0 mole %

Contact Time gm.ml. ⁻¹ sec.	S/V = 2.0 cm. ⁻¹ % YIELD	S/V = 53.5 cm. ⁻¹ % YIELD
1.38	—	0.51 %
2.07	Trace	1.02 %
4.15	~ 0.1 %	2.35 %

TABLE 3.14

EFFECTS OF SURFACE:VOLUME RATIO AFTER THE CATALYST BED
RESULTS USING CATALYST 2

15.1 gm. of Catalyst 2 ; Temperature 378°C.

C.AA = Concentration of Acrylic Acid

C.Bz _{out}	CONV.	C.Maa	CONV.	C.CO ₂	CONV.	C.AA	Contact	Carbon
m./li.	of Bz	m./li.	to Maa	m./li.	to CO ₂	m./li.	Time	Balance
(x10 ⁻³)	%	(x10 ⁻³)	%	(x10 ⁻³)	%	(x10 ⁻³)	gm.ml. ⁻¹ sec.	%

GLASS TUBULAR REACTOR : 8.16 ml. VOLUME + MINIMAL SURFACE

Concn. Bz_{in} = .80 x10⁻³ m./li. ; Concn. O_{2in} = 8.16 x10⁻³ m./li.
(1.96 mole %) (20.0 mole %)

.0032	99.0	.637	80.0	2.23	279.	.001	4.15	102.
.034	95.6	.607	75.9	2.08	260.	Trace	2.07	98.5
.0875	89.1	.563	70.1	2.00	250.	Trace	1.38	100.

GLASS TUBULAR REACTOR : 8.16 ml. VOLUME + 437.0 cm²

OF STONE SURFACE

Concn. Bz_{in} = .80 x10⁻³ m./li. ; Concn. O_{2in} = 8.16 x10⁻³ m./li.
(1.96 mole %) (20.0 mole %)

.032	96.1	.555	69.5	2.472	308.	.018	4.15	102.
.113	86.0	.494	61.8	2.12	265.	.007	2.07	99.5
.211	73.7	.422	52.8	1.824	228.	.003	1.38	100.5

Tubular Reactor ; Temperature : 378°C.

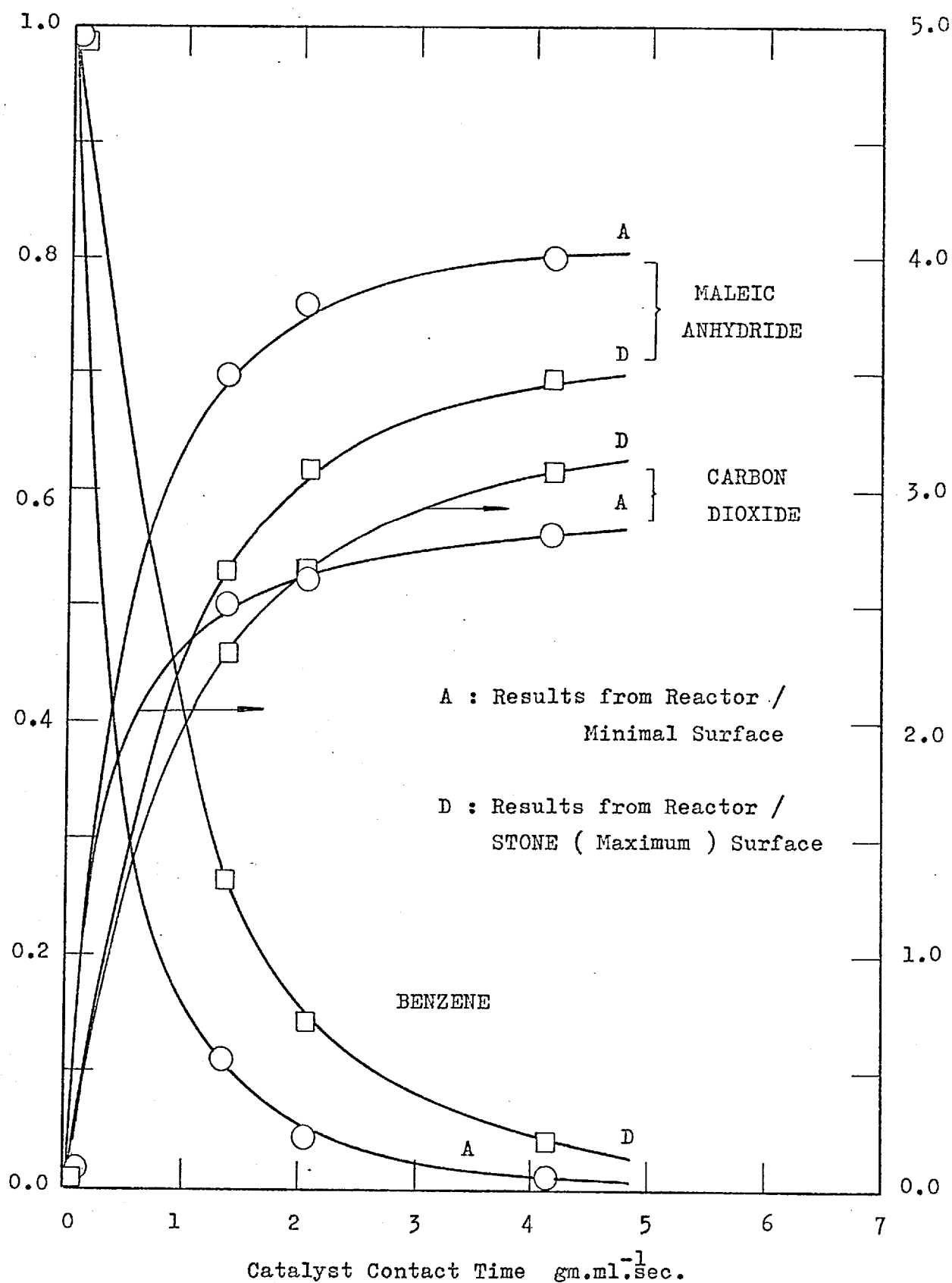


FIGURE 3.16 : The Effect of Surface:Volume Ratio after the Catalyst Bed on Product Conversion.

Results using CATALYST 2

Feed Conditions : $\text{C.Bz}_{\text{in}} = 1.96 \text{ mole\%}$
 $\text{C.O}_{2\text{in}} = 20.0 \text{ mole\%}$

THE VARIATION OF SELECTIVE CARBON YIELD OF MAA WITH OVERALL CONVERSION
RESULTS FROM GLASS TUBULAR REACTOR STUDIES.

15.11 gm. of Catalyst 1 ; 8.16 ml. FREE VOLUME ; 415°C.

Concn. $Bz_{in} = 2 \times 10^{-3} \text{ m./li.}$; Concn. $O_{2in} = 24.3 \times 10^{-3} \text{ m./li.}$

CONVERSION OF BENZENE	:	87.8	84.2	71.2	61.8	54.75	49.0
SELECTIVE CARBON YIELD OF MAA	:	22.4	20.9	21.1	22.7	23.8	24.4

Concn. $Bz_{in} = 4.08 \times 10^{-3} \text{ m./li.}$; Concn. $O_{2in} = 20.4 \times 10^{-3} \text{ m./li.}$

CONVERSION OF BENZENE	:	85.5	80.0	63.7	52.0	42.3	35.5
SELECTIVE CARBON YIELD OF MAA	:	17.0	17.6	21.9	27.6	30.0	33.3

Concn. $Bz_{in} = 7.7 \times 10^{-3} \text{ m./li.}$; Concn. $O_{2in} = 7.7 \times 10^{-3} \text{ m./li.}$

CONVERSION OF BENZENE	:	35.0	28.8	22.2	11.75	10.1	9.1
SELECTIVE CARBON YIELD OF MAA	:	40.2	42.8	50.3	66.0	66.0	58.5

15.11 gm. of Catalyst 1 ; 16.32 ml. FREE VOLUME ; 415°C.

Concn. $Bz_{in} = 1.94 \times 10^{-3} \text{ m./li.}$; Concn. $O_{2in} = 24 \times 10^{-3} \text{ m./li.}$

CONVERSION OF BENZENE	:	88.0	84.45	81.2	68.5	63.0	53.5
SELECTIVE CARBON YIELD OF MAA	:	22.2	20.5	17.7	18.8	20.4	22.8

Concn. $Bz_{in} = 4.08 \times 10^{-3} \text{ m./li.}$; Concn. $O_{2in} = 20.2 \times 10^{-3} \text{ m./li.}$

CONVERSION OF BENZENE	:	86.0	84.0	70.4	58.2	48.0	39.1
SELECTIVE CARBON YIELD OF MAA	:	16.3	15.5	16.45	18.4	21.9	26.1

Concn. $Bz_{in} = 7.7 \times 10^{-3} \text{ m./li.}$; Concn. $O_{2in} = 7.7 \times 10^{-3} \text{ m./li.}$

CONVERSION OF BENZENE	:	36.0	29.9	24.3	13.25	10.6	10.0
SELECTIVE CARBON YIELD OF MAA	:	27.3	26.7	26.7	32.4	32.5	29.6

(contd./over)

15.11 gm. of Catalyst 1 ; 8.16 ml. / 156 cm² of GLASS SURFACE : 415°C.

Concn. Bz_{in} = 2.04×10^{-3} m./li. ; Concn. O_{2in} = 24.5×10^{-3} m./li.

CONVERSION OF BENZENE	:	85.1	81.0	70.1	60.3	50.0
SELECTIVE CARBON YIELD OF MAA	:	11.7	10.3	11.1	11.95	13.3

Concn. Bz_{in} = 4.08×10^{-3} m./li. ; Concn. O_{2in} = 20.4×10^{-3} m./li.

CONVERSION OF BENZENE	:	81.5	74.0	57.6	44.3	28.1
SELECTIVE CARBON YIELD OF MAA	:	11.1	13.0	20.6	26.6	37.5

Concn. Bz_{in} = 8.41×10^{-3} m./li. ; Concn. O_{2in} = 8.01×10^{-3} m./li.

CONVERSION OF BENZENE	:	27.9	23.0	15.5	9.15	6.7
SELECTIVE CARBON YIELD OF MAA	:	38.0	45.8	56.4	63.0	58.3

15.11 gm. of Catalyst 1 ; 8.16 ml. / 437 cm² of STONE SURFACE : 415°C.

Concn. of Bz_{in} = 2×10^{-3} m./li. ; Concn. O_{2in} = 24.3×10^{-3} m./li.

CONVERSION OF BENZENE	:	61.2	43.7	34.3
SELECTIVE CARBON YIELD OF MAA	:	1.0	3.93	6.35

Concn. Bz_{in} = 4.05×10^{-3} m./li. ; Concn. O_{2in} = 20.5×10^{-3} m./li.

CONVERSION OF BENZENE	:	44.5	26.0	20.0
SELECTIVE CARBON YIELD OF MAA	:	3.8	14.0	18.9

Concn. Bz_{in} = 7.77×10^{-3} m./li. ; Concn. O_{2in} = 7.7×10^{-3} m./li.

CONVERSION OF BENZENE	:	15.35	6.6	5.75
SELECTIVE CARBON YIELD OF MAA	:	23.6	43.2	40.5

15.1 gm. of Catalyst 2 ; C.Bz_{in} = 1.96, C.O_{2in} = 20 mole % ; 378°C.

8.16 ml. / MINIMAL 8.16 ml. / 437 cm² STONE

CONVERSION OF BENZENE	:	99.0	95.6	89.1	96.1	86.0	73.7
SELECTIVE CARBON YIELD OF MAA	:	53.4	52.8	52.6	48.2	48.0	47.8

4 Kinetics of the Oxidation of Maleic Anhydride

4A Introduction

Studies, reported in 3C1, have shown the oxidation of maleic anhydride to carbon dioxide to be relatively unimportant except in the presence of metal surfaces and this observation holds both in the gas phase and over the catalyst. Even at high benzene conversions observed using catalyst 2, the over-oxidation of maa was not significant.

In order to explain the initial results obtained in the S.G.S.R. using cruciform and circular baskets (2B and 2C), it is necessary to develop some quantitative information for the steel catalysed oxidation of maleic anhydride. Although the oxidation should be thought of in terms of a surface initiated combustion reaction, catalyst surface in the S.G.S.R. will play an important role in either promotion or inhibition of the combustion process. It is necessary therefore to obtain the kinetics of the maleic oxidation reaction both in the presence and absence of catalyst. It was decided to ascertain the kinetics of the reaction using the S.G.S.R. in preference to the stainless steel tubular reactor packed with catalyst. The reasons for the choice are based on the inherent advantages of the S.G.S.R. over tubular reactors for the evaluation of catalytic rate data, and these have been described in some detail in the Introduction.

4B Oxidation in the presence of catalyst

4B1 Effects of temperature on rates of reaction:

The oxidation of maleic anhydride was studied at four temperatures over a 79° range: at 372°C, 391°C, 417°C and

15.11 gm. of Catalyst 1 ; Stirrer Speed : 3000 r.p.m.

C.Maa IN	C.O ₂ IN	Contact Time	C.Maa OUT	C.O ₂ OUT	C.CO ₂ m./li.	Maa Oxd. Rate	CO ₂ Prod. Rate	Carbon Balance
m./li. (x10 ⁻³)	m./li. (x10 ⁻³)	gm.ml. ⁻¹	m./li. (x10 ⁻³)	m./li. (x10 ⁻³)	m./li. (x10 ⁻³)	m.gm.sec. ⁻¹ (x10 ⁻⁸)	m.gm.sec. ⁻¹ (x10 ⁻⁸)	%

TEMPERATURE : 372°C.

.208	26.5	1.68	.188	26.0	.060	1.190	3.57	97.5
.223	26.5	2.80	.20	26.1	.093	.822	3.32	100.
.118	26.5	4.21	.093	26.0	.102	.594	2.43	101.
.05	8.16	1.66	.044	8.15	.021	.379	1.26	97.5
.145	8.1	2.72	.124	8.1	.068	.772	2.50	97.
.11	8.0	4.08	.085	7.8	.085	.612	2.08	99.
.15	4.07	1.65	.137	4.0	.05	.790	3.03	100.
.238	4.1	2.72	.21	4.0	.102	1.030	3.75	98.
.35	4.1	4.15	.287	3.95	.205	1.515	4.95	96.5
.39	16.9	2.75	.351	16.5	.153	1.420	5.56	100.
.239	12.0	4.06	.195	11.9	.153	1.08	3.77	102.

TEMPERATURE : 391°C.

.17	26.3	1.64	.148	26.0	.068	1.37	4.15	97.5
.16	26.1	2.76	.134	26.1	.0933	.95	3.38	98.
.148	25.9	4.03	.112	25.0	.136	.90	3.37	99.
.072	8.1	1.61	.064	8.05	.034	.50	2.11	101.
.10	8.16	2.71	.082	8.01	.0678	.665	2.50	99.
.118	8.07	4.02	.0874	7.91	.102	.76	2.54	95.5
.268	4.09	1.63	.243	4.07	.076	1.53	4.68	97.5
.273	4.05	2.69	.229	4.02	.102	1.63	3.80	93.
.21	4.01	3.99	.170	3.88	.1525	1.00	3.83	99.
.29	16.85	2.69	.244	16.55	.1525	1.71	5.67	97.
.393	12.0	3.99	.310	11.7	.238	2.08	5.96	94.5

TABLE 3.16 : Oxidation of MAA in the presence of V₂O₅ catalyst.
Results from the S.G.S.R.

15.11 gm. of Catalyst 1 ; Stirrer Speed : 3000 r.p.m.

C.Maa IN	C.O ₂ IN	Contact Time	C.Maa OUT	C.O ₂ OUT	C.CO ₂ OUT	Maa Oxd. Rate	CO ₂ Prod. Rate	Carbon Balance
m./li. (x10 ⁻³)	m./li. (x10 ⁻³)	gm.ml. ⁻¹ sec.	m./li. (x10 ⁻³)	m./li. (x10 ⁻³)	m./li. (x10 ⁻³)	m.gm. ⁻¹ sec. ⁻¹ (x10 ⁻⁸)	m.gm. ⁻¹ sec. ⁻¹ (x10 ⁻⁸)	%

TEMPERATURE : 417°C.

.30	26.5	1.59	.261	26.1	.119	2.46	7.51	97.
.25	26.0	2.59	.207	25.8	.153	1.66	5.91	98.
.172	26.5	3.97	.128	26.0	.187	1.11	4.71	102.
.13	8.18	1.57	.109	8.15	.059	1.34	3.77	95.
.10	8.05	2.57	.074	7.9	.085	1.01	3.31	95.
.066	8.2	3.91	.044	8.2	.102	.563	2.61	104.5
.322	4.1	1.57	.284	3.9	.102	2.43	6.52	96.
.415	4.1	2.62	.361	4.1	.220	2.06	8.42	100.
.433	4.08	3.92	.333	3.65	.271	2.55	6.92	92.5
.365	16.6	2.55	.298	16.5	.229	2.63	8.99	97.5
.552	11.9	3.81	.437	11.3	.390	3.02	10.25	97.

TEMPERATURE : 451°C.

.087	26.5	1.51	.063	26.2	.085	1.60	5.62	97.
.116	26.5	2.47	.075	26.3	.1525	1.66	6.17	91.
.138	25.9	3.70	.063	25.7	.271	2.02	7.35	95.5
.098	8.15	1.49	.075	8.05	.093	1.55	6.26	100.
.08	8.15	2.48	.05	8.09	.102	1.21	4.12	95.
.081	8.2	3.74	.041	8.05	.144	1.07	3.85	95.
.232	4.08	1.48	.195	4.03	.1525	2.50	10.30	100.
.254	4.06	2.41	.18	3.88	.220	3.07	9.14	93.5
.207	4.16	3.79	.122	3.82	.271	2.29	7.16	92.
.432	16.6	2.42	.311	16.1	.387	5.00	16.00	* 95.
.535	12.0	3.65	.355	11.2	.625	4.93	17.10	* 95.5

(* indicates large Traces of FORMALDEHYDE , not
included in the Carbon Balance)

TABLE 3.17

451°C. The same catalyst, used for all previous experimental work, was held in the circular basket of the S.G.S.R. Feed concentrations of maa were varied between 0.125 and 2.0 mole %, this range covering the usual concentrations of maa produced during the oxidation of benzene. Oxygen feed concentration was adjusted accordingly.

The only products of reaction were carbon dioxide and water, traces of formaldehyde being found only occasionally. Full tables of results are presented in Tables 3.16, 3.17, including calculated rates of reaction and carbon balances. Although the majority of carbon balances are within $\pm 5\%$, the occasional value outside these limits is a result of temperature fluctuations in the maa feed system, which proved very difficult to control at times.

Logarithmic plots of maa oxidation rates and carbon dioxide production rates versus maa reacting concentration are shown in Figures 3.17, 3.18.

These values were obtained from the exit concentrations of the reactor (Introduction: theory of the S.G.S.R.). Least squares analyses were completed for each set of points and the resulting rate expressions are given in Table 3.18.

4B2 Energy of Activation for maa oxidation:

Constant-order kinetics over the whole of the temperature range facilitate the calculation of an energy of activation for maa removal (or carbon dioxide production). Figure 3.19 shows the correlation between the calculated rate constants and the inverse of the reacting temperature. The energy of activation for maa oxidation in the presence of catalyst is seen to be 13.5 Kcal./mole (± 0.25).

FIGURE 3.17 : ORDER Plots for the Oxidation of MAA in the presence of Catalyst

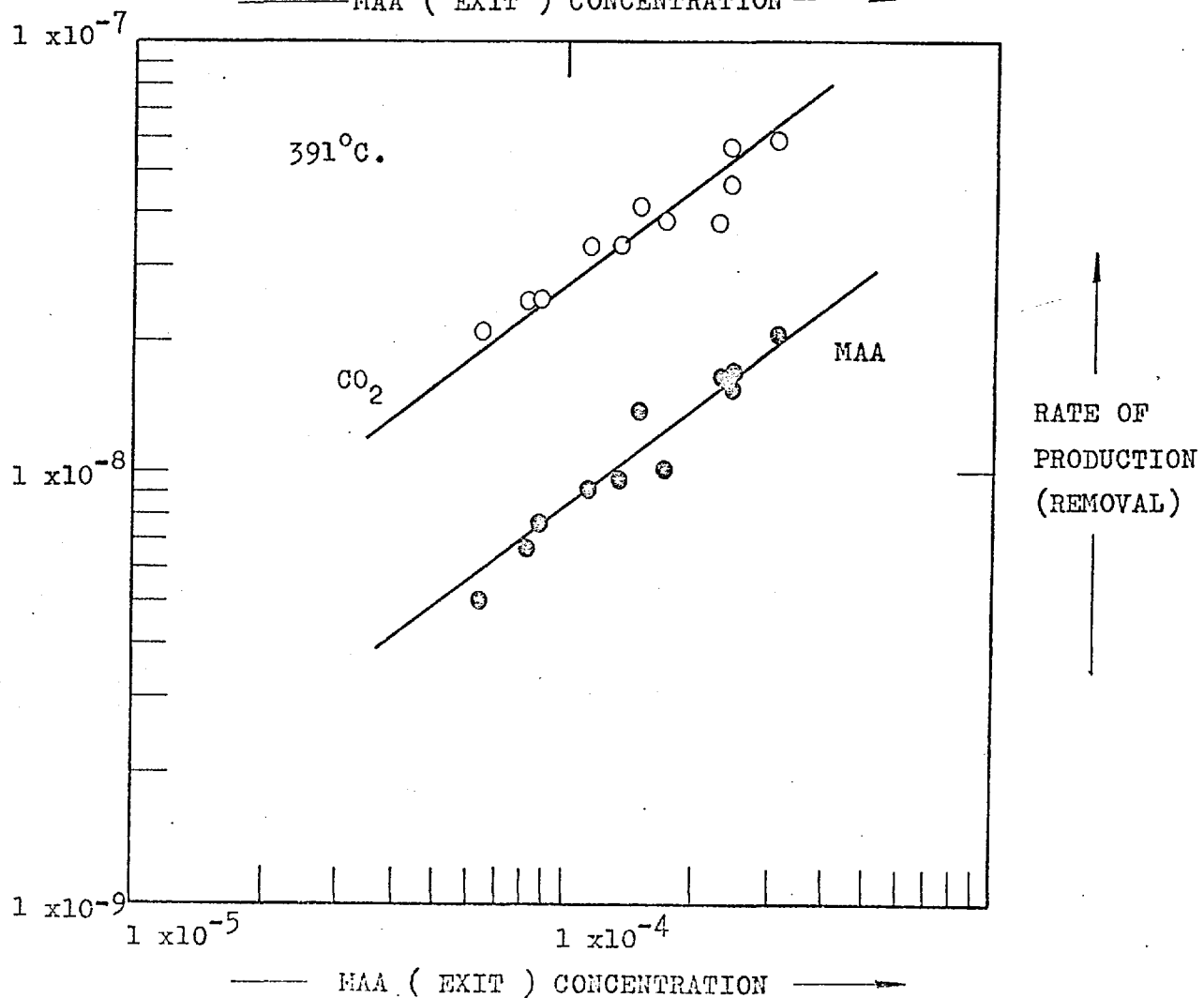
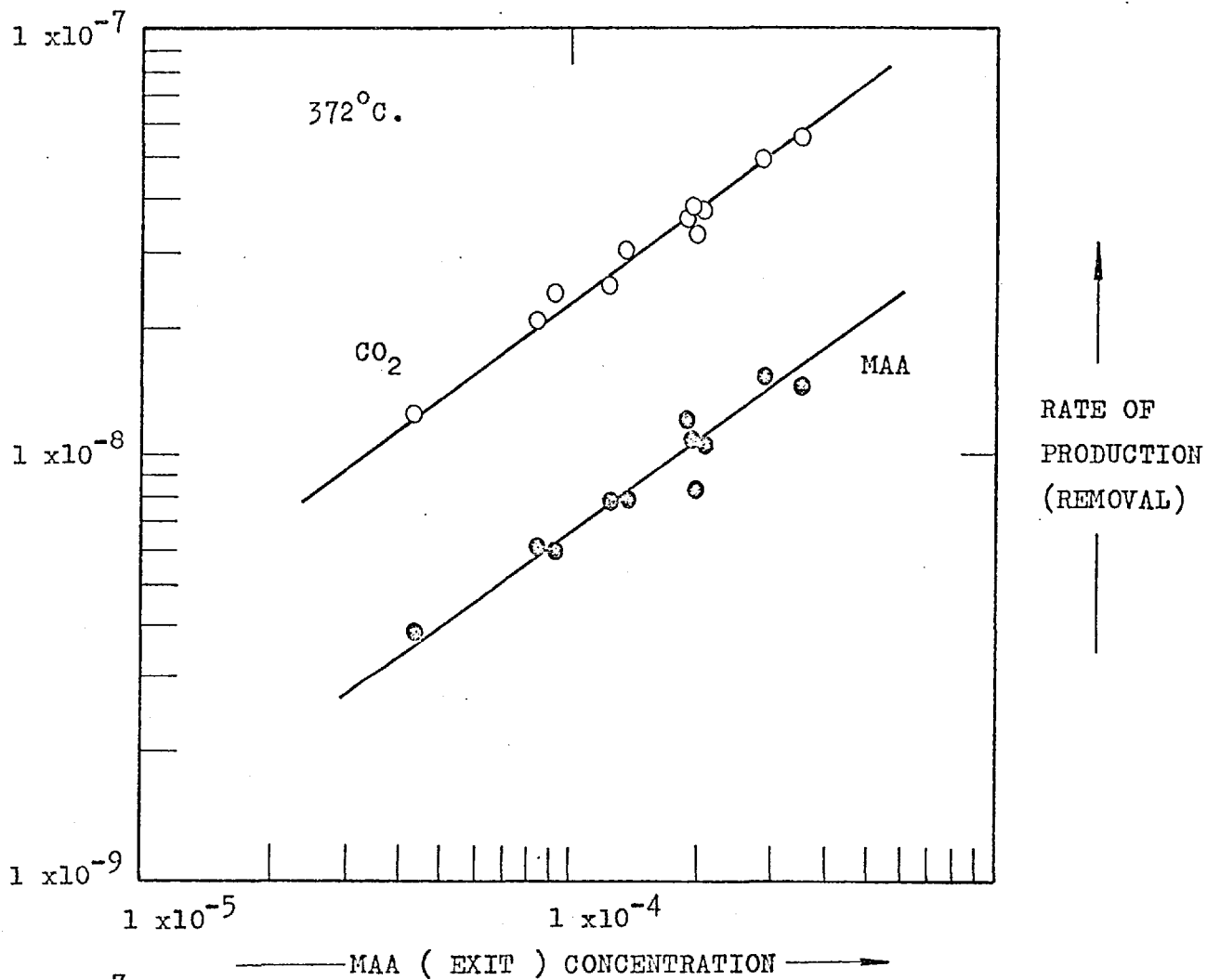
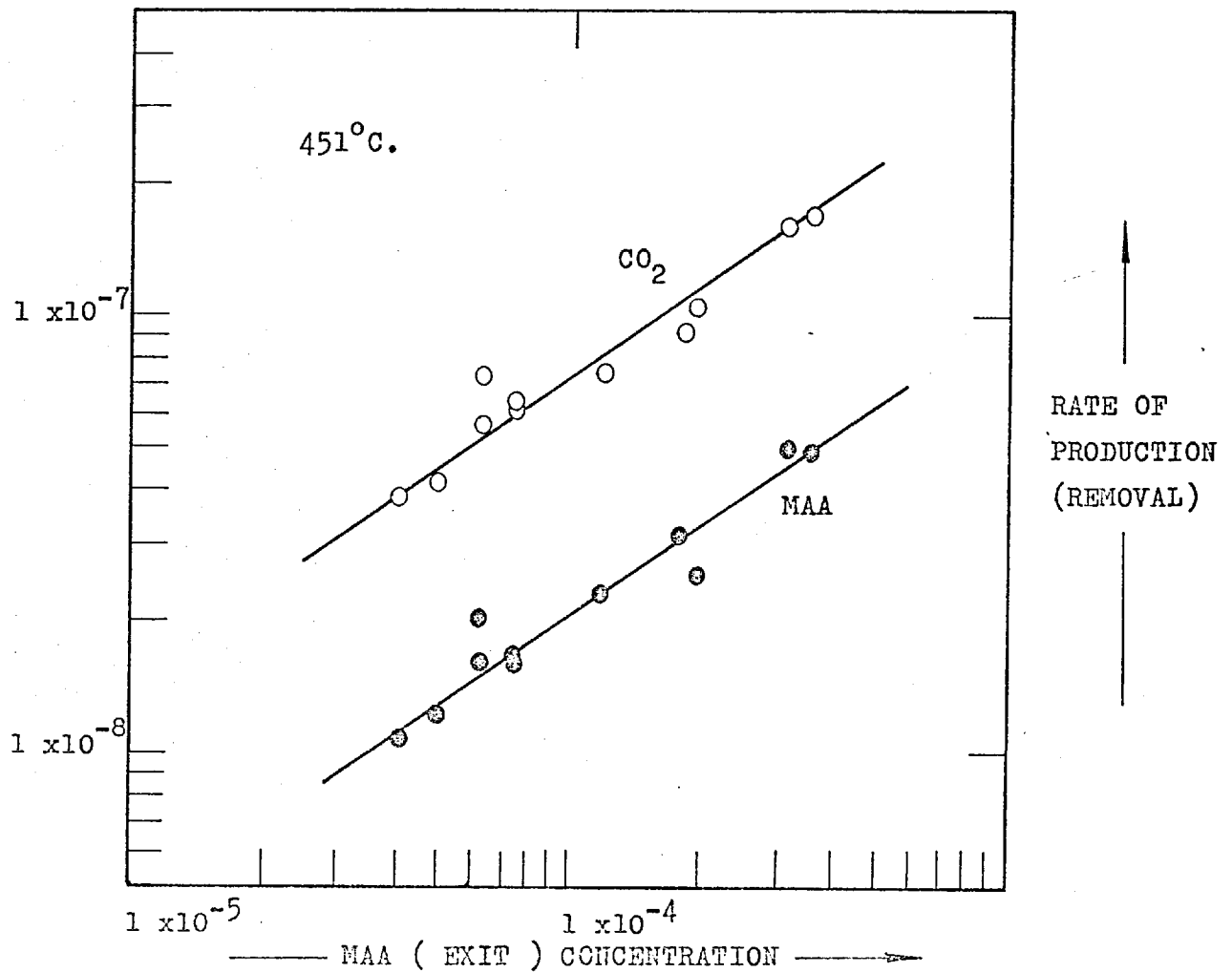
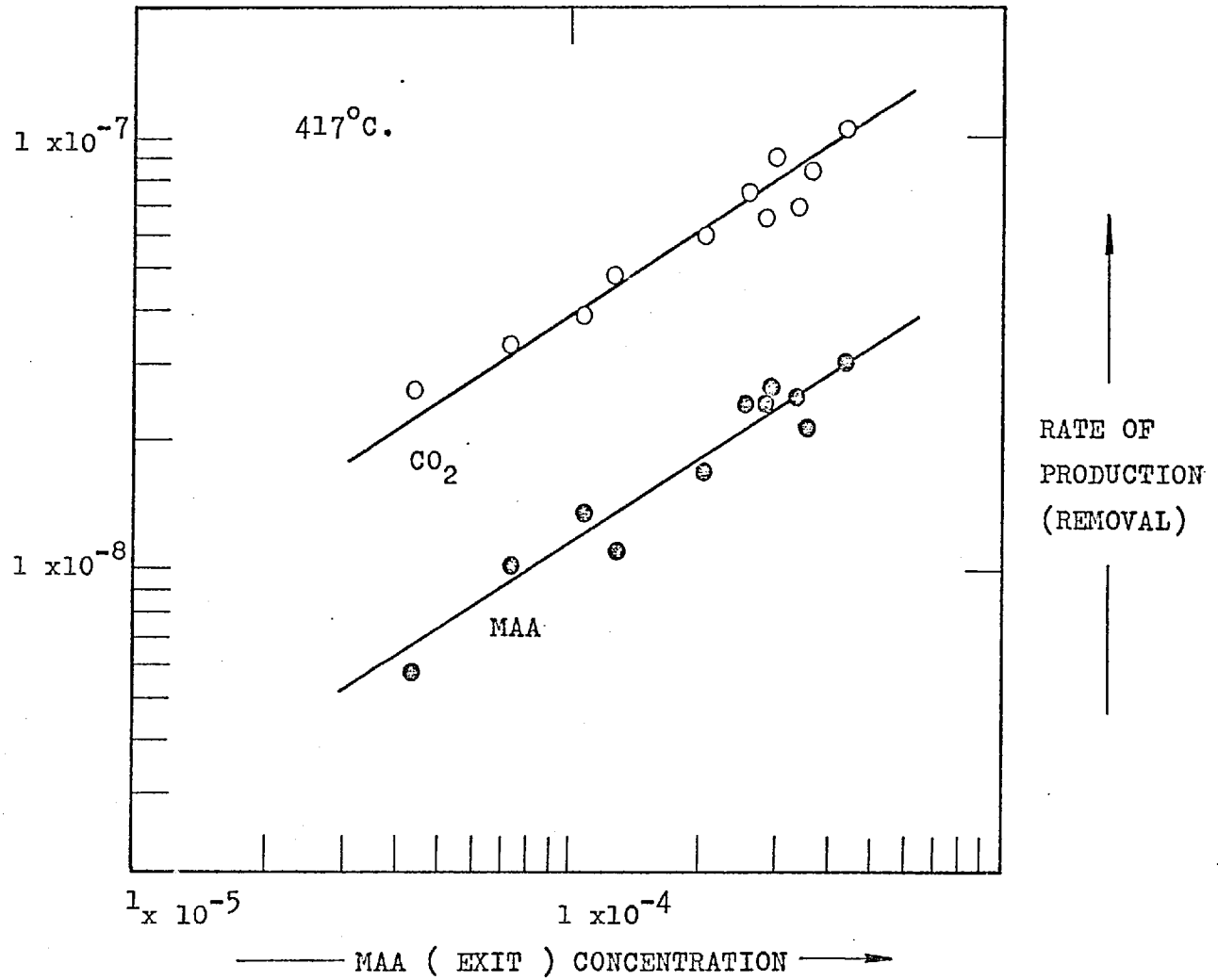


FIGURE 3.18 : ORDER Plots for the Oxidation of MAA in the presence of Catalyst



THE INFLUENCE OF TEMPERATURE ON THE RATE OF OXIDATION OF
MALEIC ANHYDRIDE TO CO₂ IN THE PRESENCE OF CATALYST.

The General Form of the Rate Expression is ,

$$r = k \times (\text{concn. of Maa})^n$$

where , the Rate (r) has units of $\frac{\text{m.gm.}}{\text{sec.}}$ ^{-1 -1}
the Rate Constant (k) has units of $\frac{\text{m. li.gm.}}{\text{sec.}}$ ^{1-n n -1 -1}
Concentration (Maa) has units of m./li.
and n is the order of reaction w.r.t. Maa concn.

The values of the Rate Constants and orders of reaction were
calculated using Unweighted Least Squares techniques.

<u>RATE EXPRESSION</u>	<u>TEMPERATURE</u>
$\frac{d\text{Maa}}{dt} = - 3.03 \times 10^{-6} (\text{Maa})^{0.67}$	----- 372°C.
$\frac{d\text{CO}_2}{dt} = 1.065 \times 10^{-5} (\text{Maa})^{0.67}$	
$\frac{d\text{Maa}}{dt} = - 4.06 \times 10^{-6} (\text{Maa})^{0.67}$	----- 391°C.
$\frac{d\text{CO}_2}{dt} = 1.48 \times 10^{-5} (\text{Maa})^{0.67}$	
$\frac{d\text{Maa}}{dt} = - 6.03 \times 10^{-6} (\text{Maa})^{0.67}$	----- 417°C.
$\frac{d\text{CO}_2}{dt} = 2.02 \times 10^{-5} (\text{Maa})^{0.67}$	
$\frac{d\text{Maa}}{dt} = - 9.35 \times 10^{-6} (\text{Maa})^{0.67}$	----- 451°C.
$\frac{d\text{CO}_2}{dt} = 3.29 \times 10^{-5} (\text{Maa})^{0.67}$	

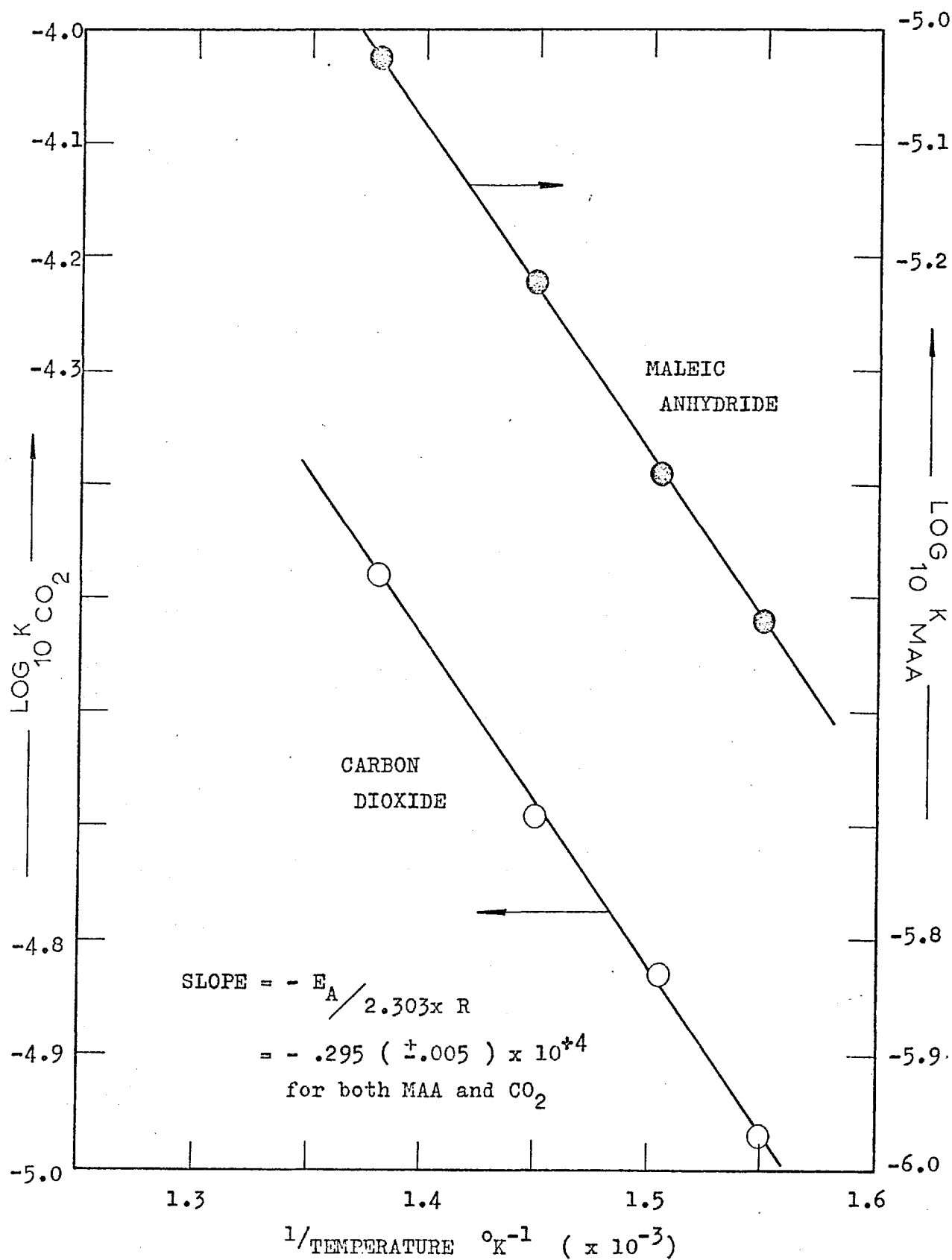


FIGURE 3.19 : ARRHENIUS PLOT FOR MAA OXIDATION IN THE PRESENCE OF CATALYST.

From the SLOPE of the plots , the ENERGY OF ACTIVATION (E_A) was calculated to be 13.5 ($\pm .25$) K.cal./mole.

4C Oxidation in the absence of catalyst

The previous experiments were repeated under identical conditions with the catalyst replaced by an exactly equal weight of $3/16''$ "Alundum" pellets. This resulted in a similar surface:volume ratio for the reactor operation, thus enabling differences in product yield and rate of reaction to be attributed to nature rather than extent of surface.

Tables 3.19 , 3.20 show the results obtained over the 79° temperature range. Increased amounts of formaldehyde were found in the product stream. Logarithmic order plots were constructed (see Figures 3.20 , 3.21), but the results show constant order kinetics only above 410°C . Below this temperature, the order of reaction changes with the maa reacting concentration. Strictly speaking, the order plots at 376°C and 393°C are best represented by curves, but approximations to linear dependence have been attempted above and below a maa reacting concentration of $0.3 \times 10^{-4} \text{ m/li}$

Least square analysis has been completed for each set of data obtained and the resulting rate expressions are given in Table 3.21.

Using the rate expressions developed from results at the two temperatures studied above 410°C , (constant order kinetics), an approximate value of the energy of activation was found to be $14.0 \text{ Kcal./mole } (\pm 0.5)$.

The most remarkable result derived from this series of experiments is seen from a comparison of rates of oxidation, above 400°C in the presence and in the absence of V_2O_5 catalyst surface. Comparison of the rate constants show

TABLE 3.19 : Oxidation of MAA in the ABSENCE of
catalyst : Results from the S.G.S.R.

15.12 gm. of ALUMINA Support Material held in the
Circular Basket of the S.G.S.R. ; Stirrer Speed : 3000 r.p.m.

C.Maa IN	C.O ₂ IN	Contact Time	C.Maa OUT	C.O ₂ OUT	C.CO ₂ OUT	Maa Oxd. Rate	CO ₂ Prod. Rate	Carbon Balance
m./li. ($\times 10^{-3}$)	m./li. ($\times 10^{-3}$)	gm.ml. ⁻¹ sec.	m./li. ($\times 10^{-3}$)	m./li. ($\times 10^{-3}$)	m./li. ($\times 10^{-3}$)	m.gm. ⁻¹ sec. ⁻¹ ($\times 10^{-7}$)	m.gm. ⁻¹ sec. ⁻¹ ($\times 10^{-7}$)	%

TEMPERATURE : 376°C.

.389	26.1	1.67	.227	25.5	.628	.97	3.76	*100.
.185	26.2	2.79	.0273	25.7	.593	.565	2.13	95.
.0475	8.2	1.65	.011	8.15	.136	.221	.825	95.5
.080	8.2	2.75	.0141	8.07	.237	.240	.832	* 93.
.089	8.16	4.15	.0102	7.86	.295	.191	.712	95.5
.272	4.07	1.66	.154	3.62	.466	.711	2.81	*100.
.236	4.05	2.75	.062	3.42	.688	.633	2.51	* 98.5
.281	4.08	4.17	.044	3.28	.825	.569	1.98	* 92.5
.060	4.02	4.12	.0065	3.88	.203	.130	.493	98.
.101	16.75	2.74	.0123	15.8	.339	.324	1.24	96.
.700	16.75	2.74	.448	15.6	1.150	.920	4.20	*105.
.133	12.1	4.11	.015	11.7	.475	.287	1.16	101.
.980	11.4	3.88	.492	10.0	1.800	1.260	4.64	* 96.
.612	11.15	3.79	.306	10.7	1.050	.807	2.77	* 93.5
.936	11.9	4.04	.530	10.55	1.420	1.005	3.51	* 94.5

TEMPERATURE : 393°C.

.085	26.2	1.63	.0123	25.7	.288	.446	1.77	99.
.100	25.9	2.69	.0082	25.2	.322	.369	1.20	* 89.5
.080	26.4	4.10	.0041	25.9	.288	.185	.70	95.
.163	8.15	1.62	.022	7.65	.509	.870	3.14	* 98.
.220	4.03	1.60	.063	3.56	.610	.981	3.81	* 98.
.160	4.13	2.73	.0165	3.62	.543	.526	1.99	* 95.
.130	4.03	4.12	.008	3.67	.458	.297	1.11	* 95.
.570	16.5	2.62	.221	14.8	1.250	1.330	4.78	* 93.5
.838	12.15	4.02	.240	10.0	2.340	1.490	5.82	* 98.
.175	20.05	1.90	.038	19.3	.543	.721	2.85	100.
.590	17.9	2.83	.188	16.6	1.42	1.420	5.01	* 92.5
.326	20.3	1.61	.112	19.3	.73	1.325	4.53	* 93.5

(* indicates large Traces of Formaldehyde, not included in the
Carbon Balance.)

