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STATISTICAL STUDY OF THE BENZENE OXIDATION PROCESS
IN A FLUIDIZED BED REACTOR

Dissertation

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of the Ohio State University

by

PHASOOK KULLAVANIJAYA, B. Ch. E., M. S.

* * * * *

The Ohio State University
1966

Approved by

[Signature]

Advisor
Department of Chemical Engineering
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VITA

May 18, 1934. Born - Bangkok, Thailand

1957. E. Ch. E., The Ohio State University, Columbus, Ohio

1958. M. S., The Ohio State University, Columbus, Ohio

1963-1964. Teaching Assistant, Chemistry Department, The Ohio State University, Columbus, Ohio

1964-1966. Research Assistant, Engineering Experiment Station, The Ohio State University, Columbus, Ohio

FIELDS OF STUDY

Major Field: Chemical Engineering

Minor Field: Industrial Engineering
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CHAPTER I

INTRODUCTION

In problems involving heterogeneous catalysis, particularly when several reactions occur simultaneously, many factors are involved and the reaction mechanisms become too complex to be solved in the classical manner. In such a case, an empirical method must be used to solve the problem for technical purposes. However, the empirical method has an inherent disadvantage in that a large number of experiments is needed to correctly define the basic relationship among the factors. Even then, the interdependence of factors may still be overlooked.

The empirical method can be improved by using a statistically designed set of experiments to determine the relationship between factors. This method enables one to cut down on the number of experiments and also to make some statistical inference as to the basic mechanisms of the process. In addition, the statistical method will allow one to maximize the yield of products or any other desired quantity with regard to the process variables.

The catalytic oxidation of benzene to form maleic anhydride has been known commercially for quite some time (1-5). In this process, benzene is oxidized in a fixed bed reactor using vanadium pentoxide catalysts. The reaction mechanism is quite complex, since there are side products formed from both simultaneous and consecutive reactions. Another interesting fact is that, while the process is commercially
feasible in a fixed bed reactor, the fluidized bed reactor has not been successful in spite of several attempts at development (6-7). On the other hand, both the fixed bed and the fluidized bed reactors have been successfully employed in the production of phthalic anhydride and maleic anhydride from toluene and xylene, even though these processes are quite similar to the benzene oxidation process (8-11).

The fluidized bed reactor has some inherent advantages over the fixed bed reactor, such as temperature uniformity and ease of handling of reaction products (7). In addition, fluidized bed reactors could be operated in such a way that the catalysts are recycled and new catalysts added continuously, thus eliminating much of the shutdown time necessary for changing catalysts in a fixed bed reactor. On the other hand, the fluidized bed reactor has a limited range of operation depending on the catalyst particle's properties and the tube diameter. For example, in a 6" diameter reactor, cracking catalysts of the silica-alumina type could be fluidized at an optimum superficial gas velocity of about 0.2-0.4 ft./sec. for a maximum reaction efficiency (12). The optimum velocity, of course, decreases with an increase in the reactor diameter. Detailed correlations of fluidization rates with respect to catalyst properties may be found in Ref. 13.

In addition, due to the wider spread of the residence time distribution in the fluidized bed, its optimum reaction efficiency is lower than that of the fixed bed. This means that the percentages of yield and selectivity are lower, especially for products of intermediate reaction steps. This point will be discussed later in this study.

In this paper, an attempt will be made to determine the basic
relationships underlying the benzene oxidation process in a fluidized bed reactor. By using a statistically designed set of experiments, optimization of the yield of maleic anhydride will be made, and from the yield contour derived, the basic mechanism of the process will be inferred. In addition, an attempt will be made to compare the fluidized bed process with the fixed bed one. Statistical work on the fixed bed reactor have been made by Benjamin Yao of this Department in 1964 (14).
CHAPTER II

HISTORICAL

2.1) Oxidation of benzene

According to Marek and Hahn (15), it had been known since Kekule's time that benzene could be oxidized to form maleic acid and its anhydride. In the 1920's, Weiss and Downs undertook the investigation that put the process on a commercial scale with the aim of producing maleic anhydride (1-5). The two important factors in this process were the temperature of the reaction and the types of the catalysts. Over the years, various types of catalysts were tried, the most successful ones being mixtures of vanadium and molybdenum oxides. Other important factors were the reactant ratio and the time of contact.

Weiss and Downs found the temperature range to be 400 - 500 °C with vanadium pentoxide catalysts. The pressure had no significant effect on the yield but should be slightly higher than atmospheric. The products were maleic anhydride, quinone, CO and CO₂. No phenol was isolated, though Weiss and Downs claimed to have smelled it. The yield of maleic acid was about 60 lbs. per 100 lbs. of benzene input, or about 40 mol %. Weiss and Downs speculated that the reaction path would be:

\[
\begin{align*}
(1) & \quad \text{benzene} + \frac{1}{2} O_2 \rightarrow O=\equiv=O + H_2O \\
(2.1) & \quad O=\equiv=O + 3 O_2 \rightarrow C=O + H_2O + 2 CO_2 \\
(3) & \quad C=O + 3 O_2 \rightarrow 4 CO_2 + H_2O
\end{align*}
\]
Various side reactions occurred, with formations of phenol, formaldehyde, fumaric acid, etc.

The reaction was highly exothermic with the heat of oxidation from benzene to maleic acid equal to 10,533 Btu./lb. of benzene. For complete oxidation, \( \Delta H = 18,093 \) Btu./lb. Weiss, Downs and Burns (2) also investigated the effect of air/benzene ratio on vanadium oxides. Their findings indicated that there was a definite ratio of \( V_2O_5 \) to \( V_2O_4 \) for any given ratio of air/benzene regardless of the original composition of oxides in the catalyst. At an air/benzene ratio greater than 14:1, the percentage of \( V_2O_5 \) in the catalyst approached an asymptotic value of 98.5\%. For a given temperature, the ratio of complete oxidation products to partial oxidation products also remained constant. It was thought that the rate of reaction might depend on the rate at which activated oxygen was supplied by the dissociation of \( V_2O_5 \). More discussion will be made on this point later.

Pigulevski and Yarzhemskaya, in the 1930's, proposed that the reaction rate constant was proportional to \( (P_{O_2})^n \) where \( n < 1 \) for the reactions involving oxidation of quinone and maleic anhydride (16-17). These were the rate controlling steps, since they were slower than that of oxidation of benzene to quinone.

In 1952, Hammar (18), using an annular fixed bed reactor, proposed that the oxidation occurred in two simultaneous paths, namely:

a. Partial oxidation

\[
\begin{align*}
(1) & \quad \text{CH}_2 & \quad \rightarrow \quad (X) & \quad \rightarrow \quad \text{CO} + \text{CO}_2 + \text{H}_2\text{O} \\
(2.2) & \quad \text{C} & \quad \rightarrow \quad (X) & \quad \rightarrow \quad \text{CO} + \text{CO}_2 + \text{H}_2\text{O}
\end{align*}
\]
b. Complete oxidation

\[ (2,2) \quad (3) \quad \square \rightarrow (X)_3 \rightarrow CO + CO_2 + H_2O \]

Reaction (1) was controlled by mass transfer (i.e., \( k_1 \) was proportional to \( k_g \)). Reaction (2) was independent of mass transfer, and the controlling step was either the re-adsorption of maleic anhydride or the surface reaction (probably the former with complex order). The only product Hammar found was maleic anhydride, with only traces of carbonyl compounds but no oxalic acid. It was also found that maleic anhydride could be oxidized further even in the absence of catalysts. No confirmation of any mechanism was possible, since Hammar made only 12 experiments which were not enough for a curve fitting.

In 1954, Holsen (19), using a fixed bed reactor, confirmed that both phenol and quinone were formed as intermediate products in the oxidation of benzene to maleic anhydride. His data were consistent with Hammar's proposal that the oxidation occurred in two simultaneous but separate reactions, one leading to products of partial oxidation (i.e., phenol, quinone and maleic anhydride), the other to products of complete combustion (i.e., CO and CO_2). Holsen proposed that the partial oxidation resulted in the formation of an appreciable amount of CO in addition to CO_2, whereas the complete oxidation resulted primarily in the formation of CO_2. Holsen also oxidized phenol, quinone and maleic anhydride in the same reactor. He found that at 400° C about 99% of phenol was oxidized, compared to about 50% for quinone, 14% for benzene, and 12% for maleic anhydride. The yield of maleic anhydride (i.e., the percentage of maleic anhydride formed from the benzene input)
was about 7%, which was quite low. Another interesting point was that
the ratio of CO over CO₂ formed in the oxidation of benzene was essenti-
ally the same as the ratio of CO to CO₂ formed in the oxidation of
maleic anhydride, whereas for oxidation of quinone and phenol, the ratio
CO/CO₂ was much lower. This seemed to contradict his proposal that the
complete oxidation of benzene gave more CO₂ than the partial oxidation
step. Maleic anhydride was formed in both phenol and quinone oxidations.

In 1954, Mars and van Krevelen (20-21) tried the oxidation of
several aromatic compounds in a fluidized bed. The reactor was 43 mm.
in diameter (about 1.7 in.), and the bed height was 11 cm. (about 4.3
in.), and was considered to be an integrating reactor. These two authors
considered that the limiting reaction was the surface reaction between
the aromatic compound and the oxygen present on the underlying catalyst
surface. Hence, the important reactions would be:

1. Aromatic compound oxidized catalyst
   \[ k_1 \rightarrow \text{oxidation product} + \text{reduced catalyst}. \]

2. Reduced catalyst + oxygen \[ k_2 \rightarrow \text{oxidized catalyst}. \]

The first reaction was assumed to be first order with respect to
the aromatic compounds, and the second reaction was assumed to be of
n_th order with respect to oxygen. At equilibrium between the two
reactions, a reaction rate equation similar to a Langmuir-type adsorp-
tion equation was developed and fitted to the data. The overall assump-
tion of Mars and van Krevelen was that the rate was determined mainly
by the re-oxidation of the catalyst, i.e., equation (2) above. Hence,
the oxidation of several aromatic compounds, such as naphthalene to
phthalic anhydride, benzaldehyde to benzoic acid, and toluene to benzoic acid would show good "yield" at the same temperature. The activating energy of their catalyst was found to be about 22 kcal./mol based on the results of naphthalene oxidation. It should be pointed out, however, that Mars and van Krevelen did not oxidize all aromatic compounds at the same temperature. In fact, for the benzene homolog series, benzene was oxidized at 337° and 377°C, naphthalene at 337°C, and anthracene at 280°C. Of course, if the second reaction was indeed controlling, its reaction rate constant would be the same for the oxidation of any aromatic compounds at the same temperature. Unfortunately this point was not proven conclusively. The series of experiments for benzene and naphthalene at 337°C were made with different weights of catalysts (though with the same range of gas flow rates). With the space velocity thus varied, the reaction rate constants for the second reaction for benzene and naphthalene oxidations differed widely. The given values for benzene oxidation were $k_2$ (i.e., the reaction rate constant for the second reaction) = 0.008 l./hr. g. of catalyst, the weight of the catalyst being 48 g., and the gas flow rate being about 100 l./hr. at STP. For the naphthalene oxidation, $k_2$ was reported as 0.15 l./hr. g., with the catalyst weight being 100 g., and the gas flow rate at 100 l./hr. STP (pp. 66, 86-87, Ref. 21). The reaction rate constant for the first reaction ($k_1$) varied widely as expected, being 0.034 l./hr. g. for benzene and 8.3 for naphthalene. In spite of this discrepancy, the derived equation did fit each separate group of data quite well.

In the related area of maleic anhydride oxidation, Mars and van
Krevelen had presented data which showed the rate of oxidation of the anhydride (to CO and CO₂) to be 3-10 times less than that at which CO and CO₂ were formed in the benzene oxidation (at the same temperature, gas flow rate and amount of catalyst).

Tarama (22), using an X-ray diffraction technique, concluded that V₂O₅ began to change to V₂O₄ at around 250 - 350°C; and the diffusion of "O ions" to the catalyst surface was the rate-controlling step for benzene oxidation. This confirmed the findings of Mars and van Krevelen.

In 1954, Ioffe and Sherman (21), using a high-density catalyst in a fixed-bed reactor, proposed that the controlling rate was the diffusion of the reactants into the pores of the catalyst. For more porous catalyst, the oxidation and reduction of V₂O₅ could be controlling. They also proposed that complete oxidation occurred in one single step (i.e., from benzene to CO and CO₂), whereas the partial oxidation occurred in several consecutive steps.

From these various studies it could be concluded that the oxidation of benzene occurred in two simultaneous paths, one composed of several consecutive steps with phenol and quinone as intermediates, and resulting in the formation of maleic anhydride. The second path probably consisted of one single step leading to the formation of CO and CO₂ as the complete oxidation products. The controlling factor in all of these reactions seemed to be the capacity of the catalysts to supply "O ions" to the catalyst surfaces. Thus, the rate-controlling step was thought to be the reaction between O₂ and the reduced catalyst surface. However, the oxidation process was also found to depend on the concentration of benzene in the gas stream to the first order. As was found out by Mars and van Krevelen (21), the highest ultimate yield (or selectivity) of
maleic anhydride (i.e., the ratio: maleic anhydride formed/benzene oxidized) was obtained at lower benzene concentrations. The effects of other process variables such as space velocity, amount of catalyst, ratio of reactants, etc., were not well defined.

2.2). Related Areas

Of interest were the related studies of the catalytic oxidation of naphthalene. One resemblance was the same type of catalyst used. The other point was that naphthalene was also oxidized in two separate reaction paths. According to Calderbank (8), one reaction led to the formation of phthalic anhydride; the other, simultaneous but separate, path, led to the formation of naphthoquinone. Both of these reactions were controlled by the partial pressure of oxygen. Some other side products were also formed, such as maleic anhydride, CO and CO$_2$. Calderbank also developed the controlling-rate equation based on the chemisorption of oxygen. Using a Langmuir-type equation, Calderbank found the rate to be proportional to $(P_{O_2})^N$, where $N = 0.96 - 0.98$. This was essentially the same as Pigulevski's findings (16-17) for the oxidation of benzene. Calderbank found the activating energy for his catalysts to be 26 kcal/mol.