TABLE 3.20

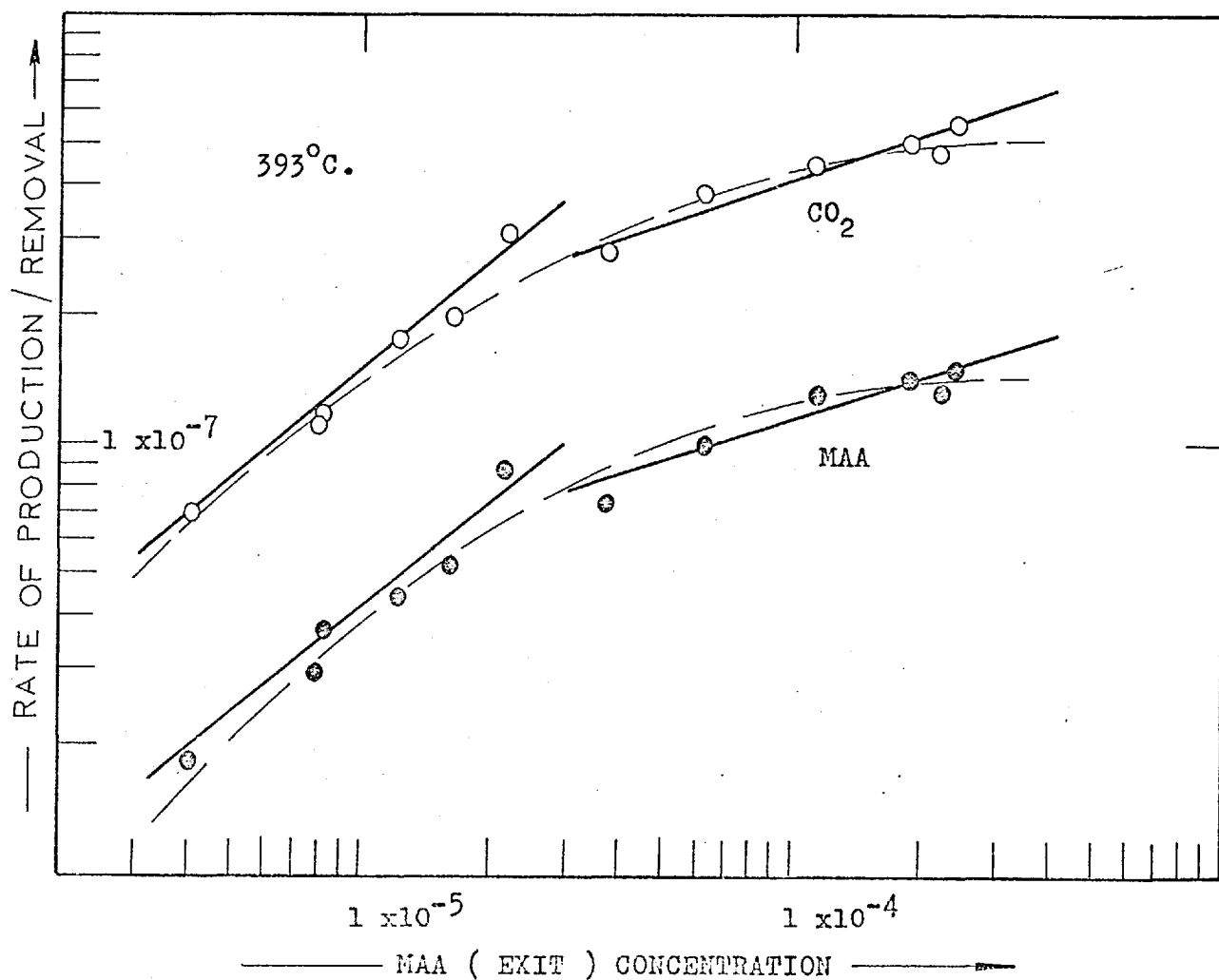
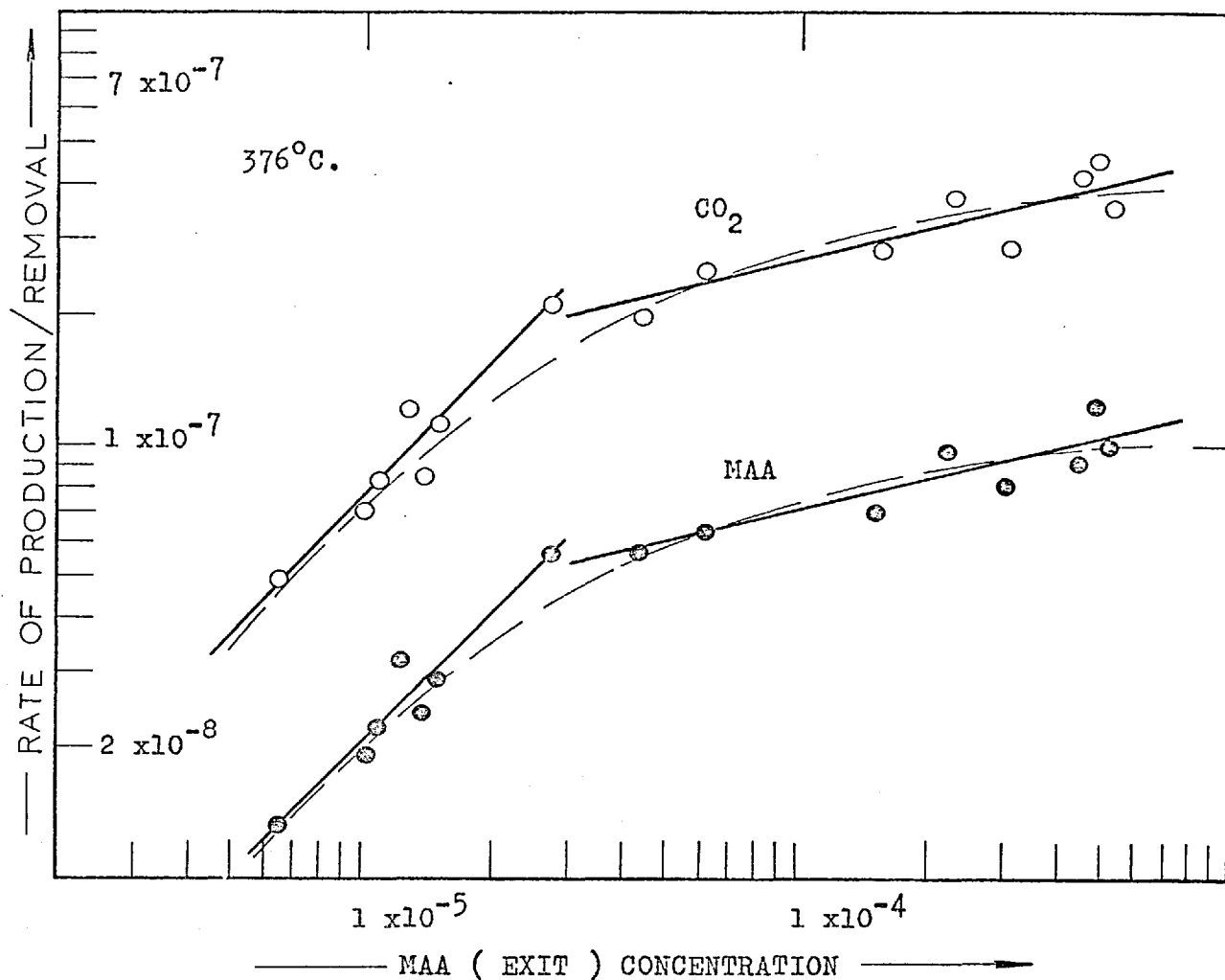
15.12 gm. of ALUMINA Support Material held in the
Circular Basket of the S.G.S.R. ; Stirrer Speed : 3000 r.p.m.

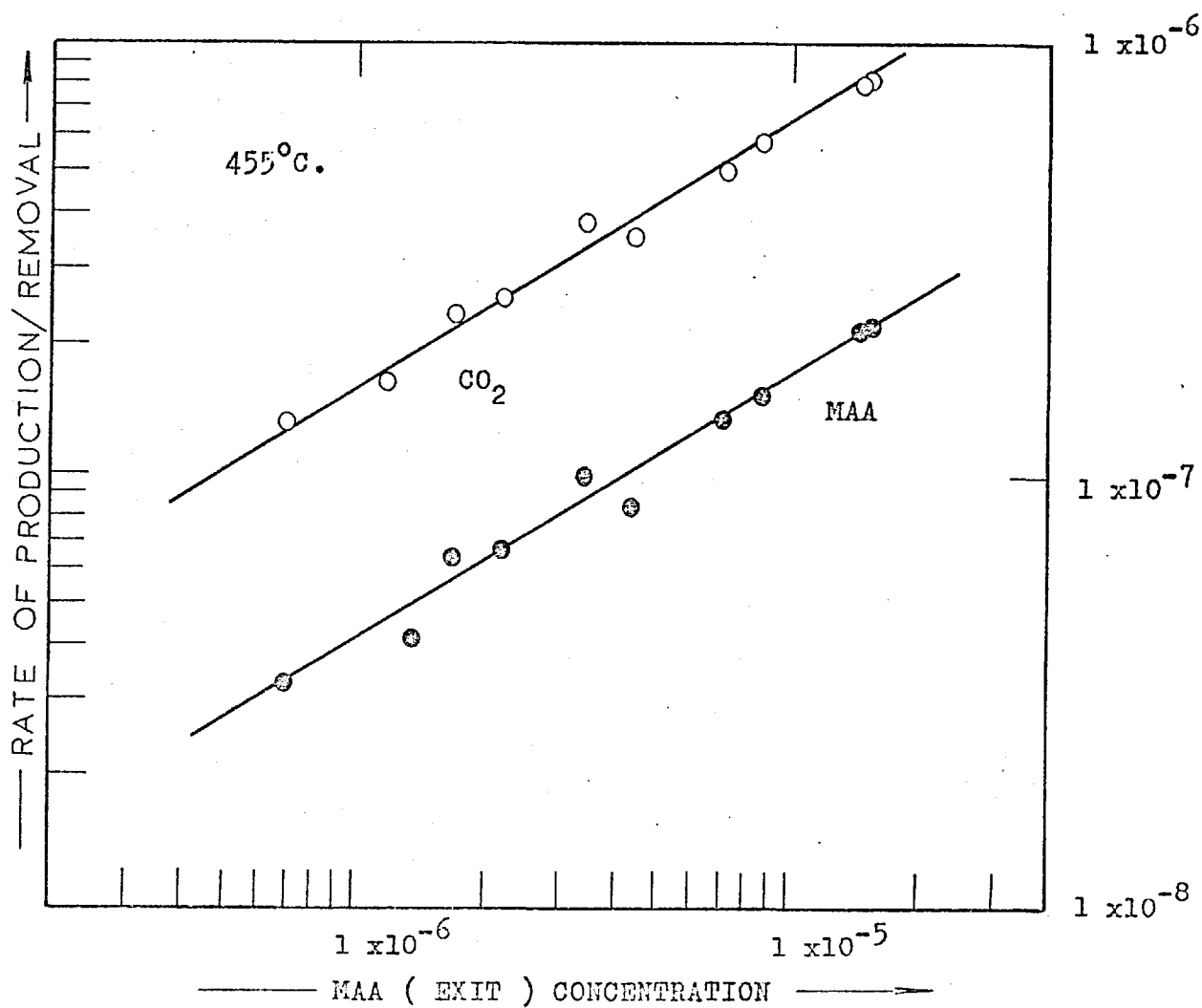
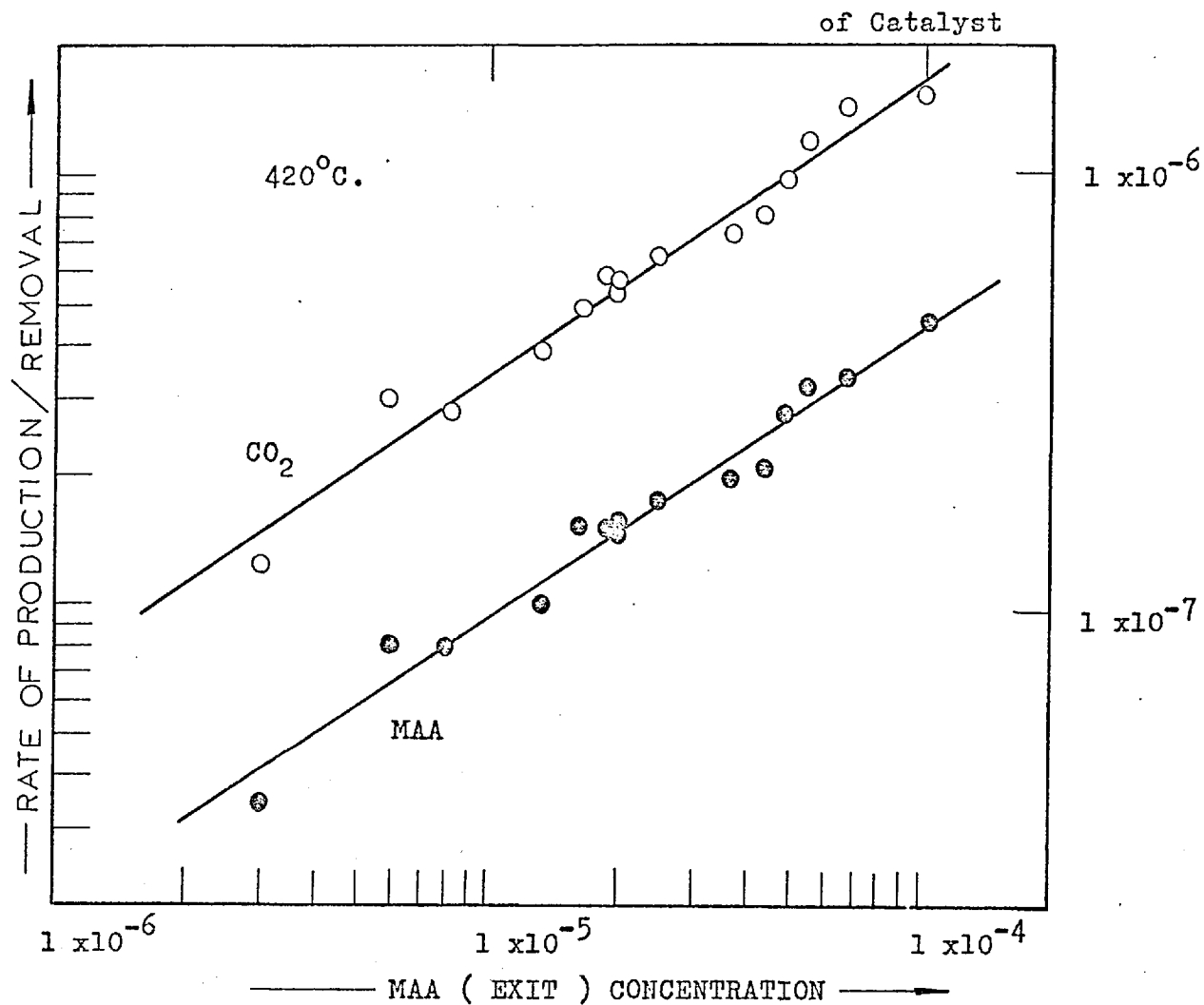
C.Maa IN	C.O ₂ IN	Contact Time	C.Maa OUT	C.O ₂ OUT	C.CO ₂ m./li.	Maa Oxd. Rate	CO ₂ Prod. Rate	Carbon Balance
m./li. (x10 ⁻³)	m./li. (x10 ⁻³)	gm.ml. ⁻¹ sec.	m./li. (x10 ⁻³)	m./li. (x10 ⁻³)	m./li. (x10 ⁻³)	m.gm. ⁻¹ sec. ⁻¹ (x10 ⁻⁷)	m.gm. ⁻¹ sec. ⁻¹ (x10 ⁻⁷)	%
TEMPERATURE : 420°C.								
.37	26.3	1.57	.044	25.0	1.27	2.07	8.10	98.
.48	26.0	1.55	.049	24.3	1.525	2.78	9.90	* 90.5
.60	25.9	1.55	.068	24.0	2.24	3.43	14.45	104.5
.55	26.0	2.59	.037	24.2	1.90	1.98	7.33	* 93.
.70	26.2	3.77	.025	23.5	2.44	1.79	6.48	* 91.5
.25	7.99	1.53	.0165	7.09	.747	1.525	4.88	100.
.211	7.99	2.55	.006	7.12	.78	.804	3.05	96.
.250	4.06	1.55	.019	3.31	.90	1.49	5.81	97.5
.265	3.96	2.52	.0135	3.07	.97	1.00	3.85	* 97.
.209	3.97	2.53	.0082	3.37	.71	.791	2.80	* 91.
.138	4.15	3.97	.003	3.68	.492	.34	1.24	92.5
.42	16.9	2.59	.020	15.6	1.475	1.545	5.70	* 93.
1.80	11.85	3.77	.104	5.65	5.75	4.51	15.25	* 95.5
.25	20.8	1.57	.020	20.0	.848	1.47	5.41	* 93.
.545	19.8	1.53	.055	18.3	1.84	3.21	12.10	* 95.5

TEMPERATURE : 455°C.								
.151	26.3	1.49	.0034	25.7	.56	.984	3.76	* 95.5
.161	26.3	2.48	.0017	25.2	.577	.641	2.33	* 91.
.125	26.5	3.74	.0007	25.9	.492	.334	1.315	99.
.230	4.05	1.47	.0087	3.32	.848	1.50	5.77	97.
.167	4.08	2.47	.0022	3.52	.628	.667	2.54	96.5
.150	4.02	3.63	.0012	3.52	.594	.411	1.64	100.
.339	16.8	2.44	.0071	15.0	1.22	1.36	5.00	* 92.5
.532	16.4	2.38	.0148	14.5	1.90	2.17	7.98	* 92.
.301	11.9	3.59	.0044	10.45	1.255	.826	3.50	105.5
.335	20.3	1.47	.0153	19.4	1.20	2.18	8.16	* 94.

(* indicates large Traces of Formaldehyde , not included in
the Carbon Balance.)

FIGURE 3.20 : ORDER Plots for the Oxidation of MAA in the
absence of Catalyst





THE INFLUENCE OF TEMPERATURE ON THE RATE OF OXIDATION OF
MALEIC ANHYDRIDE TO CO₂ IN THE ABSENCE OF CATALYST.

The General Form of the Rate Expression is ,

$$r = k \times (\text{concn. of Maa})^n$$

where , the Rate (r) has units of $\frac{\text{m.gm.}}{\text{sec.}}$
the Rate Constant (k) has units of $\frac{\text{m. li.gm.}}{\text{sec.}}$
Concentration (Maa) has units of $\frac{\text{m.}}{\text{li.}}$
and n is the order of reaction w.r.t. Maa concn.

The values of the Rate Constants and orders of reaction were
calculated using Unweighted Least Squares techniques.

RATE EXPRESSION		TEMPERATURE
Reacting (exit) Maa Concs. $3 \times 10^{-5} \text{m./li.}$	Reacting (exit) Maa Concs. $3 \times 10^{-5} \text{m./li.}$	
$\frac{d\text{Maa}}{dt} = -2.15 \times 10^{-3} (\text{Maa})^{1.0}$	$\frac{d\text{Maa}}{dt} = -5.84 \times 10^{-7} (\text{Maa})^{0.23}$	--- 376°C.
$\frac{d\text{CO}_2}{dt} = 8.28 \times 10^{-3} (\text{Maa})^{1.0}$	$\frac{d\text{CO}_2}{dt} = 2.37 \times 10^{-6} (\text{Maa})^{0.23}$	
$\frac{d\text{Maa}}{dt} = -7.93 \times 10^{-4} (\text{Maa})^{0.86}$	$\frac{d\text{Maa}}{dt} = -1.44 \times 10^{-6} (\text{Maa})^{0.27}$	--- 393°C.
$\frac{d\text{CO}_2}{dt} = 3.05 \times 10^{-3} (\text{Maa})^{0.86}$	$\frac{d\text{CO}_2}{dt} = 4.73 \times 10^{-6} (\text{Maa})^{0.27}$	
$\frac{d\text{Maa}}{dt} = -1.97 \times 10^{-4} (\text{Maa})^{0.67}$		----- 420°C.
$\frac{d\text{CO}_2}{dt} = 8.00 \times 10^{-4} (\text{Maa})^{0.67}$		
$\frac{d\text{Maa}}{dt} = -3.63 \times 10^{-4} (\text{Maa})^{0.67}$		----- 455°C.
$\frac{d\text{CO}_2}{dt} = 1.38 \times 10^{-3} (\text{Maa})^{0.67}$		

that homogeneous oxidation of maa, initiated by steel surface, is reduced by a factor of 30-40 times by the introduction of catalyst.

The conclusion emerges that the vanadia-molybdena surface is removing chain-propagating species necessary for the continuing combustion of maleic anhydride, initiated on the stainless steel surface.

5 Kinetics of the overall oxidation of Benzene to Maleic Anhydride in the S.G.S.R. system

5A Introduction

It is important in a study of this kind to measure the effect of temperature on the overall reaction kinetics of benzene oxidation to maa. Results in tubular reactors have conclusively shown the presence of homogeneous reactions other than maa over-oxidation. Therefore the influence of temperature on the homogeneous rate must be investigated as the activation energies for homogeneous and heterogeneous reaction routes will presumably be different. This difference will be reflected in differing product selectivity at various temperatures. It was decided to study the effects of temperature variation on overall rates of reaction in the S.G.S.R. system for the following reasons. Apart from the advantages gained from the relative ease of interpretation of data, the S.G.S.R. allowed the study of free volume effects in the presence of active catalyst surface. This is not possible in tubular reactors where free volume and surface:volume effects can only be studied after the reacting

gases have left the catalyst bed. In any catalyst bed, gas-phase reactions will be subject to catalytic surface effects, therefore use of the S.G.S.R. should give results of more realistic value.

Experiments were carried out with catalyst loaded in the circular basket, as evaluation of maa over-oxidation kinetics had previously been determined using this basket and incorporation of these results into present studies was envisaged.

The oxidation reactions were studied over a 77° temperature range; at 376°C, 393°C, 415°C and 453°C. Earlier work in the S.G.S.R. system at 376°C and 453°C, where the influence of free volume on overall product conversion had been studied (2B and 2C), meant that it was only necessary to perform further experiments at temperatures of 393°C and 415°C. As before, benzene feed concentrations were varied from 1.5 to 20 mole %, and the total throughput was varied for each fixed benzene input concentration using total flows of 100, 150 and 250 ml.min⁻¹. A stirrer speed of 3000 r.p.m. was used and the total reactor pressure was ca 1 atmosphere in all cases.

5B Influence of temperature on product conversion and reaction rate

A full list of results for experiments performed under the above conditions appears in Tables 3.22, 3.23 (plus Tables 3.1, 3.2 from 2B and 2C). Product conversion for a fixed benzene input concentration is shown as a function of catalyst contact time in Figures 3.22, 3.23, 3.24. Conversion as a function of temperature is shown at constant

C.Bz _{in}	C.O _{2in}	Contact Time	C.Bz _{out}	C.O _{2out}	C.Maa	C.CO ₂	Carbon Balance
m./li. (x10 ⁻³)	m./li. (x10 ⁻³)	gm.ml. ⁻¹ sec.	m./li. (x10 ⁻³)	m./li. (x10 ⁻³)	m./li. (x10 ⁻³)	m./li. (x10 ⁻³)	%

Temperature : 376°C.

.584	27.0	1.67	.444	26.15	.059	.609	100.5
1.87	25.3	1.66	1.57	25.3	.106	1.36	100.
3.73	22.8	1.68	3.28	19.8	.136	2.55	101.5
7.98	11.95	1.68	7.6	8.7	.09	1.715	99.5
.628	27.0	2.77	.405	25.8	.095	1.055	102.5
1.6	25.3	2.77	1.21	23.6	.146	1.8	100.
3.29	22.8	2.83	2.63	20.7	.238	2.75	99.
6.28	11.2	2.93	5.76	8.66	.125	2.44	99.5
.629	27.2	4.16	.30	26.2	.124	1.292	95.5
1.82	26.0	4.16	1.20	24.0	.254	2.69	100.
3.12	23.2	4.27	2.35	20.3	.295	3.57	100.5
6.48	13.1	4.38	5.57	8.58	.19	3.565	97.

Temperature : 393°C.

.73	26.2	1.62	.516	25.2	.099	.882	100.
1.91	25.4	1.61	1.50	23.6	.182	1.765	101.
3.67	22.8	1.64	3.13	19.8	.224	2.44	101.
7.12	11.1	1.68	6.47	8.55	.144	2.3	97.
.606	26.75	2.71	.32	25.15	.125	1.162	98.5
1.66	24.8	2.71	1.145	22.1	.245	2.325	103.5
3.55	22.8	2.74	2.735	19.6	.337	3.505	100.
6.66	11.75	2.83	5.90	8.45	.242	3.66	101.
.606	27.8	4.06	.23	26.2	.16	1.56	98.5
1.575	24.5	4.06	.94	21.6	.292	2.98	103.5
3.10	23.1	4.17	2.13	18.5	.372	4.38	100.
6.49	13.0	4.26	5.10	8.7	.325	5.025	95.

Stirrer Speed : 3000 r.p.m. , 15.11 gm. of Catalyst 1 .

TABLE 3.22 : Effect of Temperature on the Oxidation of Benzene.

Results from S.G.S.R. / Circular Basket.

C.Bz _{in}	C.O _{2in}	Contact Time	C.Bz _{out}	C.O _{2out}	C.Maa	C.CO ₂	Carbon Balance
m./li. (x10 ⁻³)	m./li. (x10 ⁻³)	gm.ml. ⁻¹ sec.	m./li. (x10 ⁻³)	m./li. (x10 ⁻³)	m./li. (x10 ⁻³)	m./li. (x10 ⁻³)	%

Temperature : 415°C.

.63	27.6	1.56	.40	26.0	.101	.955	100.
2.0	25.6	1.54	1.45	24.2	.24	2.29	99.5
3.52	22.7	1.58	2.79	20.1	.316	3.12	100.
6.5	12.1	1.62	5.62	8.65	.227	2.83	96.5
.59	27.6	2.59	.264	26.2	.136	1.36	98.5
1.44	25.9	2.59	.871	24.0	.259	2.465	101.
3.63	23.2	2.62	2.53	20.0	.445	4.69	99.5
6.81	13.1	2.68	5.53	8.65	.323	4.60	95.5
.605	27.8	3.89	.183	26.8	.157	1.742	95.5
1.66	25.6	3.89	.838	22.8	.336	3.93	103.
3.4	23.4	3.96	2.07	19.5	.493	6.09	100.
6.5	13.1	4.06	4.84	8.45	.39	6.50	95.5

Temperature : 453°C.

.606	27.6	1.475	.32	25.9	.106	1.29	99.
1.875	26.0	1.465	1.16	23.9	.26	3.25	100.
3.56	23.2	1.495	2.39	18.8	.48	5.175	100.
7.06	14.4	1.525	5.62	8.45	.522	6.07	99.
.653	27.5	2.47	.242	25.2	.144	1.95	102.
1.662	25.6	2.47	.82	23.0	.329	4.06	103.
3.44	23.4	2.50	1.95	17.3	.56	6.71	100.
7.07	14.75	2.54	5.20	8.45	.648	8.61	99.
.63	28.0	3.69	.168	26.5	.159	2.27	103.5
1.67	26.05	3.69	.634	21.3	.317	5.02	101.
3.12	23.1	3.78	1.44	16.1	.555	7.86	100.
6.68	14.4	3.86	4.42	8.4	.642	11.00	101.

Stirrer Speed : 3000 r.p.m. , 15.11 gm. of Catalyst 1 .

TABLE 3.22 (contd.)

TEMPERATURE : 376°C.

CONV. OF BZ	BENZENE OXD. RATE -1 -1 m.gm.sec.	CONV. TO MAA %	CONV. TO CO ₂ %
24.0	.842 x10 ⁻⁷	10.00	104.5
16.05	1.810	5.77	72.7
12.05	2.680	3.65	68.4
4.8	2.270	1.13	21.5
35.5	.806	15.10	168.0
24.4	1.410	9.13	112.5
20.0	2.330	7.25	83.6
8.3	1.785	1.99	38.8
52.0	.790	19.75	205.0
34.0	1.490	13.95	148.0
24.7	1.800	9.46	114.5
14.0	2.070	2.93	55.0

TEMPERATURE : 393°C.

CONV. OF BZ	BENZENE OXD. RATE -1 -1 m.gm.sec.	CONV. TO MAA %	CONV. TO CO ₂ %
29.3	1.32 x10 ⁻⁷	13.56	120.7
21.5	2.545	9.55	92.3
14.7	3.290	6.10	66.5
9.1	3.880	2.06	32.3
47.1	1.055	20.60	191.8
31.0	1.900	14.75	140.0
23.0	2.970	9.50	98.8
11.5	2.690	3.65	55.0
62.0	.926	26.50	257.0
40.3	1.565	18.50	189.0
31.2	2.330	12.00	141.5
21.4	3.260	5.00	77.5

TEMPERATURE : 415°C.

CONV. OF BZ	BENZENE OXD. RATE -1 -1 m.gm.sec.	CONV. TO MAA %	CONV. TO CO ₂ %
36.5	1.475 x10 ⁻⁷	16.00	151.5
27.5	3.57	12.00	114.5
20.75	4.63	8.95	88.6
13.5	5.93	3.50	43.6
55.25	1.26	23.10	231.0
39.5	2.19	18.00	171.0
30.3	3.82	12.25	129.0
18.8	4.77	4.75	67.6
69.8	1.085	25.90	287.0
49.5	2.11	20.25	237.0
39.0	3.36	14.50	179.0
25.5	4.08	6.00	100.0

TEMPERATURE : 453°C.

CONV. OF BZ	BENZENE OXD. RATE -1 -1 m.gm.sec.	CONV. TO MAA %	CONV. TO CO ₂ %
47.1	1.94 x10 ⁻⁷	17.5	213.0
38.2	4.87	14.0	173.0
33.0	7.83	13.5	145.5
20.4	9.49	7.5	86.0
63.0	1.67	22.1	299.0
50.7	3.43	19.75	244.0
44.6	5.97	16.3	195.0
26.5	7.38	9.2	121.5
73.5	1.25	25.2	360.0
62.0	2.82	19.0	300.0
53.9	4.45	17.8	252.0
33.9	5.86	9.6	165.0

TABLE 3.23

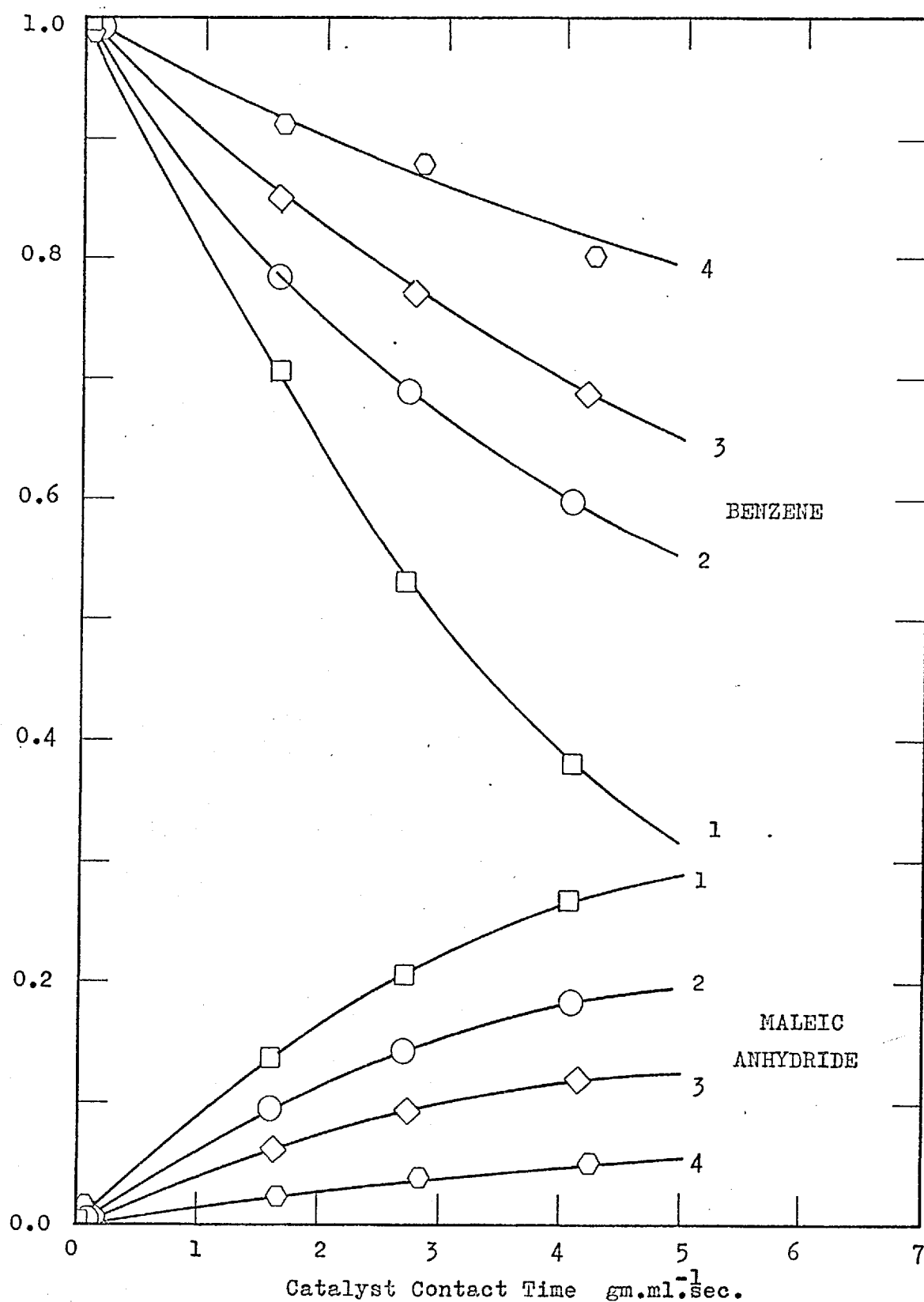


FIGURE 3.22 : Product Conversion vs. Contact Time at 393°C .
for a variety of input O_2/Fuel Ratios.

Feed Conditions : 1 ; $\text{C.Bz}_{\text{in}} = .70 \times 10^{-3}$; $\text{C.O}_{2\text{in}} = 27 \times 10^{-3} \text{ m./li.}$
 2 ; $\text{C.Bz}_{\text{in}} = 1.7 \times 10^{-3}$; $\text{C.O}_{2\text{in}} = 24.8 \times 10^{-3} \text{ m./li.}$
 3 ; $\text{C.Bz}_{\text{in}} = 3.5 \times 10^{-3}$; $\text{C.O}_{2\text{in}} = 22.8 \times 10^{-3} \text{ m./li.}$
 4 ; $\text{C.Bz}_{\text{in}} = 6.8 \times 10^{-3}$; $\text{C.O}_{2\text{in}} = 12 \times 10^{-3} \text{ m./li.}$

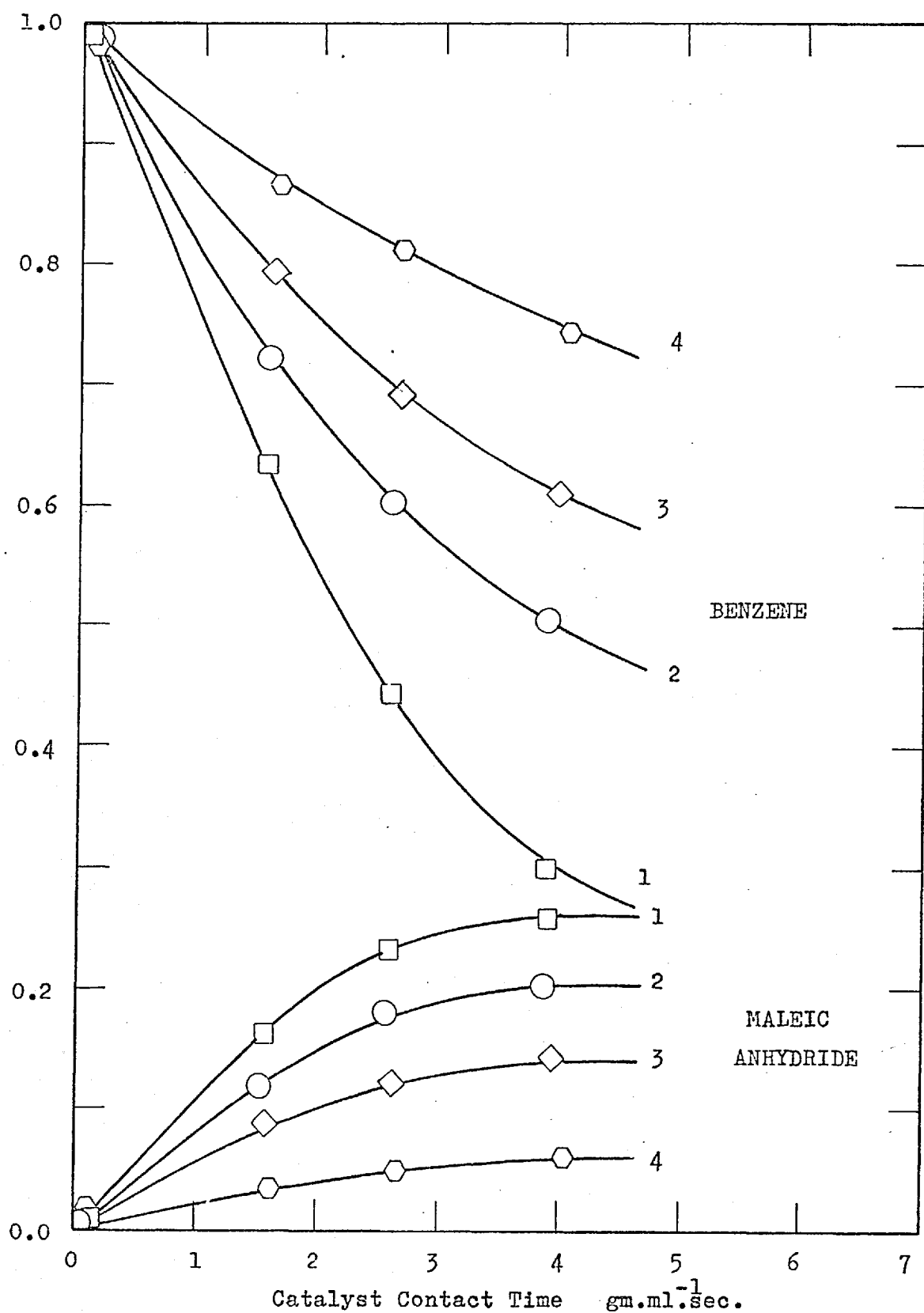
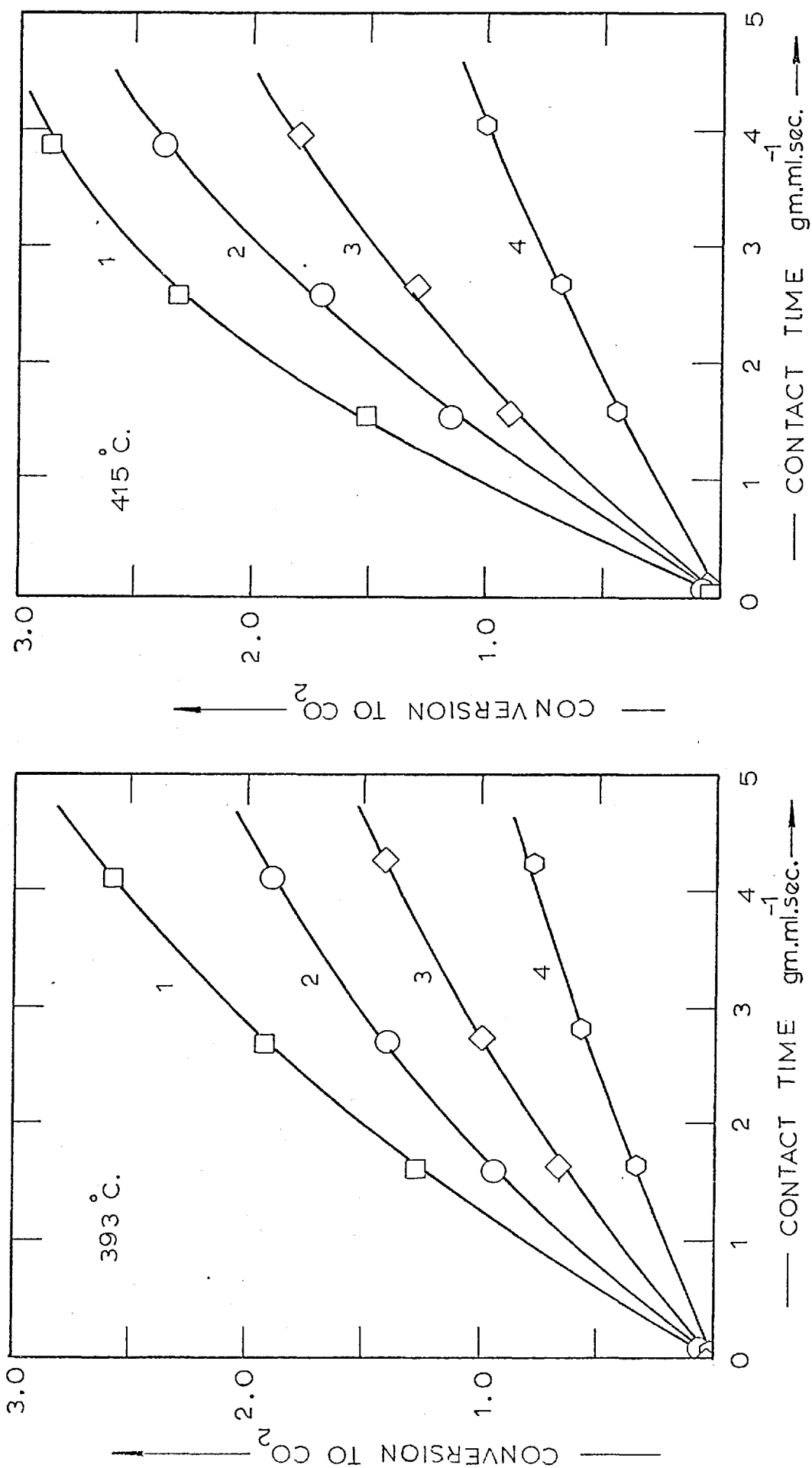


FIGURE 3.23 : Product Conversion vs. Contact Time at 415°C .
for a variety of input O_2/Fuel Ratios.

Feed Conditions : 1 ; $\text{C.Bz}_{\text{in}} = .61 \times 10^{-3}$; $\text{C.O}_{2\text{in}} = 27.8 \times 10^{-3} \text{ m./li.}$
 2 ; $\text{C.Bz}_{\text{in}} = 1.7 \times 10^{-3}$; $\text{C.O}_{2\text{in}} = 25.6 \times 10^{-3} \text{ m./li.}$
 3 ; $\text{C.Bz}_{\text{in}} = 3.5 \times 10^{-3}$; $\text{C.O}_{2\text{in}} = 23.1 \times 10^{-3} \text{ m./li.}$
 4 ; $\text{C.Bz}_{\text{in}} = 6.6 \times 10^{-3}$; $\text{C.O}_{2\text{in}} = 12.8 \times 10^{-3} \text{ m./li.}$

FIGURE 3.24 : Conversion to CO_2 vs. Contact Time at 393°C .
and 415°C . for a variety of input O_2/Fuel Ratios.