Mars and van Krevelen (21) proposed a reaction mechanism based on the reaction between oxygen and the reduced catalyst surface (i.e., equation 2.3). In fact, these two authors used this type of equation for various aromatic oxidation processes such as benzene, toluene, naphthalene, anthracene, and a few other oxidations on non-aromatic compounds as well. Their contention was that the process was basically that of re-oxidation of the vanadium catalysts. They cited, as their
main support, the change in colors of the catalysts from greenish to yellowish brown at high temperatures, indicating the occurrence of $V_2O_4$. This was the same findings as those of Weiss, Downs, and Burns in the 1920's (2). However, Mars and van Krevelen found that the reaction rate also depended on the concentration of naphthalene to the first order, and the highest ultimate yield (i.e., ratio: phthalic anhydride formed/naphthalene oxidized) occurred at lower concentrations of naphthalene. This was quite similar to the oxidation of benzene. Another interesting point was that the reaction rate constant, $k_1$, of the first reaction in equation (2.3) was always higher for at least one magnitude than $k_2$, the rate constant of the second reaction for both benzene and naphthalene oxidations. The activation energy for the first reaction, however, could not be calculated, since the values of $k_1$ were scattered widely. The activation energy of the second reaction was estimated at 22 kcal/mol.

By using the Mars and van Krevelen's model, some qualitative conclusions could be made, namely:

1. The oxidation processes of naphthalene and benzene were controlled by the equality between the rate of oxidation of the aromatic compounds and the rate of oxidation of the reduced catalysts.

2. Comparison of the temperature range of operation showed that naphthalene could be oxidized at 300°- 350° C, whereas benzene could be oxidized at 400°- 450° C. This is due to the inherent stability of benzene over that of naphthalene.

Since both the rate of oxidation of benzene and that of naphthalene were presumably matched with the rate of re-oxidation of the catalysts
at equilibrium. It could be inferred that the activation energy (overall, Arrhenius type) for naphthalene oxidation would be higher than that of benzene. Thus, the rate constant $k_1$ for naphthalene would rise quickly and its rate of oxidation matched the catalyst's re-oxidation rate at a lower temperature. On the other hand, the activation energy for benzene oxidation would be smaller, since the matching of the two rates were made at a higher temperature.

3. By considering the high values of the activation energy ($20 - 30 \text{ k cal/mol}$) of the re-oxidation equation, one could then exclude the possibility of diffusion being the rate controlling step. Mars and van Krevelen postulated that the adsorption of oxygen onto the catalyst surface could be the rate controlling step. However, this could not be conclusively shown.

The resemblances between the naphthalene and benzene processes were also carried into the theory of the aromatic oxidation itself. According to Ioffe and Sherman (23), the naphthalene oxidation proceeded as followed:

$$
\begin{align*}
\text{(2.4)} & \\
\end{align*}
$$

Similarly, the benzene oxidation, according to Holsen (19), was the following:

$$
\begin{align*}
\text{(2.5)} & \\
\end{align*}
$$
where \( x_i \) represented an unknown intermediate.

In the naphthalene process, the products were phthalic anhydride, naphthoquinone (small amount), and maleic anhydride. On the other hand, the benzene process resulted in maleic anhydride plus some trace amounts of quinone and phenol (depending on the catalysts). The fact that more intermediate products were found in the case of naphthalene could be due to the resonance stabilization that the broken naphthalene molecule (i.e., benzenoid structure) had over the broken benzene molecule (i.e., vinyl structure), and to the lower reacting temperature.

Ioffe and Volkenstein (24) had proposed a theory on the behavior of the \( V_2O_5 \) catalysts. According to this theory, \( V_2O_5 \) and most other metal oxides were electron semiconductors. This meant that they had electrons (or positive valence) roving about its surface. When benzene was adsorbed on the surface, one of the C=C bond was broken as in Fig. 2-1a. Thus, an ion radical and a stray hole (i.e., the \( \oplus \)) were formed.

![Figure 2.1 — C = C Reaction](image)

In (b), the stray hole, \( \oplus \), was eliminated by a stray electron, leaving only the ion radical which would be attacked by a stray oxygen.
ion radical of the surface as in (c). The result was dihydro-endoxy-
benzene which would break down further to maleic anhydride and two 
molecules of carbon monoxide.

In contrast, if, instead, when benzene was absorbed, a C - H 
bond was broken, there would form a phenyl radical which could be dis-
lodged easily by a stray electron, or reacted with a stray oxygen ion 
radical to form phenol. Ioffe claimed that once phenol was formed, 
further successive reactions would result in the formation of carbon 
monoxide. If one used the Ioffe-Volkenstein theory to modify the Holsen 
model (eq. 2.5), the result would be:

\begin{align*}
\text{Holsen's model:} \\
\text{Benzene} & \xrightarrow{k_1} \text{Maleic anhydride} \\
& \xrightarrow{k_2} \text{Phenol} \\
& \xrightarrow{k_3} \text{CO + CO}_2
\end{align*}

The supporting evidence for this model (eq. 2.6) was that in both 
Holsen's and Mars and van Krevelen's work, the percent yield of CO and 
CO$_2$ (i.e., the ratio of CO and CO$_2$ formed/reactant input) for the oxida-
tion of maleic anhydride by itself was about the same magnitude as 
that obtained from the oxidation of benzene.

The main difference between the Ioffe model (eq. 2.6) and the Holsen 
model (eq. 2.5) could be shown in a simplified diagram as followd:

**Figure 2.2 Benzene Oxidation Models**

a) Holsen model

\[
\text{Benzene} \xrightarrow[\text{Maleic anhydride}]{} \text{CO + CO}_2
\]
b) Ioffe model

\[
\begin{align*}
\text{Benzene} & \xrightarrow{k_1} \text{maleic anhydride} \\
\text{CO} + \text{CO}_2 & \xrightarrow{k_2}
\end{align*}
\]

Both of these models were based on the assumption that both benzene and oxygen were absorbed on the catalyst's surface, an assumption which seemed to be agreed upon by all the workers in this field. This was shown in Figure 2.3.

**Figure 2.3 Catalyst Mechanism**

Pinchbeck et al. (28-30) made a study of the naphthalene oxidation in a fixed-bed reactor along a different approach. Using a statistically-designed set of experiment, Pinchbeck developed equations defining the yield contour of phthalic anhydride in terms of process variables such as temperature, contact time, air/naphthalene ratio, etc. From the yield contour and the reaction model of equation (2.4), the kinetic mechanism was found to be controlled by "surface kinetics" up to 400°C, diffusion of the reactants into the pores could be controlling. The data was best fitted by assuming a half order for the disappearance of naphthalene, and first order for all other steps. The yield contour showed a "col" or "minimax" point at 400°C. This meant that the contour showed a maximum for two variables and a minimum with respect to the third (i.e., temperature). The maximum yields at various temperatures increased slowly both above and below the minimax temperature of 400°C.
The change in mechanism at about 400°C was considered to result from the change in the catalyst structure. Along this line, Tandy (31), in his study of vanadium catalysts on the oxidation of sulfur dioxide, found that most common V_2O_5 catalysts contained some K_2SO_4 in the mol ratio of V_2O_5: K_2SO_4 of 2:5. These catalysts melted at about 400°- 410°C, but the melting point was not sharp. K_2SO_4 (and some other sulfates) was used with V_2O_5 as a "promoter", and its immediate effect was to lower the melting point of the catalyst mixture. Boreskov (32) also found that V_2O_5 - K_2SO_4 formed a compound of 1:1 mol ratio with a melting point of about 500°C. The eutectic point between this compound and K_2SO_4 lay below 430°C, and corresponded to an approximate composition of 0.4 mol fraction V_2O_5.

The major function of the alkali metal sulfate promoters was to stabilize the V_2O_5. However, the sulfate salts also lowered the melting point of the mixture. The lowering of the melting point decreased from Na salt to K salt to Cs salt.

Other metal oxides were also added to the V_2O_5 catalysts. Most of these were oxides of the Group IV metals, notably MoO_3. Presumably, MoO_3 acted as a "de-activator" to lower the activity of V_2O_5. As shown by Tarama (33), the activating energy of V_2O_5-MoO_3 catalyst was about 32.4 kcal/mol. compared to 20 kcal/mol. for pure V_2O_5. The total rate of reaction of benzene was also slower in the mixed catalyst, but the yield of maleic anhydride was higher.

Most of the catalysts used at the present time were mixtures of V_2O_5, K_2SO_4 and MoO_3 in various compositions. These were impregnated on either silica gel or alumina. Pinchbeck (29) also made a study of
the effect of $\text{K}_2\text{SO}_4$ on $\text{V}_2\text{O}_5$ catalysts. His results showed that the important factor in catalyst effectiveness was its apparent density rather than the actual composition.

Of interest was the studies of the homogeneous oxidation of benzene by Fort and Hinshelwood (34). The reaction was supposed to proceed by a chain mechanism to some extent, since an increase in the surface area of the vessel seemed to retard the reaction. Rapid oxidation was favored by high concentrations of benzene. The primary products probably gave rise to chain molecules by reacting with more hydrocarbons, but did not react readily with oxygen. The final products were mostly $\text{H}_2\text{O}$, $\text{CO}$, and a smaller proportion of $\text{CO}_2$, even at around $500^\circ\text{C}$. This indicated that the direct oxidation of $\text{CO}$ to $\text{CO}_2$ was slow.

2.3) Statistical Experiment

Though the use of statistics in chemical study had been well established, it was mostly confined to error analysis, iteration, et cetera. The actual use of statistics in planning a chemical experiment had not been extensively documented in the literatures. This was partly due to the fact that the early statistical theories were well suited only for discrete units and linear empirical relationships. Some experiments of this type would be, for example, the comparisons between different equipments or materials of production based on empirical variables, such as abrasive resistance, hardness, et cetera. Several designs of experiments were developed, such as the Latin Square, the Youden Square, et cetera, all of which were suited for works in the industrial engineering field, but not in a basic chemical study where continuous relationships were desired. All of these designs would develop an equation of
the form:

\[ Y = a_0 + a_1 x_1 + a_2 x_2 + \ldots \]

where \( Y \) = dependent variable (e.g., yield, tensile strength, etc.)

\( x_1 \)'s = independent variables (e.g., temperature, methods of production, reaction time, etc.).

\( a_i \)'s = constants to be determined from the experiments.

In the 1950's, Box and Wilson (35), and later Davies (36) had further developed the statistical theories and upgraded the experimental designs to the point where they could be used in a chemical study. Though these designs still involved a large number of tests for any one experiment compared to the classical approach, there was an improvement in reliability plus a reduction in the amount of work compared to the earlier designs (such as the "one variable at a time" design, or the factorial design). Basically, the new designs employed a sequential technique whereby the number of tests was not decided \textit{a priori}, but was determined from the results of an earlier work. After each group of tests, a re-assessment of the position was made before the direction of future work was decided. A special application of sequential techniques, developed by Box and Wilson, and later modified by Davies, sought to maximize or minimize some measurable quantity, such as the yield of the desired product. The starting point of this technique was a two-level factorial design in the total number of variables. The experimental variables and the measured yield could be plotted as the co-ordinates of a space. Thus, the relationship between the yield and the variables would be represented by a surface. Such a surface could be visualized as a part of a relief map, the lines of constant yield being the equiva-
The two-level factorial design represented a study of a small part of this surface, and from the results obtained, the direction in which the yield increased most rapidly was estimated (the direction of the steepest ascent). The position of new tests was determined along a line in this direction and the experiments repeated until the maximum value was passed.

In the region of the highest yield found by the steepest ascent method, a different approach had to be made. Usually, this region was "near stationary", i.e., the rate of change of the yield with any one variable was small. Thus, the new objective would be to obtain information on the shape of the surface—and in particular on its curvature—near the stationary point. To obtain this information, a 3-level composite design on each of the variables had to be used. In the neighborhood of the stationary point, the yield surface could often be approximated by a quadratic equation of the form:

\[
Y = a_0 + a_1 x_1 + a_2 x_2 + a_{11} x_1^2 + a_{22} x_2^2 + a_{12} x_1 x_2 + a_{13} x_1 x_3 + a_{23} x_2 x_3 + a_{24} x_2 x_4 + \ldots
\]

where the terms, \(x_i\)'s and \(a_i\)'s had the same meanings as those in equation (2.7).

This type of experiment allowed one to estimate the "interaction" of the variables, i.e., the \(x_i x_j\) terms. It should be pointed out here that the term "interaction", in the statistical sense, meant the effect that one variable had on the other variable at various levels.
(or values) of the former. Thus, if a two-factor interaction was present, the effect on the yield due to one variable would differ at different values of another variable. Theoretically, three-or-more-factor interactions were possible, but these were considered an exception (36).

The new designs made it possible to adapt the statistical technique to the chemical field. As was well known, a simple linear relationship rarely existed in a chemical study; and, at least a quadratic equation was needed.

Nor was the sequential technique limited only to form a quadratic equation involving but two-factor interactions. The same number of tests needed to form an equation such as (2.8) could be used to form an equation involving three-or-more-factor interactions, though in such cases, there was a decrease in efficiency and capacity of error analysis. Of course, to find a cubic or higher powered equation, a larger number of tests would be needed, and the interpretation of the results would be quite complicated. Thus, in most cases, a quadratic equation of the type (2.8) was sufficient to describe a relationship in a limited range near the stationary point (36).

Though the sequential technique was an improvement over the earlier linear models, the equation derived from it was still of an empirical nature. Along this line, Davies had pointed out that some basic mechanisms between the variables could be inferred from an empirical equation. However, unless there was a clear choice between two different basic mechanisms, only qualitative generalities could be inferred. It remained for Pinchbeck et al. (28-30) to demonstrate that the sequential technique could be used together with some prior knowledge of chemical
reactions to locate the possible mechanisms of the classical nature.

Pinchbeck used the statistical technique to develop a yield equation for phthalic anhydride from naphthalene. He then compared the empirical equation with several reaction rate equations containing the same variables. The rate equations which produced axial slopes of the yield contour differing from that of the empirical equation were then eliminated. By this method, Pinchbeck could deduce that the reaction rate of the oxidation of naphthalene was controlled by "surface kinetics" up to about 400°C. The first step of oxidation, i.e., the disappearance of naphthalene, was of fractional order, whereas all subsequent steps were of first order.

It should be pointed out that, for an inferral between the empirical equation and the basic kinetic mechanism to be meaningful, some models of the chemical reaction had to be constructed, also the rate constants for each step in the models had to be known or could be calculated. This did not mean the duplication of statistical and classical kinetic experiments, however, for in a reaction as complex as the oxidation of naphthalene or benzene, several models could be constructed and different rate constants computed. The statistical method then was used to locate the most probable model and reaction paths. What was needed from the classical experimentation was the various rate constants derived from the oxidations of the intermediate products. In this way, the empirical equation was used as an overall check for the feasibility of the different kinetic models.
CHAPTER III

STATISTICAL DESIGN

3.1) Simple linear regression equation

A complete statistical theory underlying the design of experiments will not be discussed in this study. The concepts of experimental design have been explained in detail in Reference Nos. 37-39. Likewise, the mathematical backgrounds for the Least Square method and the analysis of variance could be found in Reference No. 40. The method for determining the optimum conditions and the composite design used in this study are explained in more details in Reference Nos. 35-36. Brief resume of the analysis of variance is also given in Appendix B.

If one considers a relationship between a dependent variable, such as the yield of maleic anhydride, and the various process variables, such as temperature, initial concentration of benzene, etc.,

\[(3.1) \eta_j = f(x_1, x_2, x_3, \ldots, x_k)\]

where \(\eta\) represents the true response or value of the yield.

\(x_1\)'s represent the process variables

\(k\) represents the total number of independent variables.

The actual experimental results can then be defined by:

\[(3.2) y_j = \eta + e_j \quad (j = 1, 2, \ldots, n)\]

where \(y_j\) = observed value of the yield in the jth test (or run).

\(e_j\) = random experimental variability associated with the jth run.
This is a normal random variable with a mean "0", and an unknown variance of "$\sigma^2$". (The normal distribution, however, is not a required assumption).

Before any test could be made, a model of the relationship between $\eta$ and $x_i$'s has to be assumed. In a narrow region, a linear model could be made as follows:

(3.3) $\eta = \alpha_0 + \alpha_1 x_1 + \alpha_2 x_2 + \cdots + \alpha_k x_k$

where $\alpha_i$'s are constants (called "effects" in statistical terms).

The observed value of $\eta$ for the $j$th set of $x_i$'s will then be:

(3.4) $Y_j = \alpha_0 + \alpha_1 x_{1j} + \alpha_2 x_{2j} + \cdots + \alpha_k x_{kj} + \epsilon_j$

The minimum number of runs needed to evaluate all the constants, $\alpha_i$'s would be $n = k + 1$. By disregarding the error term for the time being, a matrix involving all the test runs could be set up as follows:

$$
\begin{align*}
Y_1 &= \alpha_0 + \alpha_1 x_{11} + \alpha_2 x_{21} + \cdots + \alpha_k x_{k1} \\
Y_2 &= \alpha_0 + \alpha_1 x_{12} + \alpha_2 x_{22} + \cdots + \alpha_k x_{k2} \\
\vdots &= \vdots \\
Y_j &= \alpha_0 + \alpha_1 x_{1j} + \alpha_2 x_{2j} + \cdots + \alpha_k x_{kj} \\
Y_n &= \alpha_0 + \alpha_1 x_{1n} + \alpha_2 x_{2n} + \cdots + \alpha_k x_{kn}
\end{align*}
$$

where the number of runs are indicated by $1, 2, \ldots, j, \ldots, n$.

From (3.5), an estimate of the true correlation equation (3.3) could be made by using the method of the Least Square (36). The result is a regression equation (3.6).

(3.6) $Y = a_0 + a_1 x_1 + a_2 x_2 + \cdots + a_k x_k$

where $Y$ is an estimate of the true response "$\eta$" $a_i$'s are estimates of the effects, $\alpha_i$'s.
3.2) Error analysis

In the case where \( n \) is equal to \( k + 1 \), the total number of constants to be estimated, the error variability could not be evaluated independently. To find the error variance, \( \sigma^2 \) or its estimate, \( s^2 \), the number of runs must be greater than \( k + 1 \). The extra number of runs beyond (\( k + 1 \)) represents the "degree of freedom" for calculation of the error variance (or any additional effects). The higher the degree of freedom, the more accurate the estimate \( s^2 \) will be.

The basic assumption for the calculation of \( s^2 \) is that the individual error, \( \sigma_j^2 \), for each run is normally distributed and independent of each other. This is not a rigorous assumption, but one that compliments the method of Least Square and requires the least effort in calculation. It is conceivable, for example, that the errors may be distributed binomially, in which case, the regression equation (3.6) will have to be determined with the principle of maximum likelihood suited for the binominal distribution (instead of the Least Square method which is based on the maximum likelihood principle for the normal distribution).

The estimate of the error variance is given in eq. 3.7.

\[
(3.7) \quad s^2 = \frac{\sum_{j=1}^{n} (y_j - \bar{y})^2}{n-k-1} \text{; degree of freedom } = n - k - 1.
\]

The square root of the error variance is called the standard deviation of error, \( s \), and is used in calculating the confidence limits of the regression equation.

The error variance could also be found by repeating a run several times (with the same set of \( x_i \)'s). This provides an independent check on the value of \( s^2 \). In the repetition method, the estimate of the
variance is given by:

\[
(3.8) \quad s^2 = \frac{1}{n-1} \sum_{j=1}^{n} (y_j - \bar{y}_j)^2
\]

where \( n \) = number of repetition (number of identical tests).

\( \bar{y}_j \) = average value of response from runs.

\( y_j \) = individual response (all from the same set of \( x_i \)'s).

\( n-1 \) = degree of freedom.

The value of "\( s^2 \)" found in this way is usually more reliable than that found in (3.7) which may contain some other process variability not accounted for in the model.

3.3) **Confidence limits**

Having found the standard deviation of error "\( s \)" one may calculate the confidence limits in which future test results (i.e., prediction) are expected to fall, given a certain assurance of probability.

This is done with the aid of a \( t \) - statistic Table (found in most statistic textbooks). For example, given a probability of 95\%, the "\( t \)" value is 1.96 (for degree of freedom equal to infinity). This means that in 95\% of the time, the future test result will fall within the range of \( Y \pm 1.96s \), when \( Y \) is the prediction calculated from eq. (3.6).

The \( t \) - statistics have been tabulated for various values of probability.

3.4) **Correlation coefficient**

The term "correlation coefficient" is used to signify the level of dependence between the dependent variable and a process variable or a set of process variables. For example, a correlation coefficient of 0.80 for the whole set of process variables would mean that 80\% of the changes or variability in \( Y \) could be accounted for from the effects of
all \( x_i \)'s. A correlation coefficient of 1.0 would mean that the regression equation fits all the data perfectly, and the set of process variables, \( x_i \)'s, together with their constants would describe the response \( Y \) completely.

The mathematical equation for the correlation coefficient, \( r \), is:

\[
(3.9) \quad r = \frac{\sum_{i=1}^{n} (x_{ij} - \bar{x}_i)(y_j - \bar{y})}{\sqrt{\left[ \sum_{i=1}^{n} (x_{ij} - \bar{x}_i)^2 \right] \left[ \sum_{j=1}^{n} (y_j - \bar{y})^2 \right]^{1/2}}}
\]

where \( \bar{x}_i = \frac{1}{n} \sum_{j=1}^{n} x_{ij} \)

\( \bar{y} = \frac{1}{n} \sum_{j=1}^{n} y_j \)

3.5) Second order regression equation

The first order regression equation (3.6) is limited to only the cases when the effects of the process variables can be assumed to be independent of each other. To give an example, such a model involving two process variables would give a series of parallel straight lines for the response contour. In the experimental region far away from the optimum (i.e., maximum or minimum) response, such a model may be adequate. However, as one moves closer to the optimum point, curvatures of the response surface have to be expected. The simplest regression model that could be used in such a case would be the second-order linear regression equation of the form:

\[
(3.10) \quad Y = a_0 + a_1 x_1 + a_2 x_2 + \ldots + a_{1k} x_1 x_k + a_{12} x_1 x_2 + a_{13} x_1 x_3 + \ldots + a_{1k} x_1 x_k + a_{23} x_2 x_3 + \ldots + a_{2k} x_2 x_k + \ldots + a_{k-1,k} x_{k-1} x_k
\]
The two-factor interaction effects (i.e., the terms $a_{ij}$'s) can now be calculated. In brief, these terms measure the changes in the first-order effect with respect to a second effect.

As could be seen, the number of constants (or effects) have increased rapidly. To calculate the constants, $a_i$'s and $a_{ij}$'s, the minimum number of runs must still be equal to the total number of constants. For example, with 4 process variables ($k = 4$), the total number of constants is 11, and the minimum number of runs needed is 12 (including an extra one for error calculation).

In spite of the seemingly complex form of eq. 3.10, the treatment for its solution is still the same as in eq. 3.5. This is possible since one could replace the $x_i x_j$'s terms with a new set of "transformed process variables." Thus, eq. 3.10 may be replaced by:

$$Y = a_0 + a_1 x_1 + a_2 x_2 + \cdots + a_k x_k + a_{12} x_{12} + a_{13} x_{13} + \cdots + a_{k-1,k} x_{k-1,k}$$

where $x_{12}$ represents $x_1 x_2$, and so on.

The solution of eq. 3.11 may be made by drawing a matrix similar to eq. 3.5 and using the method of Least Square as before. It should be remembered, however, that $k + 1$ does not now represent the total number of constants, but only the total number of actual process variables. In fact, the total number of constants is now $\frac{(k+1)k}{2}$. This new value must be used in calculating the error variance (eq. 3.7) and the correlation coefficient (eq. 3.9) accordingly.

Equation (3.10) may also be expanded to include the quadratic terms for each factor. The equation now has the form:
(3.12) \[ Y = a_0 + a_1 x_1 + a_2 x_2 + \ldots + a_k x_k \]
\[ + a_{12} x_1 x_2 + a_{13} x_1 x_3 + \ldots + a_{1k} x_1 x_k \]
\[ + a_{23} x_2 x_3 + \ldots + a_{2k} x_2 x_k \]
\[ + \ldots + a_{k-1,k} x_{k-1} x_k \]
\[ + a_{11} x_1^2 + a_{22} x_2^2 + \ldots + a_{kk} x_k^2 \]

The total number of constants in this case is \( \frac{2k + 1 + \frac{k(k+1)}{2}}{2(k-2)} \)

The method of solving this equation, however, is still the same as before.

Thus, theoretically, it is possible to expand the regression equation to cover as many terms as desired. In actual practice, however, only a second-order regression equation is considered sufficient to represent the contour found in most chemical studies (36).

In addition, the larger the number of terms, the more tests would be needed to complete even a preliminary experiment. The design and treatment of, for example, a cubic regression model are complicated and the gain in accuracy is usually small, since in most cases, the variables, \( x_i \)'s could be transformed into other mathematic functions such as log \( x_i \)'s, etc., such that its quadratic model would suffice.

3.6) The principle of Least Square

Suppose, for the generalized linear model of eq. (3.1), \( n \) observations are made, a table of the values of the independent process variables, \( x_i \)'s and the observed responses, \( y_j \)'s could then be made as follows:
Table 3.1 Matrix of independent variables

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Observed response, y</th>
<th>Independent variables</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>y_1</td>
<td>x_{11} x_{21} ... x_{i1} x_{k1}</td>
</tr>
<tr>
<td>2</td>
<td>y_2</td>
<td>x_{12} x_{22} ... x_{i2} x_{k2}</td>
</tr>
<tr>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>n</td>
<td>y_n</td>
<td>x_{1n} x_{2n} ... x_{in} x_{kn}</td>
</tr>
</tbody>
</table>

In this case, each x_i will represent one process variable, either in its direct form, or its mathematical function. For example, x_1 may represent \((t \text{C} - 390) / 10\); x_2 may represent the concentration of benzene, etc. Each x_i, of course, should be independent of each other. However, this is not a rigorous requirement. Thus, x_4 may represent x_1^2, and x_5 may represent x_1 x_2, etc.

To develop a regression equation (3.6), an assumption has to be made that the estimated constants, a_i's are linear functions of the observations, y_i's, i.e., the estimates are of the form:

\[(3.13) \quad a_i = b_{1i} y_1 + b_{12} y_2 + \ldots + b_{1n} y_n,\]

where b_{ij}'s are constants. Thus, if it is supposed that the estimates a_i's are found by some method, it is then possible by way of eq. (3.6) to calculate an estimated response, \(Y_j\), for each value of the observed response, y_j, i.e.,

\[Y_j = a_0 + a_1 x_{1j} + a_2 x_{2j} + \ldots + a_k x_{kj}\]

The method of Least Square consists of choosing the estimates such that the term \(\sum_{j=1}^{n} (y_j - Y_j)^2\) is a minimum. In order that this condition
be realized, the following set of equations (called the Normal equations) must be satisfied:

\[
\begin{align*}
 c_{00} a_0 + c_{01} a_1 + c_{02} a_2 + \ldots + c_{0k} a_k &= c_{y0} \\
 c_{10} a_0 + c_{11} a_1 + c_{12} a_2 + \ldots + c_{1k} a_k &= c_{y1} \\
 c_{k0} a_0 + c_{k1} a_1 + c_{k2} a_2 + \ldots + c_{kk} a_k &= c_{yk}
\end{align*}
\]

(3.14) 

where the coefficients \( c_{11}, c_{12}, \ldots \) are the sums of squares and products between the elements in the columns of the matrix of independent variables (Table 3.1). Thus, \( c_{11} = \sum_{i=1}^{n} x_{ij}^2 \) and \( c_{12} = \sum_{i=1}^{n} x_{ij} x_{2j} \) (and has the same value as \( c_{21} \)). The coefficients \( c_{00}, c_{01}, \ldots \) are found by assuming a new process variable \( x_0 \), where \( x_0 = 1 \) for all observations. Thus, \( c_{00} = \sum_{i=1}^{n} x_{i0} \) (or \( c_{00} = n \)), and \( c_{01} = \sum_{i=1}^{n} x_{i0} x_{ij} \) and so on. Similarly, \( c_{y0} = \sum_{j=1}^{n} y_j x_{0j} \) and \( c_{yl} = \sum_{j=1}^{n} y_j x_{lj} \).

The solution of eq. (3.14) will thus provide the values of the estimated constants, \( a_i \)'s which could then be used to form the regression equation (3.6).

\[
Y = a_0 + a_1 x_1 + \ldots + a_k x_k
\]

(3.6)

The method for solving eq. (3.14) involves a process called matrix inversion. This is covered in detail in most textbooks on matrices and determinants, and also in Ref. 36.