Feed Conditions : 1, 2, 3 and 4 have values as in FIGS. 3.22, 3.23



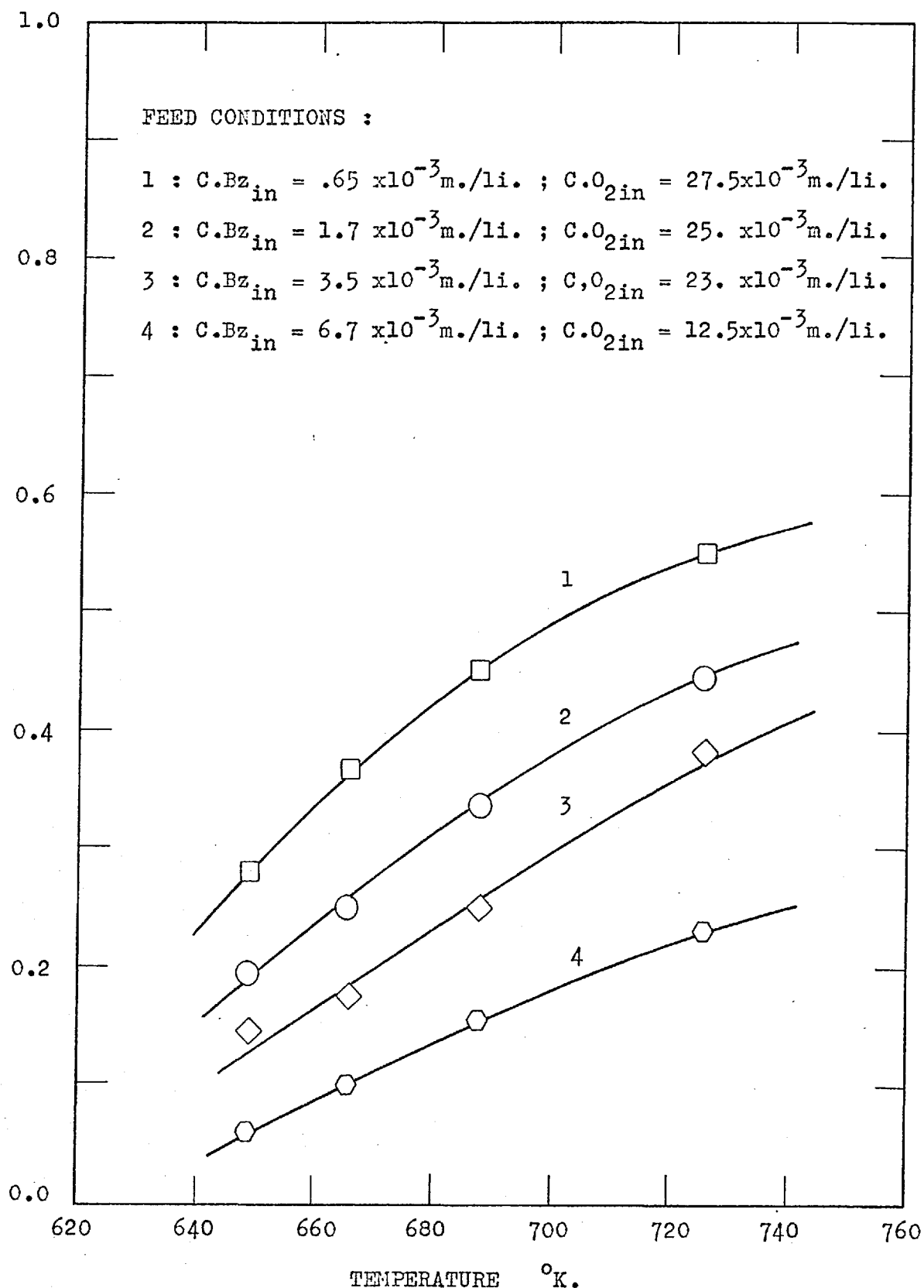


FIGURE 3.25 : Benzene Conversion as a Function of Temperature
Results at a constant Contact Time of
2 gm.ml⁻¹.sec.

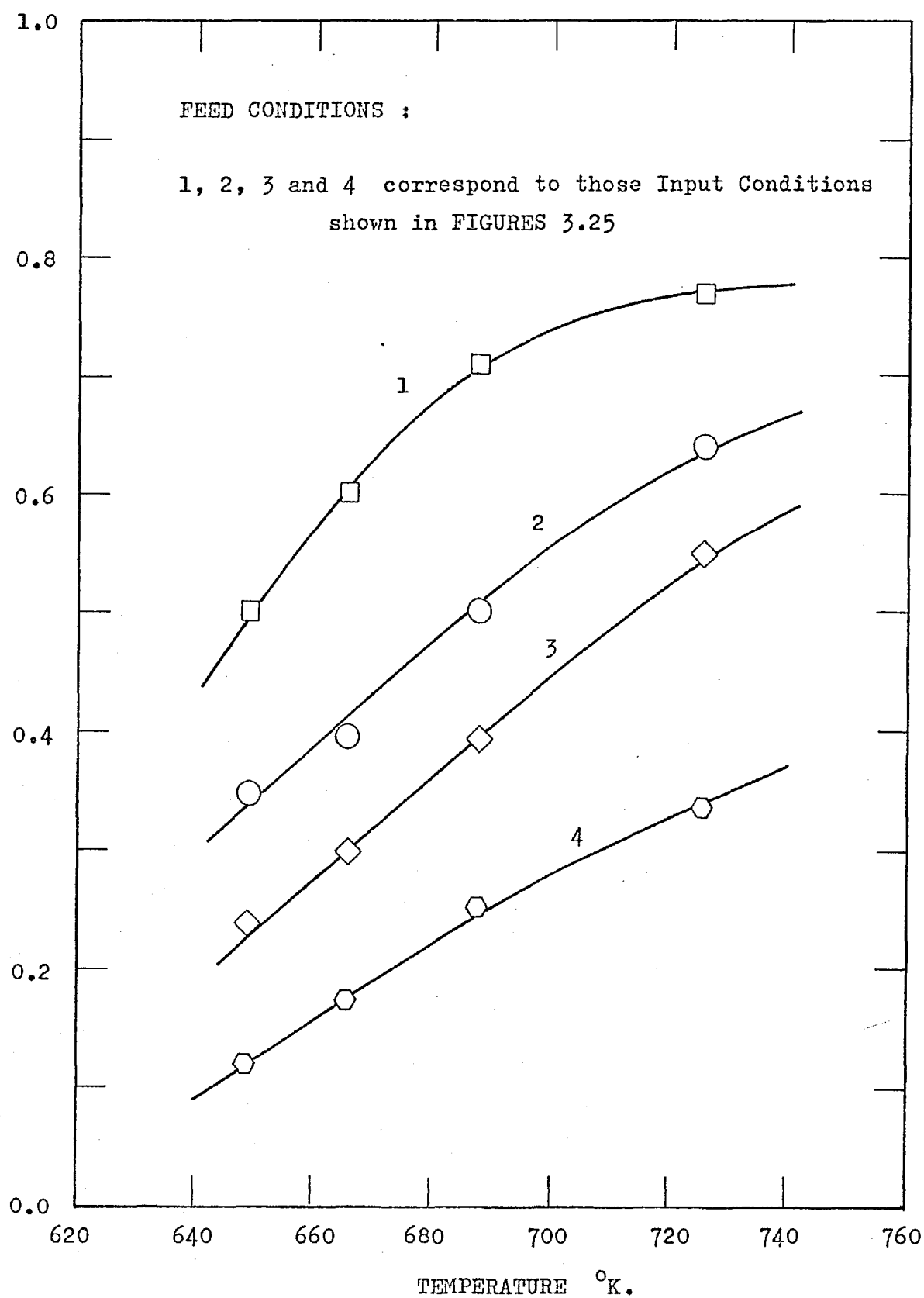


FIGURE 3.26 : Benzene Conversion as a Function of Temperature
Results at a constant Catalyst Contact Time
of $4 \text{ gm.ml.}^{-1}\text{sec.}$

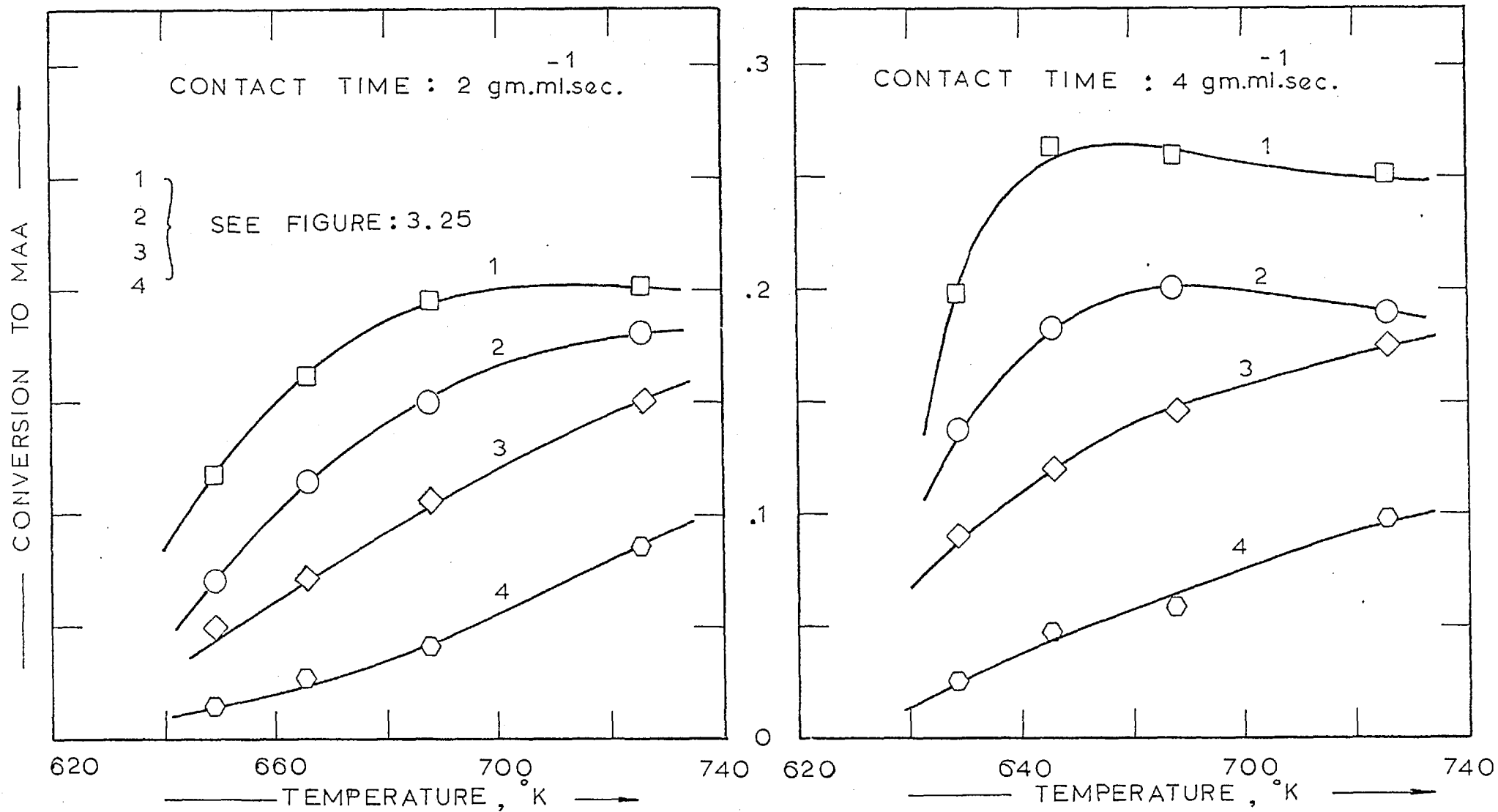


FIGURE 3.27 : Conversion to MAA as a Function of Temperature.

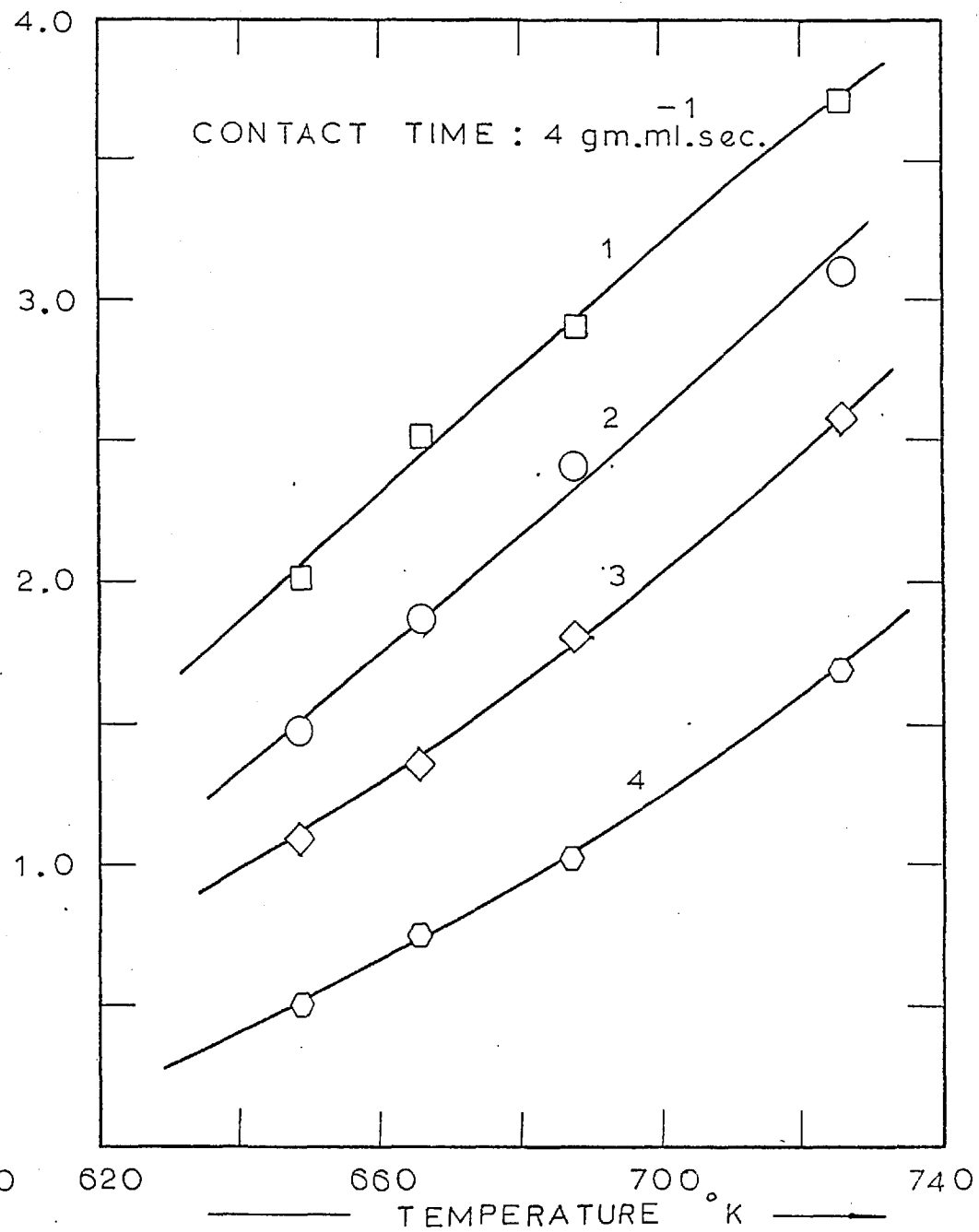
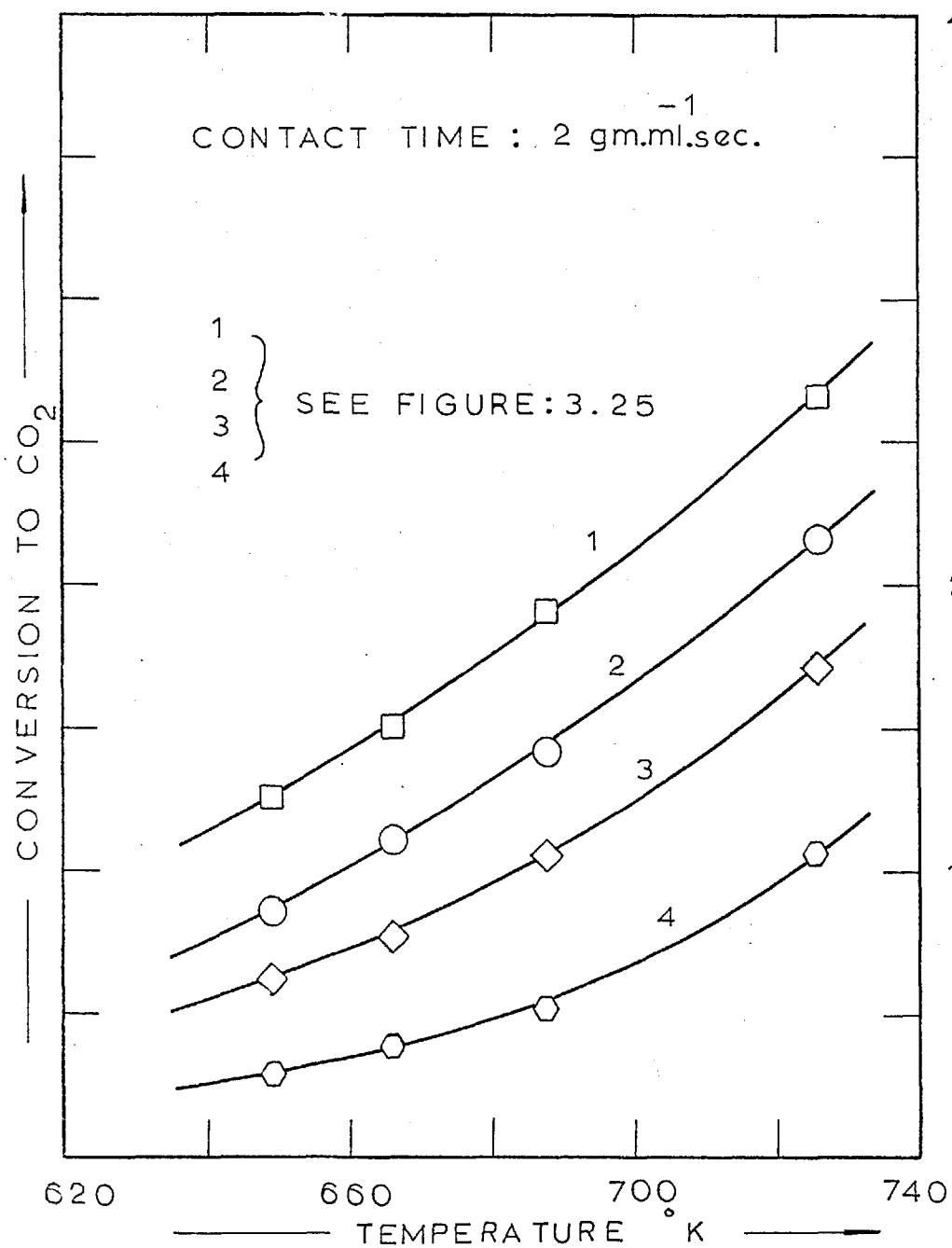


FIGURE 3.28 : Conversion to CO_2 as a function of Temperature.

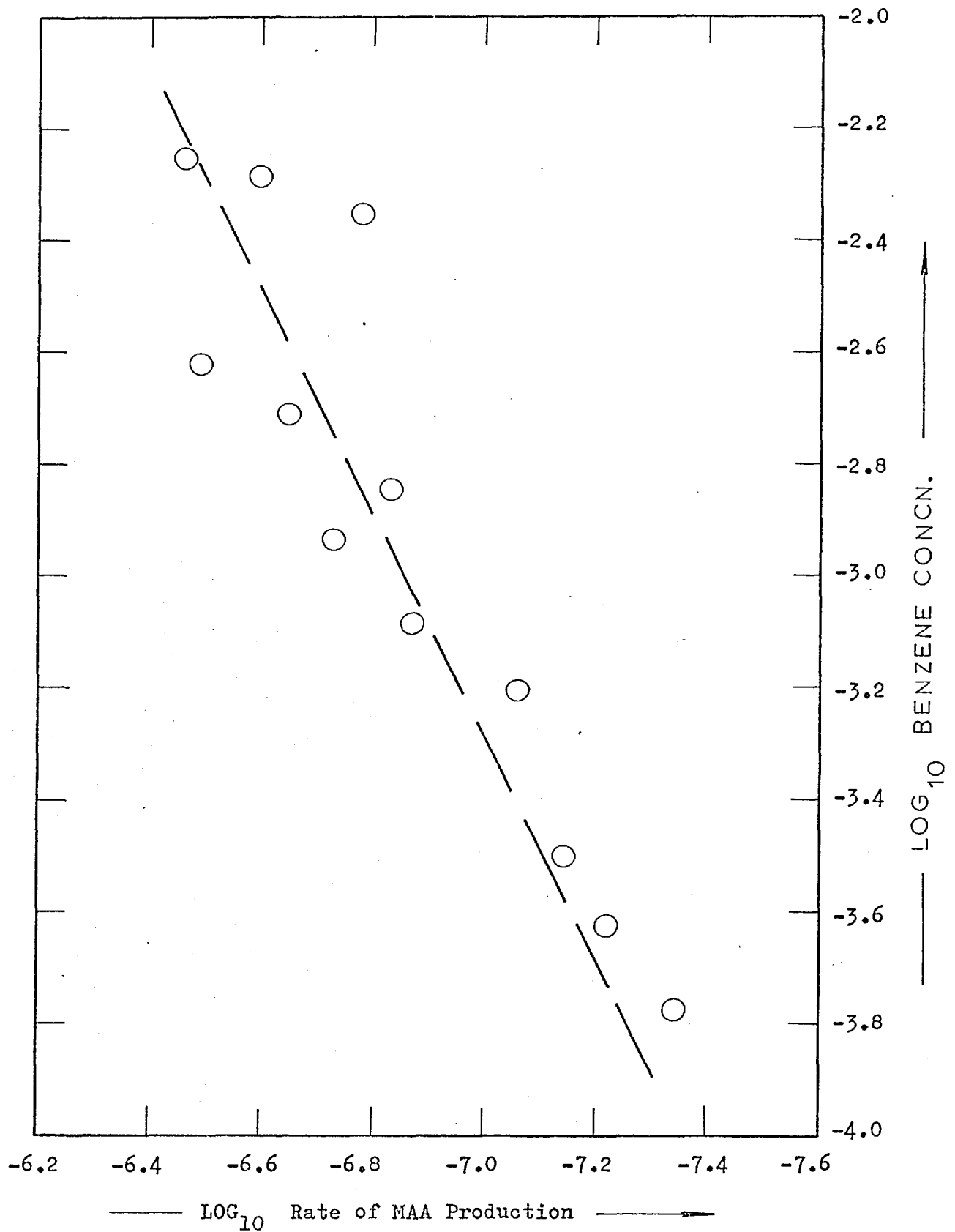


FIGURE 3.29 : ORDER Plot for the Production of MAA at 453°C. showing the scatter of experimental data.

S.G.S.R. ; Temperature : 376°C.

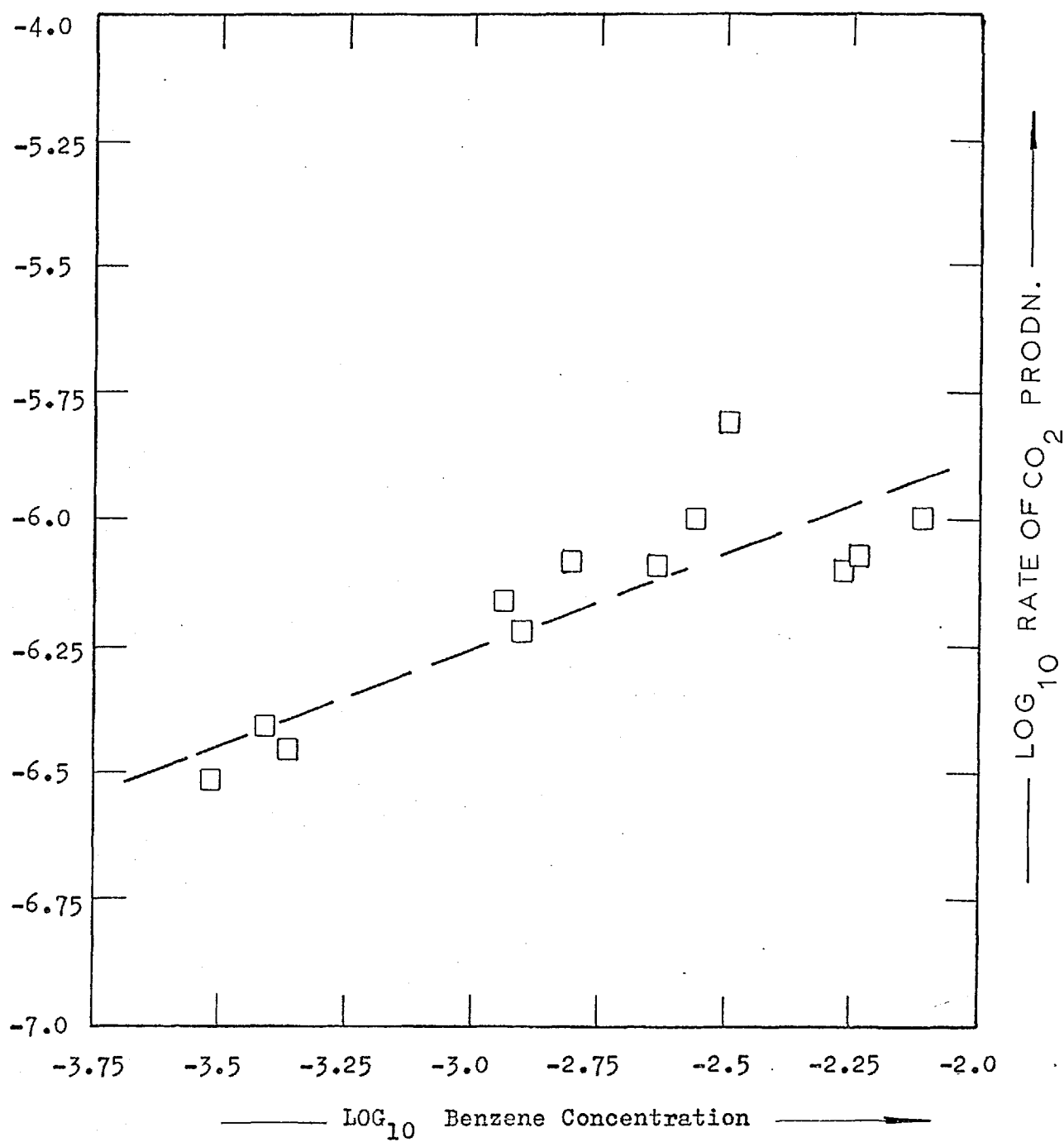


FIGURE 3.30 : ORDER Plot for the Production of CO_2 at 376°C.
showing the scatter of experimental data.

catalyst contact time in Figures 3.25 to 3.28. Figure 3.27 shows the marked over-oxidation of maa at relatively high contact times under conditions of high oxygen:benzene input ratios.

Typical logarithmic plots of reaction rate versus benzene outlet (reacting) concentration are shown in Figures 3.29, 3.30. Due to the large scatter of data, which could not be explained solely on the grounds of the oxygen dependence of the rate, least squares analyses were not attempted at this stage.

5C Incorporation of maa data in the S.G.S.R. results

5C1 Distinction between total and net rates of production of maa:

For each run of the S.G.S.R. under a set of given conditions, the amount of maa leaving the reactor system is equal to that amount formed from homogeneous-heterogeneous reactions involving benzene minus the amount oxidised due to the stainless steel surface present in the reactor. The latter may be calculated using the appropriate rate equations developed in 4B1 and 4B2. Maa present in the reactor will oxidise at a rate proportional to its concentration in the gas-phase which will be equal to the measured exit concentration. Therefore, at any temperature, knowledge of the maa concentration leaving the reactor will allow the calculation of the total amount of maa that would have been formed had over-oxidation not taken place.

Table 3.24 illustrates the calculation of total amounts of maa formed in the absence of over-oxidation, which in turn gives the 'true' rate of formation of maa from the

TABLE 3.24

INCLUSION OF OVER-OXIDATION DATA IN THE S.G.S.R.
RESULTS FOR THE PRODUCTION OF MALEIC ANHYDRIDE.

Use of the Rate Equation : $-\frac{d\text{Maa}}{dt} = k_T \times (\text{C.Maa}_{\text{exit}})^{0.67}$, (see Table), and the use of the relevant Activation Energy of 13.5 Kcal./mole to obtain values of k_T , allows the calculation of the amount of Maa over-oxidised in the S.G.S.R. under reacting conditions.

C.Maa _{ex.}	Contact Time	(C.Maa _{ex.}) ^{0.67}	Amount of Maa Oxidised	Total Maa Formed	"True" Maa Prod. Rate
m./li. (x10 ⁻³)	gm.ml. ⁻¹ sec.	(x10 ⁻³)	m./li. (x10 ⁻³)	m./li. (x10 ⁻³)	m.gm. ⁻¹ sec. ⁻¹ (x10 ⁻⁷)

TEMPERATURE : 376°C. ; $k_{376} = 3.16 \times 10^{-6}$

.059	1.67	1.51	.008	.067	.402
.106	1.66	2.23	.012	.118	.713
.136	1.68	2.64	.014	.150	.893
.090	1.68	2.01	.0107	.107	.638
.095	2.77	2.08	.018	.113	.408
.146	2.77	2.77	.024	.170	.613
.238	2.83	3.84	.0344	.272	.961
.125	2.93	2.49	.023	.148	.505
.124	4.16	2.48	.0326	.157	.377
.254	4.16	4.00	.0525	.307	.738
.295	4.27	4.42	.0595	.355	.832
.190	4.38	3.30	.0457	.236	.538

TEMPERATURE : 393°C. ; $k_{393} = 4.17 \times 10^{-6}$

.099	1.62	2.13	.0144	.113	.698
.182	1.61	3.21	.0215	.204	1.265
.224	1.64	3.68	.025	.249	1.520
.144	1.68	2.74	.019	.163	.975
.125	2.71	2.50	.0283	.153	.565
.245	2.71	3.91	.044	.289	1.065
.337	2.74	4.84	.0553	.392	1.430
.242	2.83	3.88	.0457	.288	1.015
.160	4.06	2.94	.0497	.210	.517
.292	4.06	4.40	.074	.366	.872

contd./over

C.Maa _{ex.}	Contact Time	(C.Maa _{ex.}) ^{0.67}	Amount of Maa Oxidised	Total Maa Formed	"True" Maa Prod. Rate
m./li. (x10 ⁻³)	gm.ml. ⁻¹ sec.	(x10 ⁻³)	m./li. (x10 ⁻³)	m./li. (x10 ⁻³)	m.gm. ⁻¹ sec. ⁻¹ (x10 ⁻⁷)

TEMPERATURE : 393°C. / contd.

.372	4.17	5.17	.0896	.462	1.110
.325	4.26	4.72	.0838	.409	.961

TEMPERATURE : 415°C. ; $k_{415} = 5.82 \times 10^{-6}$

.101	1.56	2.16	.0196	.121	.776
.240	1.54	3.86	.0346	.275	1.790
.316	1.58	4.63	.0425	.359	2.280
.227	1.62	3.71	.035	.262	1.615
.136	2.59	2.64	.0398	.176	.680
.259	2.59	4.06	.061	.320	1.235
.445	2.62	5.81	.0886	.534	2.040
.323	2.68	4.70	.0733	.396	1.480
.157	3.89	2.90	.0656	.222	.571
.336	3.89	4.81	.109	.445	1.145
.493	3.96	6.22	.143	.636	1.605
.390	4.06	5.32	.1255	.516	1.270

TEMPERATURE : 453°C. ; $k_{453} = 9.4 \times 10^{-6}$

.106	1.48	2.23	.031	.137	.930
.260	1.47	4.06	.056	.316	2.160
.480	1.495	6.12	.086	.566	3.780
.522	1.525	6.47	.0928	.615	4.030
.144	2.47	2.75	.0638	.208	.843
.329	2.47	4.76	.1105	.440	1.780
.560	2.50	6.78	.160	.720	2.880
.648	2.54	7.47	.178	.826	3.250
.159	3.69	2.93	.1015	.261	.706
.317	3.69	4.65	.1615	.479	1.300
.555	3.78	6.73	.239	.794	2.100
.642	3.86	7.43	.269	.911	2.360

TABLE 3.24 (contd.)

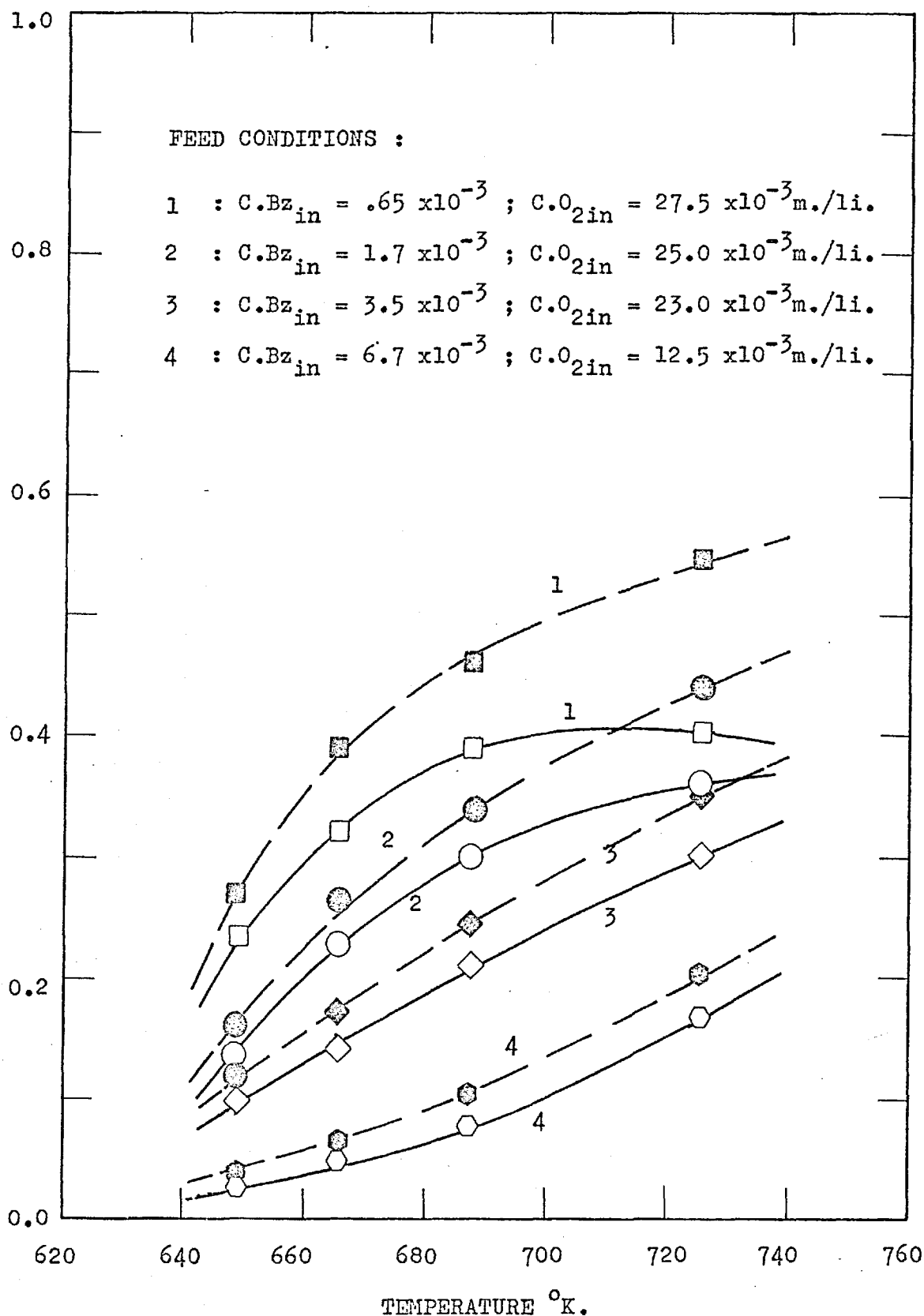


FIGURE 3.31 : Conversion to MAA as a Function of Temperature showing the Effects of Over-oxidation.
Results at a Catalyst Contact Time of $2 \text{ gm.ml.}^{-1}\text{sec.}$
NET (measured) CONVERSION to MAA - solid line
TOTAL CONVERSION to MAA - dashed line

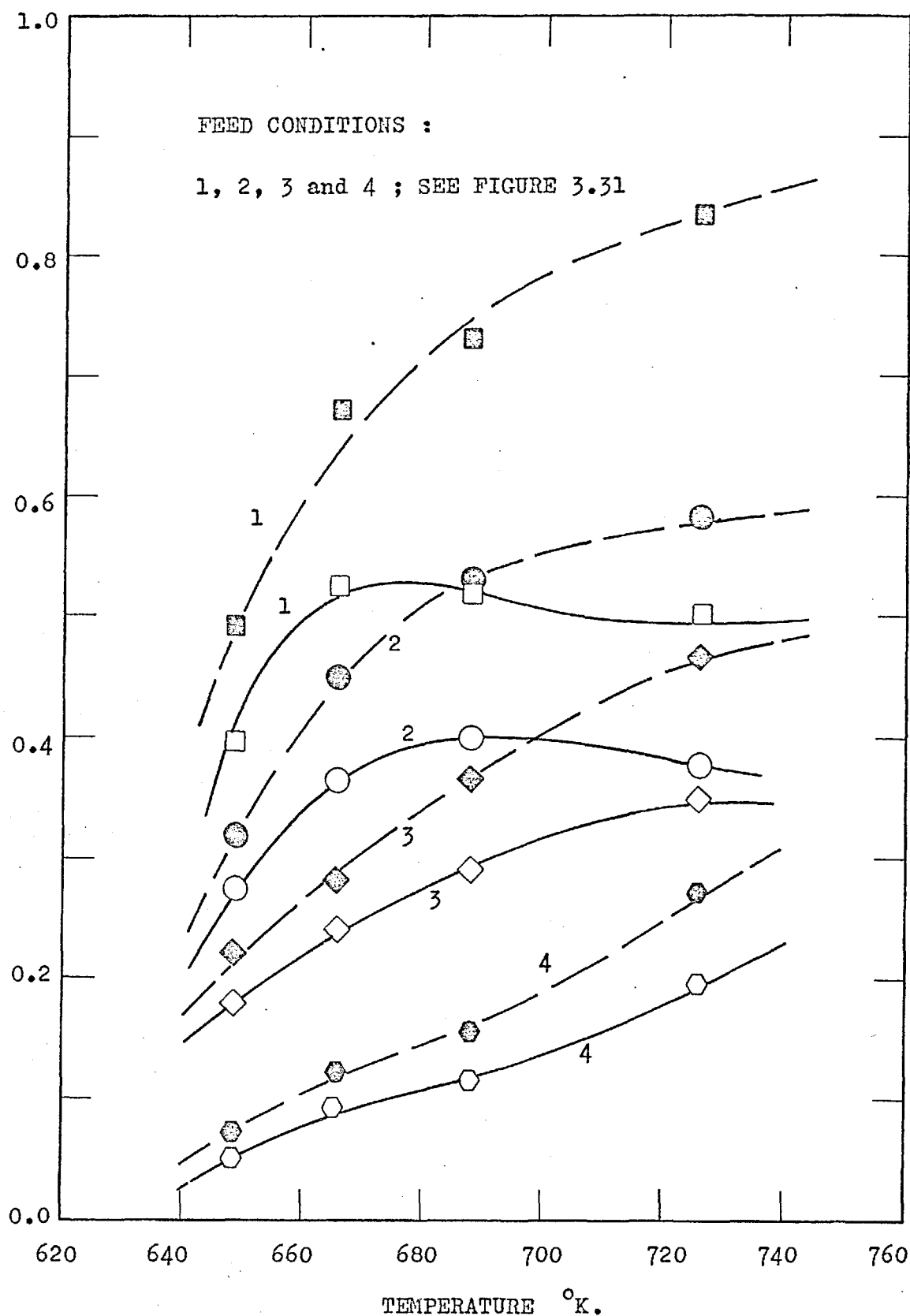


FIGURE 3.32 : Conversion to MAA as a Function of Temperature showing the Effects of Over-oxidation.
 Results at a Catalyst Contact Time of $4 \text{ gm.ml}^{-1}\text{sec.}$
 NET (measured) CONVERSION to MAA - solid line
 TOTAL CONVERSION to MAA - dashed line

oxidation of benzene. Figures 3.31, 3.32 show the effects of over-oxidation of maa in the S.G.S.R. at constant contact times for various temperatures. At a contact time of $4\text{gm.cc}^{-1}\text{sec.}$, under conditions of very high oxygen:fuel input ratio, the loss of maa due to steel initiated over-oxidation is seen to be almost 41% at 453°C . Table 3.25 shows the selective yield of maa as a function of overall benzene conversion for the temperatures studied. Selectivity is markedly constant at approximately 50% for almost all oxygen:fuel ratios studied and would appear not to be temperature dependent.

Redrawing of the logarithmic order plots, using as ordinate the rate of ''total'' maleic production, improves the scatter of data previously found, and the oxygen dependence of the rate is more apparent. First order dependence on oxygen over the whole of the temperature range studied fits the data extremely well, and the resulting plots of $\log (''total'' \text{ maleic rate} \div \text{oxygen concentration})$ versus $\log$ reacting benzene concentration are shown in Figure 3.33. Least squares analyses on each set of data points leads to the rate expressions shown in Table 3.26. The change in order w.r.t. benzene concentration is plotted as a function of temperature in Figure 3.34. A rough value of the energy of activation for maa production from benzene is derived from the Arrhenius plot in Figure 3.35, where constant order kinetics have been assumed.

5C2 Distinction between total and net rates of production of carbon dioxide:

Amounts of carbon dioxide leaving the S.G.S.R. system originate from at least three separate and distinct reactions.

THE SELECTIVE YIELD OF MAA AS A FUNCTION OF OVERALL CONVERSION.
 S.G.S.R. RESULTS / CIRCULAR BASKET / OVER-OXIDATION DATA INCLUDED.

C.BZ _{IN}	CONV. OF BZ	"NET" CONV. TO MAA	"TOTAL" CONV. TO MAA	"TRUE" SELECTIVE YIELD OF MAA
m./li. ($\times 10^{-3}$)	%	%	%	%

TEMPERATURE : 376°C.

.584	24.00	10.00	11.45	47.8
1.87	16.05	5.77	6.31	39.4
3.73	12.05	3.65	4.02	33.3
7.98	4.80	1.13	1.34	28.2 *
.628	35.50	15.10	18.00	50.7
1.60	24.40	9.13	10.60	43.6
3.29	20.70	7.25	8.26	41.1
6.28	8.30	1.99	2.35	28.5 *
.629	52.00	19.75	24.95	47.7
1.82	34.00	13.95	16.85	49.5
3.12	24.70	9.46	11.40	46.2
6.48	14.00	2.93	3.64	26.0 *

TEMPERATURE : 393°C.

.730	29.3	13.56	15.50	52.8
1.91	21.5	9.55	10.70	49.7
3.67	14.7	6.10	6.75	46.1
7.12	9.1	2.06	2.29	25.1 *
.606	47.1	20.60	25.25	53.4
1.66	31.0	14.75	17.40	56.1
3.55	23.0	9.50	11.05	48.2
6.66	11.5	3.65	4.32	37.9 *
.606	62.0	26.50	34.60	55.9
1.575	40.3	18.50	23.10	57.2
3.10	31.2	12.00	14.90	47.8
6.49	21.4	5.00	6.31	29.5 *

(* Results at relatively low oxygen concentrations ; all other runs had a reacting concentration of oxygen in excess of fuel concentration.)

TABLE 3.25 (contd.)

C.BZ _{IN}	CONV. OF BZ	"NET" CONV. TO MAA	"TOTAL" CONV. TO MAA	"TRUE" SELECTIVE YIELD OF MAA
m./li. ($\times 10^{-3}$)	%	%	%	%

TEMPERATURE : 415°C.

.630	36.5	16.0	19.20	52.7
2.00	27.5	12.0	13.75	50.0
3.52	20.75	8.95	10.20	49.2
6.50	13.5	3.5	4.03	29.8 *
.590	55.25	23.1	29.90	54.0
1.44	39.5	18.0	22.20	56.2
3.63	30.3	12.25	14.70	48.6
6.81	18.8	4.75	5.82	30.9 *
.605	69.8	25.90	36.70	52.6
1.66	49.5	20.25	26.80	54.1
3.40	39.0	14.5	18.70	48.0
6.50	25.5	6.0	7.94	31.1 *

TEMPERATURE : 453°C.

.606	47.1	17.5	22.60	48.0
1.875	38.2	14.0	16.85	44.2
3.56	33.0	13.5	15.90	48.3
7.06	20.4	7.5	8.70	42.7 *
.653	63.0	22.1	31.90	50.7
1.662	50.7	19.75	26.40	52.1
3.44	44.6	16.3	20.90	48.3
7.07	26.5	9.2	11.65	44.2 *
.630	73.5	25.2	41.40	56.5
1.67	62.0	19.0	28.70	46.3
3.12	53.9	17.8	25.40	47.2
6.68	33.9	9.6	13.60	40.4 *

(* Results at relatively low oxygen concentrations ;
all other runs had a reacting concentration of oxygen
in excess of fuel concentration.)