(3.7) Orthogonality

From eq. (3.14), it is seen that the coefficients, \( c_{01}, c_{12}, \ldots \) are functions only of the process variables, \( x_1 \)'s, and not of the observed responses, \( y_1 \)'s. Thus, selections of the values of \( x_1 \)'s could be made such that the sum of products between any two columns of \( x_1 \)'s would be zero. That is to say, \( c_{ik} = 0 \), when \( i \neq k \). In such a case, each
constant $a_1$ may then be calculated directly from the sum of squares of its corresponding $x_1$, without any entanglement from other process variables. Equation (3.14) is reduced to only:

$$c_{00} a_0 = c_{y0}$$
$$c_{11} a_1 = c_{y1} \text{ etc.}$$

Such a selection of $x_1$'s is called an orthogonal design of experiment, and represents the most efficient type of design. For a given number of tests, the error variance of the orthogonal design will be a minimum (compared to other selections of $x_1$'s). In addition, the calculations of the constants $a_1$'s are greatly simplified. In an orthogonal design, the constant $a_1$ is found by:

$$(3.15) \quad a_1 = \mathop{\sum}
_{j=1}^{n} (x_1^2)_{j} = \mathop{\sum}
_{j=1}^{n} (y_j x_1 j)$$

The mathematical definition of orthogonality is:

$$(3.16) \quad \mathop{\sum}
_{j=1}^{n} (x_1 x_k)_{j} = 0$$

where $x_1$, $x_k$ represent any pair of process variables, and $j$ represents the numbering of the tests.

3.8) **Factorial design**

One of the designs (i.e., the selection of the values of $x_1$'s for Table 3.1) that would yield orthogonality is the "factorial design." In this design, the values or levels of each variable $x_1$ are spaced equally, and all the combinations of the levels for all $x_1$'s are tested. Thus, for example, if there are three process variables, $x_1$, $x_2$, $x_3$, each of which are represented by four values or levels, the total number of observations will be $4^3 = 64$, corresponding to the number of combinations possible. This number is found by considering that,
for the variable $x_1$ being set at the level "1", there are 4 possible values of $x_2$ and 4 possible values of $x_3$, or 16 possible combinations of $x_2$ and $x_3$. Thus, for 4 levels of $x_1$, the total number of combinations will then be 64. In general, the number of observations will be the products of the number of levels in each variable.

The number of observations needed to complete a factorial design is usually much larger than the minimum needed to estimate all the constants. For this reason, the factorial design is usually employed only with 2 levels for each variable. This will give sufficient data for calculating a linear regression equation including equations involving interactions. However, for quadratic terms, the 2-level factorial design must be supplemented with more observations forming a "composite design." This will be taken up later.

3.9) Preliminary Experiments

Before any test can be made, some decisions have to be made regarding the relationship between the dependent variable and the process variables. This includes choice of dependent variable to be studied, what process variables and how many are needed (or could be properly handled), and the approximate ranges of each variable, etc. The relationship between the dependent variable and the process variables is usually assumed to be a quadratic regression equation involving only two-factor interactions. This is considered sufficient in most instances (Ref. 36), and, in addition, the resulting regression equation could be changed into other and more meaningful forms, or plotted to show contours (if the number of process variables is less than three).
The preliminary experiment is usually started in an area away from the expected maximum value of the response. In this area, it could be expected that the higher-order differentials of $Y$ (with respect to $x_i$’s) will have small values compared to the first-order ones. This is to say the response contour is relatively flat with response surfaces (for different values of $Y$) being parallel to each other. Hence, in this region, the model may be reduced to the simple linear regression of equation (3.6), i.e.,

$$ (3.6) \quad Y = a_0 + a_1 x_1 + a_2 x_2 + \ldots + a_k x_k. $$

The design needed in this area will be the 2-level factorial design. Either a complete factorial or a fractional factorial design may be used. However, the complete factorial design probably will give more information on error analysis which may become useful later on. Table 3.2 shows one form of the complete 2-level factorial design in four variables.

### Table 3.2 Complete Factorial Design for 4 Variables at 2 Levels

<table>
<thead>
<tr>
<th>Trial No.</th>
<th>Values of independent variables</th>
<th>Observed response</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$x_1$</td>
<td>$x_2$</td>
</tr>
<tr>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>3</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>7</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>8</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>9</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>10</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>11</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>12</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>13</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>14</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>15</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>16</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>
As explained earlier (Sect. 3.6), \( x_1 \) may represent a process variable in the direct form, or as its mathematical function. In Table 3.2, each \( x_1 \) represents a function, \( f(U_1) \), where \( U_1 \) is the true value of the process variable. Thus, it is possible to set the values of \( x_1 \) to be either +1 or -1. For example, if \( U_1 \) represents the temperature variable, \( x_1 \) may be a function \( f(U_1) \) such that:

\[
f(U_1) = \frac{U_1 - 390^\circ}{10} = x_1
\]

When the temperature is 380°C, \( x_1 \), of course, has the value of -1, and when the temperature is 400°C, \( x_1 \) will be +1. Similar transformations are made for the other \( x_1 \)'s.

The advantage of such transformations is that the variables are now orthogonal to each other. Thus, for any two columns of \( x_1 \)'s, the following orthogonal condition is true:

\[
\sum_{j=1}^{16} (x_{1i} \cdot x_{1k})_j = 0, \text{ when } i \neq k.
\]

The orthogonality also extends to the dummy variable, \( x_0 \), needed to calculate the constant \( a_0 \) (eq. 3.14). \( x_0 \) is, of course, set equal to +1 for all runs. The constants, \( a_i \)'s, may then be calculated using eq. (3.15) as follows:

\[
a_i \cdot \sum_{j=1}^{16} (x_{1i}^2)_j = \sum_{j=1}^{16} y_j x_{1i}, \quad i = 0, 1, \ldots, 14.
\]

The term \( \sum_{j=1}^{16} (x_{1i}^2)_j \) has a value of 16 for all \( x_1 \)'s. Thus, the constant, \( a_1 \) for example, may be found by summing up all 16 observed responses according to the signs of \( x_1 \), then dividing by 16. The other \( a_i \)'s including \( a_0 \) are found in the same manner.

It should be mentioned here that the design in Table 3.2 is also capable of locating all interaction effects (i.e., the terms \( a_{12}, a_{13}, \ldots \)).
a_{123}, etc.). These constants are found by summing up the observed responses, \( Y_j \)'s, according to the signs of the products of the corresponding \( x_i \)'s terms, and dividing by 16. For example, \( a_{123} = \frac{1}{16} \sum_{j=1}^{16} (x_1 x_2 x_3 x_4 - y_j) \). These terms are needed in case the design of Table 3.2 is used to fully define the response contour as a final model, but are not needed in a preliminary investigation.

3.10) **Path of steepest ascent**

After the preliminary set of runs is made, and the constants, \( a_0, \ldots, a_4 \) estimated, the directions of future experiments may then be found (41). The new values of \( x_i \)'s are estimated in incremental steps along a line that will insure the largest increase in the response.

Thus, if it is considered that in the preliminary region, the 4-variable response contour is represented by:

\[
(3.17) \quad \hat{Y} = \hat{a}_0 + \hat{a}_1 \hat{x}_1 + \hat{a}_2 \hat{x}_2 + \hat{a}_3 \hat{x}_3 + \hat{a}_4 \hat{x}_4,
\]

in a new adjacent region, the new estimate to the response may be given in a form of Taylor equation as:

\[
(3.18) \quad \tilde{Y} = \tilde{a}_0 + \frac{\partial Y}{\partial x_1} \bigg|_{x_1=\hat{x}_1} (\hat{x}_1 - \tilde{x}_1) + \frac{\delta Y}{\delta x_1} \bigg|_{x_1=\hat{x}_1} (\hat{x}_1 - \tilde{x}_1)^2
\]

where \( \frac{\delta Y}{\delta x_1} \bigg|_{x_1=\hat{x}_1} \) are the first-order differentials of \( Y \) with respect to \( x_1 \)'s at the points, \( \hat{x}_1 \)'s. In fact, these differentials are the estimated constants, \( \hat{a}_1 \)'s of the first region. It could be shown (41) that for a maximum increase in response, i.e., for maximum value of \( \tilde{Y} - \hat{Y} \), the following condition must be satisfied:

\[
(3.19) \quad \frac{(\hat{x}_1 - \hat{x}_1)}{(\delta Y / \delta x_1)/x_1} = \frac{(\hat{x}_2 - \hat{x}_2)}{(\delta Y / \delta x_2)/x_2} = \frac{(\hat{x}_n - \hat{x}_n)}{(\delta Y / \delta x_n)/x_n} = \hat{x}_n
\]
By using eq. 3.19 as a guideline, a new set of $x_i$'s may be found at which a test run is made. The process is repeated until no gain in the observed response could be made, indicating that a region where the response is near-stationary has been reached.

3.11) Experiments near The Optimum Point

As one approaches the optimum point (which presumably lies somewhere in the near-stationary region), the method of steepest ascent will be less effective. The gain in the observed response will become smaller with each successive step. It could also be assumed that, in this region, the first-order effects will be small. Thus, at this stage, a more comprehensive design is needed to obtain more accuracy, and to account for the quadratic effects. The basic assumption is that the contour is curved, giving rise to an optimum point, or an optimum ridge which may be defined by a second-order regression equation.

There is, at present, no systematic method to cover the case where there are two or more optima in the contour. One possible way in such a case would be to make some exploratory test runs in areas away from the optimum region. However, a more reliable method is perhaps to consider only a small experimental region with the aid of some theoretical backgrounds as to the possible nature of the contour.

For an experiment with 2 or 3 process variables, a factorial design of 3 levels may be used to define the contour in the optimum region. However, with 4 or more variables, such a design will mean an unnecessarily large number of runs. For example, for 4 variables, the number of runs needed is $3^4 = 81$, whereas the number of the first
and second order constants to be determined is only 15.

One suitable type of design is called the "composite design." This is basically a 2-level factorial design with extra runs added. The number of extra runs needed is \((2k + 1)\), where \(k\) is the number of process variables. For an experiment with 4 variables, the procedure is, first, to complete a 2-level factorial design (Table 3.2), then, add on 9 more runs to finish the composite design. The settings of the extra runs are given in Table 3.3.

Table 3.3

<table>
<thead>
<tr>
<th>Trial No.</th>
<th>Values of independent variables</th>
<th>Observed response</th>
</tr>
</thead>
<tbody>
<tr>
<td>17</td>
<td>0 0 0 0</td>
<td>(Y_{17})</td>
</tr>
<tr>
<td>18</td>
<td>+2 0 0 0</td>
<td>(Y_{18})</td>
</tr>
<tr>
<td>19</td>
<td>-2 0 0 0</td>
<td>(Y_{19})</td>
</tr>
<tr>
<td>20</td>
<td>0 +2 0 0</td>
<td>(Y_{20})</td>
</tr>
<tr>
<td>21</td>
<td>0 -2 0 0</td>
<td>(Y_{21})</td>
</tr>
<tr>
<td>22</td>
<td>0 0 +2 0</td>
<td>(Y_{22})</td>
</tr>
<tr>
<td>23</td>
<td>0 0 -2 0</td>
<td>(Y_{23})</td>
</tr>
<tr>
<td>24</td>
<td>0 0 0 +2</td>
<td>(Y_{24})</td>
</tr>
<tr>
<td>25</td>
<td>0 0 0 -2</td>
<td>(Y_{25})</td>
</tr>
</tbody>
</table>

As in Table 3.2, \(x_1\)'s represent functions of the actual process variables. For example, \(x_1\) may represent a function of temperature such that \(x_1 = \frac{t^\circ C - 450}{5}\). Thus, for \(x_1 = 0\), the temperature of the test will be 450 \(\circ C\); for \(x_1 = 2\), the temperature of the test will be 460 \(\circ C\), and so on.
There is no special preference for the values of +2 or -2 in the design of Table 3.3. To preserve orthogonality in the total design (i.e., both Tables 3.2 and 3.3), the non-zero values of Table 3.3 should be equal to ±√2 (Ref. 36). However, this may not be desirable since the levels may become too close together, and the determination of the quadratic effects is less accurate. If other values are chosen, the design will not be orthogonal among the quadratic effects, but the accuracy is better. Another method (39) is to choose the value to be \( \left( \frac{n_c}{2} \right)^{3/4} \) where \( n_c \) = number of runs in the 2-level factorial design. This allows the calculation of the constants to be proceeded in steps, depending on the parts of the design completed. At any rate, the loss of orthogonality is not serious since calculations of the results can be computerized in a standard manner (42).

After the additional tests (Table 3.3) are completed, the regression equation is calculated based on the least-square method as before (Sect. 3.6). The final equation (for 4 variables) which defines the contour space near the optimum region will be of the form:

\[
Y = a_0 + a_1 x_1 + a_2 x_2 + a_3 x_3 + a_4 x_4 \\
+ a_{12} x_1 x_2 + a_{13} x_1 x_3 + a_{14} x_1 x_4 + a_{23} x_2 x_3 + a_{24} x_2 x_4 \\
+ a_{34} x_3 x_4 \\
+ a_{11} x_1^2 + a_{22} x_2^2 + a_{33} x_3^2 + a_{44} x_4^2.
\]

No contour mapping is possible with four variables. In such a case, contour mapping is possible only when one variable is set at a fixed value, and equation (3.20) reduced to a 3-variable form.
CHAPTER IV

KINETIC CONSIDERATIONS

From the available literatures, a brief summary of the catalytic action of the $V_2O_5$ catalyst on aromatic substances may be made (43). This is shown in Section 4-1. However, with regard to the specific reaction paths that benzene undergoes in forming maleic anhydride, the situation is not entirely clear (44). Different reaction paths could be deduced from the works of different authors. The same situation occurs with regard to the rate-controlling step. The most reliable method seems to be to assume a pseudo-first order rate on a very simplified model. Even in this case, correlations between the rate constants, the mass flow rate, and the catalyst/feed rate ratio are poor. This may be due in part to the differences in the catalysts used by various authors. It is conceivable that catalysts of different compositions may promote one reaction rate over another, thus resulting in different rate-controlling step. The oxidation of benzene per se will be discussed in Section 4.2.

4.1) Reactions of $V_2O_5$ catalysts

Vanadium oxides are regarded as belonging to the n-type semiconductor catalyst. This is typified by a stoichiometric excess of metal compared to oxygen. Mobile quasi-free electrons in the lattice occur due to lattice oxygen defects. Thus, oxygen gas may be converted to $O^-$ or $O^{2-}$ ions at the surface, and diffused into the lattice itself.
In the case of vanadium oxides, the metal excess occurs due to the presence of $V_{2O_4}$ which acts as an impurity in the $V_{2O_5}$ lattice. The mobility of electrons increases sharply and occurs through out the bulk of catalyst at around 350°C. Below this temperature, the mobility occurs only along the surface (26). Various controlling mechanisms have been proposed for the adsorption of oxygen in the absence of aromatic gases. The situation differs, however, when an aromatic gas is present. The adsorption of oxygen depends not only on the presence of aromatics, but also on the type of the aromatic gas.

With regard to the adsorption of aromatic gases on the catalyst surface, no theory has been proposed. An aromatic molecule such as benzene is rich in electrons and would tend to be a donor of electrons to the catalyst surface rather than an acceptor (such as oxygen). Such a molecule could also be adsorbed since at high temperatures, the mobility of the metal protons is also great.

The simplified oxidation reactions between aromatics and $V_{2O_5}$ catalysts are:

1. Aromatics + oxidized catalyst

\[ \text{oxidation products + reduced catalyst} \]

\[ \text{(4.1)} \]

2. reduced catalyst + oxygen $\rightarrow$ oxidized catalyst.

The first part of eq. (4.1) may be represented by:

\[ r_B = k_1 P_B^m \beta^n \]

\[ \text{(4.2)} \]

where $r_B$ = rate of oxidation of benzene

$k_1$ = reaction rate constant

$P_B$ = partial pressure of benzene in the system

$\beta$ = degree of occupation of oxygen on the catalyst surface.

$m, n$ = constants.
Similarly, the second part of (4.1) may be represented by:

\[(4.3) \quad r_{O_2} = k_2 P_{O_2}^p (1 - \beta)^q \]

where \( r_{O_2} \) = rate of re-oxidation of the catalyst  
\( k_2 \) = reaction rate constant  
\( P_{O_2} \) = partial pressure of oxygen in the system  
\( p, q \) = constants.

If, for the oxidation of one benzene molecule, \( \alpha \) molecules of oxygen are required, it follows that:

\[(4.4) \quad r_B = \frac{\alpha}{\alpha} r_{O_2} \]

At steady state, equations (4.2) and (4.3) must be equal. Thus,

\[(4.5) \quad \alpha k_1 P_B^m \beta^n = k_2 P_{O_2}^p (1 - \beta)^q \]

The solutions of the rate equations could not be made except in the more simplified cases. Thus, in the case where benzene is not adsorbed on the catalysts, (i.e., \( q = 0 \)), the resulting rate equation for benzene disappearance is:

\[(4.6) \quad r_B = \frac{1}{\alpha} k_2 P_{O_2}^p - - - (q = 0) \]

When benzene is assumed to be adsorbed on the catalysts' surface (i.e., when \( q > 0 \)), the most simplified case is when both \( q \) and \( n \) are equal to 1. In this case, the result is:

\[(4.7) \quad r_B = \frac{1}{\alpha k_2 P_{O_2}^p} + \frac{1}{k_1 P_B^m} \]

For use in a steady-state catalytic process, the rate equations (4.6) and (4.7) have to be integrated with respect to the catalyst weight and the percent conversion. Following the method used by Hougen and Watson (27), and assuming that the change in the total number of molecules during the reaction is negligible, equation (4.6) is changed...
to:

\[
\frac{W}{F} = -\frac{1}{k_2 \Pi^P} \int \frac{d \frac{C_{O_2}}{C_{O_2}^p}}{C_{O_2}^p}
\]

where, \( W \) = weight of catalyst, g.

\( F \) = mol. flow rate of total input, mol./hr.

\( \Pi \) = total pressure of the system, atm.

\( C_{O_2} \) = mol fraction of oxygen

\( k_2 \) = rate constant for the disappearance of oxygen.

In the special case where \( p = 1 \), equation (4.8) is changed to:

\[
\frac{W}{F} = \frac{1}{k_2 \Pi} \ln \left( \frac{C_{O_2}^i}{C_{O_2}^o} \right)
\]

where, \( (C_{O_2}^i) \) = mol fraction of oxygen at the inlet

\( (C_{O_2}^o) \) = mol fraction of oxygen at the outlet.

For \( p > 1 \), equation (4.8) is integrated to:

\[
\frac{W}{F} = \frac{1}{k_2 (p-1) \Pi^P} \left[ \frac{1}{(C_{O_2})_o^p} - \frac{1}{(C_{O_2})_i^p} \right]
\]

Similarly, when benzene is assumed to be adsorbed on the catalysts' surface, and all reactions are supposed to be first-order (i.e., \( p = q = m = n = 1 \)), equation (4.7) is changed to:

\[
\frac{W}{F} = \frac{1}{\Pi} \left[ \frac{1}{k_1} \ln \left( \frac{C_B}{(C_B)_o} \right) + \frac{1}{k_2} \ln \left( \frac{C_{O_2}^i}{(C_{O_2})_o} \right) \right]
\]

where \( C_B \) = mol fraction of benzene.

It should be pointed out that the series of equations (4.6) - (4.11), though mathematically precise, are not exact in the actual situation. This is because the intermediate products of the reaction also undergo further oxidation, resulting in a smaller value for the mol fraction of oxygen in the outlet.
4.2) Oxidation of benzene

Due to the complexity of the various intermediate reactions in the oxidation process of benzene, no exact model for the oxidation of benzene could be constructed. At best, only a simplified model could be assumed. This is:

\[ K_1 \quad M \quad B = \text{benzene} \]
\[ K_2 \quad D \quad M = \text{maleic anhydride} \]
\[ D = \text{CO} + \text{CO}_2 \]

The symbols, \( K_1, K_2, K_3 \), are reaction rate constants which are different than those discussed in Section 4.1.

By assuming that the rate of disappearance of benzene is irreversible and first order with regard to oxygen and benzene, the following equation can be set up:

\[ r_B = K_0 p_{O_2} p_B \]

where \( r_B \) = rate of disappearance of benzene,

and, \( K_0 = K_1 + K_2 \).

In most cases, the partial pressure of oxygen, \( p_{O_2} \), is quite large compared to \( p_B \) and thus, could be assumed to be constant. By using the method of Hougen and Watson (27), and assuming that the change in the total number of molecules during the reaction is negligible, the following integrated equation is found:

\[ (Y_B/100) = 1 - \frac{-K_0 T^2 (C_{O_2})_{ave} (W/F)}{\rho} \]

where \( (Y_B/100) \) = (mol. of benzene reacted) / (mol. of benzene input).

Similarly, for the formation of maleic anhydride, by using similar assumptions as to the orders of the reactions, the following equation
may be found:

\[
\frac{Y_M}{100} = \frac{K_1}{K_3 - (K_1 + K_2)} \left[ 1 - \frac{Y_B}{100} - \frac{K_3 Y^2}{(C_{O_2})_{ave}} \left( \frac{h}{F} \right) \right]
\]

where \( Y_M \) = percent yield of maleic anhydride, i.e.,

\[
(Y_M/100) = \frac{\text{mol. of maleic anhydride formed}}{\text{mol. of benzene input}}.
\]

The derivation of equations (4.13) and (4.14) are shown in Appendix E.

Before equation (4.14) could be solved, the value of \( K_3 \) must be known independently. This is because the third equation available from the model (i.e., equation for the yield of \( CO \) and \( CO_2 \)) is simply a stoichiometric combination of the first two, i.e.,

\[
Y_D = 6Y_B - 4Y_M
\]

where \( Y_D \) = yield of \( CO + CO_2 \) (in percent)

\[
= 100 \left( \frac{\text{mol. of } CO + CO_2}{\text{mol. of benzene input}} \right).
\]
CHAPTER V

EXPERIMENTAL

5.1) Equipment and Materials

Figure 5.1 shows the photograph of the equipment set-up. The flow diagram is represented in Figure 5.2, and a detailed sketch of the reactor itself is shown in Figure 5.3. The 2" diameter reactor (approx. 5 cm.) and all connecting lines were made of pyrex.

Benzene (reagent grade) was pumped into the pre-heater I by a positive-displacement Milton-Roy pump whose capacity was from 0.05-130 ml/min. under pressure. The flow of benzene could be assumed to be continuous since the pump operated at 96 strokes / minute. However, precaution had to be made to insure stability of flow. This was done as shown in Figure 5.4. The pump had to be operated with an outlet head higher than that of the inlet. However, it was found that the flow would be stable only if both the inlet and outlet of the pump were under constant pressures. For this purpose, the pressure at the outlet section of the reactor was applied to the pump inlet, and the pump outlet, of course, was connected to the pre-heater section before the reactor. Thus, the pressure differential between the outlet and the inlet of the pump was essentially the pressure differential of the bed itself. For a given flow rate, this differential would be constant during each run.

The rate of flow of benzene was measured by checking the levels
FIGURE 5.1 --- Equipment Setup
of benzene in the calibrated pipette and timing them with a stopwatch. Attempts to calibrate the pump were not successful, since the pump delivery rate depended on both differential pressure and the piston setting. Thus, the piston had to be reset and the flow rate checked for each run. By periodic checking and re-setting, the flow rate could be maintained to within ± 5% of the desired value during any run. Usually, the flow rate was around 1 ml./min.

Ordinary laboratory air was filtered and measured with an orifice meter before being mixed with benzene in the pre-heater I. The rate of air was from 5-6 l./min. Control of air flow was readily made with a fine-control valve. The calibration of the orifice meter was shown in Appendix A.

After mixing, the reactant mixture was pre-heated in the pre-heater II to about 350°C before reaching the reactor chamber. Separate powerstats were used to control the temperatures in each section and also in the reactor itself. The entering mixture had to be at the temperature lower than that of the reactor because of the large heat of reaction liberated. However, an additional amount of heat still had to be supplied by a powerstat connected to the reactor section. This was used to control the reactor temperature. Figure 5-5 shows the heat-control sections and locations of the thermocouples (Chromel-Alumel) in the system. Temperature recordings were made with a single-pen G.E. recorder (oscillographic type). A control switch was used so that all eight thermocouples could be recorded. Temperatures could be controlled to within ±5°C.
FIGURE 5.2 --- Flow diagram.
CONNECTIONS: Ball and socket

MATERIAL: Pyrex

FIGURE 5.3 --- Reactor.
Pressure from outlet section of reactor

Calibrated burette 50 ml.

Benzene reservoir, 250 ml.

Air

Jet, 1mm. diam.

Pre-heater I

Milton Roy pump

FIGURE 5.4 --- Benzene Injection System.
FIGURE 5.5 --- Heat Control Diagram.
Keys to FIGURE 5.5

Positions of thermocouples in the reactor

<table>
<thead>
<tr>
<th>Thermocouple No.</th>
<th>Height from the bottom fritted disk, cm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>T2</td>
<td>-2.5</td>
</tr>
<tr>
<td>T3</td>
<td>2.5</td>
</tr>
<tr>
<td>T4</td>
<td>32.5</td>
</tr>
<tr>
<td>T5</td>
<td>60.0</td>
</tr>
<tr>
<td>T6</td>
<td>87.5</td>
</tr>
</tbody>
</table>
From reactor ——> To main vent

Sampling line

Three ice traps in series, 0°C.

Ground glass joints

To vent

Wet-test gas meter

Four gas sample collectors (300 ml. each).

Mercury

FIGURE 5.6 --- Sampling System
After the reactor, the gaseous products went through a fritted-glass finger which filtered out the catalyst powder. The products were kept at 250 - 200°C to prevent any condensation of maleic anhydride before they reached the sampling line.

About one-third of the gaseous products was shunted into the sampling line. The sampling rate was about 100 - 120 l./hr. The rest of the products was sent out the vent in the hood. On the main vent line, just after the sampling leg, was located the pressure-control valve which was used to maintain constant pressure in the system. The pressure was maintained so that the average density of the reacting mixture was about 0.575 g. / l. (about 0.036 lb./cu. ft.) for all runs. The reason for this will be shown in Section 5.3.

Figure 5.6 shows the diagram of the sampling system. The gaseous sample passed through three traps in series, wherein maleic anhydride was condensed out. Afterwards, the gas flowed through the gas sample collector, then through a wet-test meter and was vented to the hood.

The catalyst was added to the reactor either through the side arm or by opening the ball and socket joint at the reactor section. The catalyst, designated type V-X-L 2103 - 11P, was obtained from the Harshaw Chemical Company, Cleveland, Ohio. It contained a total of 10% metal oxides on an inert alumina support. The composition of metal oxides was 2 parts V₂O₅ to 1 part MoO₃. This was the same type of catalyst (except for the size distribution) that Yao used in his work (14). The various physical properties of this catalyst were as followed:
a) Size distribution:

- 0 - 10 microns ----- 0.2%
- 10 - 20 " ----- 6.2%
- 20 - 40 " ----- 28.6%
- 40 - 80 " ----- 41.0%
- larger than 80 " ----- 24.0%

By plotting the "cumulative weight percent under" vs. particle diameter on a log probability coordinate, as suggested by Zenz (13), the mean particle diameter, \( D_p \), was found to be 50 microns (0.002 in.).

b) Densities:

1. Bulk density, \( \rho_b \) = 1.144 g/ml.
2. Absolute density, \( \rho_a \) = 3.79 g/ml.
3. Apparent density, \( \rho_p \) = 1.98 g/ml.

c) Fluidizing properties:

1. Loose-bed density, \( \rho_{mf} \) = 0.809 g/ml.

This was the density of the reactor bed just before the onset of fluidization. In other words, it was the bed density at the loosest packing state, when the catalyst particles just barely touched each other.

2. Minimum fluidization void fraction, \( \epsilon = 0.592 \). This was the void fraction corresponding to the loose-bed density above.

5.2) Analytical method

1) Gas sample - About 300 ml. of the gas which passed through the condensers was kept in a mercury sample collector. This gas was analyzed for percents of nitrogen, oxygen, CO and CO\(_2\) in a Beckman "GC-2" gas chromatograph equipped with dual columns. A molecular sieve
column was used to separate $O_2$, $N_2$ and $CO$. The column was 6 mm. O.D. by 1.5 m. long, and packed with 1.2 m. of 40-60 mesh molecular sieve 5A (Linde Products) plus 15 cm. of 50-50 mesh silica gel (Davidson Catalyst Dept., W. R. Grace and Co.) on each end for absorption of water vapor. The other column, 6 mm. O.D. by 45 cm. long, was packed with silica gel (same as above) for $CO_2$ determination. Both columns were operated at 40°C. Calibrations for the gas chromatograph were shown in Appendix A. The analytical results were based on at least two analyses using air as a standard. The accuracy of these analyses was about ±1% for $O_2$ and $N_2$ and about ±3% for $CO$ and $CO_2$. This method of analysis was used in all runs. Summary Tables for the data of all runs are shown in Appendix D.