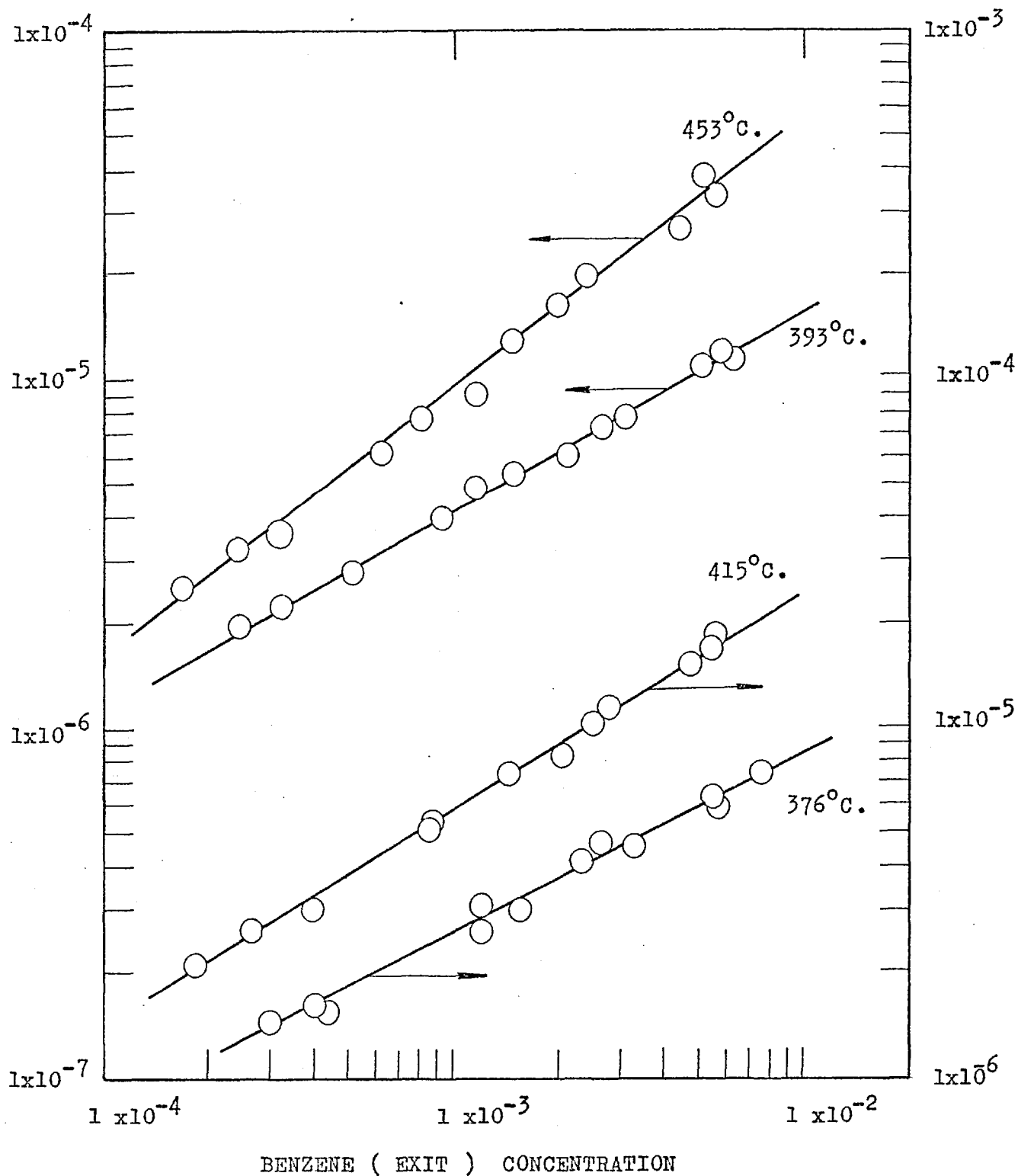


FIGURE 3.33 : ORDER Plots for MAA Production in the S.G.S.R. :

"Corrected" MAA Rate / Oxygen Concn. plotted
against Reacting Benzene Concn.

Rate has units of $\text{m.gm.}^{-1}\text{sec.}^{-1}$; Concn. in m./li.

TABLE 3.26

RATE OF PRODUCTION OF MAA AS A FUNCTION OF TEMPERATURE
RESULTS FROM THE S.G.S.R. / CIRCULAR BASKET

The General Form of the Rate Expression is ,

$$r = k_T \times (\text{Concn. } O_2)^m \times (\text{Concn. Bz})^n$$

where , the Rate (r) has units of m.gm.sec.^{-1}

the Rate Constant (k_T) at a temperature T, has units of $\text{li. m. gm.sec.}^{-n+m-1}$

the concentrations of O_2 and Bz are the reacting (exit) concentrations in units of m./li.

m and n are the orders of reaction w.r.t. O_2 and Bz respectively. (m = unity in all cases)

<u>RATE EQUATION</u>	<u>TEMPERATURE</u>
$\frac{dMaa}{dt} = 9.29 \times 10^{-5} (C.O_2)^{1.0} (C.Bz)^{0.522}$	376°C.
$\frac{dMaa}{dt} = 1.95 \times 10^{-4} (C.O_2)^{1.0} (C.Bz)^{0.554}$	393°C.
$\frac{dMaa}{dt} = 3.87 \times 10^{-4} (C.O_2)^{1.0} (C.Bz)^{0.609}$	415°C.
$\frac{dMaa}{dt} = 1.99 \times 10^{-3} (C.O_2)^{1.0} (C.Bz)^{0.775}$	453°C.

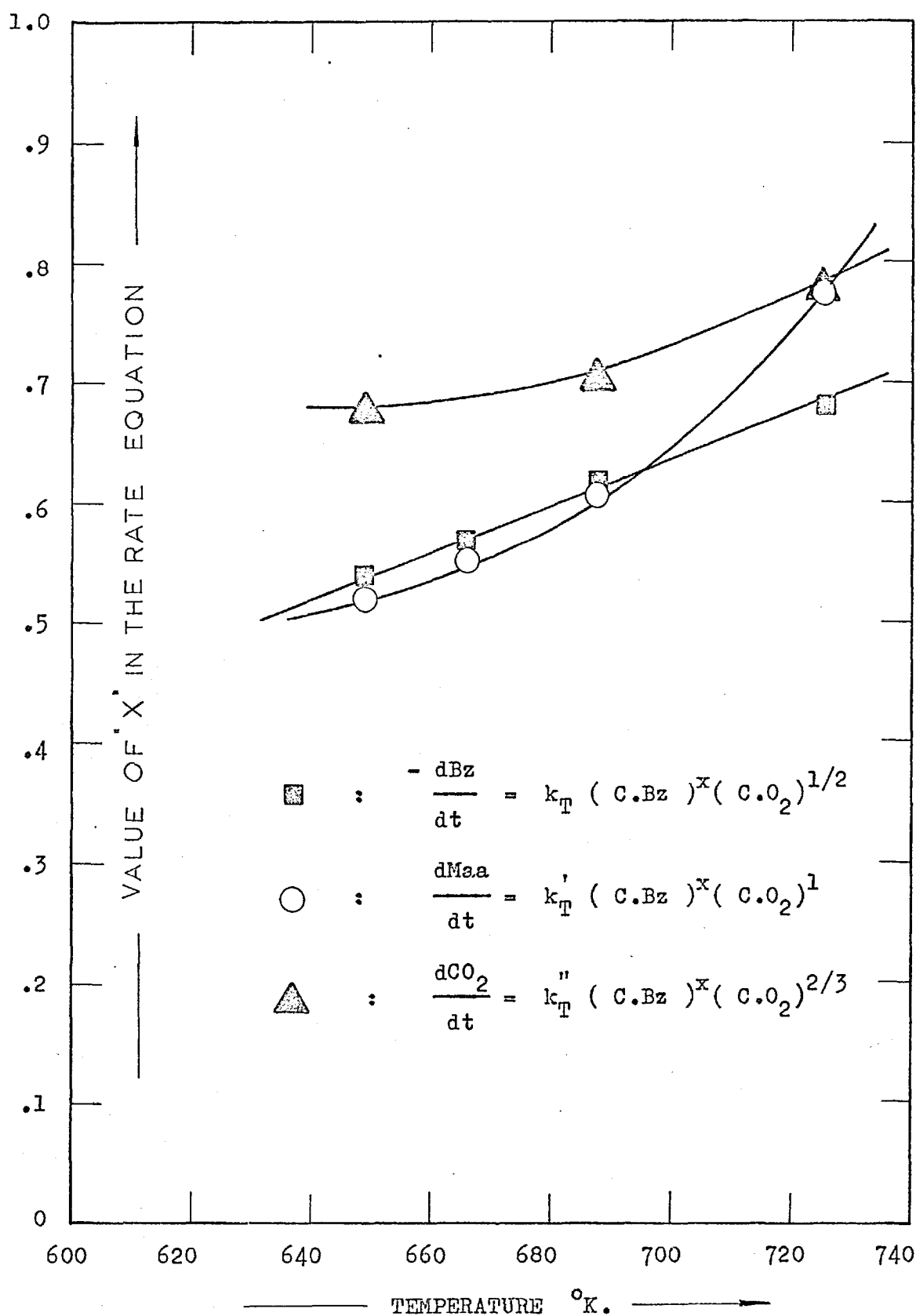


FIGURE 3.34 : The Change in Order (x) w.r.t. Reacting Benzene Concentration as a Function of Temperature.

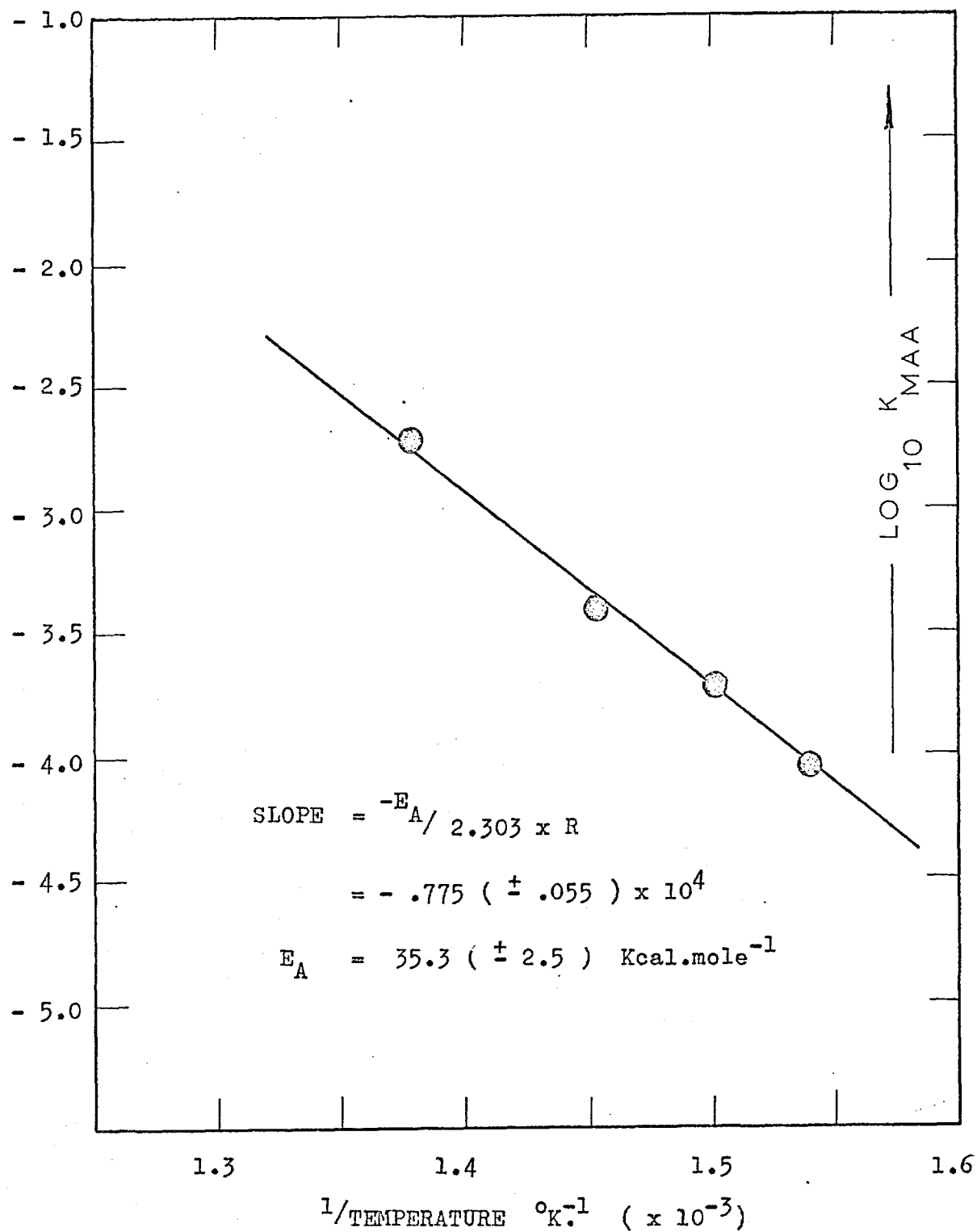


FIGURE 3.35 : ARRHENIUS PLOT FOR MAA PRODUCTION FROM THE OXIDATION OF BENZENE IN THE S.G.S.R.

(Constant order kinetics assumed)

From the SLOPE of the plot, the ENERGY OF ACTIVATION (E_A) was calculated to be $35.3 (\pm 2.5) \text{ K.cal./mole}$

(i) some will be formed directly from benzene, either by a homogeneous-heterogeneous reaction or by wholly catalytic reaction.

(ii) for each maleic anhydride molecule formed, by whatever reaction path, two carbons will be made available for subsequent reaction. In all experiments, performed both in the S.G.S.R. and tubular reactors, negligible amounts of carbon monoxide were found and it has been assumed that these two carbons ultimately give carbon dioxide as the only stable product.

(iii) carbon dioxide is the only product of maa over-oxidation occurring on the steel of the S.G.S.R.

Knowledge of the total maa produced in the S.G.S.R. under any set of conditions will give a direct measure of the amount of carbon dioxide contributed from (ii), and knowledge of the rate of maa oxidation will give a measure of the contribution from (iii).

Table 3.27 shows experimental and calculated results made on this basis, and Figures 3.36, 3.37 show net carbon dioxide yield (total - amount from (ii) and (iii)) as well as total yield, as a function of catalyst contact time for fixed benzene input concentrations. Figures 3.38 and 3.39 illustrate net and total conversions to carbon dioxide as functions of temperature for fixed catalyst contact times.

As for the maleic anhydride rate data, a "true" rate of production for CO_2 may be calculated and plotted logarithmically versus reacting benzene concentration. Again, there is a vast improvement in scatter, and oxygen dependence can be accounted for - although in a less simple

PRODUCTION OF CARBON DIOXIDE IN THE S.G.S.R.
CORRECTION OF CO₂ RESULTS USING MAA PRODUCTION AND OVER-OXIDATION DATA

Assumptions :- (i) 2 moles of CO₂ formed for each mole of Maa produced
(ii) 4 moles of CO₂ produced for each mole of Maa oxidised

C.CO ₂ (EXIT)	Contact Time	C.CO ₂ FROM MAA PRODUCTION	C.CO ₂ FROM MAA OXIDATION	C.CO ₂ (NET)
TOTAL (1)		(2)	(3)	(1 - (2+3))
m./li (x10 ⁻³)	gm.ml. ⁻¹ sec. ⁻¹	(m./li. (x10 ⁻³))	m./li. (x10 ⁻³)	m./li (x10 ⁻³)

TEMPERATURE : 376°C.

.609	1.67	.134	.032	.443
1.360	1.66	.236	.047	1.075
2.550	1.68	.300	.056	1.493
1.715	1.68	.214	.043	1.455
1.055	2.77	.226	.073	.755
1.800	2.77	.340	.096	1.365
2.750	2.83	.546	.137	2.070
2.440	2.93	.296	.092	2.050
1.292	4.16	.314	.130	.848
2.690	4.16	.614	.210	1.865
3.570	4.27	.710	.238	2.620
3.565	4.38	.472	.183	2.910

TEMPERATURE : 393°C.

.882	1.62	.226	.057	.559
1.765	1.61	.408	.086	1.270
2.440	1.64	.498	.100	1.840
2.300	1.68	.326	.076	1.900
1.162	2.71	.306	.113	.743
2.325	2.71	.578	.177	1.570
3.505	2.74	.784	.221	2.500
3.660	2.83	.576	.183	2.900
1.560	4.06	.420	.200	.937
2.980	4.06	.728	.297	1.950
4.380	4.17	.924	.360	3.100
5.025	4.26	.818	.335	3.870

C.CO ₂ (EXIT)	Contact Time	C.CO ₂ FROM MAA PRODUCTION	C.CO ₂ FROM MAA OXIDATION	C.CO ₂ (NET) (1 - (2+3))
TOTAL (1)		(2)	(3)	(1 - (2+3))
m./li (x10 ⁻³)	gm.ml. ⁻¹ sec. ⁻¹	m./li. (x10 ⁻³)	m./li. (x10 ⁻³)	m./li (x10 ⁻³)

TEMPERATURE : 415°C.

.955	1.56	.242	.080	.634
2.290	1.54	.550	.138	1.602
3.120	1.58	.718	.170	2.232
2.830	1.62	.524	.140	2.170
1.360	2.59	.352	.160	.848
2.465	2.59	.640	.245	1.580
4.690	2.62	1.068	.354	3.270
4.600	2.68	.792	.293	3.510
1.742	3.89	.444	.262	1.034
3.930	3.89	.890	.436	2.604
6.095	3.96	1.272	.573	4.250
6.500	3.96	1.032	.502	4.970

TEMPERATURE : 453°C.

1.29	1.475	.274	.124	.892
3.25	1.465	.632	.224	2.394
5.175	1.495	1.132	.344	3.700
6.07	1.525	1.230	.371	4.470
1.95	2.47	.416	.256	1.278
4.06	2.47	.880	.442	2.738
6.71	2.50	1.440	.640	4.630
8.61	2.54	1.652	.712	6.246
2.27	3.69	.522	.406	1.342
5.02	3.69	.958	.646	3.416
7.86	3.78	1.588	.956	5.316
11.00	3.86	1.822	1.076	8.102

TABLE 3.27

(contd./over)

TABLE 3.27 (contd.)

TEMPERATURE : 376°C.

TEMPERATURE : 393°C.

TOTAL CONV. TO CO ₂ %	NET CONV. TO CO ₂ %	"TRUE" CO ₂ PROD. RATE m.gm. ⁻¹ sec. ⁻¹	TOTAL CONV. TO CO ₂ %	NET CONV. TO CO ₂ %	"TRUE" CO ₂ PROD. RATE m.gm. ⁻¹ sec. ⁻¹
104.5	76.0	.266 x10 ⁻⁶	120.7	82.1	.370 x10 ⁻⁶
72.7	57.6	.650	92.3	66.5	.788
68.4	40.0	.880	66.5	50.2	1.122
21.5	18.2	.868	32.3	26.7	1.135
168.0	120.0	.273	191.8	122.5	.274
112.5	85.4	.493	140.0	94.4	.580
83.6	63.1	.732	98.8	70.5	.913
38.8	32.7	.700	55.0	43.6	1.025
205.0	134.5	.204	257.0	154.0	.233
148.0	102.5	.448	189.0	124.0	.480
114.5	84.0	.615	141.5	100.0	.744
55.0	45.0	.665	77.5	59.6	.908

TEMPERATURE : 415°C.

TEMPERATURE : 453°C.

TOTAL CONV. TO CO ₂ %	NET CONV. TO CO ₂ %	"TRUE" CO ₂ PROD. RATE m.gm. ⁻¹ sec. ⁻¹	TOTAL CONV. TO CO ₂ %	NET CONV. TO CO ₂ %	"TRUE" CO ₂ PROD. RATE m.gm. ⁻¹ sec. ⁻¹
151.5	100.5	.406 x10 ⁻⁶	213.0	147.0	.605 x10 ⁻⁶
114.5	80.1	1.040	173.0	127.5	1.635
88.6	63.4	1.415	145.5	104.0	2.470
43.6	33.1	1.330	86.0	63.4	2.930
231.0	143.5	.328	299.0	195.5	.517
171.0	110.0	.610	244.0	165.0	1.110
129.0	90.1	1.250	195.0	134.5	1.850
67.6	51.6	1.310	121.5	88.5	2.460
287.0	171.0	.266	360.0	213.0	.364
237.0	157.0	.669	300.0	204.0	.925
179.0	125.0	1.073	252.0	170.0	1.405
100.0	76.5	1.225	165.0	121.0	2.100

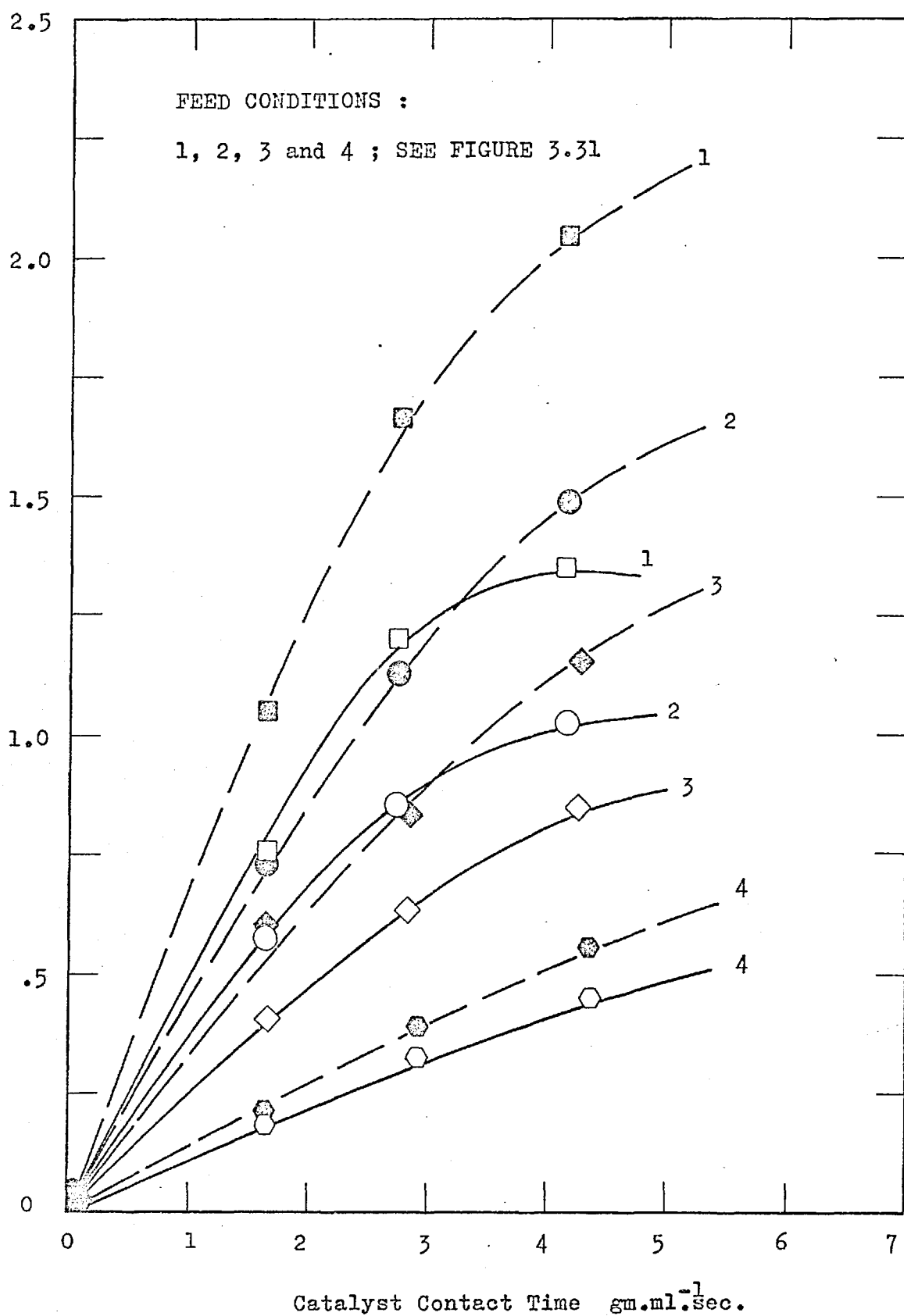


FIGURE 3.36 : NET CONVERSION (solid line) and TOTAL CONVERSION (dashed line) to CARBON DIOXIDE as a Function of Contact Time, for different O_2/FUEL input ratios. Results at 376°C .

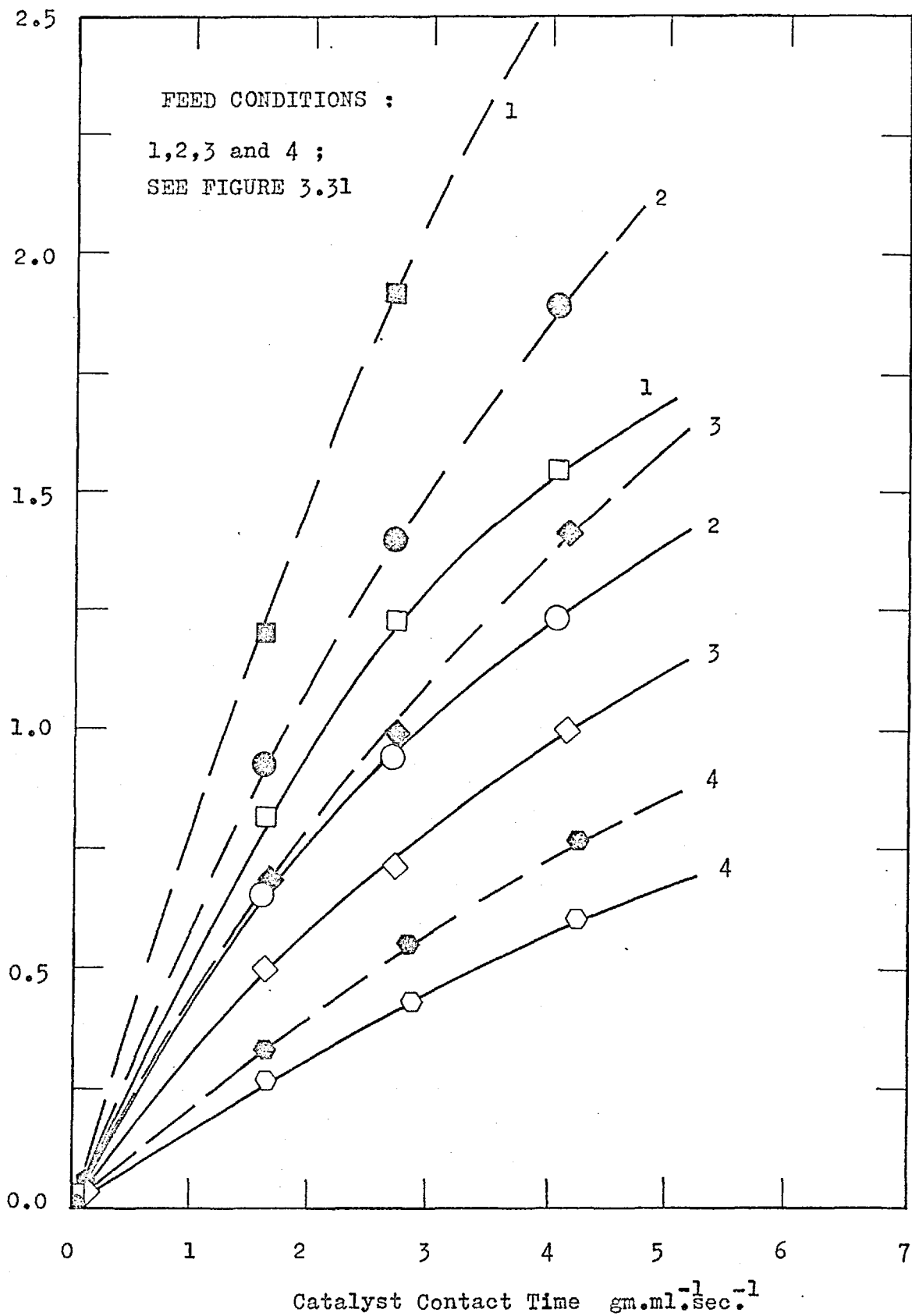


FIGURE 3.37 : NET CONVERSION (solid) and TOTAL CONVERSION (dashed line) to CARBON DIOXIDE as a Function of Contact Time, for different O_2 /FUEL input ratios. Results at 393°C.

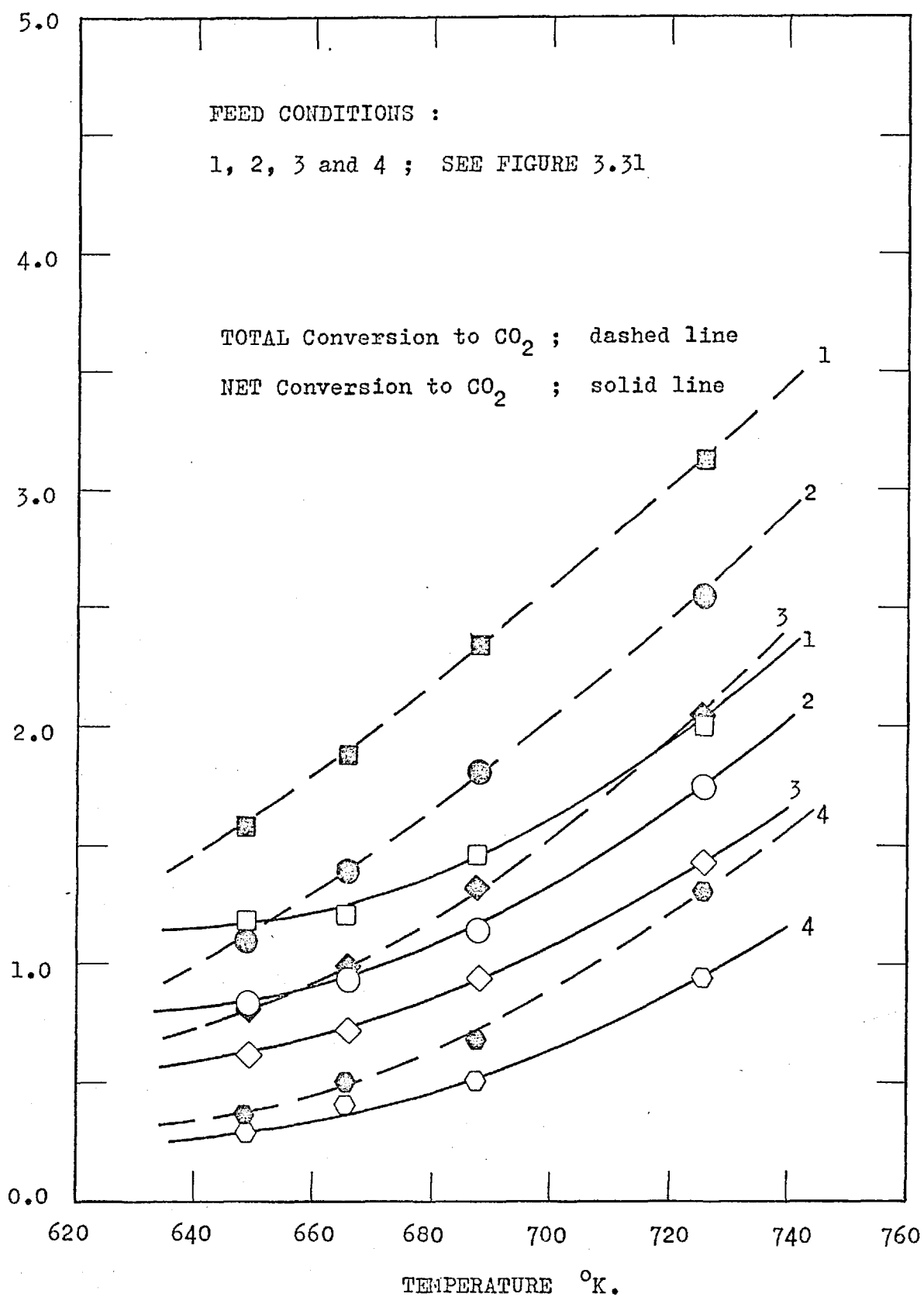


FIGURE 3.38 : NET and TOTAL CONVERSION to CO_2 as a Function of Temperature , for a Constant Catalyst Contact Time of $2.65 \text{ gm.ml}^{-1}\text{sec.}$

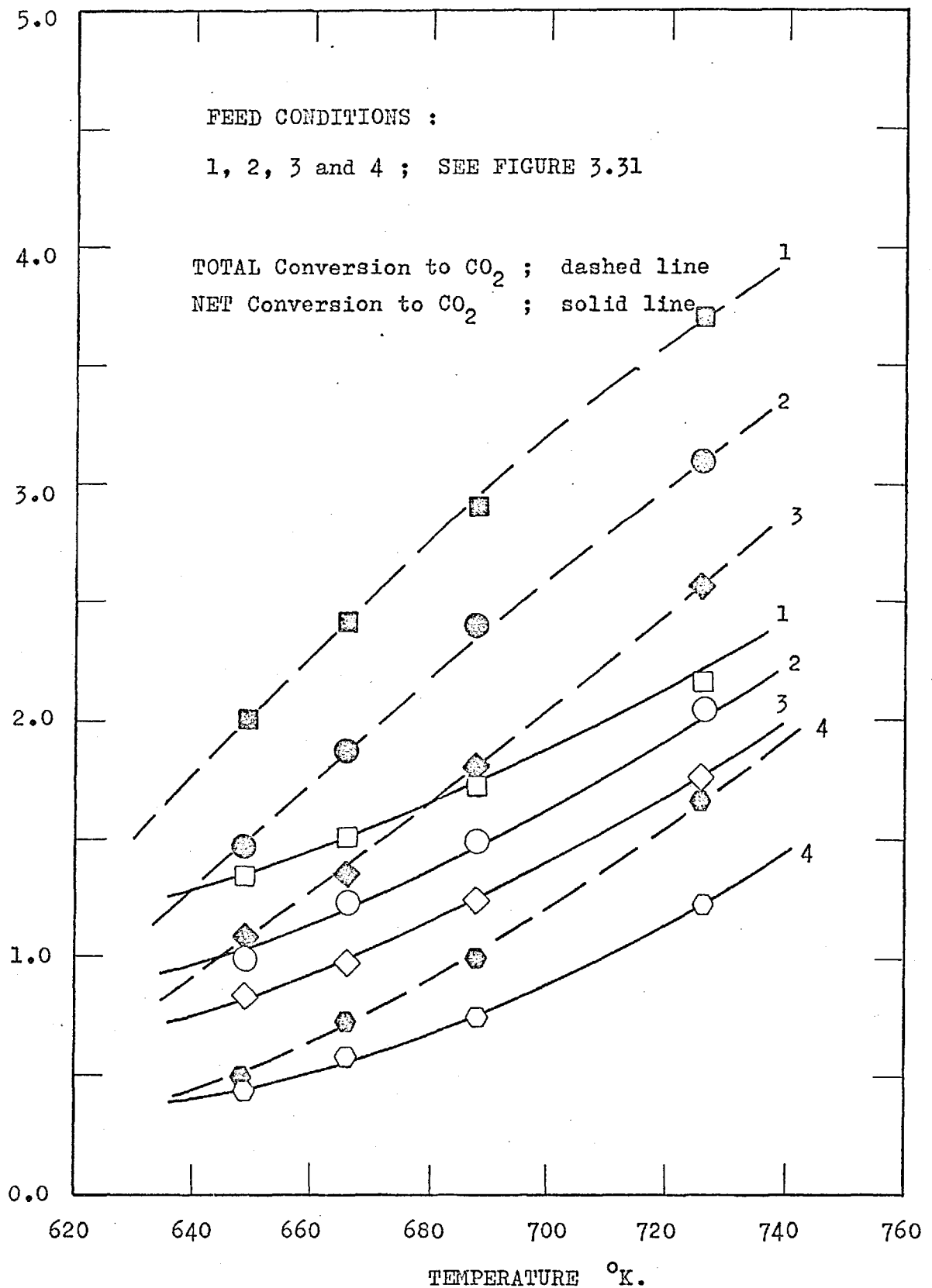


FIGURE 3.39 : NET and TOTAL CONVERSION to CO_2 as a Function of Temperature , for a Constant Catalyst Contact Time of 4 gm.ml.⁻¹.sec.

fashion. Oxygen concentration raised to the power of 0.66 gave the best fit and the plots to determine the order w.r.t. benzene concentration are shown in Figure 3.40 . Least square analyses of each set of points leads to rate expressions shown in Table 3.28. The change in order w.r.t. benzene is plotted as a function of temperature in Figure 3.34 , and a rough value of the energy of activation for CO_2 production is obtained from the Arrhenius plots in Figure 3.41 .

5D Evaluation of benzene oxidation rate

Unlike the data for maa and carbon dioxide, it is not possible to improve the results obtained for benzene other than by evaluating the probable oxygen dependence of the rate. Indeed, although the maa data may be adjusted by taking over-oxidation into account, and the CO_2 data may be corrected by considering both the parallel production with maa and the subsequent formation by oxidation of maa, it is not possible to separate the homogeneous and heterogeneous reactions involved in the production of these compounds. The rate expressions shown in Table 3.28 are overall relationships. Similarly, although benzene is known to react in the gas-phase (from the results of 3C2), it is not possible to distinguish between the wholly catalytic reaction and the reaction in the free gas space.

Oxygen dependence of the rate has been investigated and best fit to the data was found by assuming a dependence of the rate on oxygen concentration to the power 0.5. The plots to determine the order w.r.t. benzene concentration are shown in Figure 3.42 . Scatter of the points is a

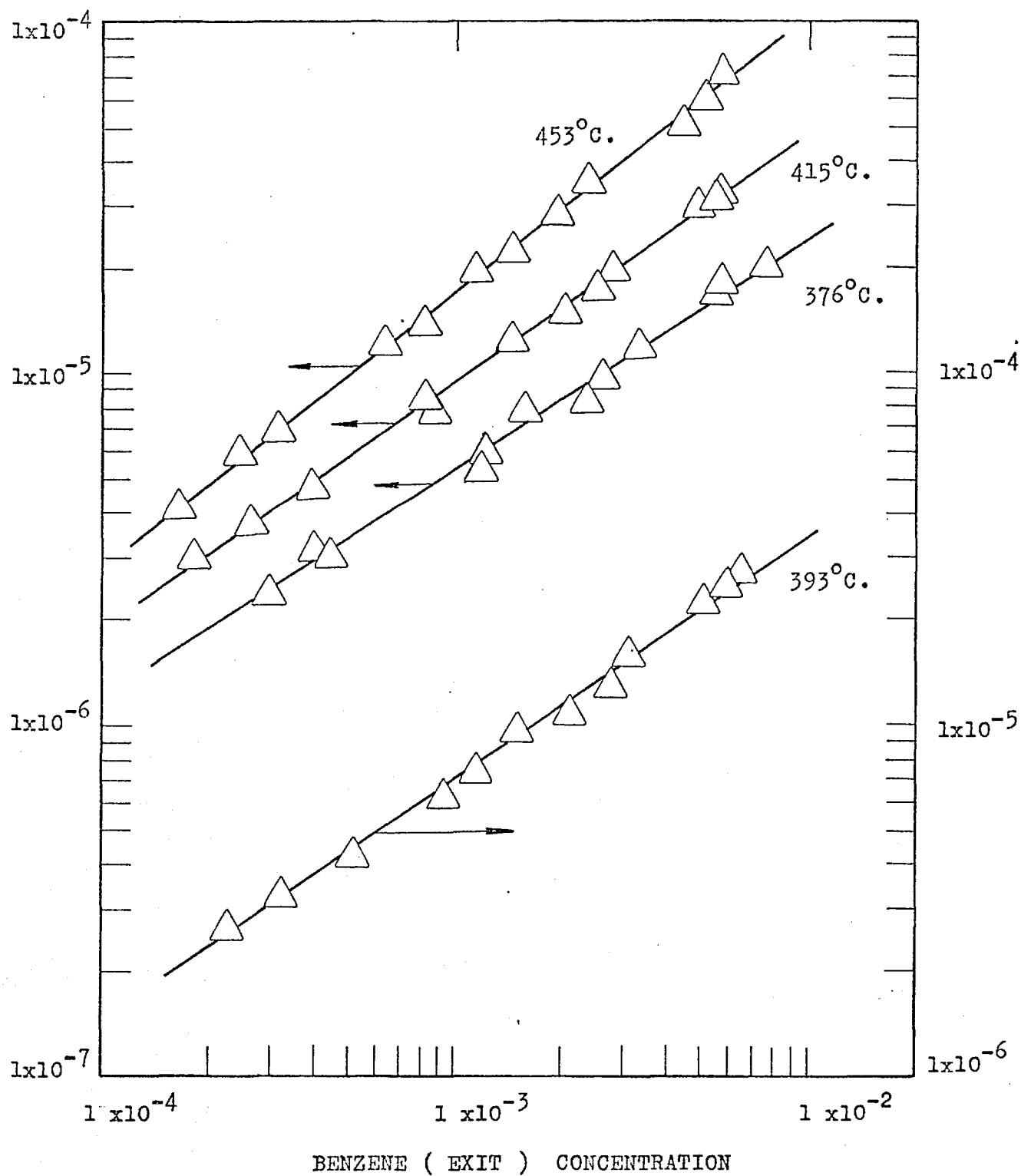


FIGURE 3.40 : ORDER PLOTS FOR CO_2 PRODUCTION IN THE S.G.S.R.
 "Corrected" CO_2 Rate / (Oxygen Concn.)^{2/3}
 plotted against Reacting Benzene Concentration.
 Rate has units of $\text{m.gm.}^{-1}\text{sec.}^{-1}$; Concn. in m./li.

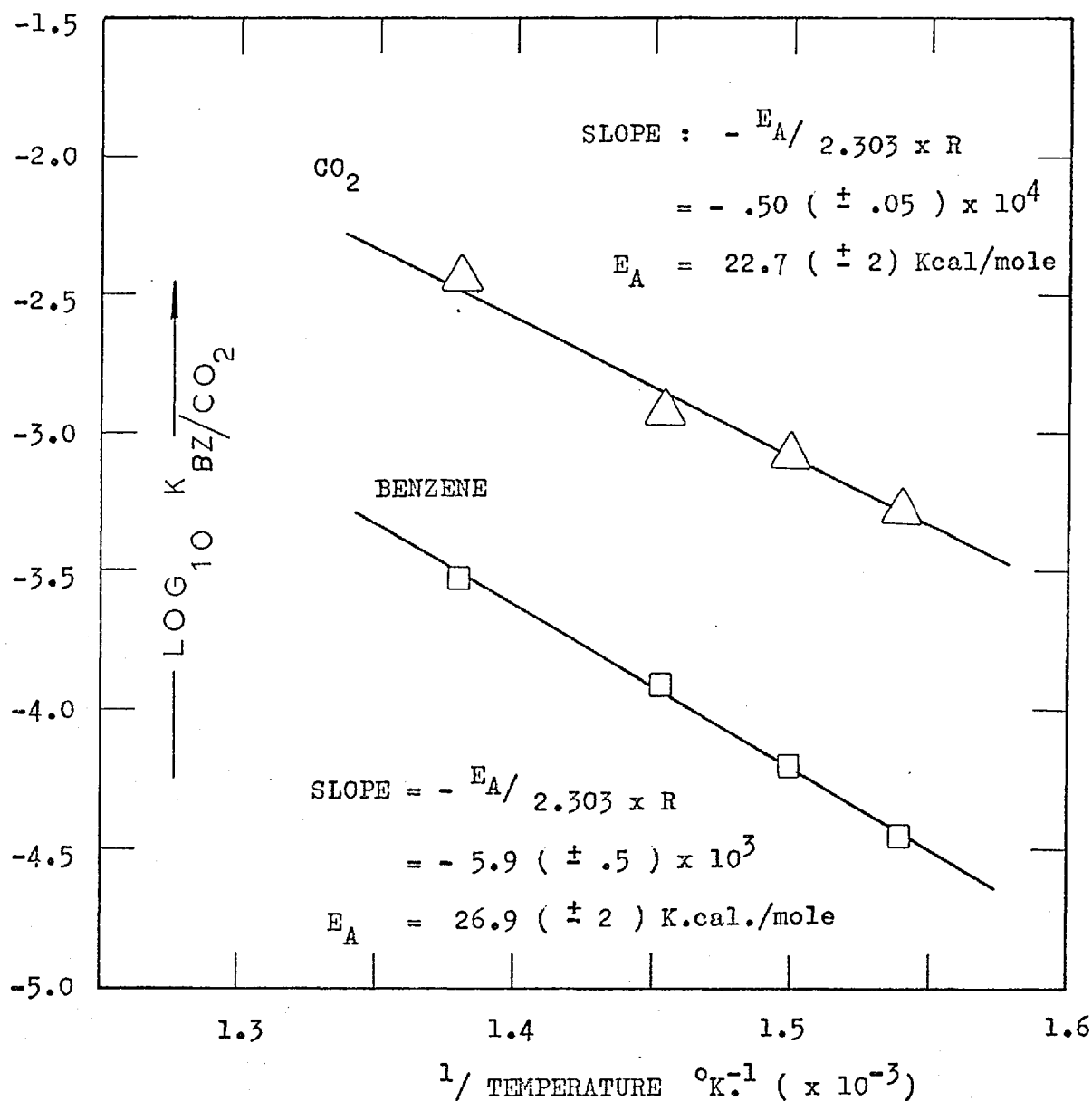


FIGURE 3.41 : ARRHENIUS PLOTS FOR BENZENE REMOVAL AND CO₂ PRODUCTION IN THE S.G.S.R.

(Constant order kinetics assumed)

From the SLOPES of the plots, the ENERGY OF ACTIVATION (E_A) for BENZENE REMOVAL is seen to be $26.9 (\pm 2) \text{ K.cal./mole}$ and for CO₂ PRODUCTION is $22.7 (\pm 2) \text{ K.cal./mole}$.

TABLE 3.28

RATE OF PRODUCTION OF CO₂ AS A FUNCTION OF TEMPERATURE
RESULTS FROM THE S.G.S.R. / CIRCULAR BASKET

The General Form of the Rate Expression is ,

$$r = k_T \times (\text{Concn. } O_2)^a \times (\text{Concn. Bz})^b$$

where , the Rate (r) has units of $\frac{m.gm.}{sec.}$

the Rate Constant (k_T) at a temperature T , $\frac{a+b}{1-a-b} \frac{1}{m. gm. sec.}$
has units of $\frac{li. m.}{gm. sec.}$

the concentrations of O₂ and Bz are the reacting (exit)
concentrations in units of m./li.

a and b are the orders of reaction w.r.t. O₂ and Bz
respectively. (a = 0.67 in all cases)

<u>RATE EQUATION</u>	<u>TEMPERATURE</u>
$\frac{dCO_2}{dt} = 5.63 \times 10^{-4} (C.O_2)^{0.67} (C.Bz)^{0.676}$	376°C.
$\frac{dCO_2}{dt} = 8.25 \times 10^{-4} (C.O_2)^{0.67} (C.Bz)^{0.692}$	393°C.
$\frac{dCO_2}{dt} = 1.18 \times 10^{-3} (C.O_2)^{0.67} (C.Bz)^{0.702}$	415°C.
$\frac{dCO_2}{dt} = 3.67 \times 10^{-3} (C.O_2)^{0.67} (C.Bz)^{0.778}$	453°C.

little more marked than for the corresponding maa and CO_2 plots, but least squares analyses gave a reasonably good fit of the data to the expressions shown in Table 3.29 . As before, changes in order are shown as a function of temperature in Figure 3.34 , and a value of the energy of activation for benzene removal was calculated, assuming constant order kinetics, from the Arrhenius plot in Figure 3.41 .

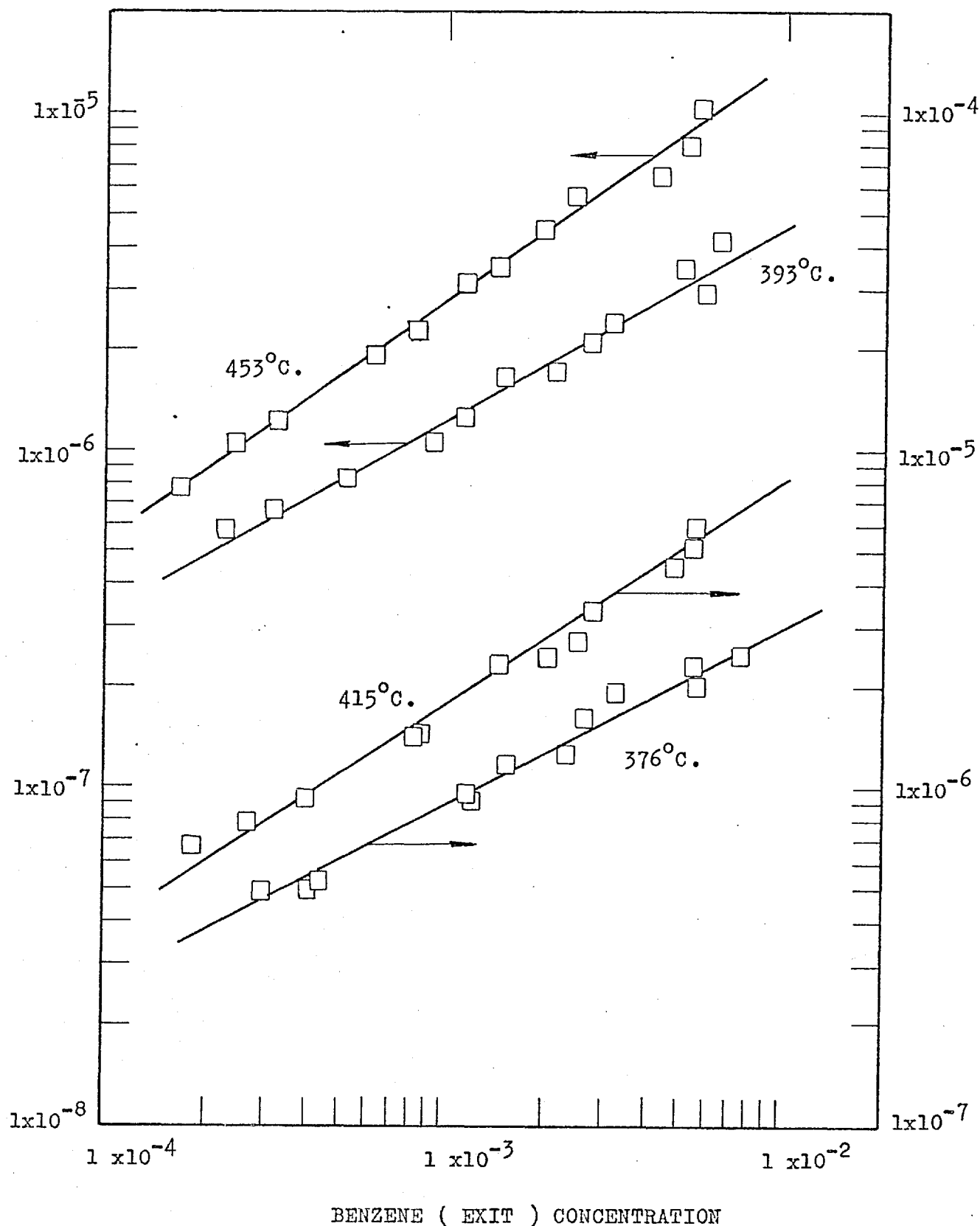


FIGURE 3.42 : ORDER PLOTS FOR BENZENE REMOVAL IN THE S.G.S.R.

Benzene Oxidation Rate / (Oxygen Conc.)^{1/2}
plotted against Reacting Benzene Concentration.

Rate has units of m.gm.⁻¹.Sec.⁻¹; Concn. in m./li.

TABLE 3.29

RATE OF OXIDATION OF BENZENE AS A FUNCTION OF TEMPERATURE
RESULTS FROM THE S.G.S.R. / CIRCULAR BASKET

The General Form of the Rate Expression is ,

$$r = k_T \times (\text{Concn. } O_2)^p \times (\text{Concn. Bz})^q$$

where , the Rate (r) has units of $\text{m.gm.}^{-1}\text{sec.}^{-1}$

the Rate Constant (k_T) at a temperature T, $\text{p+q } 1-\text{p}-\text{q } -1 \text{ } -1$
has units of li. m. gm.sec.

the concentrations of O_2 and Bz are the reacting (exit)
concentrations in units of m./li.

p and q are the orders of reaction w.r.t. O_2 and Bz
respectively. ($p = 0.5$ in all cases)

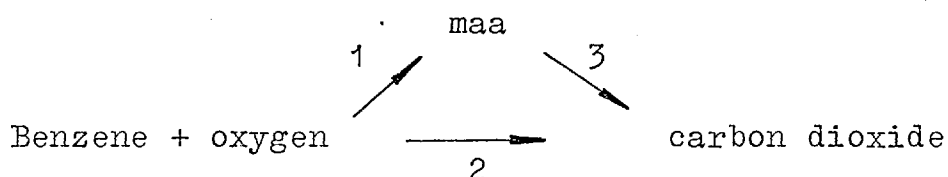
<u>RATE EQUATION</u>	<u>TEMPERATURE</u>
$\frac{dBz}{dt} = - 3.53 \times 10^{-5} (C.O_2)^{0.5} (C.Bz)^{0.54}$	376°C.
$\frac{dBz}{dt} = - 6.30 \times 10^{-5} (C.O_2)^{0.5} (C.Bz)^{0.57}$	393°C.
$\frac{dBz}{dt} = - 1.23 \times 10^{-4} (C.O_2)^{0.5} (C.Bz)^{0.62}$	415°C.
$\frac{dBz}{dt} = - 2.88 \times 10^{-4} (C.O_2)^{0.5} (C.Bz)^{0.68}$	453°C.

DISCUSSION

- Section A Evidence of Interacting Gas and Gas-Solid
Reactions
- Section B Development of Surface Adduct Theory
- Section C Development of Kinetic Data for the Homogeneous
Reactions and the Discussion of a General
Mechanism
- Section D Explanation of the S.G.S.R. Results in terms
of the Surface Adduct Theory
- Section E Application of a general Reduction-Oxidation
Mechanism to the S.G.S.R. Results
- Section F General Conclusions

A Evidence of Interacting Gas and Gas-Solid Reactions

The oxidation of benzene to maleic anhydride (maa) and to carbon dioxide has, in the past, been discussed in terms of the concurrent and consecutive catalytic reactions 1, 2, and 3 shown below.



The present results show that this is at best an oversimplification, for two reasons. Firstly, and in contradiction of previous reports, the oxidation of maa to carbon dioxide has been found to be relatively unimportant except in the presence of metal surfaces (section 3C1). This apparently anomolous observation can be resolved by inspection of previous papers. In every case, with the possible exception of work by Ioffe et al.(34 , 52), the reactor used was either made from or contained steel, the minimal quantity of which (37) corresponding to the minimal over-oxidation of maa. The present results show that over-oxidation of maa in a glass reactor is not significant even at the high conversions observed over catalyst 2, except in the presence of steel surface, and that this observation holds both in the gas phase and over the catalyst. Indeed, results in the S.G.S.R. system using a feed of maa and air, led to the surprising conclusion that the presence of catalyst surface leads to a decrease in the rate of maa oxidation initiated by the steel surface. It must therefore be concluded that

the vanadia surface plays an active part in removing species necessary for the continued oxidation of the anhydride.

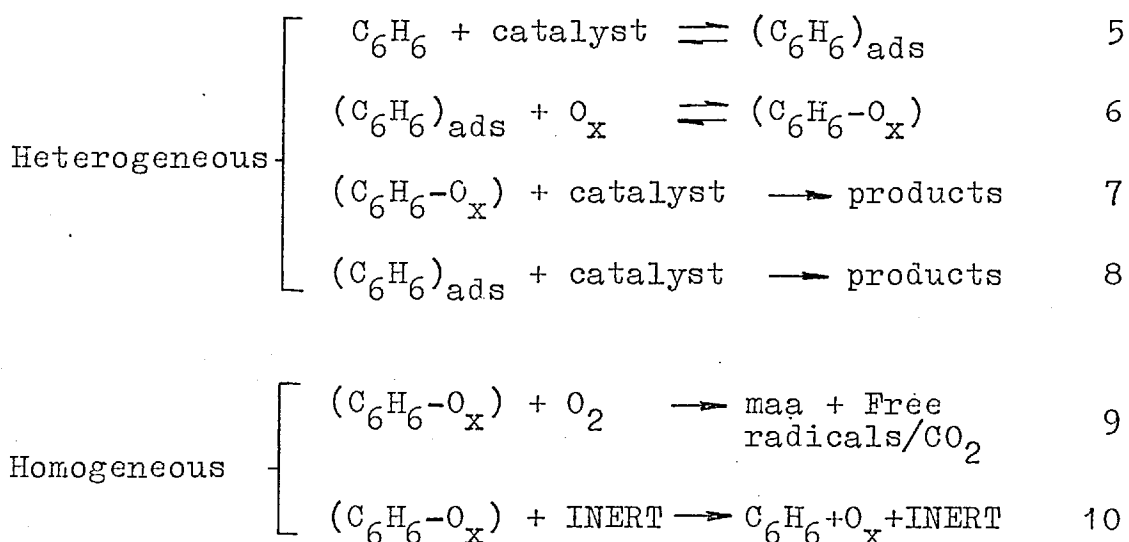
The second, and most theoretically interesting oversimplification, refers to the oxidation of benzene to maa. The present results show unambiguously that this oxidation involves interacting gas-solid (heterogeneous) and gas (homogeneous) reactions. This interaction is seen most clearly from the results given in Figures 3.13 and 3.16. Using exactly the same catalyst and a fixed contact time, increasing the amount of inert surface after the bed led to increasing quantities of benzene and decreasing quantities of maa in the final products. Since benzene is not oxidised in the gas phase at these temperatures (section 3B), and very great care was taken to check that no change in the activity of the catalyst had occurred between runs, the only possible inference is that some other process is occurring in the gas phase which is initiated on the catalyst surface. The effect of the "inert" packing is to prevent this reaction.

Results from the S.G.S.R., where the effect of increasing reactor free volume was studied using circular and cruciform baskets, also show the presence of a gas phase reaction involving benzene (section 2B). At identical catalyst contact times, (and therefore differing gas phase residence times), the conversion of benzene in the cruciform basket was always less than in the circular, and the conversion to maa was also considerably reduced (Figures 3.2,3.3). Although the drop in maa yield could possibly be explained in terms of increased over-oxidation due to the relative increase of steel surface:volume ratio, the corresponding decrease in ben-

zene converted can only be accounted for in terms of a gas phase reaction involving benzene, and one which must be linked to the overall catalytic reaction. Studies in the S.G.S.R. at a higher reaction temperature (453°C) gave results which reflected the relatively increased contribution of the homogeneous part of the supposed homogeneous-heterogeneous interacting reactions (section 2C).

catalyst but reacting to form maa in the gas phase. As discussed below, this intermediate may well be a benzene-oxygen adduct formed by reaction of adsorbed benzene with oxygen either from the gas phase or from the catalyst.

Details of the mechanism can perhaps best be considered in the light of the proposed scheme which involves the catalytic production of the intermediate followed by a gas phase reaction to produce maa.



Although there are some difficulties, this network does seem to explain the experimental observations. Considering first the results in Figures 3.13 and 3.16, increased inert packing would be expected to favour reaction 10 at the expense of reaction 9, leading to the isolation of more benzene and less maa in the final products. Semiquantitative estimation of the importance of reactions 7 and 8 show that the wholly catalytic production of maa is not of major importance (see below). In this case the relation between heterogeneous reactions producing the adduct, and homogeneous reactions favouring the decomposition of the adduct to maa, is clearly seen.

The above explanation involving a catalytically formed benzene-oxygen adduct which is free to undergo reaction in the gas phase, would also explain the results from the S.G.S.R. studies (section 2). Despite maleic anhydride over-oxidation, due to a steel catalysed combustion reaction, there would also be an effect of free volume on the homogeneous rate of decomposition of the adduct to maa. Because of the necessarily higher residence/contact times involved in the use of the S.G.S.R. as opposed to the tubular reactors, secondary reactions involving the adduct would obviously be encouraged. Unfortunately, the reacting gases are never free from the influence of catalyst surface (as they are in the tubular reactor studies), and collision of the benzene/oxygen adduct with catalyst surface may not necessarily give benzene and oxygen, but rather they may give products of complete oxidation. This cannot be completely true or, at constant catalyst contact time, free volume should have no influence on benzene conversion. Experimental results (section 2B) show that such an effect does exist. It is significant, however, that at high temperatures the differences in benzene conversion at high oxygen to fuel input ratios as a result of free volume changes are remarkably small (see Figure 3.4). This would indicate that, at such temperatures and in the presence of an excess of oxygen, once the benzene/oxygen adduct has been formed there is little chance of adduct decomposition back to benzene and oxygen.

Since these proposals satisfy many of the experimental observations, it is rewarding to consider scientific support for the ideas. The arguments split naturally into two parts: the catalytic production of the intermediate and its subse-

quent reactions.

The only positive evidence that the intermediate is a benzene-oxygen adduct comes from the observation that the intermediate breaks down only to benzene and oxygen on collision with inert surface. The only possible alternatives for such an intermediate would seem to be an adduct or a peroxide/hydroperoxide with the latter being less likely to break down to the original components on collision (6, 71, 87). Possible structures of the adduct are discussed later.

The catalytic production of adduct may result from the reaction of positively charged adsorbed benzene with negatively charged oxygen species, the resulting neutral adduct desorbing easily from the surface. Alternatively, adsorbed hydrocarbon may react with oxygen from the gas phase. In either case, the hydrocarbon is probably adsorbed by an electron donating mechanism leading to a drain of electrons at the point of adsorption. Since V^{5+}/V^{4+} is known to be the active centre (44, 45, 48, 56, and 57) the possibility of molecular benzene being adsorbed in a planar fashion seems unlikely on steric grounds. Considering the relative sizes of a benzene ring (diameter $3\overset{\circ}{\text{Å}}$), and the separation between the vanadium ions ($1.8\overset{\circ}{\text{Å}}$ on the (001) face), the benzene ring set planar on the (001) face would interact with something like seven vanadium ions. It has been suggested that this disturbance would appear to be too great (86). It is easier to believe that the benzene adsorption is specific to one V^{5+}/V^{4+} ion with the bond being formed by the donation of electrons from the pi-bond of the benzene ring into the empty d_{z^2} orbital of the V^{5+} . A back dona-

tion of these electrons through the dxz and dyz orbitals into the anti-bonding orbitals would have the net effect of weakening the ring. The benzene will be adsorbed, therefore, at one point with the remainder of the molecule flapping in space. Oxygen attack from either the gas phase or by surface oxidic species will be at the ring positions of smallest electron density (oxygen acceptor), opposite the point of attachment of the benzene ring. The formation of two carbon-oxygen bonds could release sufficient energy in the ring to cause the RO_x species to desorb, leaving a residual V^{4+} surface ion requiring further oxidation. Homogeneous oxidation of the active RO_x species to maleic anhydride would presumably follow since it is probable that the desorbed RO_x would react with gaseous oxygen before it readsorbed, providing the concentration of surface was not very high.

Gas phase reactions of this type are normally considered to be unselective while the production of maa under typical conditions can be highly selective. Table 4.2 shows the selective carbon yields of maa and CO_2 for different tubular reactor configurations. The selectivity of the homogeneous reaction, obtained by subtracting the results for maximum surface after the bed from those for minimum surface after the bed, is seen to be a maximum for maa formation at high oxygen to fuel ratios.

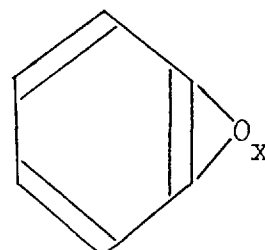
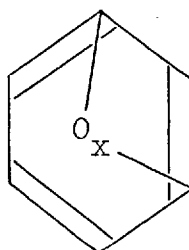
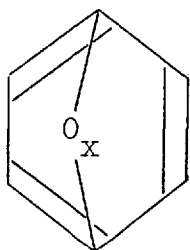
It seems possible, however, that this selectivity is closely associated with the structure of the adduct, which may be formed specifically on the surface of the catalyst. Since inert packing placed after the bed leads to breakdown

of the adduct to benzene and oxygen, the overall structure must be fairly simple. The most satisfactory explanation would appear to involve oxygen addition across the ring:-

1 , 4 addition

1 , 3 addition

1 , 2 addition

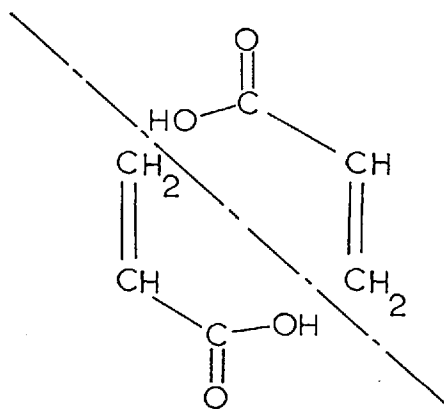
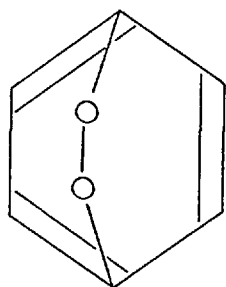


where x may be 1 or 2, with $x=2$ being favoured by the observation that the adduct decomposes only to benzene and oxygen.

1, 2 and 1, 4 addition have previously been suggested to occur both in the gas phase as a precursor to the hydroquinone (39, 41, 42, 87), and on the surface of the catalyst (38, and 87) where the 1, 2 structure was postulated to be an adsorbed precursor of products of complete oxidation and the 1, 4 complex to be the adsorbed intermediate necessary for maa formation.

It is not easy to suggest which of these adducts would be formed nor to predict the decomposition mechanism leading specifically to maleic anhydride, although the most obvious route would start from the 1, 4 adduct. It is possible, however, to relate the formation of some minor products with the alternative adducts above. Thus, for example, phenol may originate entirely from a completely gas phase reaction (6, 43 and 71), or from the further reactions of

adduct C. Again, there is a marked similarity between the structure of adduct A, and two molecules of acrylic acid, which is produced in the reaction under some reaction conditions (section 3C2).



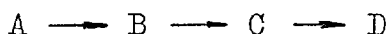
This similarity was sufficient to be tested experimentally. Acrylic acid was observed in every case when the surface: volume ratio after the catalyst bed was increased (Table 3.1), the acid being observed only in trace quantities at high conversions when this ratio was low. The yield of acrylic acid increased as the flow of gas through the reactor decreased, although over-oxidation of the acid under these conditions is known to be important. No trace of acrylic acid could be observed when maa, alone or with oxygen, was used as a fuel.

There seems little doubt that acrylic acid is only observed when acid over-oxidation is inhibited, as, for example, by increasing the surface after the bed. Unfortunately, the results are consistent with two mechanistic routes: either the acrylic acid is formed on the surface of the catalyst (reaction 7 or 8) and overoxidises in the gas phase, the reaction being inhibited by surface. Alternatively an adduct, which may or may not be the same as that responsible for the production of maa, is formed on the catalyst and

decomposes to acrylic acid in the gas phase. In the latter case, increase in surface after the bed would be expected to yield less acrylic acid (as for maa), not more. However, since the oxidation of acrylic acid occurs in the gas phase, the comparative efficiency of the surface in quenching the decomposition and the over-oxidation may lead to a net increase in the yield of acid observed.

C Development of Kinetic Data for the Homogeneous Reactions
and the Discussion of a General Mechanism

It is possible to obtain a semiquantitative measure of the importance of the interaction and of the kinetics of the homogeneous reactions from the experimental results. The ''initial rate'' approach, where the measured rate at zero catalyst contact time is equated to the input concentrations of the feed (assumed constant when dealing with very small conversions), was discarded at an early stage in the work as being unsuitable for use for the following reasons. In consecutive reactions of any kind the use of ''initial rate'' techniques can be applied with confidence only for the disappearing reactant and the primary product B.



By analogy with our reaction system, the disappearance of benzene may be studied in any of the tubular reactors used, but unfortunately one of the further products of B (the benzene/oxygen adduct) is benzene itself (and in large amounts if ample inert surface is present). Similarly maleic anhydride and some of the carbon dioxide produced are both further products of B which makes the basis of an ''initial rate'' approach unsound.

Evaluation of the homogeneous reactions of the adduct leading to maa, to carbon dioxide or back to benzene are based on numerical differences in results obtained for two extreme cases, where the catalyst was taken with 8.16 ml. Free space (a) with minimal surface and (b) with ca 420cm² of stone surface. Decomposition of the adduct to benzene and

Table 4.1 : KINETICS OF THE GAS PHASE REACTIONS
TYPICAL RESULTS FOR THE 12 : 1 OXYGEN
TO FUEL RATIO.

Concn. $Bz_{in} = 2.0 \times 10^{-3} \text{ m./li.}$; Concn. $O_{2in} = 24.5 \times 10^{-3} \text{ m./li.}$

CONTACT TIME	DIFFERENCES IN CONVERSION				DIFFERENCES IN CONCENTRATION				RES.
	BZ	MAA	CO ₂	AA	BZ	MAA	CO ₂	AA	TIME
$\frac{\text{gm.ml.}^{-1}}{\text{sec.}}$	$(\text{ all m./li. } \times 10^{-3})$								sec.
.5	.080	.080	.10	.001	.16	.16	.20	.002	.27
1.0	.140	.125	.20	.002	.28	.25	.40	.004	.54
1.5	.170	.160	.40	.0033	.34	.32	.80	.0066	.81
2.0	.185	.185	.55	.0046	.37	.37	1.10	.0092	1.08
2.5	.205	.210	.60	.006	.41	.42	1.20	.012	1.35
3.0	.215	.230	.65	.0071	.43	.46	1.30	.0142	1.62
3.5	.225	.240	.65	.0081	.45	.48	1.30	.0162	1.89
4.0	.230	.255	.65	.009	.46	.51	1.30	.018	2.16
4.5	.230	.260	.66	.0096	.46	.52	1.32	.0192	2.43

Differences in conversion are those obtained by subtracting results over catalyst + 8.16 ml. free volume / 437 cm² surface, from corresponding results over catalyst + 8.16 ml. / minimal surface.

Catalyst Contact Time = mass of catalyst / flow at reactor temperature.

Residence Time = volume of space after the bed / flow at reactor temperature.

As the mass of catalyst was 15.11 gm. in both cases, and the free space after the catalyst bed was always 8.16 ml. , we have

$$\text{RESIDENCE TIME} = 0.54 \times \text{CONTACT TIME}$$

$$(\text{sec.}) \quad \left(\frac{\text{ml}}{\text{gm}} \right) \quad \left(\frac{\text{gm.ml.}^{-1}}{\text{sec.}} \right)$$

(contd./over)

SELECTIVITY OF THE HOMOGENEOUS DECOMPOSITION
REACTION TO MAA AND CARBON DIOXIDE.

Concn. $Bz_{in} = 2 \times 10^{-3}$ m./li. ; Concn. $O_{2in} = 24.5 \times 10^{-3}$ m./li.

CONTACT TIME (gm.ml. ⁻¹ sec. ⁻¹) :	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5
SELECTIVE CARBON									
YIELD OF MAA :	66.7	60.0	63.0	66.7	68.0	71.0	72.0	73.0	74.0
SELECTIVE CARBON									
YIELD OF CO ₂ (1)* :	33.3	30.0	31.5	33.5	34.0	35.5	36.0	36.5	37.0
SELECTIVE CARBON									
YIELD OF CO ₂ (2)* :	-	-	7.8	16.2	14.6	14.8	12.5	9.5	9.5

Concn. $Bz_{in} = 4.08 \times 10^{-3}$ m./li. ; Concn. $O_{2in} = 20.4 \times 10^{-3}$ m./li.

CONTACT TIME (gm.ml. ⁻¹ sec. ⁻¹) :	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5
SELECTIVE CARBON									
YIELD OF MAA :	61.5	50.5	45.5	39.5	37.0	36.5	35.5	35.5	35.5
SELECTIVE CARBON									
YIELD OF CO ₂ (1) :	30.7	25.0	23.0	20.0	18.5	18.0	17.7	17.7	17.7
SELECTIVE CARBON									
YIELD OF CO ₂ (2) :	7.7	12.5	34.0	45.0	50.5	52.0	50.0	48.0	48.0

Concn. $Bz_{in} = 7.7 \times 10^{-3}$ m./li. ; Concn. $O_{2in} = 7.7 \times 10^{-3}$ m./li.

CONTACT TIME (gm.ml. ⁻¹ sec. ⁻¹) :	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5
SELECTIVE CARBON									
YIELD OF MAA :	37.5	43.0	44.5	44.5	36.0	29.5	29.0	30.0	31.0
SELECTIVE CARBON									
YIELD OF CO ₂ (1) :	19.0	22.0	22.5	22.5	18.0	15.0	14.5	15.0	15.5
SELECTIVE CARBON									
YIELD OF CO ₂ (2) :	2.1	-	-	5.6	9.0	33.5	43.0	49.0	53.0

* (1) refers to that CO₂ produced with each mole of maa.

(2) refers to that CO₂ produced directly from adduct.

oxygen need not be complete in the latter case if differences between the two experiments are used to calculate the efficiency of reaction 10. Since the same amount of adduct is produced catalytically in both cases, the differences in benzene conversion give a measure of the amount of adduct that would have gone to maa and carbon dioxide had the packing not been there.

The differences in concentration between the two cases were obtained from results such as are presented in Figures 3.12, 3.13 and Tables 3.5, 3.10. Typical results for an oxygen:benzene ratio of 12 : 1 are presented in Table 4.1 where values of the differences of benzene (adduct concentration), maa and CO_2 are shown as a function of time. Also shown are the selective carbon yields of the homogeneous decomposition reactions to maa and CO_2 .

Differences in benzene and maleic conversion as a function of time are shown graphically for all three O_2 :fuel ratios used in Figures 4.1, 4.2. Since the amounts of adduct produced catalytically are the same in both cases, it is convenient to redefine the time variable in terms of residence in the free volume after the bed. Similar plots may be constructed for carbon dioxide, and all the plots were found to be linear at low residence times when traces of acrylic acid were considered as part of the carbon dioxide yield (see Figure 4.3). It was assumed that each 'molecule' of adduct leading to maa also gave two molecules of carbon dioxide and this was accounted for in selectivity and initial rate calculations.

Assuming that only one benzene molecule is produced by the decomposition of an adduct molecule, it is then possible

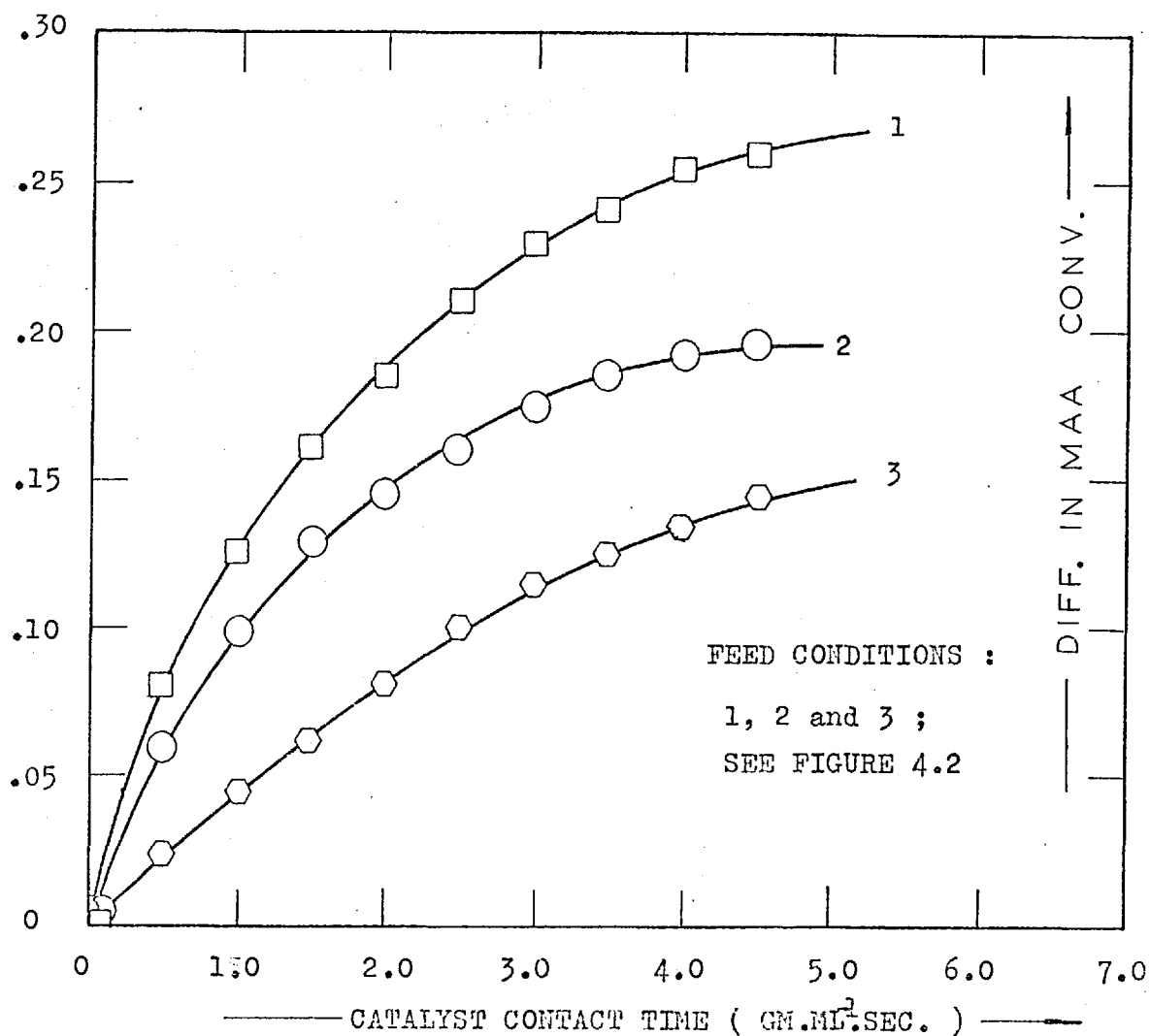
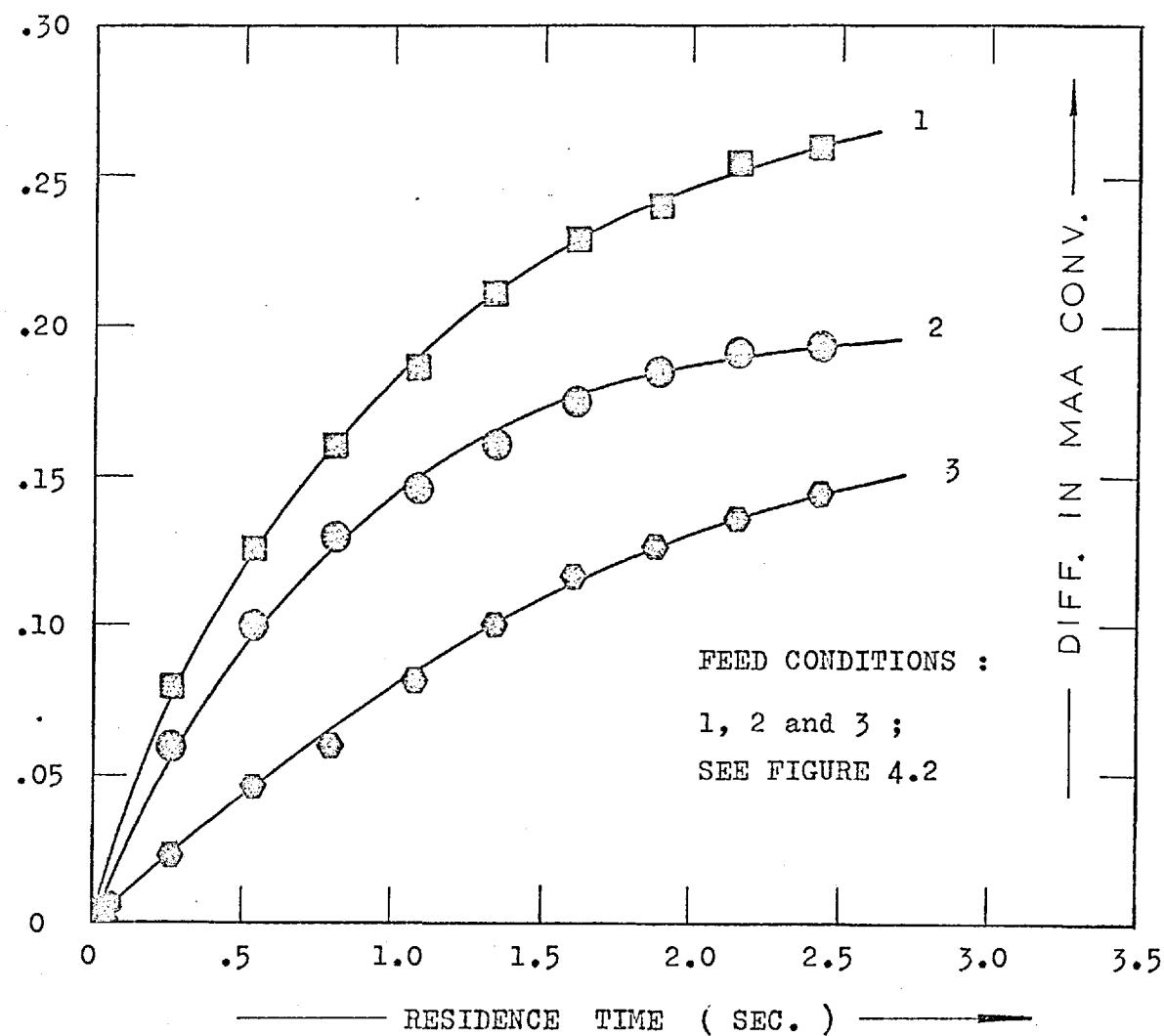
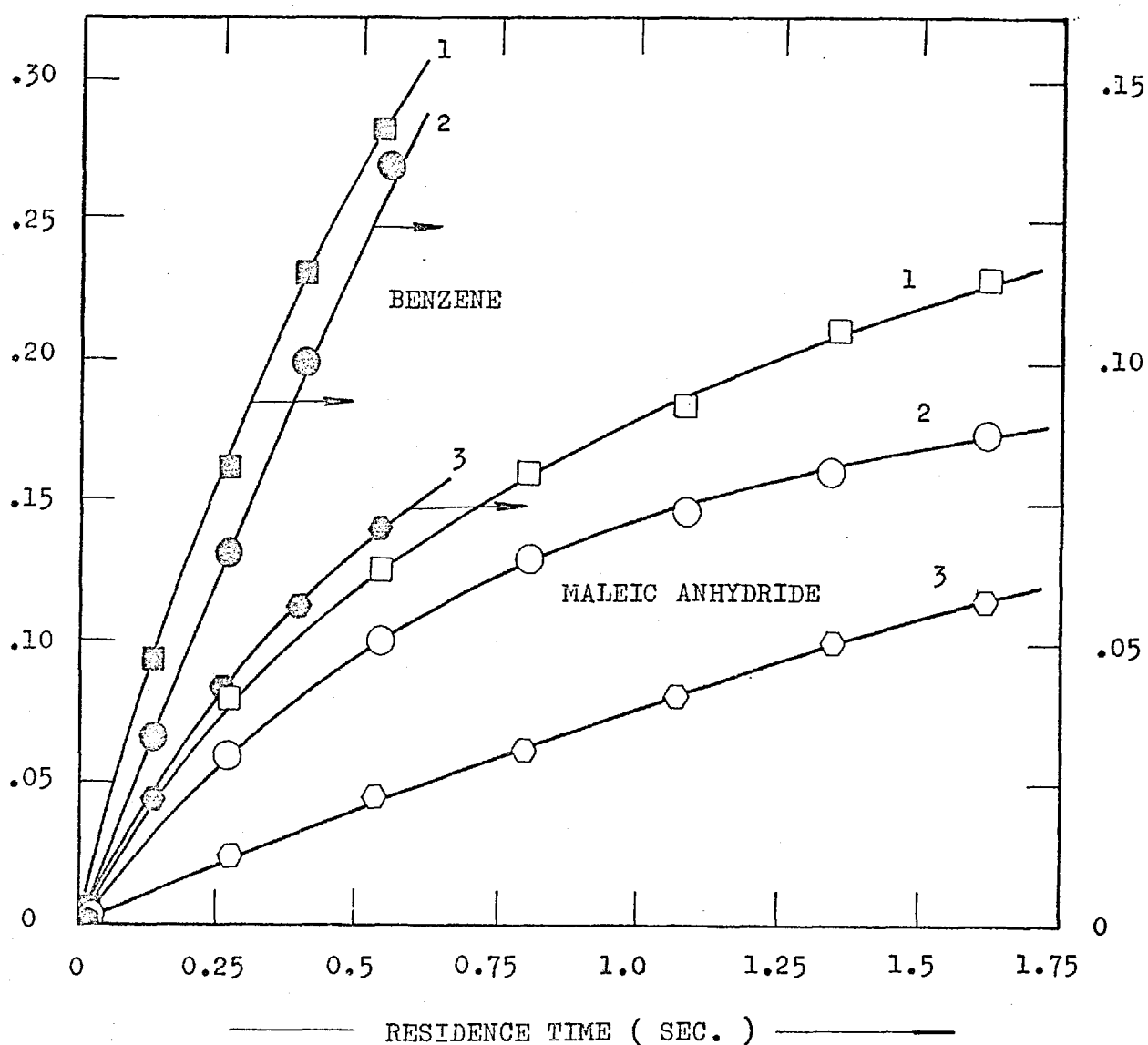


FIGURE 4.1 : DIFFERENCES IN MAA CONVERSION WITH TIME

FIGURE 4.2 : DIFFERENCES IN BENZENE AND MAA CONVERSION AS A FUNCTION OF TIME, FOR DIFFERENT O_2 /FUEL RATIOS

Results shown are those for the initial time (residence time) period. This facilitates the calculation of respective "Initial Rates".

Differences in Conversion are obtained by subtracting results using ' catalyst + 8.16 ml. / maximum surface' from results using ' catalyst + 8.16 ml. / minimum surface'.



FEED CONDITIONS :

- 1 : $C.BZ_{in} = 5 \text{ mole\%}$; $C.O_2 = 60 \text{ mole\%}$
- 2 : $C.BZ_{in} = 10 \text{ mole\%}$; $C.O_2 = 50 \text{ mole\%}$
- 3 : $C.BZ_{in} = 18.9 \text{ mole\%}$; $C.O_2 = 18.9 \text{ mole\%}$

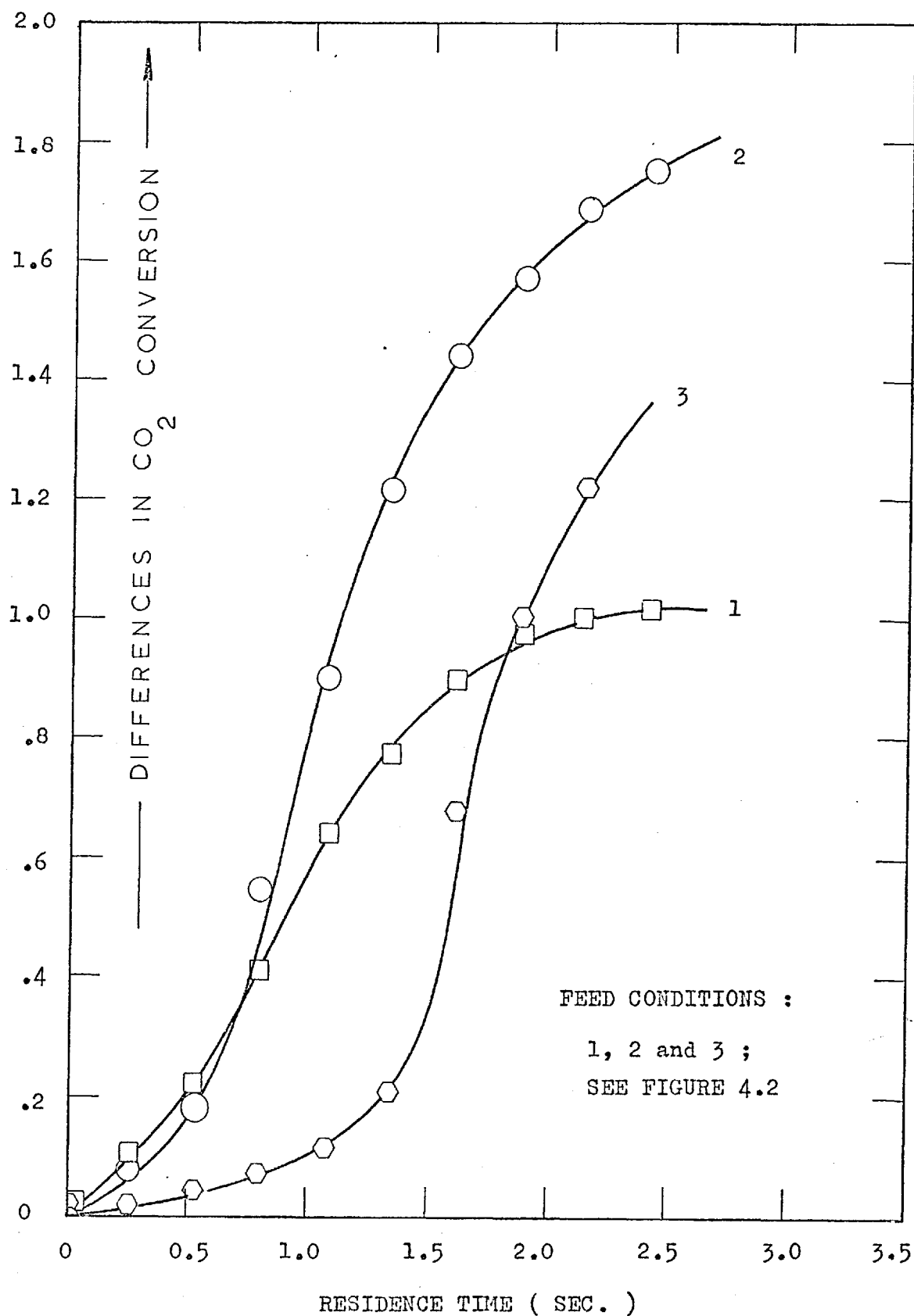


FIGURE 4.3 : DIFFERENCES IN CO₂ CONVERSION AS A FUNCTION OF TIME, FOR DIFFERENT O₂/FUEL RATIOS.