2) Liquid sample - The condensates in the three traps were rinsed out with acetone and combined. Two procedures were used in analyzing the condensate, depending on the temperature of the traps.

a) Dry ice-acetone traps: - Earlier in the experimental program (Runs Nos. 2 and 3), dry ice-acetone traps (-50°C) were used. Here, the condensate included both benzene and maleic anhydride. The amount of each component was found by analyzing in a Hy-Fi hydrogen-flame gas chromatograph. However, it was found that benzene loss in the traps and in subsequent handling was high (30-50%). Hence, this method was abandoned.

b) Ice traps: - Here, the condensate was composed of only maleic anhydride (and water). After rinsing with acetone, the condensate was analyzed for maleic anhydride in the Hy-Fi gas chromatograph as before. The ice traps were used in all runs except Nos. 2 and 3.
The column used was 3 mm. O.D. by 2.4 m. long, packed with 30% silicone grease and Apiezon L on Chromosorb W solid support. The calibration curve for maleic anhydride solution in acetone is shown in Appendix A.

The accuracy of the Hy-Fi unit was about ±8%. However, it was difficult to maintain the unit in top condition at all times. Hence, this method of analysis was used only in Runs Nos. 1A, and 4-16.

From Runs No. 17 on, the liquid condensate was analyzed for maleic anhydride by titrating the condensate-acetone solution with a standard NaOH solution (0.25N), using a Fisher electrolytic titrimeter. The accuracy was about ±1% provided that the titration was made within 24 hours. A sample of the titration curve is shown in Appendix A.

3) Benzene analysis:— In Runs Nos. 2 and 3 when dry ice-acetone traps were used, benzene was analyzed in the liquid form by injecting 1 ul of the condensate-acetone solution into the Hy-Fi unit. However, this method was not very successful and was abandoned, the reasons being the extremely small sample size required, and the interference from acetone.

In Runs Nos. 1A and 4-16, benzene was analyzed from gas samples at the main vent (this portion of the gas did not pass through the traps). At least 10 gaseous samples of 50 ul. each were taken and analyzed in the Hy-Fi unit. The accuracy of these analyses was about ±8%. Larger samples could not be used since column flooding occurred. The calibration curve for the analysis of benzene in air mixture was given in Appendix A.

From Run No. 17 on, the amount of benzene input was low, and the
amount of unreacted benzene in the exit gas stream was too small (around 0.1% or less) to be analyzed effectively with the Hy-Fi unit. Hence, this method was dropped. It was also found that the percentage of benzene in the off-gas had no effect on the material balance, being so small as to be negligible. Thus, in Runs Nos. 17-45, no benzene analysis was made. The amount of unreacted benzene was found from the difference between the benzene input and the amounts of products formed. Only the material balance on oxygen was made.

To check whether the material balance on oxygen alone could indicate the degree of accuracy of the results, benzene analysis was again made in Runs Nos. 46-53. This time, the off-gas samples containing benzene were analyzed in the Beckman GC-2 gas chromatograph at 80°C. The column used was 6 mm. O.D. by 1.5 m. packed with 5% carbowax and stearic acid on Anachrome ABS. The amount of gas samples injected was 1.0 ml. each, and so, the accuracy of the analysis was much better than in the Hy-Fi unit where the samples had to be smaller (50 ul). The new Anachrome ABS column allowed benzene analyses to be made in the GC-2 unit (which was of thermal conductivity type) without interference from water vapor. With this type of packing, water was eluted from the column at a much slower rate than benzene. The procedure was to inject three gas samples into the unit at a 7 minute interval, then to wait about 35 - 40 minutes before all the water was eluted out. Benzene had an elution time of 4-6 minutes, whereas water had an elution time of 25-35 minutes. One inherent advantage of the GC-2 unit over the Hy-Fi was that the GC-2 was equipped with a pre-calibrated injection valve whereas injections into the Hy-Fi had to be made with a hand-held syringe. The accuracy obtained with the Anachrome column
in the GC-2 was ±3% based on two analyses for each sample. The calibration equation for this method of analysis is given in Appendix A.

The results of Runs Nos. 46-53 showed that the material balance on oxygen could be used to indicate the degree of accuracy of the results. In all cases, the material balance on benzene followed that of oxygen closely. A sample of the material balance calculation is given in Appendix D.

In no runs were naphthoquinone and phenol detected. From the analytical procedure, it could be concluded that both naphthoquinone and phenol, if present, were less than 0.1% of the amount of maleic anhydride in a sample.

5.3) Fluidization Study

Since no visual observation could be made of the inside of the reactor during the operation, informations concerning bed heights and degrees of fluidization had to be found from other sources.

A mock fluid-bed reactor of acrylic tubing was built, having the same dimensions as the actual reactor. The catalyst was fluidized in this reactor at various flow rates, using air and helium at room temperature. The data from the mock reactor were then correlated using both Leva's and Zenz's methods (45, 13). These correlations were based essentially on the densities and viscosities of the fluidizing gases. The fluidization data are shown in Appendix C.

Leva correlated the term "bed height ratio", \( R_b \), vs. the reduced mass rate, \( \dot{W}_f/\dot{W}_{mf} \), using the ratio \( (\rho/\mu)^{0.91} \) as a parameter. The various terms were defined as followed:

\[
R_b = \text{bed height ratio} = \frac{L_f}{L_{mf}}
\]
L_f = Bed height during fluidization

L_{mf} = Bed height at the minimum fluidization (i.e., at loose-bed density).

W_f = Mass flow rate of the fluidizing gas

W_{mf} = Mass flow rate at minimum fluidization

(\phi/u)_f = Ration of density vs. viscosity of the gas.

The mass flow rate at minimum fluidization could be calculated from an empirical equation (given in Ref. 45). However, this method did not produce a suitable correlation of the experimental data for air, helium and reactor gas. This might be due to the fact that the range of fluidization undertaken in this study was beyond that at which Leva had correlated.

Zenz's method (13) offered a different approach to the problem. Instead of basing one's correlation on the fluidizing properties at minimum fluidization, one calculated first the free-fall velocity of a single particle (i.e., the gas velocity at which a single particle would be blown out of the reactor). This was the point where \( \varepsilon \), the void fraction, = 1, and represented the upper limit of fluidization. The actual fluidization rate was found from Zenz's graph of \((R_0/C_d)^{1/3}\) and \((C_dR_0^2)^{1/3}\) with \( \varepsilon \) and \( R_0 \) as parameters, whereby:

\[
(5.1) \quad (R_0/C_d)^{1/3} = \left[ \frac{4}{3} \frac{\mu \left( \phi_p - \phi_f \right) D_p}{\phi_f^2} \right]^{1/3}
\]

and,

\[
(5.2) \quad (C_dR_0^2)^{1/3} = \frac{\varepsilon + \zeta}{D_p} \left[ \frac{3 \mu^2}{4 g (\phi_p - \phi_f) (\phi_f^2)} \right]^{1/3}
\]

where,

\( R_0 = \) Reynolds number, \( (D_p \varepsilon C_f) / u \)

\( C_d = \) Drag coefficient, \( 4gD_p (\phi_p - \phi_f) / (3 \phi_f^2 v^2) \)
For the given catalyst and any superficial velocity, the values of $(R_0 / C_d)^{1/3}$ and $(C_d R_0^2)^{1/3}$ could be calculated for both air and helium, and the corresponding values of $\varepsilon$, the fluid voidage, could be read off Zenz's chart. A plot of $\varepsilon$ vs. $V$ could then be made and compared with the actual plot of $\varepsilon$ vs. $V$ as directly observed from the experiment with the mock reactor. As could be seen in Figures 5.7 and 5.8, the actual data did not agree with Zenz's correlation. However, by using the shape factor, $J$, as a correction term, a definite trend could be found. The shape factor, $J$, was then used to correct Zenz's correlation in the case of the reactor gas. This was shown in Figure 5.9 which was used to give approximate values of the fluid voidages in the actual fluidized bed. Detailed calculations for Figures 5.7, 5.8 and 5.9 were shown in Appendix C. These were made in the F.P.S. system to be consistent with Zenz's method (13).

The correlation of Figure 5.9 was based on an estimated gas density of 0.036 lb./cu. ft. (0.575 g/l.). This number was arrived at from the average conditions of temperature and pressure existing in the actual reactor. In order that the correlation of Figure 5.9 would hold true, all runs in the actual reactor were then made at such
Void Fraction

1.0
0.9
0.8
0.7
0.6

Superficial Velocity, ft./sec.

Note: To convert ft./sec. to cm./sec., multiply by 30.5.

FIGURE 5.7 — Fluidization with Air, Zenz's Method (13).
Superficial Velocity, ft./sec.*

*Note: To convert ft./sec. to cm./sec., multiply by 30.5

FIGURE 5.8 --- Fluidization with Helium, Zenz's Method (13).
FIGURE 5.9 --- Fluid Voidage Vs. Superficial Velocity for Reactor Gas.

Superficial Velocity, ft./sec.*

* Note: To convert ft./sec. to cm./sec., multiply by 30.5.
a pressure that the reaction gas mixture would always have a density of about 0.036 lb./cu. ft. The average reactor pressure was varied from 870-930 mm. from run to run depending on the temperature desired, and the composition of the inlet gas. The variation in pressure could be justified since pressure was considered to have no effect on the yield of maleic anhydride (2). In the same way, an average value of 0.035 cp was used for the fluid viscosity of the reactor gas mixture in the calculation of Figure 5.9. The change in the fluid viscosity due to gas composition and temperature was small, and its effect in equations 5.1 and 5.2 was negligible.

5.4) Choice of Variables

In a statistical study to determine the "optimum conditions" of a process, the first task was, of course, to define the dependent variable (i.e., the term to be optimized). Several terms could be considered, such as the concentration of maleic anhydride in the outlet gas stream, the yield of maleic anhydride, or its selectivity. (In this study, the term "yield" was defined as the mol ratio of the product / benzene input. "Selectivity" was defined as the mol ratio of the product / benzene reacted). With regard to kinetic consideration and comparison with existing literatures, the "yield" of maleic anhydride would be the most appropriate term to be optimized.

The selection of independent variables was more difficult, since the number of variables that could be handled was limited. Some of the factors, such as the size of reactor, type of baffles, etc., certainly could not be evaluated with the present equipment set-up. For a given catalyst, and the present equipments, the following variables
were considered:

a. Temperature — This was the obvious variable. From the literature survey, the range of temperature for the process was around 400-450°C. Thus, the starting levels for temperature were set at 380-400°C for the preliminary set of runs.

b. Molecular ratio of air to benzene — Apart from the obvious importance of the composition of the feed, this particular term was used for ease of calculation and comparison with the existing literatures. The value of the mol. ratio was reported to be in the range of 50-200 for a fixed bed process (15). This was, of course, in excess of the stoichiometric ratio needed for the oxidation of benzene. The stoichiometric ratio between air and benzene for partial oxidation was 17.5 and for complete oxidation was 37.5. For the preliminary set of runs, the levels of this variable was set at 50-100.

c. Superficial gas velocity — This was defined as the velocity of the gaseous feed over the empty cross section of the reactor, at the reacting temperature and average reactor pressure. From the fluidization study, it was necessary to keep the density of the reacting gas mixture constant at 0.575 g/l by varying the pressure of the system to allow for the change in the temperature of the reactor. One resulting advantage was that, with the gas density constant, the superficial gas velocity was then directly proportional to the mass flow rate.

The mol. ratio and the superficial velocity would completely define the reactant stream. In addition, as could be seen from Fig. 5.9, the average bed voidage, \( \varepsilon \), was found to be a function of \( V \), the superficial velocity. Thus, \( V \) would also represent one
property of the fluidizing bed.

The choice of the range of $V$ depended on the characteristics of both the catalyst particles and the gaseous feed. An upper limit of $V$ was placed at 0.35 fps. (10.5 cm./sec.). Beyond this value, more than half of the catalyst particles would be blown out of the bed. The lower limit of $V$ was, theoretically, the minimum fluid voidage velocity, but, in practice, the limit would depend on the capability of the equipment system, particularly, the benzene pump, to deliver accurately-measured small volumes. The lower limit of $V$ was assumed to be around 0.15 fps. (4.5 cm./sec.).

d. Weight of catalysts, $W$ - In a fixed bed process, the ratio $W/F$ (catalyst weight over mass flow rate) was used to define the contact time or space velocity. This implied constant fluid voidage in the bed. However, in a fluidized system, the actual contact time was also a function of the fluid voidage. Here, the term "contact time" was used as synonymous to the term "hold-up time", i.e., the average time a small particle of gas stayed in bed zone, and could be calculated by taking the ratio of the bed height over the superficial velocity, taking into account the fluid voidage and the assumption of plug flow. Thus, the average contact time, $\tau$, would be defined by:

$$\tau = \left(\frac{\varepsilon}{1-\varepsilon}\right) \cdot \frac{W}{F} \cdot \frac{\rho_f}{\rho_p}$$

As could be seen from Figure 5.9, the fluid voidage, $\varepsilon$, was a function of $W$ and $V$.

5.5) Contact time distribution

Though $\tau$ gave a closer approximation (than $W/F$) to the actual time a gas particle stayed in a bed zone, it still did not give a true
picture of the actual conditions in the bed. One would also have to consider the backmixing of the gas and the distribution of the catalyst particles in the bed zone. The gas backmixing and lateral movements would increase the actual time that a particle of gas stayed in the bed zone, while the distribution of catalyst powder would indicate the actual encounter between the gas and the catalyst. Thus, the fluid voidage, $\varepsilon$, would be a function of time also.

If one defined "t" as the time that a particle of gas stayed in a bed zone (i.e., residence time), the following relationship would hold:

$$\frac{W}{F} = \frac{C}{S_f} \cdot \frac{1-\varepsilon}{\varepsilon} \cdot t$$

where $\varepsilon = \varepsilon(\Theta)$, $\Theta$ being the time variable.