(The CO₂ conversion includes acrylic acid contributions, and takes into account that CO₂ formed with each mole of Maa.)

to obtain rates of reaction from the tangents to the slopes at an 'adduct' concentration as measured from the benzene difference curve. Results may be obtained in the initial rate period for the three oxygen:fuel ratios, and these may be used to generate log rate versus log concentration plots. The 'initial' concentration of adduct is taken as the mean value over the time range where the benzene concentration / time curves are sensibly linear ie. where rate of adduct decomposition to benzene divided by adduct concentration is about constant. Using a trial and error procedure it is possible to fit an oxygen dependence and to establish appropriate rate expressions. Typical calculations showing the evaluation of the rate of maa production from adduct and from benzene are shown in Table 4.3 . The relevant order plots for adduct decomposition, maa and carbon dioxide production are shown in Figure 4.4 , from which the relationships, shown below, were established.

$$\frac{d(\text{benzene})}{dt} = k_{10}(M)(\text{adduct})^1 (\text{O}_2)^0$$

where M = third body

$$\frac{d(\text{maa})}{dt} = k_9 (\text{adduct})^1 (\text{O}_2)^{0.5}$$

$$\frac{d(\text{CO}_2)}{dt} = k_{11}(\text{adduct})^1 (\text{O}_2)^1$$

where, at 415°C, $k_{10}(M) = 4.00 \text{ sec}^{-1}$, $k_9 = 26.7 \text{ li.}^{1/2} \text{ m.}^{-1/2} \text{ sec}^{-1}$, and $k_{11} = 2.25 \times 10^2 \text{ li.m.}^{-1} \text{ sec}^{-1}$.

Although the decomposition of adduct to benzene and oxygen is heterogeneous in nature, providing the concentration of inert surface is taken as if it were a third body in the gas

EVALUATION OF A RATE EXPRESSION FOR THE PRODUCTION
OF MAA FROM THE HOMOGENEOUS DECOMPOSITION OF ADDUCT

Initial Rate of Homogeneous MAA formation *	Initial Adduct (Bz/O ₂) Concn. ⁺	(Oxygen Concn.) ^{1/2}	I.Rate MAA <u>(C.Bz/O₂)¹</u>	I.Rate MAA <u>(C.O₂)^{1/2}</u>
(m.li. ⁻¹ .sec. ⁻¹)	(m./li.)	(m./li.)	(sec. ⁻¹)	(m. ^{-1/2} li. ^{-1/2} sec. ⁻¹)
0.556 x 10 ⁻³	1.45 x 10 ⁻⁴	0.1565	3.83	3.55 x 10 ⁻³
0.946 x 10 ⁻³	2.55 x 10 ⁻⁴	0.143	3.71	6.61 x 10 ⁻³
0.703 x 10 ⁻³	3.10 x 10 ⁻⁴	0.0883	2.27	7.96 x 10 ⁻³

* Initial Rates are calculated from tangents to the Maa concentration curves at zero residence time.

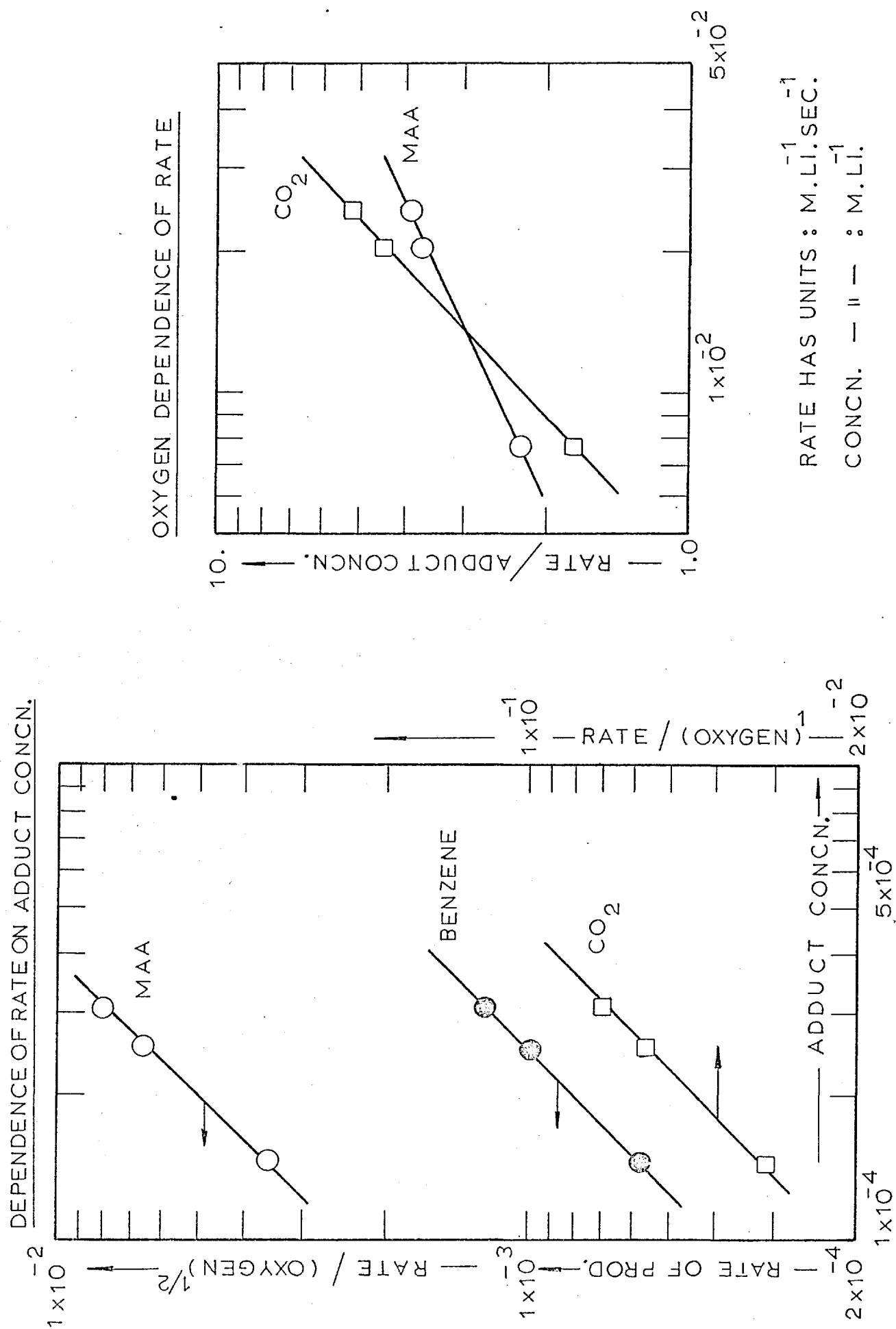
⁺Initial Adduct concentrations are calculated from average values of differences in benzene conversion over the initial time period. (0 to 0.54 sec. i.e. 0 to 1.0 gm.ml.⁻¹.sec.)

$$\text{RATE EXPRESSION : } \frac{d\text{Maa}}{dt} = 26.7 (C.\text{Bz}/O_2)^1 (C.O_2)^{1/2}$$

and has units of m.li.⁻¹.sec.⁻¹

TABLE 4.3

FIGURE 4.4 : KINETICS OF THE HOMOGENEOUS DECOMPOSITION OF
ADDUCT TO (a) BENZENE (b) MAA (c) CO_2



phase (such as nitrogen diluent), then the above may be considered to be homogeneous rate expressions. This proves very useful in that appropriate pre-exponential A factors, available in the literature for such specific hydrocarbon oxidation reactions, may be used to calculate respective energies of activation.

Using values of $6 \times 10^{10} \text{ li.m.}^{-1}\text{sec}^{-1}$ for bimolecular collisions and 10^{13} sec^{-1} for monomolecular collisions (88 and 89) the appropriate energies of activation were calculated to be:-

$$E_{A_{10}} = 36.4 \text{ Kcal/mole}$$

$$E_{A_9} = 29.9 \text{ Kcal/mole}$$

$$E_{A_{11}} = 25.3 \text{ Kcal/mole}$$

Despite the inaccuracy associated with the average value of the A factor, the adduct appears to be very stable and should show up in a suitably chosen chromatographic column. However, the decomposition reaction is almost certain to be catalysed by any steel surface the adduct meets before reaching the detector.

The initial rate procedure is also successful in evaluating the dependence of the rate of maleic production on benzene concentration. Calculations are shown in Table 4.4 and this leads to the appropriate order plots shown in Figure 4.5 . The final rate expression is

$$\frac{d(\text{Maa})}{dt} = k_m (\text{Benzene})^1 (\text{O}_2)^1$$

where, at 415°C , $k_m = 1.157 \text{ li.m.}^{-1}\text{sec}^{-1}$.

THE HOMOGENEOUS PRODUCTION OF MAA AS A FUNCTION
OF BENZENE AND OXYGEN FEED CONCENTRATIONS.

EVALUATION OF A RATE EXPRESSION.

Initial Rate of Homogeneous MAA formation *	Benzene Concn.	Oxygen Concn.	I.Rate MAA $(C.Bz_{in})^1$	I.Rate MAA $(C.O_{2in})^1$
(m.gm. ⁻¹ Sec. ⁻¹)	(m./li.)	(m./li.)	(li.gm. ⁻¹ Sec. ⁻¹)	(li.gm. ⁻¹ Sec. ⁻¹)
0.300×10^{-6}	2.0×10^{-3}	24.5×10^{-3}	0.15×10^{-3}	1.225×10^{-5}
0.511×10^{-6}	4.08×10^{-3}	20.5×10^{-3}	0.125×10^{-3}	2.49×10^{-5}
0.380×10^{-6}	7.77×10^{-3}	7.7×10^{-3}	0.049×10^{-3}	4.90×10^{-5}

* Initial Rates are calculated from tangents to the Maa concentration curves at zero catalyst contact time.

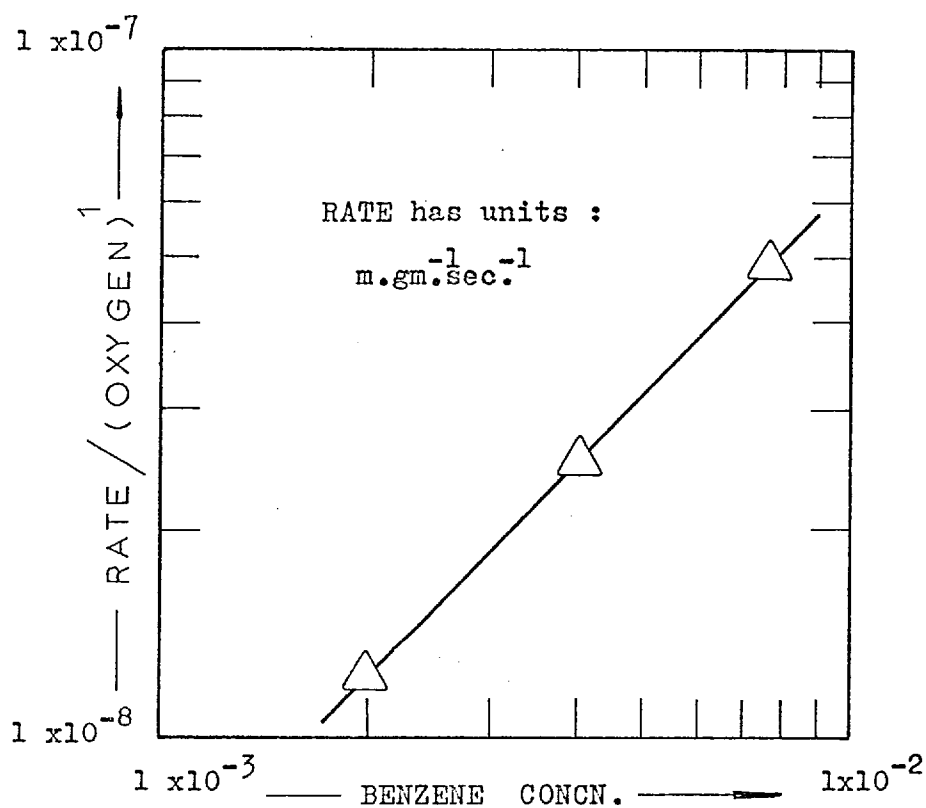
The resulting Rate Expression has units of m.gm.⁻¹Sec.⁻¹, but as the reaction is homogeneous in nature the relationship between residence time and catalyst contact time was used.

$$\text{RATE EXPRESSION : } \frac{dMaa}{dt} = 1.157 (C.Bz_{in})^1 (C.O_2)^1$$

and has units of m.li.⁻¹Sec.⁻¹

TABLE 4.4

DEPENDENCE OF RATE ON BENZENE CONCN.



DEPENDENCE OF RATE ON OXYGEN CONCN.

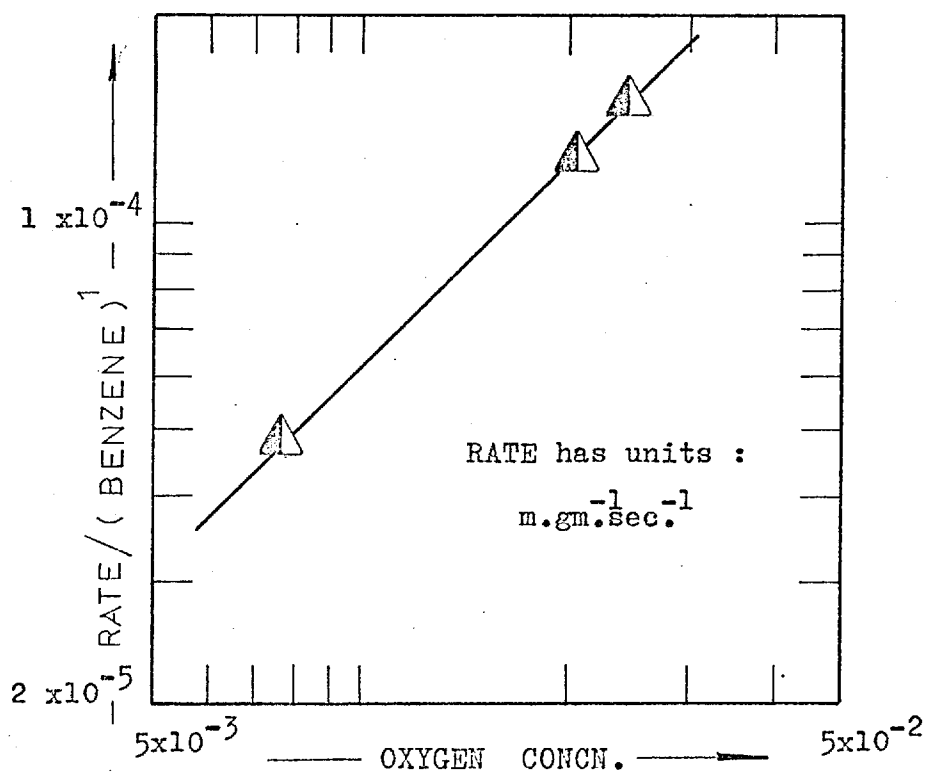


FIGURE 4.5 : THE HOMOGENEOUS PRODUCTION OF MAA AS A FUNCTION OF BENZENE AND OXYGEN FEED CONCENTRATIONS.

Using the appropriate A factor for bimolecular collision, the energy of activation is calculated to be 33.7 Kcal/mole. It is interesting to compare this value with that obtained from S.G.S.R. studies presented in the results, section 5C1. Although constant order kinetics had to be assumed for the evaluation of E_A , Figure 3.35 gave a value of $35.3(\pm 2.5)$ Kcal/mole, in good agreement with the above.

The amount of maa that originates from the homogeneous-heterogeneous reaction is open to some doubt, but the indications are that only small amounts originate from a pure heterogeneous reaction (reaction 8 above). Although results in the presence of high inert surface areas (Figures 3.13, 3.16) show that significant quantities of maa appear to have been generated catalytically, it is important to remember that the voidage in the catalyst bed itself is of the order of 3 ml. Order of magnitude calculations show that the residence time of the adduct in this voidage would be sufficient to explain the production of maa in the catalyst bed in terms of mixed homogeneous-heterogeneous oxidation.

The production of carbon dioxide, on the other hand, appears to involve both gas phase and purely catalytic reactions, as can be seen by inspection of the selectivities of the various reactions. Table 4.1 shows the selective carbon yields of the homogeneous reactions to maa, to CO_2 (formed with each maa), and to CO_2 directly from adduct (by reaction 11). Although this table shows selectivity varying a little with contact/residence time, it is seen that the selectivity of the homogeneous reaction to maa compared with that to carbon dioxide is dependent on the fuel:oxygen ratio,

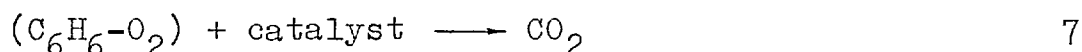
TABLE 4.2

SELECTIVE CARBON YIELDS OF MAA AND CARBON DIOXIDE
FOR DIFFERENT REACTOR CONFIGURATIONS.

Typical results for a constant Residence Time in the Free Space
after the bed of 1.08 sec. (equivalent to a catalyst contact
time of $2 \text{ gm.ml.}^{-1} \text{sec.}^{-1}$) Temperature : 415°C .

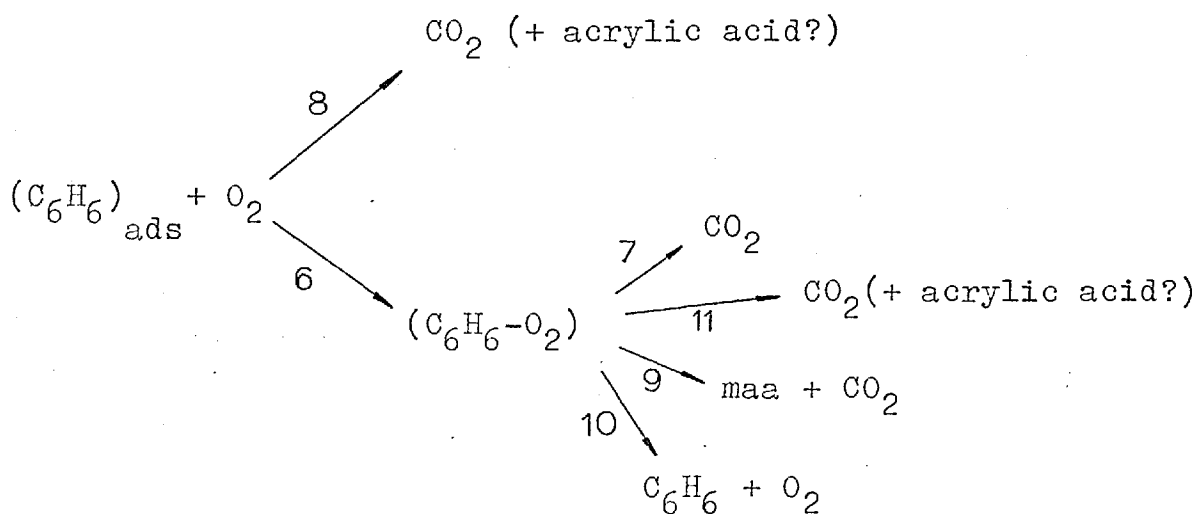
	$\text{C.Bz}_{\text{in}} = 2 \times 10^{-3} \text{ m./li.}$ $\text{C.O}_{2\text{in}} = 24.5 \times 10^{-3} \text{ m./li.}$		$\text{C.Bz}_{\text{in}} = 4.08 \times 10^{-3} \text{ m./li.}$ $\text{C.O}_{2\text{in}} = 20.4 \times 10^{-3} \text{ m./li.}$	
REACTOR CONFIGURATION	SELECTIVITY TO MAA	SELECTIVITY TO CO_2	SELECTIVITY TO MAA	SELECTIVITY TO CO_2
Catalyst + Free Space + minimal surface (a)	22.7	66.2	27.6	66.0
Catalyst + Free Space + maximum surface (b) (stone packed)	3.93	86.0	14.0	79.0
Homogeneous Reaction ie. (a) - (b)	66.7	16.2	39.5	45.0

(this is obvious from the kinetic equations above), varying from $S_{\text{maa}}/S_{\text{CO}_2} \cong 5$ at an oxygen:fuel ratio of 12, to $S_{\text{maa}}/S_{\text{CO}_2} \cong 0.75$ at a ratio of 1. However, comparison of the selectivities obtained in different reactor systems for the same oxygen:fuel ratios show marked differences (Table 4.2). It can be seen that the homogeneous reaction is considerably more selective to maa than the reaction in which the homogeneous reaction is minimised. Quenching of the homogeneous reaction, either on the catalyst or on an inert surface, obviously favours the production of carbon dioxide relative to maa. The inference that carbon dioxide is produced in the catalyst bed, either on the catalyst (reaction 8) or by quenching ie.



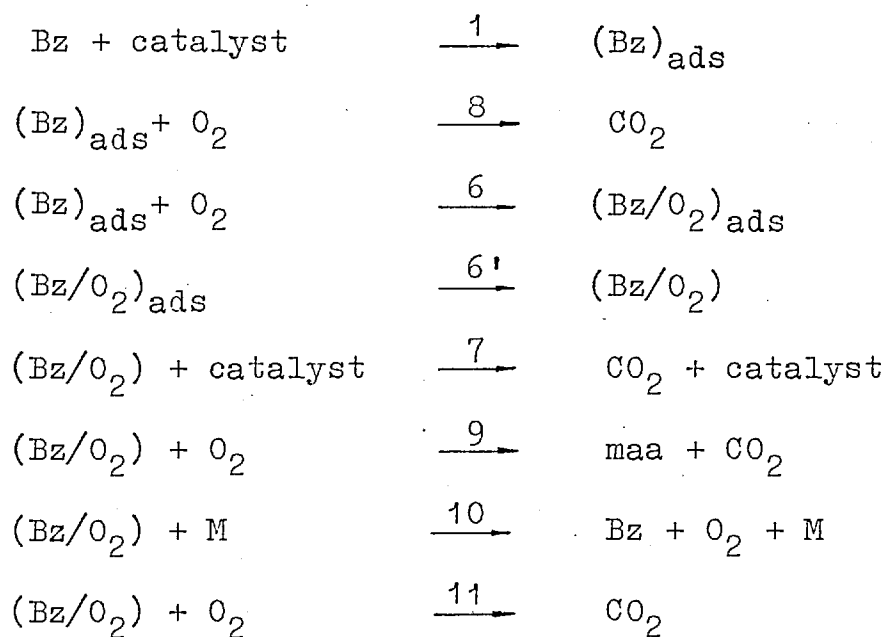
is inescapable.

To summarise then, the experimental results show that the production of maa and carbon dioxide involves both surface and gas phase reactions and these results are consistent with the reaction scheme,



of which either reaction 8 or 11 may account for the production of acrylic acid. To maximise the production of maa, a catalyst should be selected that favours the production of the benzene/oxygen adduct selectively and in high yield. Any subsequent reaction between the adduct and the catalyst will result in a decrease in the overall selectivity of the reaction to maa.

Examining the proposed mechanism in a more rigorous fashion, it may be possible to quantify the effects of inert surface using an analytical approach. Another useful quantitative result would be obtained if the development of an inter-relationship between overall disappearance of reactant benzene and production of the desired maa could be achieved. Listing the more important reactions, numbered as before:-



The following mass balances are easily derived,

$$\frac{d(\text{Bz})_{\text{ads}}}{dt} = k_1(\text{Bz})^a - k_8(\text{Bz})_{\text{ads}}^b(\text{O}_2)^c - k_6(\text{Bz})_{\text{ads}}^d(\text{O}_2)^e - (a)$$

$$\frac{d(\text{Bz/O}_2)_{\text{ads}}}{dt} = k_6(\text{Bz})_{\text{ads}}^d(\text{O}_2)^e - k_{6'}(\text{Bz/O}_2)_{\text{ads}}^f - (b)$$

$$\begin{aligned} \frac{d(\text{Bz/O}_2)}{dt} = & k_{6'}(\text{Bz/O}_2)_{\text{ads}}^f - k_7(\text{Bz/O}_2)^g - k_9(\text{Bz/O}_2)^h(\text{O}_2)^i \\ & - k_{11}(\text{Bz/O}_2)^j(\text{O}_2)^k - k_{10}(\text{Bz/O}_2)^l(\text{M})^m - (c) \end{aligned}$$

where k_i ($i = 1, 6, \dots, 11$) are respective heterogeneous and homogeneous rate constants, and $a, b, c, \dots, m$ are the orders of reaction w.r.t. to concentrations shown.

At the steady state, assuming that $\frac{d(\text{Bz})_{\text{ads}}}{dt}$, $\frac{d(\text{Bz/O}_2)_{\text{ads}}}{dt}$ and $\frac{d(\text{Bz/O}_2)}{dt}$ all equal zero,

$$k_1(\text{Bz})^a = k_8(\text{Bz})_{\text{ads}}^b(\text{O}_2)^c + k_6(\text{Bz})_{\text{ads}}^d(\text{O}_2)^e - (d)$$

$$(\text{Bz/O}_2)_{\text{ads}} = \frac{k_6}{k_{6'}}(\text{Bz})_{\text{ads}}^d(\text{O}_2)^e - (e)$$

Assuming further that all gas phase reactions have order w.r.t. adduct concentration of unity (experimentally 9, 10 and 11 do), and with $m=1$, we obtain:

$$(\text{Bz/O}_2) = \frac{k_6(\text{Bz})_{\text{ads}}^d(\text{O}_2)^e}{(k_7+k_9(\text{O}_2)^i+k_{11}(\text{O}_2)^k+k_{10}(\text{M}))} - (f)$$

Writing the mass balance for reacting benzene:-

$$-\frac{d\text{Bz}}{dt} = k_1(\text{Bz})^a - k_{10}(\text{Bz/O}_2)(\text{M})$$

and using (d) and (f),

$$-\frac{dBz}{dt} = k_8(Bz)_{ads}^b(O_2)^c + k_6(Bz)_{ads}^d(O_2)^e \left[1 - \frac{1}{\frac{k_7}{k_{10}}(M) + \frac{k_9(O_2)^i}{k_{10}(M)} + \frac{k_{11}(O_2)^k}{k_{10}(M)} + 1} \right] \quad - (g)$$

The effect of increasing the concentration of inert surfaces present in the reacting system is seen from studying (M) in equation (g). As (M) increases, the denominator of the last term on the R.H.S. tends to unity, and the whole of the term in brackets will therefore tend to zero. The rate of benzene conversion will fall away and finally remain constant at a value equal to $k_8(Bz)_{ads}^b(O_2)^c$, which is the rate of production of CO_2 directly from benzene by catalytic reaction.

The equivalent mass balance for maa is shown below:

$$\frac{dMaa}{dt} = k_9(Bz/O_2)(O_2)^i$$

Using (f) and rearranging leads to,

$$\frac{dMaa}{dt} = k_6(Bz)_{ads}^d(O_2)^e \left[\frac{1}{1 + \frac{k_7(O_2)^{-i}}{k_9} + \frac{k_{11}(O_2)^{k-i}}{k_9} + \frac{k_{10}(M)(O_2)^{-i}}{k_9}} \right] \quad - (h)$$

For fixed oxygen:fuel ratios, the denominator of (h) will increase with increasing (M) and the rate of production of maa will fall. Ostensibly, there will be some value for (M) which will make the rate virtually zero, although whether this

may be demonstrated practically is debatable.

Using (g) and (h) we can write,

$$-\frac{dBz}{dt} = k_8(Bz)_{ads}^b (O_2)^c + \frac{dMaa}{dt} \left[1 + \frac{k_7(O_2)^{-i}}{k_9} + \frac{k_{11}(O_2)^{k-i}}{k_9} + \frac{k_{10}(M)(O_2)^{-i}}{k_9} \right]$$

$$\times \left[1 - \frac{1}{\frac{k_7}{k_{10}(M)} + \frac{k_9(O_2)^i}{k_{10}(M)} + \frac{k_{11}(O_2)^k}{k_{10}(M)} + 1} \right]$$

Multiplying out the terms in brackets,

$$-\frac{dBz}{dt} = k_8(Bz)_{ads}^b (O_2)^c + \frac{dMaa}{dt} \left[1 + \left\{ \frac{k_7}{k_{10}(M)} + \frac{k_7^2}{k_9 k_{10}} \frac{(O_2)^{-i}}{(M)} + 2 \frac{k_7 k_{11}}{k_9 k_{10}} \frac{(O_2)^{k-i}}{(M)} + \frac{k_7(O_2)^{-i}}{k_9} + \frac{k_{11}(O_2)^k}{k_{10}(M)} + \frac{k_{11}^2}{k_9 k_{10}} \frac{(O_2)^{2k-i}}{(M)} + \frac{k_{11}(O_2)^{k-i}}{k_9} \right. \right.$$

$$\left. \left. - \frac{k_7}{k_{10}(M)} + \frac{k_9(O_2)^i}{k_{10}(M)} + \frac{k_{11}(O_2)^k}{k_{10}(M)} + 1 \right\} \right]$$

Taking out $\frac{k_7(O_2)^{-i}}{k_9}$ firstly, as a common factor, and similarly with $\frac{k_{11}(O_2)^k}{k_7}$:-

$$-\frac{dBz}{dt} = \frac{dMaa}{dt} \left[1 + \frac{k_7(O_2)^{-i}}{k_9} \cdot \left\{ 1 + \frac{k_{11}(O_2)^k}{k_7} \right\} \right] + k_8(Bz)_{ads}^b (O_2)^c$$

or,

$$-\frac{dBz}{dt} = \frac{dMaa}{dt} \left[1 + \frac{k_7(O_2)^{-i}}{k_9} + \frac{k_{11}(O_2)^{k-i}}{k_9} \right] + k_8(Bz)_{ads}^b (O_2)^c \quad - (i)$$

The relationship between rate of production of maa and rate of overall conversion of benzene is seen to be independent of the concentration of inert surface present. This rather surprising result holds not only for initial rates but also

at high reactant conversions, the only necessity being steady-state operation.

As yet it has not been possible in the discussion of the homogeneous-heterogeneous reactions, to distinguish numerically between the homogeneous decomposition to CO_2 and the wholly catalytic reaction giving this product (ie. between reactions 8 and 11). Expression (i) may be used in the following manner to give a direct measure of the rate of production of CO_2 from benzene by direct catalytic reaction - which is $k_8(\text{Bz})_{\text{ads}}^b(\text{O}_2)^e$. Present results have shown i to be 0.5 and k to be unity. Knowing k_9 and k_{11} , for a given oxygen:fuel ratio, experimental measurements give $d\text{Bz}/dt$ and $d\text{Maa}/dt$ and, keeping the last term on the R.H.S. of (i) constant, a trial and error technique may be used to fit a value for k_7 . The first guessed value could be that of the known rate constant k_{10} . Once k_7 has been evaluated it is an easy matter to calculate values of the rate $k_8(\text{Bz})_{\text{ads}}^b(\text{O}_2)^c$, for a multiplicity of oxygen:fuel ratios. Direct experimental measurement of k_7 would obviously be an advantage although it is not easy to see how this could be done.

D Explanation of the S.G.S.R. Results in terms of the
Surface Adduct Theory

The above analysis deals only with reactions that occur over a catalyst held in a glass reaction vessel - presence of steel surface, as in the S.G.S.R., will necessitate the inclusion of a suitable expression for the over-oxidation of maa.

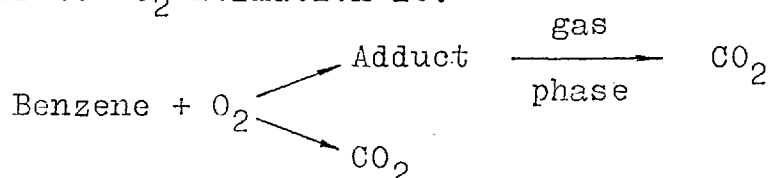
However, the reaction mechanism still remains rather more complex than for reactions in a glass vessel, as kinetic data for the effect of steel surface on adduct concentration is not available. Almost certainly the decomposition will be catalysed by steel, but it is questionable whether the products will be benzene and oxygen or products of complete oxidation. As mentioned previously, it is known that some adduct must decompose back to the two basic constituents, otherwise at constant catalyst contact time, free volume would have no effect on benzene conversion. Unfortunately, interchanging circular and cruciform baskets in the S.G.S.R. also gives differing surface:volume ratios, and it is difficult to say whether differences in conversion are a result of this effect or just of the changed volume. Results from the tubular reactor studies would indicate the former as being the more likely.

Results in the S.G.S.R. must then involve a picture of interacting gas and gas-solid reactions. Benzene disappears by a catalytic reaction to form carbon dioxide or adduct, and is possibly regenerated by subsequent collision of the adduct with the reactor walls. Maa is formed in the gas phase by homogeneous reaction of the adduct with oxygen, and a

certain amount is subsequently removed by a steel initiated combustion reaction. Carbon dioxide is formed: (a) catalytically from benzene and oxygen, (b) from the homogeneous decomposition of adduct, (c) together with each maa molecule produced and (d) from maa over-oxidation. As discussed in the results, it is possible to adjust the maa and carbon dioxide yields by accounting for maa over-oxidation and the resulting CO_2 production. A great improvement in the rate data was achieved, although this improvement could not be extended to the data for benzene conversion.

The outlet (reacting) benzene concentration is made up of two contributions: one, that amount of benzene which was not consumed by catalytic reaction and two, the amount of benzene which is regenerated from adduct decomposition. If it were possible to separate these two effects, then plotting maa and CO_2 rates of production against that concentration of benzene in the reactor should there be no regeneration, would give an even bigger improvement, especially in the maa and benzene data. Indeed, the fact that the maa rate data is as consistent as shown would indicate that regeneration of benzene from adduct in the S.G.S.R. is not as important as benzene removal by catalytic reaction.

Interpretation of the carbon dioxide rate data is made difficult by what could be described as one of the disadvantages of the S.G.S.R. system. In essence, CO_2 is produced by a parallel reaction scheme; one path being wholly catalytic in nature, the other involving a consecutive homogeneous reaction prior to CO_2 formation ie.



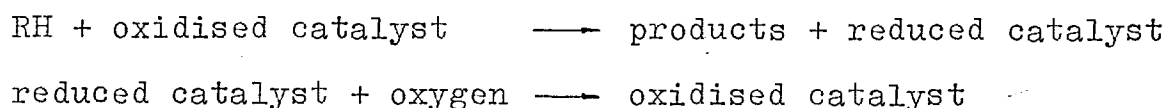
Use of the S.G.S.R., with the necessary longer contact/residence times, will obviously encourage secondary reactions and it is not possible, therefore, to separate the two rates of production when a common product is formed. Nevertheless, a reasonable fit of the results has been obtained and allows the estimation of kinetic parameters with a fair degree of accuracy (see Figure 3.40).

Although oxygen dependence of the rates is clearly marked, Figure 3.34 shows that the order of reaction w.r.t. reacting benzene concentration is a function of temperature. This is not too surprising considering the abscissae for the order plots (benzene outlet concentration) constitutes the result of heterogeneous and 'homogeneous' reactions. If these reactions could be separated, as explained above, and the rate expressions redeveloped, it is not unlikely that constant order kinetics would be obtained over the whole of the temperature range studied.

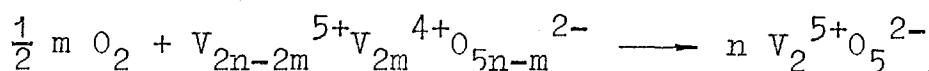
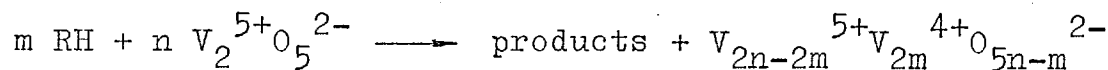
E Application of a general Reduction-Oxidation Mechanism to the S.G.S.R. Results

However, an alternative reason for the changing order can be argued on lines closely following those of Ioffe (34) and Andreikov (90), both of whom have developed a general pattern of oxidation kinetics of aromatic hydrocarbons on vanadia catalysts. Studies of the oxidation of anthracene over a V_2O_5 catalyst between 330° and $370^\circ C$ revealed the order of all reactions involved w.r.t. anthracene concentration varied with temperature in a manner much the same as in the present studies. The effect has also been noted in work on o-xylene oxidation (61 and 91). This variation was explained in terms of the influence of temperature on volume mobility of anionic vacancies in the catalyst (see Introduction, section 3). To a certain extent similar arguments can be considered for the present results.

A general mechanism of the heterogeneous reaction can be written (62 and 92);



or in terms of electron transfer processes;

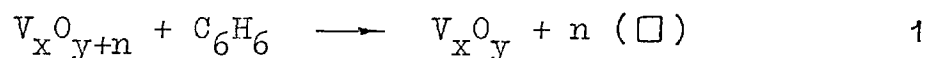


During oxidation, m gradually increases, the catalyst being reduced. When $m \cong n/6$, ie. when about one-sixth of the vanadium is tetravalent, the valency composition of the

vanadium in the catalyst corresponds to that of sodium vanadyl vanadate (92). The mechanism is not, therefore, kinetically cyclic, indicating that re-oxidation of the catalyst is rate-determining, as has been suggested previously (62).

Using the general mechanism outlined above it is possible to examine the effect of increasing temperature on anionic vacancies in the catalyst. Making the following assumptions:

(a) A small part of the benzene reacts with oxygen in the catalyst network, forming oxygen vacancies by the reaction



where ($\square$) is an oxygen vacancy.

The oxygen vacancies formed by reaction 1, together with the surface vanadium ions present, form the active catalytic reaction sites. Let the proportion of these centres be ξ .

(b) Molecular oxygen can react with the surface oxygen vacancies by two routes. It can be adsorbed on them, bonding coordinately with a neighbouring metal atom, or it can dissociate to give O^{2-} ions. Introduction of oxygen into the catalyst lattice and destruction of the active centre is shown by



(c) Benzene is 'oxidised' to the adduct by adsorbed oxygen on active catalyst centres arising from 1.

(d) Above a temperature of $340^\circ C$ the mobility of the oxygen vacancies increases abruptly (34, 47 and 90).

The kinetic equation for the disappearance of benzene to adduct may be written in a form:-

$$R_{Bz} = k_{Bz} \cdot C_{Bz}^n \cdot \xi \quad 3$$

where R_{Bz} is the rate of benzene removal, and k_{Bz} is a suitable rate constant.

By analogy with Andreikov (90), by consideration of the steady state, where

$$\frac{\partial(V_{2O_5})}{\partial t} \equiv t \cdot \frac{\partial(V_{xO_{y+n}})}{\partial t} = 0$$

then

$$\xi = \sigma \cdot \frac{V_{1sp}}{V_{1sp} + V_{2sp}} \quad 4$$

where σ is a proportionality constant, and V_{1sp} is the specific rate of formation of active centres by reaction 1 and V_{2sp} is the specific rate of destruction of active centres by reaction 2.

Since

$$V_{1sp} = k_{s1} \cdot C_{Bz} \cdot (1-C) \quad 5$$

and

$$V_{2sp} = k_{s2} \cdot C \quad 6$$

where k_{s1} and k_{s2} are the respective heterogeneous rate constants, and C is defined by Q/Q_T , where Q_T is the quantity of oxygen sites per unit surface area, and Q is the quantity of oxygen vacancies per unit surface. Therefore C is the concentration of oxygen vacancies per unit surface and $(1-C)$ is the concentration of oxygen ions per unit surface.

At the stationary state,

$$D_1 C = k_{s1} \cdot C_{Bz} \cdot (1-C) \quad 7$$

$$D_2(1-C) = k_{s2} \cdot C \quad 8$$

where D_1 is the diffusion coefficient of the oxygen vacancies in the bulk of the crystal, and D_2 the coefficient of diffusion of oxygen vacancies to the crystal surface.

From 7 ,

$$C = \frac{k_{s1} C_{Bz}}{D_1 + k_{s1} \cdot C_{Bz}}$$

$$\text{or} \quad V_{1sp} = D_1 C = \frac{k_{s1} D_1 C_{Bz}}{D_1 + k_{s1} C_{Bz}} \quad 9$$

Similarly, from 8 ,

$$V_{2sp} = D_2(1-C) = \frac{k_{s2} D_2}{D_2 + k_{s2}} \quad 10$$

Therefore ,

$$\xi = \sigma \cdot \frac{\frac{k_{s1} D_1 C_{Bz}}{D_1 + k_{s1} C_{Bz}}}{\frac{D_1 k_{s1} C_{Bz}}{D_1 + k_{s1} C_{Bz}} + \frac{D_2 k_{s2}}{D_2 + k_{s2}}} \quad 11$$

Now considering temperatures up to about $340^\circ\text{C} - 350^\circ\text{C}$,

$D_1 \ll k_{s1} C_{Bz}$ and $D_2 \ll k_{s2}$ (34 and 90),

Hence 11 reduces to, $\xi = \sigma \cdot \frac{D_1}{D_1 + D_2}$ ie. $\xi = \text{a constant}$.

As the temperature of operation increases upwards from 350°C ,

D_1 and D_2 begin to attain appreciable values, and the expression for ξ may be transformed to

$$\xi = \sigma' \cdot \left\{ \frac{C_{Bz}}{1 + \beta \cdot C_{Bz}} \right\} \quad 12$$

where $\sigma' = \sigma \cdot k_{s1} (1/k_{s2} + 1/D_2)$

and $\beta = k_{s1} (1/k_{s2} + 1/D_1 + 1/D_2)$

equation 12 may be written as

$$\xi = \sigma' \cdot C_{Bz}^{\alpha}, \text{ and } 0 < \alpha < 1 \quad 13$$

Substituting the expressions obtained for ξ in equation 3, the interesting relation is obtained, for temperatures below $340^{\circ}\text{C} - 350^{\circ}\text{C}$,

$$\underline{R_{Bz} = k'_{Bz} \cdot C_{Bz}^n} \quad 14$$

And as the temperature is increased above 350°C ,

$$\underline{R_{Bz} = k''_{Bz} \cdot C_{Bz}^{n+\alpha}} \quad 15$$

As far as the oxidation of benzene is concerned, the predictions outlined above (in particular equations 14 and 15) would seem to give a reasonable fit to the results obtained in the S.G.S.R. Obviously, as the temperature is increased diffusion considerations in the catalyst lattice will become increasingly important and the exponent $(n+\alpha)$ will increase as α increases. Examination of equations 12 and 13 reflect the non-linearity of increasing values of α and the rate of increase of α with temperature is seen to be very complex.

Equation 3 for the removal of benzene may equally have been written for production of the benzene-oxygen adduct.

$$\text{ie. } R_{(Bz/O_2)} = k_{(Bz/O_2)} \cdot C_{Bz}^n \cdot \xi \quad 16$$

An identical analysis to that outlined above will lead to analagous equations of 14 and 15 for the rate of production of adduct. Unfortunately, the exponent of benzene concentration cannot be examined as a function of temperature for adduct production since the only products from the S.G.S.R. are maa and carbon dioxide, and formation of these species involve a further series of reactions. However, the results for benzene show the increasing order effect quite distinctively (Figure 3.34), even taking into account that some benzene is regenerated by adduct decomposition.

Identical effects are also seen for both maa and carbon dioxide and it would seem, therefore, that although there are at least two reactions involved in the production of maa (and some CO_2) from benzene itself, the influence of temperature on the rate of production of adduct is such that the effect on the order w.r.t. benzene for the overall reaction to maa is still marked. As far as carbon dioxide is concerned, a great deal of it will have been produced by wholly catalytic reaction, the rate of production being of similar form to 16. The effect of changing order with temperature is therefore less surprising than for maa.

F General Conclusions

It is very important to consider the effects of present results in the context of reactor design. Conventional procedures for designing catalytic reactors are based largely on the assumption that all chemical reaction occurs on the surface of the catalyst. On this basis, pellet size and spacing in the bed, and surface, other than catalyst surface, should have no influence on product yields after making the necessary allowance for heat and mass transfer effects.

The homogeneous component in the oxidation of benzene has been suggested to consist of a benzene/oxygen adduct undergoing gas phase reaction with oxygen to give maa and carbon dioxide. This reaction is influenced by free volume both in and after the catalyst bed, and by nature and extent of surface present - therefore it is obviously important to include in any reactor design the necessary detail for the quantitative description of these effects.

As a further thought, one questions the role of the catalyst in the overall reaction. Is the adduct formation peculiar to the benzene/maa system alone, or is it some function of the V_2O_5/MoO_3 surface in operation: can similar effects be expected in other oxidative systems which make use of vanadium based catalysts? Of particular interest would be the oxidation of naphthalene to phthalic and maleic anhydrides, o-xylene to phthalic anhydride, and possibly butene to maleic anhydride - all three reaction systems use a V_2O_5/MoO_3 catalyst. It is interesting to speculate if there is in each case a common mechanism at the active surface which precedes subsequent homogeneous reaction to form the desired product.

IMPLICATIONS OF THE ADDUCT THEORY TOWARD A REACTOR DESIGN

- (a) General Considerations
- (b) Objectives for Study
- (c) General Model and Assumptions
- (d) Production of Maa from Adduct in the Free Space after
a Bed
- (e) Production of Maa by Decomposition of Adduct in
Catalyst Voids
- (f) Significance of the Equations developed for a suitable
Bed Design
- (g) Incorporation of Kinetic Data in the Design Equations
- (h) Summary: Reactor Design

(a) General Considerations

Although the design of reactors for heterogeneous catalytic processes is a well studied field, little work has been done on the design of reactors for mixed homogeneous-heterogeneous reactions. The problems can be seen from the example of the present results, which suggest that maa is produced from the gas phase reaction of a catalytically formed intermediate with molecular oxygen. The results also show that collision of this intermediate with active surface gives products of complete oxidation, and that collision with inert surface leads to the original reactants. Then, for high yields of maa, it is desirable to have large amounts of catalyst surface in order to produce lots of intermediate, but it is also necessary to allow the desorbed intermediate sufficient free space for the gas phase reaction to occur. These two requirements are opposite in the sense that large amounts of active surface are usually obtained at the expense of void size by the choice of small catalyst particles. There must, therefore, be an optimal solution for maximal active surface associated with sufficient free space for reaction to occur.

From a point of view of catalyst bed design, several other problems emerge. The first of these is the size of the catalyst pellet: is it better, in a particular cross-section of bed, to have few, large voids (large diameter pellets) as opposed to lots of voids of smaller dimensions (small diameter pellets)? Secondly, how should the bed be used: is it better to lock upon the bed as a source of active intermediate (adduct) which is then free to react in

the gas phase after the bed? In this case, the design would be such that maa would be formed principally in free spaces following alternate layers of catalyst pellets, and the catalyst bed would be designed to maximise production of the adduct. Alternatively, is it possible to design the bed in such a fashion that large amounts of maa are produced in the voids between the catalyst pellets, as well as in the free space after the bed? Adduct formation must remain high but sufficient voidage in the bed should be allowed to encourage the gas phase reaction.

In some respects, both of these aims have common ground. For example, looking upon the catalyst bed as acting as a source of adduct necessitates large voids to allow the adduct out of the bed before further reaction with the catalyst to produce carbon dioxide can occur. Similarly, if maa is to be formed in the voids in the catalyst bed, there must be enough void volume in the bed to allow the adduct a reasonable chance of reacting homogeneously.

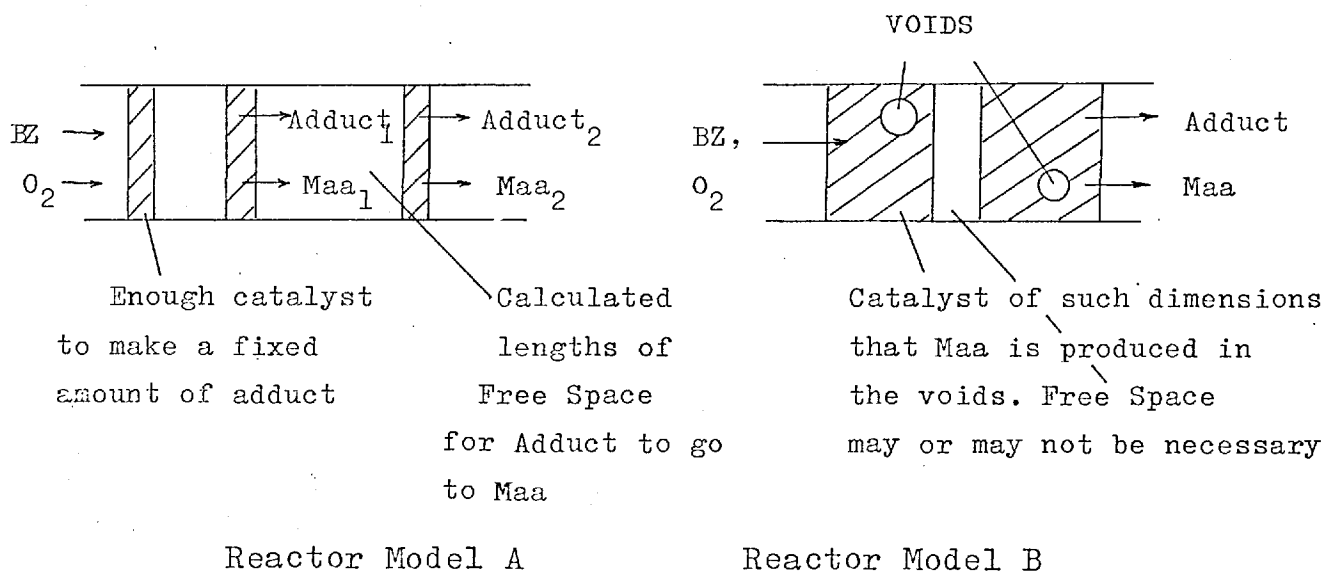
Ultimately, then, it must be decided what are the relative merits of producing maa by (a) gas phase reaction in voids, or (b) gas phase reaction in spaces free from the influence of catalyst surface.

(a) has the advantage that adduct is always being formed heterogeneously whilst being removed homogeneously (there is, therefore, always a good supply of adduct for possible gas phase reaction, but has the disadvantage that the selectivity will be lower as reaction at the catalyst surface to carbon dioxide will be more favoured due to the smaller void sizing.

(b) has the advantage that the decomposing adduct will be

less prone to wall reaction (there is much further for the adduct to diffuse), and that any wall reaction will lead to the original reactants benzene and oxygen - which may subsequently react to produce more adduct in the next catalyst section. The disadvantage is that adduct is not being formed continuously and the concentration of adduct is never greater than when leaving the preceding catalyst bed section.

The two situations that can be envisaged can be expressed diagrammatically as



One point which must be remembered is that maa does not oxidise significantly under normal conditions in the gas phase or over the catalyst. Once the adduct has reacted homogeneously to maa, there will be no significant loss in yield by passage of the maa through subsequent catalyst or free space sections, provided the reactor walls are inactive (see above)

(b) Objectives for Study

The primary objective for the present study was to distinguish between these two possible modes of production of maa, using a theoretical approach to decide which of the models will give the best overall selective yield. High conversions of benzene are obviously desired (to produce lots of adduct), and possible methods of promoting the gas phase reaction of adduct to maa rather than to other products should also be examined. To obtain quantitative results, the study must take into account reaction parameters such as diffusion, mass velocity and gas and wall reactions.

(c) General Model and Assumptions

As a general model, the arrangement shown below was chosen, assuming the reactor was fabricated from an inert material (not stainless steel - see above)

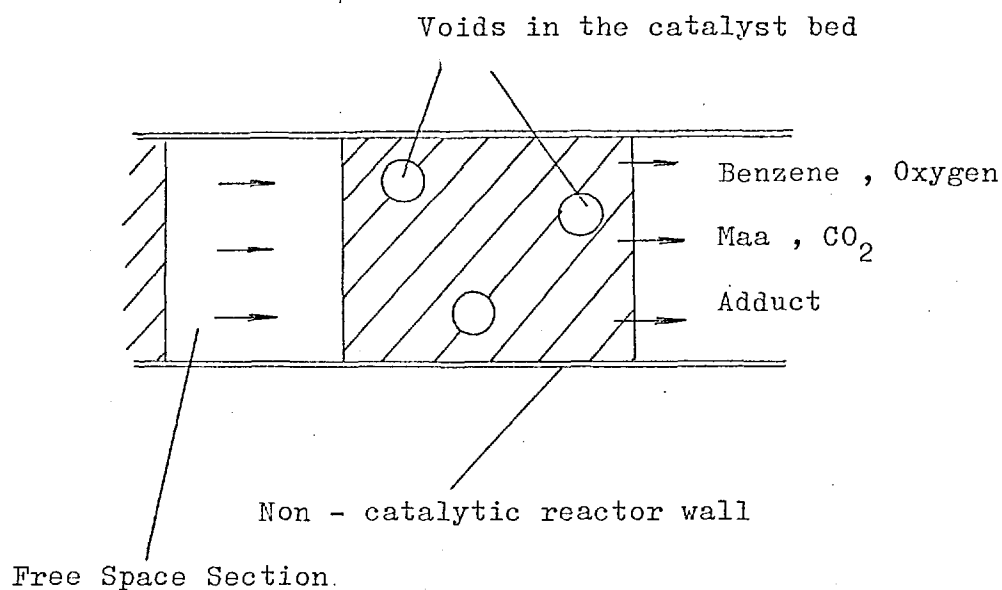


FIGURE 5.1

Alternate catalyst beds are inter-spaced by sections of free volume, where no active (catalyst) material is present.

Isothermal operation of the reactor is assumed, although more sophisticated models must obviously eliminate this constraint (most catalytic reactors operate adiabatically).

The feed to the reactor consists of benzene, air and diluent (where necessary), and a large excess of air over benzene is assumed.

Axial diffusion is neglected in the analysis as in most catalytic reactors the convective contribution to transport in the axial direction far outweighs diffusional contributions (94).

It is convenient to split the analysis into two. Firstly, the production of maleic anhydride in free spaces after catalyst sections will be considered. The extension of arguments developed in this part of the study will then be made for maa production in catalyst voids.

(d) Production of Maa from Adduct in the Free Space after
a Bed

- Considerations:
- (a) Convective transport
 - (b) Radial and Axial Diffusion
 - (c) Homogeneous reaction of adduct to maa
 - (d) Wall reaction, where adduct disappears to benzene and oxygen

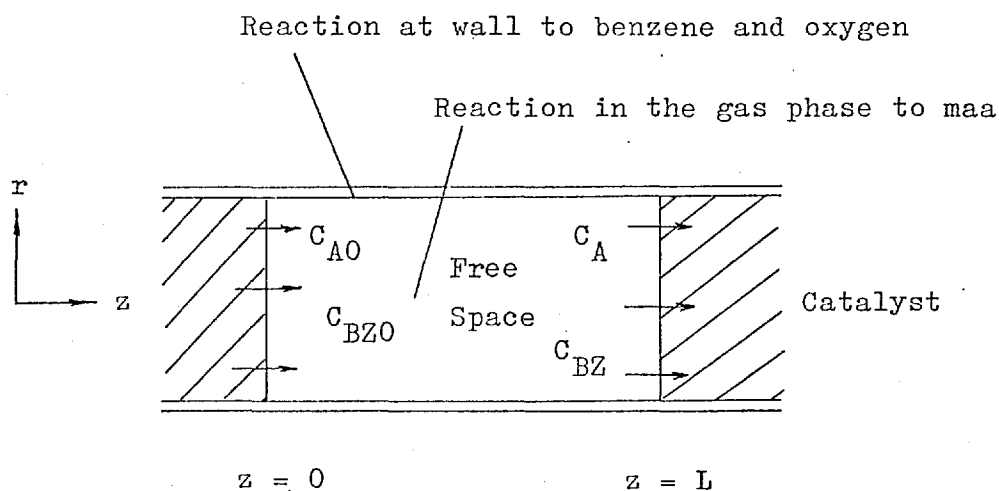


FIGURE 5.2

At the beginning of the free space section, the concentration of adduct (C_A) will be a maximum.

$$\text{Initial Condition: } z=0, 0 \leq r < a, C_A = C_{A0} \quad (1)$$

or, assuming a parabolic distribution of adduct leaving the catalyst bed

$$z=0, 0 \leq r < a, C_A = \bar{C}_{A0} (1 - r^2/a^2) \quad (2)$$

Preferably, at $z=L$, the concentration of adduct should be as small as possible.

Considering adduct flowing through the free space, at the steady state the basic transport equation may be written:

$$D \cdot \nabla^2 C_A - \underline{u} \cdot \text{div } C_A - R_A = 0 \quad (3)$$

(it is also assumed that $D \neq D(C_A)$)

The rate of removal of adduct by homogeneous reaction to maa (R_A) may be written: $R_A = k_g \cdot C_A^1$, where $k_g = k_{go} e^{-E_A/RT}$ x (Concn. O_2)^{1/2} (see Results and Discussion Sections)

The assumption of isothermal operation and high oxygen:fuel ratios makes k_g essentially constant.

For cylindrical symmetry, where $C_A = C_A(r, z)$, equation (3) reduces to

$$D \left(\frac{\partial^2 C_A}{\partial r^2} + \frac{1}{r} \cdot \frac{\partial C_A}{\partial r} \right) - u_z \cdot \frac{\partial C_A}{\partial z} - k_g \cdot C_A = 0$$

$$\text{or } u_z \cdot \frac{\partial C_A}{\partial z} = \frac{D}{r} \frac{\partial}{\partial r} (r \frac{\partial C_A}{\partial r}) - k_g C_A = 0 \quad (4)$$

The initial and boundary conditions are

$$\begin{aligned} \text{(i) } z=0; 0 \leq r < a & ; C_A = C_{A0} \text{ or } C_{A0}(1 - r^2/a^2) \quad (5) \\ \text{(ii) } z \geq 0, r=0 & ; C_A \text{ is finite} \\ \text{(iii) } z \geq 0; r=a & ; \frac{-D \partial C_A}{\partial r} = R_w \quad (6) \end{aligned}$$

where R_w is the rate of adduct removal at the wall of the reactor.

From present results, it is known that

$$R_w = k_w C_A^1$$

where $k_w = k_{wo} e^{-E_A/RT}$ x (concentration of surface)

$$\text{Therefore (6) may be written } \frac{-D \partial C_A}{\partial r} = k_w C_A$$

A solution to (4) using conditions (5) and (6) is obtainable using principles put forward by Danckwerts (93)

for problems in unsteady-state diffusion of binary liquids. Briefly, the solution makes use of the following integral relationship, that if C_{A1} is the solution of

$$u_z \cdot \frac{\partial C_A}{\partial z} = \frac{D}{r} \cdot \frac{\partial}{\partial r} \left(r \frac{\partial C_{A1}}{\partial r} \right) \quad (7)$$

then C_A is a solution of $u_z \cdot \frac{\partial C_A}{\partial z} = \frac{D}{r} \cdot \frac{\partial}{\partial r} \left(r \frac{\partial C_A}{\partial r} \right) - k_g \cdot C_A$ providing that

$$C_A = k' \cdot \int_0^z C_{A1} \cdot e^{-k'z'} \cdot dz' + C_{A1} \cdot e^{-k'z} \quad (8)$$

with $k' = k_g/u_z$, $D' = D/u_z$, and $z' =$ some arbitrary length variable.

Equation (8) is shown to hold for both boundary and initial conditions in Appendix 1.

The problem is therefore greatly reduced, as it is much easier to obtain a solution of (7), and, once C_{A1} has been obtained, use of (8) will upgrade the solution to take into account the homogeneous gas phase reaction.

Therefore, the solution of

$$\frac{\partial C_{A1}}{\partial z} = \frac{D'}{r} \cdot \frac{\partial}{\partial r} \left(r \frac{\partial C_{A1}}{\partial r} \right) \quad (9)$$

is required, subject to

- (i) $z=0$; $0 \leq r < a$; $C_{A1} = C_{A0}$ (or $\bar{C}_{A0}(1 - r^2/a^2)$)
- (ii) $z \geq 0$; $r=a$; $-\frac{D}{r} \frac{\partial C_{A1}}{\partial r} = k_w \cdot C_{A1}$
- (iii) $z \geq 0$, $r=0$; C_{A1} is finite

A solution of (9) is obtained by introducing a new variable u , which is a function of r only.

$$C_{A1} = u \cdot \exp(-D'\alpha^2 z) \quad (10)$$

where α is some arbitrary constant. This satisfies

$$(9) \quad \text{if} \quad \frac{\partial^2 u}{\partial r^2} + \frac{1}{r} \frac{\partial u}{\partial r} + \alpha^2 u = 0.$$

This is a Bessel Function of zero order, and, using (iii), the solution reduces to (taking radial symmetry into account)

$$u = A \cdot J_0(\alpha r) \quad (11)$$

where A is some determinable constant.

Now (11) must satisfy boundary condition (ii), or

$$-D\alpha \cdot A(-J_1(\alpha a)) = k_w \cdot A J_0(\alpha a)$$

and letting $h = k_w/D$,

$$\alpha \cdot J_1(\alpha a) - h \cdot J_0(\alpha a) = 0 \quad (12)$$

Therefore, to satisfy the boundary condition, values of α must be chosen to satisfy (12). In fact (12) has an infinite number of real, simple roots.

$$\text{ie.} \quad \alpha_n \cdot J_1(\alpha_n a) = h \cdot J_0(\alpha_n a) \quad (12)'$$

The solution of (9) then becomes,
$$C_{A1} = \sum_{n=1}^{\infty} A_n J_0(\alpha_n r) e^{-D'\alpha_n^2 z}$$

with values of A_n determined from the initial condition at $z=0$.

$$\text{ie.} \quad C_{A1} = C_{A0} \quad \text{or} \quad f(r), \quad \text{at } z=0$$

Taking the general case that $C_{A1} = f(r)$ at $z=0$,

$$f(r) = \sum_{n=1}^{\infty} A_n J_0(\alpha_n r)$$

Multiplying both sides of the above by $rJ_0(\alpha_n r)$ and integrating between 0 and a leads to

$$A_n = \frac{2}{a^2 [J_0^2(\alpha_n a) + J_1^2(\alpha_n a)]} \cdot \int_0^a r f(r) J_0(\alpha_n r) dr$$

To obtain A_n , use is made of the expressions

$$\int_0^a r J_0(\alpha r) J_0(\beta r) dr = 0 \quad (\text{for } \alpha \neq \beta)$$

$$\int_0^a r J_0(\alpha r) J_0(\alpha r) dr = \frac{a^2}{2} [J_0^2(\alpha_n a) + J_1^2(\alpha_n a)] \quad (13)$$

$$\text{and } \int_0^a r J_0(\alpha_n r) dr = \frac{a}{\alpha_n} J_1(\alpha_n a) \quad (14)$$

$$\text{From (12): } J_1^2(\alpha_n a) = (h^2 / \alpha_n^2) \cdot J_0^2(\alpha_n a) ,$$

and the solution for C_{A1} becomes ,

$$C_{A1} = \sum_{n=1}^{\infty} \frac{2\alpha_n^2 J_0(\alpha_n r) e^{-D' \alpha_n^2 z}}{a^2 (\alpha_n^2 + h^2) J_0^2(\alpha_n a)} \cdot \int_0^a r f(r) J_0(\alpha_n r) dr \quad (15)$$

If at $z=0$, $C_{A1} = C_{A0}$, ie. $f(r) = C_{A0}$, then, after integration

$$C_{A1} = \sum_{n=1}^{\infty} \frac{2h}{a} \cdot \frac{C_{A0} J_0(\alpha_n r) e^{-D' \alpha_n^2 z}}{(\alpha_n^2 + h^2) J_0(\alpha_n a)} \quad (16)$$

If at $z=0$, $C_{A1} = \bar{C}_{A0} (1 - r^2/a^2)$, it is necessary to

integrate the expression

$$\int_0^a r(1-r^2/a^2)J_0(\alpha_n r)dr$$

After integrating by parts twice, the final result is found to be

$$C_{A1} = \sum_{n=1}^{\infty} \frac{4\bar{C}_{A0}J_0(\alpha_n r)e^{-D'\alpha_n^2 z}}{a^2(\alpha_n^2+h^2)J_0(\alpha_n a)} \cdot \left[\frac{2h}{a\alpha_n^2} - 1 \right] \quad (17)$$

In the present study, C_{A1} is considered to be constant over all r at $z=0$, and the expression (16) for C_{A1} is applicable.

(16) satisfies the boundary condition at $r=a$, and the initial condition that $C_A = C_{A0}$ at $z=0$ is also maintained by use of the DINI series of unity (94)

$$\text{ie.} \quad \sum_{n=1}^{\infty} \frac{2h}{a} \cdot \frac{J_0(\alpha_n r)}{(\alpha_n^2+h^2)J_0(\alpha_n a)} = 1 \quad \text{for } 0 \leq r \leq a.$$

Having obtained the expression for C_{A1} , it is now possible to evaluate the corresponding expression for C_A , the concentration of adduct as a function of radial and axial position when homogeneous reaction to maa is taking place.

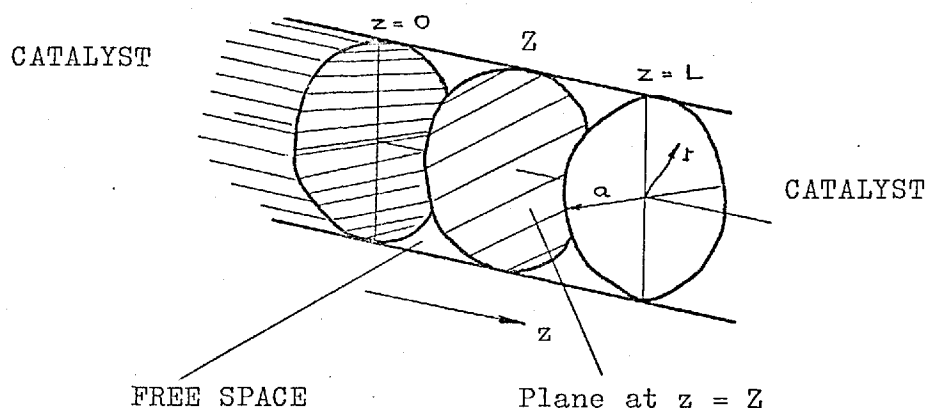
$$\text{Using (8),} \quad C_A = k' \cdot \int_0^z C_{A1} \cdot e^{-k'z'} dz' + C_{A1} \cdot e^{-k'z},$$

and, after performing the necessary integration, the final expression for C_A is ,

$$C_A = C_{A0} \sum_{n=1}^{\infty} \frac{2h}{a(\alpha_n^2 + h^2)} \cdot \frac{J_0(\alpha_n r)}{J_0(\alpha_n a)} \dots \times \left[\frac{k' + D' \alpha_n^2 e^{-(k' + D' \alpha_n^2)z}}{k' + D' \alpha_n^2} \right] \quad (18)$$

The total amount of adduct present in the free space at a distance z from the end of the catalyst bed is given

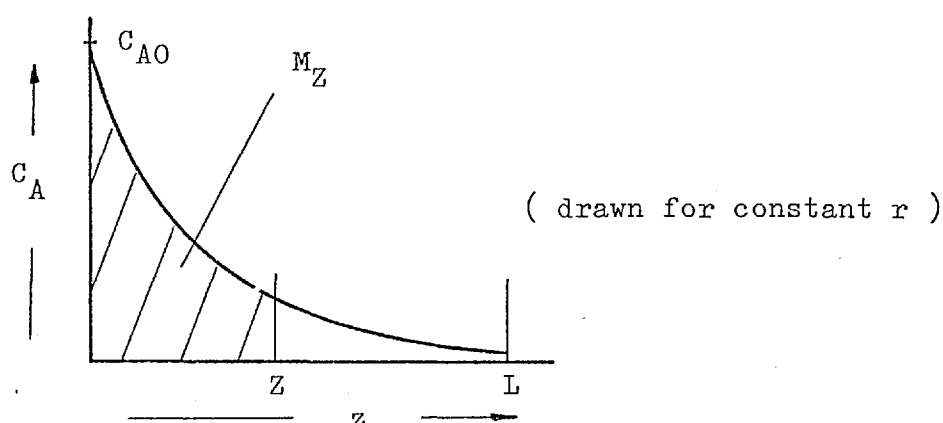
by M_z , where
$$M_z = \int_0^z \cdot \int_0^a 2\pi r C_A(r, z) dr dz$$



The total amount of adduct in the free space section, if that length of section is L , is given by

$$M_L = \int_0^L \cdot \int_0^a 2\pi r C_A(r, z) dr dz$$

One quantity of interest would be M_z/M_L , ie. the amount of adduct up to a distance z , over the total amount present. L may be chosen to be very large or very small, but the ratio M_z/M_L for small values of z would indicate the efficiency of adduct disappearance down the free space section. For example, if at small values of z the ratio of $M_z:ML$ is large, a fast "tail off" of adduct would be shown



In other words, after a certain value of z , the inclusion of more free space (by extending L) would mean only a slight gain.

A more flexible quantity by which to estimate overall adduct conversion is the difference in mass flux at the extremes of the free space section. The amount of adduct flowing into the free space at $z=0$ is given by

$$-2\pi D \int_0^a r \left(\frac{\partial C_A}{\partial z} \right)_{z=0} dr$$

Similarly, the flux out of the free space section, at

$z=L$, is given by

$$-2\pi D \int_0^a r \left(\frac{\partial C_A}{\partial z} \right)_{z=L} dr$$

Using expression (18) for C_A , using (14) gives ,

$$\text{Flux}|_{IN} = 4\pi \frac{D^2}{u_z} \sum_{n=1}^{\infty} \frac{h^2}{(\alpha_n^2 + h^2)} \cdot C_{A0} \quad (19)$$

Similarly, the total amount of adduct flowing out of the free space at a distance L along the z -axis can be written,

$$\text{Flux}|_L = 4\pi \frac{D^2}{u_z} \sum_{n=1}^{\infty} \frac{h^2}{(\alpha_n^2 + h^2)} \cdot C_{A0} e^{-(k' + D'\alpha_n^2)L}$$

For an infinitely long free space section, the flux will obviously tend to zero. In practical terms, very large values of L are not feasible, and real values of L must be dealt with, even though the flux of adduct at L should still be as small as possible.

However, by choosing (u_z/L) sufficiently large so that only the first term in the expansion of the exponential need be included, ie.

$$e^{-(k' + D'\alpha_n^2)L} \cong 1 - (k' + D'\alpha_n^2)L$$

then

$$\text{Flux}|_L = 4\pi \frac{D^2}{u_z} \sum_{n=1}^{\infty} \frac{h^2}{(\alpha_n^2 + h^2)} \cdot C_{A0} \cdot [1 - (k' + D'\alpha_n^2)L] \quad (20)$$

Expansion of (20) gives

$$\text{Flux}_L = \text{Flux}_{IN} - 4\pi \frac{D^2}{u_z} \sum_{n=1}^{\infty} \frac{h^2}{(\alpha_n^2 + h^2)} \cdot C_{AO} (k' + D' \alpha_n^2) L$$

It may be shown that $\sum_{n=1}^{\infty} \frac{h^2}{(\alpha_n^2 + h^2)} \cong \left[1/1 + 2/ah \right]$ (21)

and $\sum_{n=1}^{\infty} \frac{\alpha_n^2}{(\alpha_n^2 + h^2)} \cong \left[1/1 + ah/2 \right]$ (22)

(see Appendix 2)

Using these relationships, and remembering that $k' = k_g/u_z$, $h = k_w/D$ etc.,

$$\boxed{\text{Flux}|_L = \text{Flux}|_{IN} \times \left[1 - \left(\frac{k_g L}{u_z} \right) - 2 \left(\frac{L}{a} \right) \cdot \left(\frac{k_w}{u_z} \right) \right]} \quad (23)$$

(units of (23) are moles per unit time)

To maximise the gas phase reaction to maa in the free space after the catalyst bed, it is necessary to minimise the flux of adduct at the end of the free space (at $z=L$).

Consideration of equation (23) shows this is possible for any value of L . If the L.H.S of (23) is minimised by suitable choice of the parameters incorporated in the R.H.S. then the gas phase reaction before the plane $z=L$ will be a maximum. The parameters which may be varied consist of the dimensionless groups

$$\left(\frac{k_g L}{u_z} \right), \quad \left(\frac{L}{a} \right) \quad \text{and} \quad \left(\frac{k_w}{u_z} \right)$$

Maximising (k_w/u_z) is of little use as the wall reaction, although removing adduct, leads to benzene and oxygen, and

not to maa.

Care must be applied in maximising the group (L/a) . Large values of L are undesirable as this would lead to very long reactors, but small values of L leads to necessarily choosing an even smaller a . This has two detrimental effects. One, the rate of wall reaction would be increased, and two, the derivation of (21) and (22), necessary for development of (23) involves the assumption that sufficiently large values of a be chosen to make the Bessel Function approximation valid (see Appendix 2). The most promising group to maximise would thus appear to be $(k_g L/u_z)$. Although, at constant temperature, k_g will be fixed by the reaction kinetics of the system, choice of (L/u_z) may maximise this group, hence maximising the gas phase conversion of adduct to maa. If the assumption of isothermal operation is removed and temperature is considered as an operating variable, then $(k_g L/u_z)$ may be increased by supplying heat to the free space section. Increases in operating temperature will have a direct influence on k_g , through the relation $k_g =$

$$k_{go} e^{-E_A/RT} \times (C.O_2)^{0.5}.$$

Although the quantity $\text{Flux}|_L / \text{Flux}|_{IN}$ is a measure of the efficiency of adduct removal, the nature of disappearance of the adduct must also be investigated (ie. whether adduct proceeds by gas phase reaction to maa, or to benzene and oxygen by collision with inert surface). The overall rate of reaction to maa is given by R_g , where

$$R_g = k_g \cdot \int_0^L \int_0^a 2\pi r C_A(r,z) dr dz$$

Similarly, the overall rate of reaction to other products is given by the volumised reaction at the wall, R_w .

$$R_w = k_w \cdot \int_0^L 2\pi a C_A(a, z) dz$$

The ratio R_g/R_w is a direct measure of the selectivity of adduct decomposition to maa.

Using equation (18) for $C_A(r, z)$, and using (12) and (14) to give the relation

$$\int_0^a r J_0(\alpha_n r) = \frac{ha}{\alpha_n^2} J_0(\alpha_n a) \quad ,$$

$$R_g = 4\pi k_g C_{A0} \sum_{n=1}^{\infty} \frac{h^2}{\alpha_n^2 (\alpha_n^2 + h^2)} \left[\frac{k' L}{(k' + D' \alpha_n^2)} + \dots \dots \dots \right. \\ \left. \frac{D' \alpha_n^2}{(k' + D' \alpha_n^2)^2} \cdot [1 - e^{-(k' + D' \alpha_n^2)L}] \right]$$

For large values of (u_z/L) ,

$$1 - e^{-(k' + D' \alpha_n^2)L} \cong (k' + D' \alpha_n^2)L$$

$$\text{Hence,} \quad R_g = 4\pi k_g C_{A0} L \sum_{n=1}^{\infty} \frac{h^2}{\alpha_n^2 (\alpha_n^2 + h^2)} \quad (24)$$

$$\text{Similarly,} \quad R_w = 4\pi k_w C_{A0} L \sum_{n=1}^{\infty} \frac{h}{(\alpha_n^2 + h^2)} \quad (25)$$

It may be shown that
$$\sum_{n=1}^{\infty} \frac{h^2}{\alpha_n^2 (\alpha_n^2 + h^2)} = \frac{a^2}{4} \quad (26)$$

(see Appendix 2)

and, using the two previous results of (21) and (22), the final result is obtained

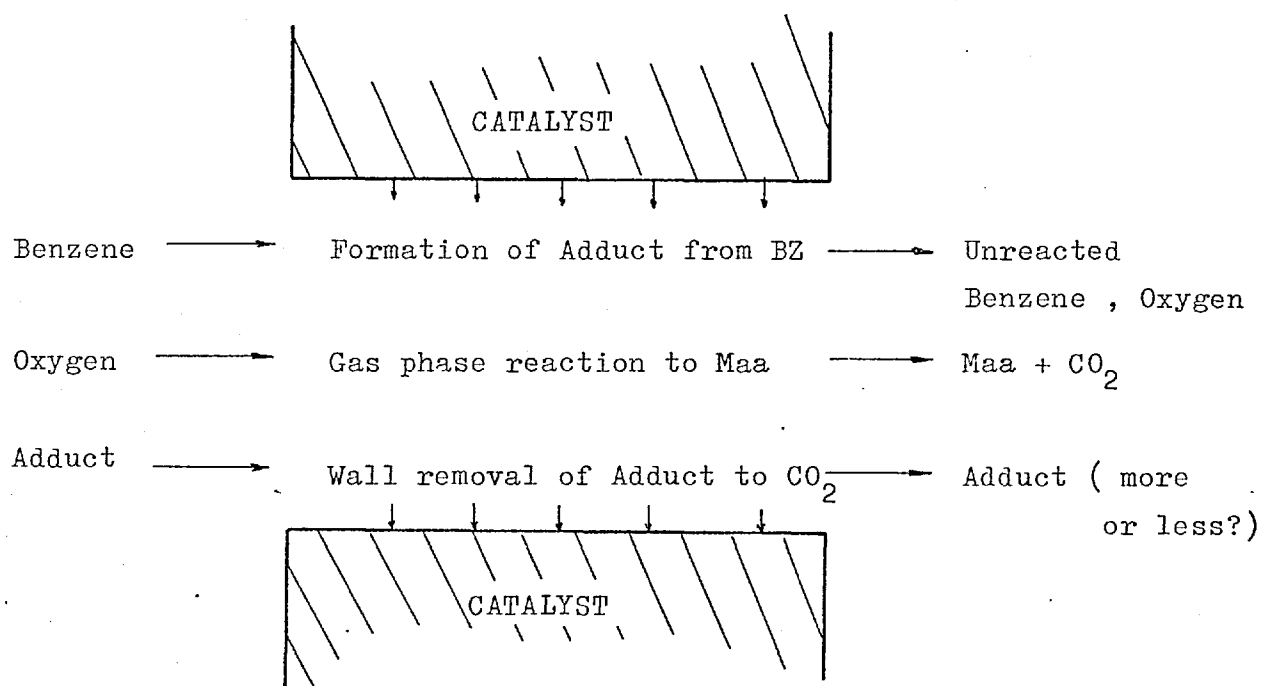
$$\boxed{R_g/R_w = k_g a / 2k_w + k_g a^2 / 4D} \quad (27)$$

This is a very interesting and important result. It would appear that the selectivity of the overall reaction to maa is not dependent on reactor length or flow velocity through the bed. In fact, selectivity to maa is apparently determined by the intrinsic kinetics of the two reactions (gas phase and wall), and by a diffusion parameter ($a^2/4D$). However, should the constraint of isothermal operation be lifted, a more complex situation arises as gas phase reaction and wall reaction will proceed at rates governed by their respective activation energies. These will be presumably different, and knowledge of their actual values must be obtained for predicting subsequent variation of the group ($k_g a / 2k_w$) with temperature.

Equations (23) and (27) are of major interest. They would suggest that although total conversion of adduct in the gas phase is a function of the length and diameter of bed and the flow velocity through the reactor, the selectivity of the adduct decomposition does not depend on these values, but only on the intrinsic kinetics of the reaction and on a diffusion parameter.

(e) Production of Maa by Decomposition of Adduct in
Catalyst Voids

Considering a typical void in the catalyst bed, it may be possible to obtain estimates of parameters which will supply information as to the best void size for maa production



Reactions to be considered are:

- (i) Diffusion of benzene and oxygen through the void, and catalytic reaction to give adduct.
- (ii) Diffusion of adduct through the void (some adduct may enter the void as a result of formation in a prior section).
- (iii) Homogeneous reaction of adduct to maa.
- (iv) Catalytic 'wall' reaction to products of complete oxidation.

(v) "'Wall'" reaction of adduct to give benzene and oxygen as products is unlikely to occur in the system (see Results section) but can be accounted for in (i). Over-oxidation of maa produced in a prior section of the bed will not occur and need not be considered.

Assumptions:

(a) Isothermal operation of the catalyst bed (and other previous assumptions) are again assumed and only cylindrical voids will be considered.

(b) From heterogeneous rate data in the Results section, the rate of production of adduct can be expressed by $k_f'(C_{BZ})^a(CO_2)^b$ where the rate has units of moles/gm.sec. For the following analysis, typical industrial operating conditions are considered where, with excess oxygen present, the reaction rate may be written $k_f''(C_{BZ})^a$. Further, it is assumed that the rate of production of adduct is first order w.r.t. benzene concentration.

Therefore, $\text{Rate of production} = k_f \cdot C_{BZ}$

where $k_f = k_f'(C.O_2)^b/S$, and S is the specific surface of catalyst, in m^2/gm .

(c) A further assumption is that adduct is removed at a catalytic surface by a reaction which is first order w.r.t. adduct concentration. This is known to be true for wall collision with inert surface, where the products are benzene and oxygen, but every indication is that adduct collision with active catalyst surface gives CO_2 , and presumably such a reaction would be directly proportional to adduct concentration.

Considering the following model:

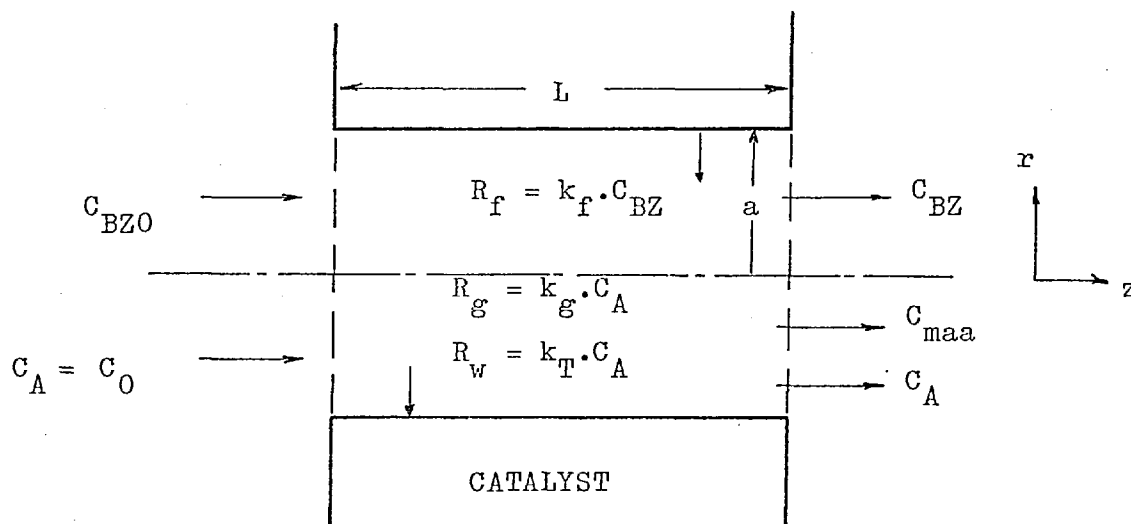


FIGURE 5.3

L is a mean void length

a is a mean void radius

Plug Flow is assumed through the voids, although, as in the previous section, the analysis may be extended to include Poiseuille Flow.

A material balance on benzene diffusing and reacting is

$$D_{BZ} \left(\frac{\partial^2 C_{BZ}}{\partial r^2} + \frac{1}{r} \frac{\partial C_{BZ}}{\partial r} \right) - u_z \cdot \frac{\partial C_{BZ}}{\partial z} = 0 \quad (28)$$

(no homogeneous reaction involving benzene takes place).

Boundary and initial conditions for the void are,

$$(i) \ z=0 \ , \ 0 < r < a \ , \ C_{BZ} = C_{BZO}$$

$$(ii) \ z>0 \ , \ r=a \ , \ -D_{BZ} \cdot \frac{\partial C_{BZ}}{\partial r} = k_f \cdot C_{BZ} \ ,$$

$$(iii) \ z>0 \ , \ r=0 \ , \ C_{BZ} \text{ is finite}$$

A solution to (28) using the above boundary conditions is obtained by similar techniques outlined in the previous

section (cf. (16))

$$C_{BZ} = C_{BZO} \sum_{n=1}^{\infty} \frac{2h_1}{a(\alpha_n^2 + h_1^2)} \cdot \frac{J_0(\alpha_n r)}{J_0(\alpha_n a)} e^{-D_{BZ} \alpha_n^2 z} \quad (29)$$

where α_n are the roots of $\alpha_n J_1(\alpha_n a) = h_1 J_0(\alpha_n a)$ (30)

with $h_1 = (k_f/D_{BZ})$

At the moment it is convenient to write (29) as

$$C_{BZ} = C_{BZO} \sum_{n=1}^{\infty} A_n J_0(\alpha_n r) e^{-D_{BZ} \alpha_n^2 z} \quad (31)$$

with

$$A_n = \frac{2J_1(\alpha_n a)}{(a\alpha_n) \{ J_0^2(\alpha_n a) + J_1^2(\alpha_n a) \}}$$

In developing expressions for adduct concentration profiles, a similar procedure as used in the previous section was followed. An expression for C_{A1} , the concentration of adduct in the absence of gas phase reaction, was obtained, and subsequent use of the equation

$$C_A = k' \int_0^z C_{A1} e^{-k'z'} dz' + C_{A1} e^{-k'z} \quad (8)$$

gives the adduct concentration when gas phase reaction to maa does take place (see section (d)).

Therefore, a solution of

$$D \left(\frac{\partial^2 C_{A1}}{\partial r^2} + \frac{1}{r} \frac{\partial C_{A1}}{\partial r} \right) - u_z \frac{\partial C_{A1}}{\partial z} = 0 \quad (32)$$

is required (cf. (9)).

The boundary and initial conditions are a little more complex, as both adduct generation and termination must be considered taking place at the surface.

$$(i) \quad z \geq 0 \quad , \quad r=0 \quad , \quad C_{A1} \text{ is finite}$$

$$(ii) \quad z=0 \quad , \quad 0 < r < a \quad , \quad C_{A1} = C_0 \text{ (a constant)}$$

C_0 may have any value, including zero, depending on the position of the void in the catalyst bed. However, for one particular void, the concentration of adduct entering the void is taken as being sensibly constant over the void width.

$$(iii) \quad z > 0 \quad , \quad r=a \quad , \quad -D \frac{\partial C_{A1}}{\partial r} = \text{rate of removal} \\ \text{at surface} - \text{rate of production at surface}$$

$$\text{ie.} \quad -D \frac{\partial C_{A1}}{\partial r} = k_T \cdot C_{A1} - k_f \cdot C_{BZ}$$

For convenience let $D \cong D_{BZ}$, (both concentration independent), therefore (iii) becomes,

$$-\frac{\partial C_{A1}}{\partial r} = h_2 C_{A1} - h_1 C_{BZ}$$

Equation (32) is homogeneous but it is not directly soluble due to the non-homogeneous boundary condition at $r=a$.