To reflect the spectrum of the residence time, $t$, a new variable $\bar{G}$ was introduced, such that

$$\bar{G} = \left[ \frac{C}{S_f} \int_0^t \frac{1-\varepsilon}{\varepsilon} d\Theta \right] / \left( \frac{W}{F} \right)$$

The new variable, $\bar{G}$, would also have a distribution function, $f(\bar{G})$, with a mean of 1, i.e., $\int_0^\infty \bar{G} f(\bar{G}) d\bar{G} = 1$. Thus, $\bar{G}$ could be thought of as a modifying factor of $W/F$, and was a dimensionless term.

Romano (46) had determined the residence time distribution functions in a 4 in. diam. fluidized bed, using cracking catalyst with an average particle diameter of 41 microns. The superficial gas velocities were 0.20, 0.375 and 0.55 ft./sec., and the bed heights were 12 and 20 inches. Air at room temperature and pressure was used for fluidization and the residence time was found by sinusoidally injecting a gas tracer (alpha particles from a Radium - D source) into the bed. This finding showed that the peaks of the distribution curves $[f(\bar{G}) \text{ vs. } \bar{G}]$
occurred at about \( f = 0.9 \) regardless of the superficial velocities. However, \( f(p) \) showed a definite tendency to become more peaked and its variance became smaller, indicating less gas mixing as the velocity was increased. There was no effect of bed height on gas mixing. This could be due to the low L/D ratio used (3.0 to 5.0). Romano's curves of residence-time distribution are shown in Appendix C.

For a first-order homogeneous reaction in a stirred tank, the fraction, \( \phi(K) \), of the reactant remaining, could be represented by:

\[
(5.6) \quad \phi(K) = \int_0^\infty e^{-K \tau} g(t) \, dt
\]

where \( t \) = holding time whose distribution was \( g(t) \).

Similarly, for a heterogeneous reaction, the fraction, \( \phi(K) \), could be represented by:

\[
(5.7) \quad \phi(K) = \int_0^\infty e^{-K \tau} h(\xi) \, d\xi
\]

where \( K = \frac{k \pi}{(H/P)} \),

and \( h(\xi) \) = "contact time" distribution of \( \xi \). The derivation of Eq. (5.7) is shown in Appendix E.

Distinction had to be made between the residence time distribution, \( f(\xi) \), and the gas-solid contact time distribution, \( h(\xi) \). The former indicated the probability of the time that a gas particle stayed in the bed zone, whereas the latter indicated the combined probability of a gas particle staying in the bed zone and contacting catalyst particles. The relationship between the two distributions would be:

\[
(5.8) \quad f(\xi) = f_b \delta(\xi) + (1-f_b) h(\xi)
\]

where \( f_b = \) fraction of the total gas stream that by-passed the bed.

\( \delta(\xi) \) represented a function such that \( \delta(0) \neq 0 \) at \( \xi = 0 \), and \( \delta(\xi) = 0 \) at \( \xi \neq 0 \), and also \( \int_0^\infty \delta(\xi) \, d\xi = 1. \)
For the fraction \( (1-f_b) \) of the total flow which was contacted chemically with the catalyst, the following would be true:

\[
\int_0^\infty h(\xi) \, d\xi = 1.
\]

If, from a set of experiments, the relationship between \( \phi(K) \) and \( K \) was found, one could, by Laplace transformation, find the function \( h(\xi) \) from eq. (5.7). To do this, it was necessary to find a mathematical relationship between \( \phi(K) \) and \( K \) from the experimental results.

Using this method, Orcutt (12) had determined the contact time distribution, \( h(\xi) \), in a 4 in. and 6 in. diameter reactors with gas velocity up to 0.5 ft./sec. The catalyst used was an oxide-impregnated silicon-alumina type which had similar physical properties to the catalyst used in this study. The reaction was the decomposition of ozone, which was a first-order heterogeneous one. For the relationship between \( \phi(K) \) and \( K \), Orcutt used a polynomical function (based on the gamma probability function) with 3 parameters, one of which was \( f_b \).

The values of \( f_b \) and the other two parameters (which had no physical meaning) were found by trial and error, and the \( \phi(K) \) vs. \( K \) curves fitted by the least-square method.

Orcutt's correlation of \( h(\xi) \) vs. \( \xi \) was shown in the Appendix C. The value of \( f_b \), the fraction bypassed, was found to be 0.05-0.078 in the 4" diam. reactor. Comparison between Romano's \( f(\xi) \) and Orcutt's \( h(\xi) \) for a 4 in. diam. reactor showed that the contact time distribution, \( h(\xi) \), had its peak at a lower value of \( \xi \), as expected. The mean value of \( \xi \) for \( h(\xi) \) was 0.78, and the variance was 0.91, compared to the mean of 1, and the variance of about 0.3-0.4 for \( f(\xi) \). The larger value of the variance of \( h(\xi) \) reflected the effects of mixing and the frequency of chemical reaction during contacts. It should be
pointed out that $f_b$ not only represented the fraction by-passing, but also the fraction of the gas that, though contacting with the catalysts, did not react.

Both the residence-time and contact-time distributions could define the behavior of a fluidized bed completely only in the case of first-order reactions. For second-order reactions, $\phi(K)$ could not be predicted from the contact time distributions. This was because in the second-order cases, the variation in the reactant concentrations between adjacent gas particles would effect the rate of reaction greatly. Any meaningful distribution would have to take into account the time-dependent variation of concentrations also. (This had no effect in the first-order cases).

In addition, though $f_b$ and its distribution functions were important in defining fluidizing properties, they could not be controlled easily. Therefore, in this study, only the velocity, $V$, and the catalyst weight, $W$, were used to control the bed characteristics, since, in the final analysis, given a fluidized system, the contact time distribution would depend on $W$ and $V$.

5.6) Procedure

Each run was made with all four variables set at predetermined values to fit in the statistical design matrix. The benzene pump, of course, had to be set and the rate measured while the reactor was in operation. The pressure in the system was adjusted until the average density of the fluidizing gas was about 0.575 g/l. depending on the temperature and gas composition desired. After the reactor was in operation with all variables at the correct levels for at least 1 hr., the sample valve was open and the products collected in the traps
while the corresponding gas samples were taken. The time of sampling was between 45-60 minutes.

The samples, both liquid and gas, were analyzed within 24 hrs. It was found that a longer waiting period resulted in an appreciable loss of CO and CO₂ in the gas sample, and also a decrease in the amounts of maleic anhydride and benzene in the liquid.

Each batch of catalysts was changed after four runs or less. The loss of catalysts after each change was about 1-2%. The loss probably was due to the fine particles being lodged in the top and connecting arm of the reactor. Reverse air flow was made after each catalyst change, but the amount of fines recovered was negligible.

Records were made of the pressure just below the catalyst supporting grid and the pressure just after the reactor proper. The average of these values was taken as the average pressure of the reactor. This was used for the calculation of fluid density.

Material balances on benzene and oxygen were based on the percentage of each gas component in the sample, and the amount of maleic anhydride found. A sample calculation was given in Appendix D.
CHAPTER VI

RESULTS

The data were divided into three parts. Part I included Runs Nos. 1-16. This was the preliminary experiment. Part II was Runs Nos. 17-25. This was the "steepest ascent" section and also included checking the validity of the first part. Part III was Runs No. 26-53 which comprised the experiment near the optimum point. In addition, Runs Nos. 42-45 also served as an error analysis, since they were made at identical controlled conditions. The complete data are shown in the Appendix D.

As explained in Chapter III, to simplify the statistical calculation, the actual values of the variables were transformed into coded values. These coded terms were as followed:

- $x_1$ represented the coded value of the temperature variable ($T^0_K$).
- $x_2$ represented the coded value of the mol ratio (air/benzene) in the inlet. The actual value of the ratio was represented by $R$.
- $x_3$ represented the coded value of the superficial velocity ($V$ in cm./sec.) of the inlet gas at the reactor conditions.
- $x_4$ represented the coded value of the weight of catalyst ($W$ in g.).

The coding in each set of experiments depended upon the size of the matrix desired. Each coded variable was changed in step or "level". Thus, in Part I, there were two levels for each factor. These were $+1$
for the high level, and -1 for the low level. In Part III, the variables were changed in five equal levels, namely, -2, -1, 0, +1 and + 2.

6.1) Preliminary experiment

The design used in this section was the complete factorial design shown in Table 3.2. The levels of each variable were set as followed:

| Table 6.1 Actual Variables in the Preliminary Experiment |
|-------------|-------------|-------------|-------------|-------------|
| Variable | High Level | Low Level | Base Level | Unit |
| T°K | 673 | 653 | 663 | 10 |
| R | 103.45 | 48.63 | 76.05 | 27.42 |
| V cm/sec | 7.86 | 5.61 | 7.24 | 0.62 |
| W, g | 75 | 50 | 62.5 | 12.5 |

Fractional values of R and V were chosen because these two variables could not be controlled exactly, and the average values for all 16 runs were used. The variations from the average values were small as could be seen in Table 6.2. Thus, each variable could be regarded as set at the predetermined level for each run.

The coded variables, x_i's were found from the following general formula (referred also to Table 6.1):

\[ x_i = \frac{U_i - \bar{U}_i}{\Delta U_i} \]

where \(U_i\) is value of the i th actual variable

\(\bar{U}_i\) is base value (i.e., value of the variable when \(x_i = 0\))

\(\Delta U_i\) is unit value

For example, the coded variable for temperature would be

\[ x_1 = \frac{(T^0 - 663)}{10}. \] In this set of experiments, the values of \(x_i\)'s would be either +1 or -1.
The small unit for velocity was necessary because the range of velocity that could be used was small (up to 10.5 cm./sec.). Also in a preliminary experiment, one would want to explore a relatively small area so that the interactions would be negligible. This is in contrast with an exploratory experiment whereby no information is known about the process under study. In such a case, a large coverage of the response area would be desirable.

The results of the runs in Part I are shown in Table 6.2. The terms in this Table have been defined in previous sections and are also summarized in Appendix F. Additional terms are as follow:

\[ F_B = \text{g.mol/hr. of benzene at the outlet} \]

\[ C_{Bi} = \text{mol \% of benzene at the inlet} \]

\[ S = \% \text{ selectivity, (mol percent of maleic anhydride formed based on moles of benzene reacted). Mathematically,} \]

\[ S = 100 \left( \frac{y_M}{y_B} \right). \]
### Table 6.2 Preliminary Experiments

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Level of Variables</th>
<th>T (°C)</th>
<th>V (cm/sec)</th>
<th>W (g)</th>
<th>W/F (g mol/hr)</th>
<th>F (g mol/sec)</th>
<th>%B</th>
<th>f</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>-1 -1 -1 -1</td>
<td>653</td>
<td>48.89</td>
<td>6.62</td>
<td>50</td>
<td>5.36</td>
<td>0.187</td>
<td>2.004</td>
<td>0.919</td>
</tr>
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<td>3</td>
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<td>673</td>
<td>48.43</td>
<td>6.62</td>
<td>50</td>
<td>5.44</td>
<td>0.186</td>
<td>2.023</td>
<td>0.919</td>
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<td>4</td>
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<td>103.35</td>
<td>6.59</td>
<td>50</td>
<td>5.36</td>
<td>0.089</td>
<td>0.949</td>
<td>0.923</td>
</tr>
<tr>
<td>5</td>
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<td>673</td>
<td>102.17</td>
<td>6.71</td>
<td>50</td>
<td>5.35</td>
<td>0.091</td>
<td>0.959</td>
<td>0.911</td>
</tr>
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<td>6</td>
<td>-1 -1 1 -1</td>
<td>653</td>
<td>48.99</td>
<td>7.80</td>
<td>50</td>
<td>4.56</td>
<td>0.220</td>
<td>2.000</td>
<td>0.933</td>
</tr>
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<td>1 -1 1 -1</td>
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<td>7.80</td>
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<td>4.57</td>
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<td>2.010</td>
<td>0.933</td>
</tr>
<tr>
<td>8</td>
<td>-1 1 1 -1</td>
<td>653</td>
<td>102.46</td>
<td>7.90</td>
<td>50</td>
<td>4.48</td>
<td>0.108</td>
<td>0.957</td>
<td>0.922</td>
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<tr>
<td>9</td>
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<td>673</td>
<td>103.13</td>
<td>7.86</td>
<td>50</td>
<td>4.49</td>
<td>0.107</td>
<td>0.960</td>
<td>0.926</td>
</tr>
<tr>
<td>10</td>
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<td>653</td>
<td>47.90</td>
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<td>75</td>
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<td>0.188</td>
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<td>1.273</td>
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<td>11</td>
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<td>6.59</td>
<td>75</td>
<td>8.08</td>
<td>0.186</td>
<td>2.006</td>
<td>1.260</td>
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<td>6.62</td>
<td>75</td>
<td>7.91</td>
<td>0.091</td>
<td>0.955</td>
<td>1.260</td>
</tr>
<tr>
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<td>103.69</td>
<td>6.62</td>
<td>75</td>
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<td>0.090</td>
<td>0.955</td>
<td>1.260</td>
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<td>7.86</td>
<td>75</td>
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<td>0.222</td>
<td>2.010</td>
<td>1.265</td>
</tr>
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<td>673</td>
<td>48.51</td>
<td>7.86</td>
<td>75</td>
<td>6.82</td>
<td>0.222</td>
<td>2.020</td>
<td>1.265</td>
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<td>7.90</td>
<td>75</td>
<td>6.86</td>
<td>0.108</td>
<td>0.961</td>
<td>1.260</td>
</tr>
<tr>
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<td>673</td>
<td>105.48</td>
<td>7.86</td>
<td>75</td>
<td>6.87</td>
<td>0.106</td>
<td>0.939</td>
<td>1.265</td>
</tr>
</tbody>
</table>
By using the method of least squares (Chapter III), a second-order linear regression equation (involving two-factor interactions only) could be made. This is of the form:

\[
Y = a_0 + a_1x_1 + a_2x_2 + a_3x_3 + a_4x_4 + a_{12}x_1x_2 + a_{13}x_1x_3 + a_{14}x_1x_4 + a_{23}x_2x_3 + a_{24}x_2x_4 + a_{34}x_3x_4
\]

where \(Y\) represents \(Y_B\), \(Y_M\) or \(S\) in percentage values.

The values of \(a_i\)'s are shown in Table 6.3. This was calculated directly by means of a 7094 IBM computer (42).