A solution has been obtained by introducing a new single variable which relates the two independent variables $C_{A1}(r,z)$ and $C_{BZ}(r,z)$. The solution is outlined in Appendix 3, and the final expression for C_{A1} is shown below

$$C_{A1} = \frac{h_1}{h_2} C_{BZ0} \sum_{n=1}^{\infty} A_n J_0(\alpha_n a) \cdot e^{-D' \alpha_n^2 z} \\ + \sum_{n=1}^{\infty} B_n J_0(\mu_n r) \left\{ \left(C_0 - \frac{h_1}{h_2} C_{BZ0} \right) e^{-D' \mu_n^2 z} + \frac{h_1}{h_2} C_{BZ0} \cdot \sum_{n=1}^{\infty} \frac{A_n \alpha_n^2 J_0(\alpha_n a)}{(\mu_n^2 - \alpha_n^2)} \dots \right. \\ \left. \dots \times (e^{-D' \alpha_n^2 z} - e^{-D' \mu_n^2 z}) \right\} \quad (33)$$

where $\alpha_n J_1(\alpha_n a) = h_1 J_0(\alpha_n a)$

$$\mu_j J_1(\mu_j a) = h_2 J_0(\mu_j a)$$

and
$$A_n = \frac{2J_1(\alpha_n a)}{(a\alpha_n) \cdot \{J_0^2(\alpha_n a) + J_1^2(\alpha_n a)\}}$$

$$B_j = \frac{2j_1(\mu_j a)}{(a\mu_j) \cdot \{J_0^2(\mu_j a) + J_1^2(\mu_j a)\}}$$

Using equation (8) and equation (33) to obtain the concentration of adduct as a $f_n(r, z)$ when gas phase reaction to maa is occurring,

$$\begin{aligned} C_A = & \frac{h_1}{h_2} C_{BZO} \cdot \sum_{n=1}^{\infty} A_n J_0(\alpha_n a) \left\{ \frac{k' + D' \alpha_n^2 e^{-(k' + D' \alpha_n^2)z}}{k' + D' \alpha_n^2} \right\} \\ & + \sum_{n=1}^{\infty} B_j J_0(\mu_j r) \left[\left(C_0 - \frac{h_1}{h_2} C_{BZO} \right) \cdot \left\{ \frac{k' + D' \mu_j^2 e^{-(k' + D' \mu_j^2)z}}{k' + D' \mu_j^2} \right\} + \dots \right. \\ & \dots \frac{h_1}{h_2} C_{BZO} \cdot \sum_{j=1}^{\infty} \frac{A_n \alpha_n^2 J_0(\alpha_n a)}{(\mu_j^2 - \alpha_n^2)} \left\{ \frac{k' + D' \alpha_n^2 e^{-(k' + D' \alpha_n^2)z}}{k' + D' \alpha_n^2} \right\} - \dots \\ & \left. \dots \frac{k' + D' \mu_j^2 e^{-(k' + D' \mu_j^2)z}}{k' + D' \mu_j^2} \right] \end{aligned} \quad (34)$$

This gives the concentration of adduct at any point in the void, and includes appropriate terms for homogeneous reaction in the gas phase, for catalytic production from benzene and oxygen and for catalytic removal to carbon dioxide. Overall,

it is difficult to predict whether there will be a net accumulation of adduct going down the void, or whether there will be a net depreciation due to removal of adduct both on the surface and in the gas phase. Ultimately, this must depend on the boundary condition at $r=a$. Once the rate of production of adduct exceeds the rate of removal to CO_2 , diffusion of adduct in the reverse direction (away from the wall) will occur. A state where adduct concentration ceases to be a function of r can then be envisaged.

Taking the analysis further, it is convenient to obtain a measure of adduct removal (or production) along a typical catalyst void. As before, this is achieved by comparing the mass flux of adduct through the void at any plane $z=L$ with the flux of adduct into the void.

The amount of adduct flowing into the void at $z=0$, and the amount flowing through a cross section at a distance L down the void, are described by equations

$$- 2\pi D \int_0^a r \left(\frac{\partial C_A}{\partial z} \right)_{z=0} dr$$

and

$$- 2\pi D \int_0^a r \left(\frac{\partial C_A}{\partial z} \right)_{z=L} dr$$

Using the following rearrangements,

$$A_n = \frac{2J_1(\alpha_n a)}{(a\alpha_n)[J_0^2(\alpha_n a) + J_1^2(\alpha_n a)]} = \frac{2h_1}{a(\alpha_n^2 + h_1^2)} J_0(\alpha_n a)$$

$$B_j = \frac{2j_1(\mu_j a)}{(a\mu_j)[J_0^2(\mu_j a) + J_1^2(\mu_j a)]} = \frac{2h_2}{a(\mu_j^2 + h_2^2)} J_0(\mu_j a)$$

and equation (34) for C_A together with (22) and (26), the following expression may be obtained,

$$\text{Flux}|_{z=0} = 2\pi D \left[(C_0 - \frac{h_1}{h_2} C_{BZO}) D' \sum_{n=1}^{\infty} \frac{2h_2^2}{\mu_j^2 + h_2^2} \right] \quad (35)$$

(cf. (19))

In developing $(\partial C_A / \partial z)_{z=L}$ the procedure is as before;

where values of (L/u_z) are small, the expanded exponential may be truncated after the second term of the series.

Relating $(\partial C_A / \partial z)_{z=L}$ to $(\partial C_A / \partial z)_{z=0}$;

$$\begin{aligned} \left(\frac{\partial C_A}{\partial z} \right)_{z=L} = \left(\frac{\partial C_A}{\partial z} \right)_{z=0} \times \{ 1 - k' L \} & - \left[- \frac{h_1}{h_2} C_{BZO} (D')^2 L \sum_1^{\infty} A_n J_0(\alpha_n a) \alpha_n^4 \right. \\ & - \sum_1^{\infty} B_j J_0(\mu_j r) \mu_j^4 (D')^2 L (C_0 \frac{h_1}{h_2} C_{BZO}) \\ & + \sum_1^{\infty} B_j J_0(\mu_j r) \mu_j^2 (D')^2 L \sum_1^{\infty} A_n J_0(\alpha_n a) \alpha_n^2 \frac{h_1}{h_2} C_{BZO} \\ & \left. + \sum_1^{\infty} B_j J_0(\mu_j r) (D')^2 L \sum_1^{\infty} A_n J_0(\alpha_n a) \alpha_n^4 \frac{h_1}{h_2} C_{BZO} \right] \end{aligned}$$

$$\text{As } \text{Flux}|_{z=L} = \text{Flux}|_{z=0} \times [1 - k' L] + 2\pi D \left[\int_0^a r dr \times \text{all terms above} \right]$$

$$\text{and } \sum_1^{\infty} \frac{B_j J_0(\mu_j a)}{\mu_j^2} = \frac{2h_2}{a(\mu_j^2 + h_2^2)} \mu_j^2 = \frac{a}{2h_2} \quad , \text{ the integrated}$$

forms of the 1st and 4th bracketed terms above cancel out.

Using the appropriate expressions for A_n and B_j , eventually,

$$\text{Flux}|_{z=L} = \text{Flux}|_{z=0} \left[1 - k'L + 2\pi D(D')^2 L \left\{ \frac{2}{2+ah_2} \cdot \frac{4h_1^2}{2+ah_1} \cdot C_{BZO} - \dots \right. \right. \\ \left. \left. \dots \frac{4h_2^2}{2+ah_2} \cdot \left(C_0 - \frac{h_1}{h_2} C_{BZO} \right) \right\} \right]$$

Equation (35) for the flux in to the void may be rewritten, using an equation analagous to (21), as

$$\frac{4\pi D(D')}{2+ah_2} \cdot \frac{ah_2^2}{2} \cdot \left(C_0 - \frac{h_1}{h_2} C_{BZO} \right)$$

Using this, and with $k' = k_g/u_z$, $D' = D/u_z$, $h_2 = k_T/D$, $h_1 = k_f/D$,

$$\text{Flux}|_L = \text{Flux}|_0 \left[1 - \left(\frac{k_g L}{u_z} \right) - 2 \left(\frac{k_T}{u_z} \right) \cdot \left(\frac{L}{a} \right) \cdot \left[1 - \left(\frac{k_f}{k_T} \right)^2 \cdot \frac{C_{BZO}}{\left(C_0 - \frac{k_f}{k_T} C_{BZO} \right) \left(2 + \frac{a k_f}{D} \right)} \right] \right]$$

(36)

This is an analagous equation to (23) where there was no formation of adduct occurring. If $k_f = 0$, or $k_T \gg k_f$ the above expression is seen to condense to (23).

Previously, minimising the flux at $z=L$ gave high conversions to maa (as gas phase reactions would be more favoured than wall reactions - further for the adduct to diffuse). In a catalyst void, it must be decided whether high conversions of adduct are required, or if, in fact, conditions should have been chosen so that more adduct is manufactured in the void. High conversion is not necessarily desirable, as this does not necessarily mean the formation of large amounts of maa - due to the small size of the voids, the wall reaction

to CO_2 would obviously be more favoured than in the previous case, where the wall reaction was to benzene and oxygen. Obviously it is important to study the selectivity of the reaction scheme to maa.

As before, the overall rate of reaction to maa is given by the local reaction rate integrated throughout the void volume.

$$R_g = k_g \int_0^L \int_0^a 2\pi r C_A(r, z) dr dz$$

and the overall rate of adduct reaction to other products is given by the volumised reaction at the wall,

$$R_T = k_T \int_0^L 2\pi a C_A(a, z) dz$$

As before, R_g/R_T is a measure of the selectivity of adduct decomposition to maa. The mathematical derivation is straight forward and the final result obtained is

$$R_g/R_T = k_g a / 2k_T + k_g a^2 / 4D \cdot \left[\frac{1}{1 + \left(\frac{h_1}{h_2}\right) \cdot \frac{C_{BZO}}{C_0 - \frac{h_1}{h_2} C_{BZO}}} \cdot \left(\frac{2+ah_2}{2+ah_1}\right) \right] \quad (37)$$

As for the expression for adduct conversion, there is a marked similarity between (37) and (27).

From (37) it can be seen that if

$$\left(\frac{h_1}{h_2}\right) \cdot \frac{C_{BZO}}{C_0 - \frac{h_1}{h_2} C_{BZO}} \cdot \left(\frac{2+ah_2}{2+ah_1}\right) > 0, \text{ then the equation}$$

approximates to

$$R_g/R_T = k_g a / 2k_T + k_g a^2 / 4D \times \left\{ \text{Factor of } < 1 \right\}$$

Therefore, the selectivity to maa in the void will be less than in a free space section of identical radius after the catalyst bed (providing that $k_T \cong k_w$, which may not necessarily be true).

However, if $\frac{k_f}{k_T} C_{BZO} > C_0$, then $\left(\frac{h_1}{h_2} \right) \frac{C_{BZO}}{C_0 - \frac{h_1}{h_2} C_{BZO}} \cdot \left(\frac{2+ah_2}{2+ah_1} \right)$

will be < 0 . Up to a value of -1 , R_g/R_T will be larger than in a tube of identical radius after the bed (no active surface present), but after this value R_g/R_T falls off again. For voids early in the catalyst bed, C_{BZO} will be $\gg C_0$ and, providing $k_T \gg k_f$, the selectivity to maa will be high. In fact, even when very high conversions of benzene have occurred and large amounts of adduct have been produced ($C_0 > C_{BZO}$), it is unlikely that $\frac{k_f C_{BZO}}{k_T}$ will ever be less

than C_0 , as, in order to produce large amounts of adduct (high C_0), k_f must necessarily be very large, and probably always greater or of the same order as k_T . However, it is possible that, at very high conversions of benzene to adduct, and for very small voids, R_g/R_T in the void will be less than in a tube of identical radius after the bed.

(f) Significance of the Equations developed for a suitable
Bed Design

To summarise, for any arbitrary void in the catalyst bed, equations have been derived describing the conversion of adduct in that void and the selectivity of the reaction to maa. In obtaining the two equations describing adduct conversion and selectivity, it was necessary to assume constant values of adduct concentration at the mouth of the void (C_{BZO} and C_O). Obviously, the values of C_{BZO} and C_O will change for different void positions down the bed. At the very first section of catalyst material, C_O will be zero, and C_{BZO} will be the value of the feed to the reactor assembly. Proceeding from section to section of bed, void to void, C_O will increase from zero as more adduct is formed, and C_{BZO} will decrease all the while. C_O will not go on increasing unrestrained, however, as conversion of the adduct in the gas phase and on the catalytic surface will become increasingly important.

Equations (29) (for benzene removal) and (34) (for adduct formation and removal) can be represented by

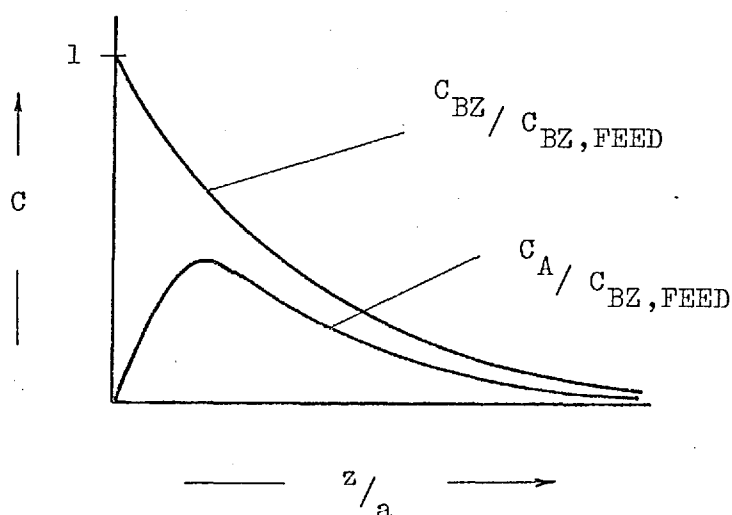


FIGURE 5.4

Numerical solutions of equations (29), (34), (36) and (37) are easily obtained, using suitable values for the various dimensionless groups involved. With the present experimental data, it is possible to assign values to all these groups, but a little more information may first be gained by inspection of the expressions for conversion of the adduct (36) and for selectivity to maa (37).

It is rewarding to consider the case when the void, and the conditions of flow through it, are such that any conversion of adduct occurring produces maa by gas phase reaction. Although this is an extreme, and may be argued theoretically as impossible to attain - some adduct will always necessarily be lost at the surface as C_A must have some finite value there - an approximation to this extreme may give some indications as to void sizing. Equation (36), which is a measure of adduct conversion, is

$$\frac{\text{Flux}|_L}{\text{Flux}|_0} = 1 - \left(\frac{k_g^a}{u_z}\right) \cdot \left(\frac{L}{a}\right) - 2\left(\frac{k_T}{u_z}\right) \cdot \left(\frac{L}{a}\right) \cdot \left\{ 1 - \left(\frac{k_f}{k_T}\right)^2 \frac{C_{BZO}}{\left(C_0 - \frac{k_f}{k_T} C_{BZO}\right) \left(2 + \frac{2}{ak_f}\right)} \right\}$$

For least conversion of adduct, and that conversion being principally to maa, the last term on the R.H.S. should tend to zero

$$\text{ie.} \quad \left(\frac{k_f}{k_T}\right)^2 \cdot \frac{C_{BZO}}{\left(C_0 - \frac{k_f}{k_T} C_{BZO}\right) \left(2 + \frac{2}{ak_f}\right)} \cong 1 \quad (38)$$

(minimisation of (L/a) and (k_T/u_z) would necessarily mean small values of (k_g^a/u_z) and small selectivity to maa ; hence it is better to minimise using (38)).

(38) may be rearranged to give

$$(C_0/C_{BZO}) = (k_f/k_T) \cdot \left\{ 1 + \left(\frac{k_f}{k_T} \right) \frac{2}{\frac{2+ak_f}{D}} \right\} \quad (38)'$$

With the kinetic data available from the Results section, values of (k_f/k_T) and (ak_f/D) give values of (C_0/C_{BZO}) where the maximum conversion to maa is taking place (but least total conversion). This implies that, for catalyst pellets of a fixed uniform size, a knowledge of the benzene concentration profile down the catalyst bed (a measure of C_{BZO} as it changes from void to void) will give, using (38)', a direct measure of adduct concentration in the bed, when the only significant reaction is to maa in the gas phase. Obviously the benzene profile through the catalyst bed will be much easier to compute directly, as benzene disappears (in the catalyst bed section) by a heterogeneous reaction, no homogeneous reaction or production taking place. Computation of equation (29) for the benzene profile is a relatively simple problem, and other results have been published for various values of the dimensionless parameters; $\left(\frac{k_f a}{D} \right)$ and $(u_z a/D)$ (96, 97)

Alternatively, maximising the selectivity to maa can be examined by consideration of equation (37)

$$\text{ie. } R_g/R_T = k_g a / 2k_T + k_g a^2 / 4D \cdot \left\{ 1 / \left(1 + \left(\frac{k_f}{k_T} \right) \frac{C_{BZO}}{C_0 - \frac{k_f}{k_T} C_{BZO}} \cdot \left(\frac{2 + \frac{ak_T}{D}}{2 + \frac{ak_f}{D}} \right) \right) \right\}$$

At constant temperature, $(k_g a / k_T)$ and $(k_g a^2 / D)$ are fixed by the kinetics of the reactions involved, and maximising

R_g/R_T is best achieved by making $\left(\frac{k_f}{k_T}\right) \cdot \frac{C_{BZO}}{\left(C_O - \frac{k_f}{k_T} C_{BZO}\right)} \cdot \left\{ \frac{2 + \frac{ak_T}{D}}{2 + \frac{ak_f}{D}} \right\}$

approach - 1 as closely as possible.

Rearrangement gives

$$\left(\frac{C_O}{C_{BZO}}\right) \cong \left(\frac{ak_f}{D}\right) \left(\frac{k_f}{k_T} - 1\right) \left\{ \frac{1}{2 + \frac{ak_f}{D}} \right\} \quad (39)$$

As the values of the kinetic parameters are fixed at constant temperature, evaluation of the R.H.S. is an easy matter.

When (C_O/C_{BZO}) for any particular void approaches this value, maximum selectivity to maa will occur.

(g) Incorporation of Kinetic Data in the Design Equations

However useful equations (29), (34), (36) and (37) may appear to be, it should be emphasised that they are only theoretical predictions and, as such, are subject to limitations imposed by the use of assumptions. The most severe of these is the assumption of isothermal operation, a situation rarely realized in practice.

Some comparison of theory with experimental results is possible, although in a limited sense. The limitations of the present results necessitate the use of experimental data together with the above theoretical predictions in order to develop further predictions which can be subject to future experimental verification. Success of the theoretical analysis can only be judged from the results of future experimental work.

Some combination of theory and experiment can be made for steady state operation, where the rate of production of adduct is assumed to equal the rate of loss to mass by homogeneous reaction and to other products by surface reaction.

$$\text{ie. } \underset{\substack{\uparrow \\ \text{cm. sec}^{-1}}}{k_f (BZ)^1} = \underset{\substack{\uparrow \frac{k_g}{S} \text{ sec}^{-1} \\ \swarrow \text{cm}^{-1}}}{k_g (C_A)^1} + \underset{\substack{\uparrow \\ \text{cm. sec}^{-1}}}{k_T (C_A)^1}$$

S is the surface area per unit volume of gas space.

Assuming that the benzene concentration is of the same order as adduct concentration for reacting conditions over the active catalyst, then,

$$\left(\frac{k_f}{k_T}\right) = \left(\frac{k_g}{S k_T}\right) + 1$$

The experimental results show that $k_g = 26.7 \times (O_2)^{1/2} \text{ sec}^{-1}$, and assuming a feed of air, together with high air to fuel ratios

$$k_g = 2.46 \text{ sec}^{-1}$$

since $(Sk_T) = 4.00 \text{ sec}^{-1}$, $(k_g/Sk_T) = 0.615$, and $(k_f/k_T) = 1.615$.

For a volumetric feed rate of 500 ml.min^{-1} , a reaction temperature of 415°C , and a bed porosity of 0.25, it follows that, in 2cm diameter reactors,

$$u_z \cong 25 \text{ cm/sec}$$

Hence, $(k_g a/u_z) \cong 0.1$

The diffusion coefficients may be calculated from published work (98), as $D_{415^\circ\text{C}} = 0.4 \text{ cm}^2/\text{sec}$. Values of $(a k_T/D)$ have been reported to fall within the range 0.1 to 10 (96, 97). Assuming a mean value of unity,

$$\left(\frac{a k_T}{D}\right) = 1.0, \text{ and } k_f = 0.646 \text{ cm/sec}$$

$$\left(\frac{a k_f}{D}\right) \text{ will then be } 1.615, \text{ and } (k_T/u_z) = 0.016.$$

Using these values for the dimensionless groups, it is possible to compute concentration profiles and selectivities in voids and in sections of free space placed after catalyst beds. Using equation (39) for example, it is possible to compute which values of (C_O/C_{BZO}) will give the best selectivity to maa. Insertion of the experimental data into (39) gives a value of 0.275. Hence, at any position down the catalyst bed, use of equations (29) and (34) with the above values of the relevant parameters will generate

values of (C_0/C_{BZO}) . These will give a direct measure of the selectivity to maa and, for values of $(C_0/C_{BZO}) \cong 0.275$, this selectivity will be a maximum.

As previously stated, (C_0/C_{BZO}) will change going from void to void down the bed, although from Figure 5.4, C_0/C_{BZO} will have a maximum value approaching unity. However, experimental results (over catalyst 2) would indicate that for very active catalysts where the rate of termination is much smaller than the rate of formation, C_0 can be several times larger than C_{BZO} . In fact, inspection of equation (38)' shows the maximum value of C_0/C_{BZO} for any void will be (k_f/k_T) .

Using the values of the kinetic parameters involved, estimates of the net reaction to maa may also be computed. Expanding (37) to use the experimental data,

$$R_g/R_T = \frac{1}{2} \left(\frac{k_g a}{u_z} \right) \left(\frac{u_z}{k_T} \right) + \frac{1}{4} \left(\frac{k_g a}{u_z} \right) \left(\frac{u_z}{k_T} \right) \left(\frac{k_T}{k_f} \right) \left(\frac{a k_f}{D} \right) \left[\frac{1}{1 + \left(\frac{k_f}{k_T} \right) \frac{C_{BZO}}{C_0 - \frac{k_f}{k_T} C_{BZO}} \cdot \left(\frac{2 + \frac{a k_T}{D}}{2 + \frac{a k_f}{D}} \right)} \right]$$

Using the calculated values of the various parameters, it is interesting to observe that at the start of the catalyst bed, where $C_0=0$, the net selectivity to maa is 92%. This compares favourably with values calculated from equation (27) which gives the selectivity of the gas phase reaction to maa in the absence of catalyst surface a constant value of 87%. However, as C_0 increases (from void to void) going down the catalyst bed, the selectivity will decrease and will eventually be less than 87%. This may be a convenient point at which to discontinue the catalyst bed and to introduce a

free space section. Selectivity will then remain constant at 87% and, as adduct is being removed in the gas phase (to maa) and by wall reaction (to BZ and O_2), " C_0 " will decrease to a point where the introduction of a new section of catalyst bed will lead once again to a selectivity of 92%.

One other point of interest would be the position, in a catalyst bed, where adduct concentration ceases to be a function of r , the radius of the void (or of the bed). This should be a well defined point, in terms of the measured parameters, and its physical significance is obvious. As more adduct is produced going down the void (and therefore the bed), there will come a point, (where formation is greater than termination), when the adduct concentration at the wall will be greater than in the centre of the void. Diffusion will take place away from the wall, until eventually the radial concentration gradient will disappear, and C_A will no longer be a function of r .

Mathematically this would imply that $(\partial C_A / \partial r) = 0$ for all r , including $r=a$. Using equation (34) for C_A as a function of r and z , after differentiation w.r.t. r and subsequent expansion of exponentials (as above),

$$- \sum_1^{\infty} B_j J_0(\mu_j a) h_z \left[(C_0 - \frac{h_1}{h_2} C_{BZO}) \cdot (1 - D' \mu_j^2 z) + \frac{h_1}{h_2} C_{BZO} \cdot \sum_1^{\infty} \frac{A_n \alpha_n^2 J_0(\alpha_n a)}{\mu_j^2 - \alpha_n^2} \cdot [D' \mu_j^2 - D' \alpha_n^2] \cdot z \right] = 0$$

Using the appropriate expressions for A_n and B_j , together with equations (21) and (22),

$$(C_0 - \frac{h_1}{h_2} C_{BZO}) = \left[h_2^2 (C_0 - \frac{h_1}{h_2} C_{BZO}) - h_1^2 C_{BZO} \frac{2}{(2 + ah_1)} \right] D' z$$

and, upon rearrangement, with $h_2 = k_T/D$, $h_1 = k_f/D$, $D' = D/u_z$,

$$(z/a) = \frac{\left(\frac{D}{ak_T}\right) \left(\frac{u_z}{k_T}\right)}{1 - \left(\frac{k_f}{k_T}\right) \cdot \frac{C_{BZO}}{C_0 - \frac{k_f}{k_T} C_{BZO}} \cdot \frac{2}{\left(2 + \frac{ak_f}{D}\right)}} \quad (40)$$

At the start of the catalyst bed, where C_0 is zero, use of the experimental data in equation (40) gives a value of (z/a) of 40. Imagining a continuous void running down the first catalyst bed ($C_{BZO} = C_{BZ}$ Feed, and $C_0 = 0$), after a distance of 40 x the mean void radius, C_A will cease to be a function of radial position.

(h) Summary: Reactor Design

Some aspects of the design of a catalyst bed involving mixed homogeneous-heterogeneous reactions have been considered. Emphasis has been placed on a clearer understanding of the physico-chemical phenomena which occur and, in particular, the effect of various parameters on overall reactant conversion and selectivity to maleic anhydride. Although the model must be viewed as preliminary and little effort has been made at correlating the theory with experimental results, the results of the analysis are encouraging. The experimental data available has been used to derive numerical results from several of the more important equations developed. These results are predictions only, and should be judged more fully when more experimental data is available; nevertheless, several possibilities for improving the design of a catalyst bed have emerged.

In particular, for isothermal operation of the bed, it has been possible to show that although reactant (and adduct) conversion may be higher in a particular section of catalyst bed, in general maximum selectivity of the overall reaction to maa should occur in a free space section which is devoid of catalyst surface. There is an exception to this, in that, for very small sections of catalyst, the concentration of adduct (formed by catalytic reaction of benzene and oxygen) may be maintained at a sufficiently low (although increasing) level so that the selectivity to maa will approach the "initial" value of 92%. As the concentration of adduct increases, the selectivity will decrease to less than 87%. This is the point at which free

space should be introduced, as selectivity will be maintained at 87%, even though the adduct concentration will steadily be reduced. Once this concentration reaches a sufficiently low level, more catalyst may be introduced, the selectivity once again approaching 92%. The most promising design that evolves from these preliminary arguments thus involves long reaction tubes with alternate layers of free space between layers of active catalyst.

APPENDICES

APPENDIX 1

If C_{A1} is the solution of $u_z \cdot \frac{dC_{A1}}{dz} = \frac{D}{r} \cdot \frac{d}{dr} \left(r \cdot \frac{dC_{A1}}{dr} \right)$ 1.

then C_A is a solution of $u_z \cdot \frac{dC_A}{dz} = \frac{D}{r} \cdot \frac{d}{dr} \left(r \cdot \frac{dC_A}{dr} \right) - k_g \cdot C_A$

providing that $C_A = k' \int_0^z C_{A1} \cdot e^{-k'z'} \cdot dz' + C_{A1} \cdot e^{-k'z}$ 2.

with $k' = k_g / u_z$, $D' = D / u_z$, and z' is some arbitrary length variable.

PROOF :

From Differentiation of 2. , $\frac{dC_A}{dz} = \frac{dC_{A1}}{dz} \cdot e^{-k'z}$ 3.

Also, $\frac{dC_A}{dr} = k' \int_0^z \frac{dC_{A1}}{dr} \cdot e^{-k'z'} \cdot dz' + \frac{dC_{A1}}{dr} \cdot e^{-k'z}$

and, $\frac{d^2C_A}{dr^2} = k' \int_0^z \frac{d^2C_{A1}}{dr^2} \cdot e^{-k'z'} \cdot dz' + \frac{d^2C_{A1}}{dr^2} \cdot e^{-k'z}$

Equation 1. may be written as $\frac{dC_{A1}}{dz} = D' \cdot \frac{d^2C_{A1}}{dr^2} + \frac{D'}{r} \cdot \frac{dC_{A1}}{dr}$

Using the above , $D' \cdot \frac{d^2C_A}{dr^2} = D' \left[k' \int_0^z \frac{1}{D'} \cdot \left(\frac{dC_{A1}}{dz} - \frac{D'}{r} \cdot \frac{dC_{A1}}{dr} \right) e^{-k'z'} \cdot dz' \right]$

$+ D' \left[\frac{1}{D'} \cdot \left(\frac{dC_{A1}}{dz} - \frac{D'}{r} \cdot \frac{dC_{A1}}{dr} \right) e^{-k'z} \right]$

and also , $\frac{D'}{r} \cdot \frac{dC_A}{dr} = k' \int_0^z \frac{D'}{r} \cdot \frac{dC_{A1}}{dr} \cdot e^{-k'z'} \cdot dz' + \frac{D'}{r} \cdot \frac{dC_{A1}}{dr} \cdot e^{-k'z}$

Therefore , $D' \left(\frac{d^2C_A}{dr^2} + \frac{1}{r} \cdot \frac{dC_A}{dr} \right) = k' \int_0^z \frac{dC_{A1}}{dz} \cdot e^{-k'z'} \cdot dz' + \frac{dC_{A1}}{dz} \cdot e^{-k'z}$

Using 3. in this equation ,

$$D' \left(\frac{d^2 C_A}{dr^2} + \frac{1}{r} \frac{dC_A}{dr} \right) = k' \int_0^z \frac{dC_A}{dz'} dz' + \frac{dC_A}{dz}$$

which is

$$u_z \frac{dC_A}{dz} = \frac{D}{r} \frac{d}{dr} \left(r \frac{dC_A}{dr} \right) - k_g \cdot C_A$$

Q.E.D.

Similarly, it can be shown that if C_{A1} satisfies the initial and boundary conditions, then so will C_A .

e.g.

(1) If the initial condition is that at $z = 0$, $C_{A1} = C_{A0}$, then inspection of 2. shows that $C_A = C_{A0}$ also.

(2) For points where $z > 0$, should $C_{A1} = C_{A0}$, then as

$$C_A = k' \int_0^z C_{A0} \cdot e^{-k'z'} dz' + C_{A0} \cdot e^{-k'z}; \text{ i.e. } C_A = C_{A0}$$

(3) For the surface condition : $\frac{dC_{A1}}{dr} = -\gamma C_{A1}$,

where γ is some arbitrary constant, using 2. it is seen

$$\text{that } \frac{dC_A}{dr} = k' \int_0^z \frac{dC_{A1}}{dr} \cdot e^{-k'z'} dz' + \frac{dC_{A1}}{dr} \cdot e^{-k'z}$$

$$\text{or } \frac{dC_A}{dr} = k' \int_0^z -\gamma C_{A1} \cdot e^{-k'z'} dz' + (-\gamma C_{A1} \cdot e^{-k'z})$$

which reduces to , as $C_A = C_{A1}$ at $z = 0$,

$$\frac{dC_A}{dr} = -\gamma C_A$$

Therefore the expression 2. for C_A satisfies the initial and boundary conditions providing that C_{A1} does also.

Evaluation of the series :
$$\sum_{n=1}^{\infty} \frac{h^2}{\alpha_n^2 + h^2} \quad \text{and} \quad \sum_{n=1}^{\infty} \frac{\alpha_n^2}{\alpha_n^2 + h^2}$$

Equation (12)' is
$$\alpha_n J_1(\alpha_n \cdot a) = h \cdot J_0(\alpha_n \cdot a)$$

Expanding the Bessel Functions in series form :-

$$J_0(\alpha_n \cdot a) = 1 - \left(\frac{\alpha_n \cdot a}{2}\right)^2 + \frac{1}{4} \left(\frac{\alpha_n \cdot a}{2}\right)^4 - \dots$$

$$J_1(\alpha_n \cdot a) = \left(\frac{\alpha_n \cdot a}{2}\right) - \frac{1}{2} \left(\frac{\alpha_n \cdot a}{2}\right)^3 + \frac{1}{12} \left(\frac{\alpha_n \cdot a}{2}\right)^5 - \dots$$

For large values of a , (for most industrial reactors this is so),

$$J_1(\alpha_n \cdot a) \cong \left(\frac{\alpha_n \cdot a}{2}\right), \quad \text{and so, from}$$

$$\alpha_n^2 \cong 2 \cdot h / a$$

Therefore,
$$\sum_{n=1}^{\infty} \frac{h^2}{\alpha_n^2 + h^2} \cong \frac{1}{1 + 2/a \cdot h} ; \quad \sum_{n=1}^{\infty} \frac{\alpha_n^2}{\alpha_n^2 + h^2} \cong \frac{1}{1 + \frac{a \cdot h}{2}}$$

Evaluation of the series :
$$\sum_{n=1}^{\infty} \frac{h^2}{\alpha_n^2 (\alpha_n^2 + h^2)}$$

The DINI - Expansion of unity is written for this case :-

$$1 = \frac{2 \cdot h}{a} \sum_{n=1}^{\infty} \frac{J_0(\alpha_n \cdot r)}{(\alpha_n^2 + h^2) \cdot J_0(\alpha_n \cdot a)}, \quad 0 \leq r \leq a$$

Multiply both sides by $r \cdot dr$ and integrate from 0 to a ;

$$\int_0^a r \cdot dr = \frac{2 \cdot h}{a} \int_0^a \frac{r \cdot J_0(\alpha_n \cdot r) \cdot dr}{(\alpha_n^2 + h^2) \cdot J_0(\alpha_n \cdot a)}$$

However, it is known from equations (14) and (12)' that

$$\int_0^a r \cdot J_0(\alpha_n \cdot r) \cdot dr = \frac{h \cdot a}{\alpha_n^2} J_0(\alpha_n \cdot a)$$

Therefore,

$$\frac{a^2}{2} = \frac{2 \cdot h}{a} \sum_{n=1}^{\infty} \frac{h \cdot a}{(\alpha_n^2 + h^2) \cdot \alpha_n^2}$$

or ,

$$\sum_{n=1}^{\infty} \frac{h^2}{(\alpha_n^2 + h^2) \cdot \alpha_n^2} = \frac{a^2}{4}$$

Q.E.D.

APPENDIX 3

A solution is required of

$$D \left(\frac{d^2 C_{A1}}{dr^2} + \frac{1}{r} \frac{dC_{A1}}{dr} \right) - u_z \frac{dC_{A1}}{dz} = 0 \quad 1.$$

subject to the following conditions :-

(i) At $r = 0$, $z = 0$, C_{A1} is finite

(ii) At $z = 0$, $0 < r < a$, $C_{A1} = C_0$

(iii) At $r = a$, $z = 0$, Net flux to the wall = Rate of removal at the wall - Rate of production.

$$\text{i.e. } -D \frac{dC_{A1}}{dr} = k_T \cdot C_{A1} - k_f \cdot C_{Bz}$$

For convenience, let $D \cong D_{Bz}$ (both independent of concentration)

$$\text{Therefore (iii) becomes } -\frac{dC_{A1}}{dr} = h_2 \cdot C_{A1} - h_1 \cdot C_{Bz} \quad -2.$$

Equation 1. is homogeneous but it is not directly soluble due to the non-homogeneous boundary condition at $r = a$.

Introducing a new variable C , defined by $C = C_{A1} - \frac{h_1 \cdot C_{Bz}(a, z)}{h_2}$ 3.

$$\text{or, } C = C_{A1} - \frac{h_1 \cdot C_{Bz0}}{h_2} \cdot \sum_{n=1}^{\infty} A_n \cdot J_0(\alpha_n \cdot a) \cdot e^{-D' \cdot \alpha_n^2 \cdot z}$$

$$\text{Therefore, } \frac{dC}{dr} = \frac{dC_{A1}}{dr}$$

$$\text{and, } \frac{dC}{dz} = \frac{dC_{A1}}{dz} + \frac{h_1 \cdot C_{Bz0}}{h_2} \cdot \sum_{n=1}^{\infty} A_n \cdot D' \cdot \alpha_n^2 \cdot J_0(\alpha_n \cdot a) \cdot e^{-D' \cdot \alpha_n^2 \cdot z}$$

4. and 5.

Hence, using these results in equation 1. , it can be seen that a solution is required of

$$\frac{D'}{r} \cdot \frac{d}{dr} \left(r \cdot \frac{dC}{dr} \right) = \frac{dC}{dz} - \frac{h_1}{h_2} \cdot C_{BZO} \cdot \sum_{n=1}^{\infty} A_n \cdot D' \cdot \alpha_n^2 \cdot J_0(\alpha_n \cdot a) \cdot e^{-D' \cdot \alpha_n^2 \cdot z} - 6.$$

Subject to the conditions :-

$$(a) \quad r = 0, \quad z = 0, \quad C \text{ is finite}$$

$$(b) \quad 0 < r < a, \quad z = 0, \quad C = C_0 - \frac{h_1}{h_2} \cdot C_{BZO} \cdot \sum_{n=1}^{\infty} A_n \cdot J_0(\alpha_n \cdot a)$$

$$\text{From the DINI - SERIES of unity,} \quad \sum_{n=1}^{\infty} A_n \cdot J_0(\alpha_n \cdot a) = 1$$

$$\text{Therefore,} \quad C = C_0 - \frac{h_1}{h_2} \cdot C_{BZO}$$

$$(c) \quad r = a, \quad z = 0, \quad -\frac{dC}{dr} = h_2 \left(C + \frac{h_1}{h_2} \cdot C_{BZ}(a, z) \right) - h_1 \cdot C_{BZ}(a, z)$$

$$\text{or,} \quad -\frac{dC}{dr} = h_2 \cdot C$$

Thus simplifying the boundary condition enables a solution of 6. to be obtained. The solution will be of the form :-

$$C = \sum_{j=1}^{\infty} b_j(z) \cdot J_0(\mu_j \cdot r) \quad -7.$$

where the $b_j(z)$ are undetermined functions of z . Using 7. in 6.

$$\begin{aligned} \frac{D'}{r} \cdot \frac{d}{dr} \left(r \cdot \frac{d}{dr} \sum_{j=1}^{\infty} b_j(z) \cdot J_0(\mu_j \cdot r) \right) &= \frac{d}{dz} \sum_{j=1}^{\infty} b_j(z) \cdot J_0(\mu_j \cdot r) \\ &\quad - \frac{h_1}{h_2} \cdot C_{BZO} \cdot \sum_{n=1}^{\infty} A_n \cdot D' \cdot \alpha_n^2 \cdot J_0(\alpha_n \cdot a) \cdot e^{-D' \cdot \alpha_n^2 \cdot z} \end{aligned}$$

or,

$$\begin{aligned} \frac{D'}{r} \cdot \frac{d}{dr} \left(-\mu_j \cdot r \sum_{j=1}^{\infty} b_j \cdot J_1(\mu_j \cdot r) \right) &= b_j'(z) \cdot J_0(\mu_j \cdot r) \\ &\quad - \frac{h_1}{h_2} \cdot C_{BZO} \cdot \sum_{n=1}^{\infty} A_n \cdot D' \cdot \alpha_n^2 \cdot J_0(\alpha_n \cdot a) \cdot e^{-D' \cdot \alpha_n^2 \cdot z} \end{aligned}$$

Making use of the general relation :- $\frac{d}{dp}(p.J_1(p)) = p.J_0(p)$

$$-\mu_j^2.D'.J_0(\mu_j.r).b_j(z) = b_j'(z).J_0(\mu_j.r) - \frac{h_1.C_{BZO}}{h_2} \sum_{n=1}^{\infty} A_n.D!\alpha_n^2.J_0(\alpha_n a).e^{-D!\alpha_n^2.z}$$

Using the orthogonality properties of Bessel Functions , multiplying each side of the above by $r.J_0(\mu_j.r)$ and integrate from 0 to a :-

$$(\text{ and using the relations } \int_0^a r.J_0(\mu_j.r).dr = \frac{a}{\mu_j}.J_1(\mu_j.a)$$

$$\text{and } \int_0^a r.J_0^2(\mu_j.r).dr = \frac{a^2}{2} \left[J_0^2(\mu_j.a) + J_1^2(\mu_j.a) \right]$$

Finally ,

$$b_j'(z) + D'.\mu_j^2.b_j(z) = \frac{2J_1(\mu_j.a)}{a.\mu_j[J_0^2(\mu_j.a) + J_1^2(\mu_j.a)]} \cdot \frac{h_1.C_{BZO}}{h_2} \sum_{n=1}^{\infty} A_n.D!\alpha_n^2.J_0(\alpha_n a).e^{-D!\alpha_n^2.z} \quad - 8.$$

(the ' indicating differentiation)

The solution to equation 8. is the sum of two solutions, one for the homogeneous equation and the second for the Particular Integral.

$$b_j(z) = d_j.e^{-D!\mu_j^2.z} + \frac{2J_1(\mu_j.a)}{a.\mu_j[J_0^2(\mu_j.a) + J_1^2(\mu_j.a)]} \cdot \frac{h_1.C_{BZO}}{h_2} \sum_{n=1}^{\infty} \frac{A_n.D!\alpha_n^2.J_0(\alpha_n a).e^{-D!\alpha_n^2.z}}{1(D!\mu_j^2 - D!\alpha_n^2)} \quad - 9.$$

where the d_j must be determined.

The d_j can be obtained from the initial condition (b)

$$\text{i.e. } C_0 - \frac{h_1.C_{BZO}}{h_2} = \sum_{j=1}^{\infty} b_j(0).J_0(\mu_j.r)$$

From 9.

$$b_j(0) = d_j + \frac{2J_1(\mu_j.a)}{a.\mu_j[J_1^2(\mu_j.a) + J_0^2(\mu_j.a)]} \cdot \frac{h_1.C_{BZO}}{h_2} \sum_{n=1}^{\infty} \frac{A_n.\alpha_n^2.J_0(\alpha_n a)}{(\mu_j^2 - \alpha_n^2)}$$

Hence ,

$$C_0 - \frac{h_1}{h_2} \cdot C_{BZO} = \int_1^{\infty} d_j \cdot J_0(\mu_j r) + \frac{2J_1(\mu_j a)}{a\mu_j [J_0^2(\mu_j a) + J_1^2(\mu_j a)]} \cdot \frac{h_1}{h_2} \cdot C_{BZO} \cdot \int_1^{\infty} \frac{A_n \alpha_n^2 \cdot J_0(\mu_j r) J_0(\alpha_n a)}{(\mu_j^2 - \alpha_n^2)}$$

Using the orthogonality properties again , i.e. multiply by $r \cdot J_0(\mu_j r) \cdot dr$ and integrate between 0 and a - after evaluation ,

$$d_j = \frac{2J_1(\mu_j a)}{a\mu_j [J_0^2(\mu_j a) + J_1^2(\mu_j a)]} \left\{ \left(C_0 - \frac{h_1}{h_2} C_{BZO} \right) - \frac{h_1}{h_2} \cdot C_{BZO} \cdot \int_1^{\infty} \frac{A_n \alpha_n^2 \cdot J_0(\alpha_n a)}{(\mu_j^2 - \alpha_n^2)} \right\}$$

Therefore

$$b_j(z) = \frac{2J_1(\mu_j a)}{a\mu_j [J_0^2(\mu_j a) + J_1^2(\mu_j a)]} \cdot \left[\left(C_0 - \frac{h_1}{h_2} C_{BZO} \right) \cdot e^{-D' \mu_j^2 z} + \dots \dots \dots \right. \\ \left. \dots \frac{h_1}{h_2} \cdot C_{BZO} \cdot \int_1^{\infty} \frac{A_n \alpha_n^2 \cdot J_0(\alpha_n a) \cdot (e^{-D' \alpha_n^2 z} - e^{-D' \mu_j^2 z})}{(\mu_j^2 - \alpha_n^2)} \right]$$

Using this in the general solution (equation 7.) , and remembering

that we defined $C = C_{A1} - \frac{h_1}{h_2} \cdot C_{BZO} \cdot \int_1^{\infty} A_n \cdot J_0(\alpha_n a) \cdot e^{-D' \alpha_n^2 z}$

The final expression for C_{A1} is :-

$$C_{A1} = \frac{h_1}{h_2} \cdot C_{BZO} \cdot \int_1^{\infty} A_n \cdot J_0(\alpha_n a) \cdot e^{-D' \alpha_n^2 z} + \int_1^{\infty} \frac{2J_1(\mu_j a) \cdot J_0(\mu_j r)}{a\mu_j [J_0^2(\mu_j a) + J_1^2(\mu_j a)]} \cdot \left[\dots \dots \dots \right. \\ \left. \dots \left(C_0 - \frac{h_1}{h_2} \cdot C_{BZO} \right) \cdot e^{-D' \mu_j^2 z} + \frac{h_1}{h_2} \cdot C_{BZO} \cdot \int_1^{\infty} \frac{A_n \alpha_n^2 J_0(\alpha_n a) (e^{-D' \alpha_n^2 z} - e^{-D' \mu_j^2 z})}{(\mu_j^2 - \alpha_n^2)} \right]$$

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