<table>
<thead>
<tr>
<th>Constants</th>
<th>(Y_B)%</th>
<th>(Y_M)%</th>
<th>(S)%</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a_0)</td>
<td>70.659</td>
<td>14.339</td>
<td>20.174</td>
</tr>
<tr>
<td>(a_1)</td>
<td>6.494</td>
<td>0.696</td>
<td>-0.924</td>
</tr>
<tr>
<td>(a_2)</td>
<td>6.336</td>
<td>1.989</td>
<td>1.092</td>
</tr>
<tr>
<td>(a_3)</td>
<td>0.998</td>
<td>1.017</td>
<td>1.719</td>
</tr>
<tr>
<td>(a_4)</td>
<td>0.741</td>
<td>-0.639</td>
<td>-1.021</td>
</tr>
<tr>
<td>(a_{12})</td>
<td>-0.992</td>
<td>0.106</td>
<td>0.338</td>
</tr>
<tr>
<td>(a_{13})</td>
<td>-0.414</td>
<td>-1.105</td>
<td>-1.547</td>
</tr>
<tr>
<td>(a_{14})</td>
<td>-0.337</td>
<td>0.436</td>
<td>0.873</td>
</tr>
<tr>
<td>(a_{23})</td>
<td>-3.786</td>
<td>-1.243</td>
<td>-0.871</td>
</tr>
<tr>
<td>(a_{24})</td>
<td>-1.371</td>
<td>-0.616</td>
<td>-0.286</td>
</tr>
<tr>
<td>(a_{34})</td>
<td>-2.196</td>
<td>-0.707</td>
<td>-0.613</td>
</tr>
</tbody>
</table>

No error analysis was made at this point, since there was no a priori standard of error to compare. The object of this set of experiment was simply to find the trend or path of steepest ascent as indicated by the first-order effects. It should be pointed out here also that, due to the orthogonal form of the design matrix, the values of the first-order effects would still be the same as in Table 5.3, even if no interaction term was calculated.
There are three response expressions for results, namely, \( Y_B, Y_M \) and \( S \). Obviously, the path to the optimum would not be the same for all expressions. As mentioned in Sect. 5.4, the yield of maleic anhydride, \( Y_M \) would be the most desirable one to be optimized. Thus, later work was made with this purpose.

6.2) The Steepest Ascent

To determine the directions of future experiments, one was concerned only with the first-order effects, i.e., the terms, \( a_1, a_2, \ldots, a_4 \), in Table 6.3. By using eq. 3.19 (Sect. 3.10), the path of the steepest ascent was calculated as shown in Table 6.4. For example, if one let the term \( \left[ \frac{\delta Y}{\delta x_1} \right] = 1 \), the value of \( \delta x_1 \) would then be equal to 0.696 (since from Table 6.3, \( a_1 = \frac{\delta Y}{\delta x_1} = 0.696 \)). In terms of the actual temperature scale, this was equivalent to 0.696 x 10 = 6.96°K. (One unit of \( x_1 \) was equal to 10°K as shown in Table 6.1). Similar calculations were made for the other three variables. A series of conditions for possible trials were then calculated starting from the base levels, and one set chosen for Run No. 17.
Table 6.1 -- Calculation of the Steepest Ascent

<table>
<thead>
<tr>
<th></th>
<th>T°K</th>
<th>R</th>
<th>V cm./sec.</th>
<th>W g*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Unit</td>
<td>10</td>
<td>27.42</td>
<td>0.62</td>
<td>12.5</td>
</tr>
<tr>
<td>2. Slope, a₁</td>
<td>0.696</td>
<td>1.989</td>
<td>1.017</td>
<td>-0.639</td>
</tr>
<tr>
<td>3. Equivalent step</td>
<td>6.96</td>
<td>54.538</td>
<td>0.63</td>
<td>-7.988</td>
</tr>
<tr>
<td>4. equivalent change per 10⁷K of change in x₁</td>
<td>10</td>
<td>78.359</td>
<td>1.02</td>
<td>-11.477</td>
</tr>
<tr>
<td>5. Path of steepest ascent as series of possible runs</td>
<td>390</td>
<td>76.05</td>
<td>7.24</td>
<td>62.5</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>154.41</td>
<td>8.26</td>
<td>51.0</td>
</tr>
</tbody>
</table>

Run 17  
| 410 | 232.78 | 9.28 | 39.5 |
| 420 | 301.13 | 10.30 | 28.0 |
| 430 | 379.49 | 11.32 | 16.5 |

Since there were large interaction effects present in the regression equation, a check had to be made for the correctness of the calculated path. This was done by making some runs away from the calculated values and comparing the resulting yields. Thus, where Run No. 17 was made on the path, Runs Nos. 18, 19 and 20 were made away from it as followed:

1. The variables V and W were changed in the opposite directions from the path; and the steps enlarged.

2. Since the variable R showed a large first-order effect, and the variable T showed an agreement with theoretical considerations (i.e., an increase in temperature resulted in an increase in the rate), these two variables were kept constant. The results of Runs Nos. 17-20 are shown in Table 6.5. It should be noted that the actual conditions for Run No. 17 were somewhat different from those calculated in Table 6.1.
(though still in the same directions). This was due to the equipment
limits on the ranges of \( R \) and \( V \). Thus, shortened steps had to be taken
for these two factors.

**Table 6.5 Results of Runs Nos. 17-20**

<table>
<thead>
<tr>
<th>Run Nos.</th>
<th>Variable</th>
<th>Result, ( Y_M )</th>
</tr>
</thead>
<tbody>
<tr>
<td>17</td>
<td>683</td>
<td>214.6 8.94 37.5 23.96</td>
</tr>
<tr>
<td>18</td>
<td>683</td>
<td>220.0 5.68 37.5 10.21</td>
</tr>
<tr>
<td>19</td>
<td>683</td>
<td>220.0 5.65 150.0 10.18</td>
</tr>
<tr>
<td>20</td>
<td>683</td>
<td>225.3 9.00 150.0 10.65</td>
</tr>
</tbody>
</table>

Since \( T \) and \( R \) were kept approximately constant in this series
of runs, a regression equation on \( V \) and \( W \) could be calculated. This is:

\[
Y_M = 13.75 + 3.56 x'_3 - 3.34 x'_4 - 3.32 x'_3 x'_4
\]

where \( x'_3 = \frac{V - 7.26}{1.71} \)

\( x'_4 = \frac{W - 93.75}{56.25} \)

and ' denotes the set of experiments from Runs 17-20.

Comparison of the constants of the above equation and the corres­
ponding terms in Table 6.3 showed that the average term, \( a_0 \), was lower
for Runs Nos. 17-20 than for Runs Nos. 1-16. The individual results of
Runs 18, 19 and 20 were all lower than that of Run 17 (which was set
on the calculated path). This indicated the correctness of the path;
and any deviation from it would result in lower conversion

The constants \( a_3 \) and \( a_4 \) in eq. (6.3) were both larger than the
corresponding values in Table 6.3. This was because the units of \( x_3 \)
and \( x_4 \) in the second set of runs were larger. Hence, their effects
must be greater. The same reasoning could be applied to the inter-
action effect, \( a_{34} \). However, it could also be argued that, in the
first set of runs, one was already near the optimum area for the
factors \( x_3 \) and \( x_4 \). In this case, the first value of \( a_{34} \) would also
be small.

The next step in the experiment was the series of runs (Nos. 17,
21-25). These were made along the directions indicated by Table 6.4.
However, some limitations had to be placed on the range of each vari-
able as followed:-

1. The variable \( R \), the mol ratio of air to benzene could be
increased up to approximately 275. At larger values, the amounts
of benzene needed was too small to be delivered accurately.

2. The variable \( V \), superficial gas velocity could be increased
to approximately 10.5-11.0 cm./sec. Beyond this, more than half of
the catalyst particles would be blown out of the bed.

3. The variable \( W \), weight of catalyst used, could be reduced
only to a certain limit. By considering the size of the reactor tube
(5 cm. diam.), and the loose-bed density of the catalyst (0.81 g/ml.),
the minimum amount of catalyst used was set at about 20 g. This would
give a minimum loose-bed height of approximately 1 cm. Of course, the
actual fluidized bed would be higher (close to 2 cm.), depending on the
superficial velocity. The minimum L/D ratio used was then close to
\( \frac{1}{2} \). The maximum value (for Runs Nos. 19-20, where \( W = 150 \text{ g.} \)) was approxi-
mately 3-4.

Therefore, only the temperature could be changed over a wide
range. For the other variables, shortened steps were taken until the
limits were reached. Table 6.6 shows the results of this series of runs.
Table 6.6 — Path of Steepest Ascent

<table>
<thead>
<tr>
<th>Run No.</th>
<th>T₀K</th>
<th>R</th>
<th>V cm./sec.</th>
<th>W g.</th>
<th>Y_M %</th>
</tr>
</thead>
<tbody>
<tr>
<td>17</td>
<td>683</td>
<td>214.6</td>
<td>8.82</td>
<td>37.5</td>
<td>23.96</td>
</tr>
<tr>
<td>21C</td>
<td>693</td>
<td>254.8</td>
<td>9.62</td>
<td>25.0</td>
<td>24.20</td>
</tr>
<tr>
<td>22</td>
<td>703</td>
<td>272.6</td>
<td>10.30</td>
<td>25.0</td>
<td>26.88</td>
</tr>
<tr>
<td>23</td>
<td>713</td>
<td>266.1</td>
<td>10.30</td>
<td>25.0</td>
<td>27.49</td>
</tr>
<tr>
<td>24</td>
<td>723</td>
<td>269.8</td>
<td>10.30</td>
<td>25.0</td>
<td>28.97</td>
</tr>
<tr>
<td>25</td>
<td>733</td>
<td>270.5</td>
<td>10.29</td>
<td>25.0</td>
<td>24.40</td>
</tr>
</tbody>
</table>

As could be seen, Y_M increased steadily from Runs 17 to 24. The limits of R, V and W were reached in Run No. 22, and thus, R, V and W could not be changed any further in Runs Nos. 23-25. As T was raised from 723 to 733 K as in Runs 24 to 25, Y_M decreased, indicating that the optimum had been passed. Thus, for T, there was an optimum range around 723 K, whereas for the other variables, the optima were simply the limits imposed by the equipment system.

6.3) Experiments in the Optimum Region

The high value of Y_M in Run 24 indicated that a near stationary region close to the optimum had been reached. A series of tests were then made in this area to determine the exact location of the optimum point, and also to give a quadratic regression equation relating Y_M to the various variables.

The design of experiment used here was the composite design of Davies (36). The first part of this design was the complete factorial matrix for 4 variables at 2 levels, as shown in Table 3.2. This was supplemented by the design matrix shown in Table 3.3. The total number
of runs was 25. As in Sect. 6.1, the actual variables were coded into the $x_i$'s form (equation 6.1). The levels and units of each variable were given in Table 6.7.

Table 6.7 Actual Variables in the Composite Design

<table>
<thead>
<tr>
<th>Variable</th>
<th>$x_i=2$</th>
<th>Level</th>
<th>$x_i=-1$</th>
<th>$x_i=0$</th>
<th>$x_i=-2$</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T^{\circ}K$</td>
<td>733</td>
<td>728</td>
<td>723</td>
<td>718</td>
<td>713</td>
<td>5</td>
</tr>
<tr>
<td>$R$</td>
<td>286.63</td>
<td>270.50</td>
<td>248.43</td>
<td>230.76</td>
<td>205.29</td>
<td>20.21</td>
</tr>
<tr>
<td>$V_{cm./sec}$</td>
<td>10.88</td>
<td>10.38</td>
<td>9.88</td>
<td>9.38</td>
<td>8.88</td>
<td>0.50</td>
</tr>
<tr>
<td>$W_{g}$</td>
<td>40</td>
<td>35</td>
<td>30</td>
<td>25</td>
<td>20</td>
<td>5</td>
</tr>
</tbody>
</table>

As before, $x_i = (U_i - \bar{U}_i)/\Delta U_i$, where $\bar{U}_i$ represented the base value, i.e., the value of the actual variable corresponding to $x_i=0$.

In addition, to find the error variance, four runs instead of one were made at the center point of the matrix (i.e., at the conditions where all $x_i$'s were set equal to zero in the same run, corresponding to Trial no. 17 in Table 3.3). The error variance was calculated from this group of four runs by using eq. (3.8), and compared with the variance obtained from the calculation of residuals (eq. 3.7, with $k=14$).

The results of this set of runs (Nos. 26-53) were shown in Table 6.8. The resulting regression equations were of the form:

$$Y = a_0 + a_1 x_1 + a_2 x_2 + a_3 x_3 + a_4 x_4$$

$$+ a_{12} x_1 x_2 + a_{13} x_1 x_3 + a_{14} x_1 x_4 + a_{23} x_2 x_3$$

$$+ a_{24} x_2 x_4 + a_{34} x_3 x_4$$

$$+ a_{11} x_1^2 + a_{22} x_2^2 + a_{33} x_3^2 + a_{44} x_4^2$$

(6.4)
### Table 6.8 Results in the Optimum Region

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Level of Variables</th>
<th>$T_{OK}$</th>
<th>$R$</th>
<th>$V$</th>
<th>$W$</th>
<th>$W/F$</th>
<th>$F_B$</th>
<th>$C_B$</th>
<th>$T$</th>
<th>$Y_B$</th>
<th>$Y_M$</th>
<th>$S$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$x_1$</td>
<td>$x_2$</td>
<td>$x_3$</td>
<td>$x_4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>26</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>718</td>
<td>229.47</td>
<td>9.40</td>
<td>25</td>
<td>1.84</td>
<td>0.059</td>
<td>0.434</td>
<td>0.531</td>
</tr>
<tr>
<td>27</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>728</td>
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<td>9.40</td>
<td>25</td>
<td>1.84</td>
<td>0.059</td>
<td>0.433</td>
<td>0.531</td>
</tr>
<tr>
<td>28</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>718</td>
<td>271.14</td>
<td>10.40</td>
<td>25</td>
<td>1.84</td>
<td>0.050</td>
<td>0.367</td>
<td>0.531</td>
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<td>-1</td>
<td>728</td>
<td>270.72</td>
<td>10.30</td>
<td>25</td>
<td>1.84</td>
<td>0.050</td>
<td>0.368</td>
<td>0.531</td>
</tr>
<tr>
<td>30</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>718</td>
<td>231.78</td>
<td>9.40</td>
<td>25</td>
<td>1.68</td>
<td>0.064</td>
<td>0.430</td>
<td>0.566</td>
</tr>
<tr>
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<td>-1</td>
<td>1</td>
<td>-1</td>
<td>728</td>
<td>231.90</td>
<td>9.40</td>
<td>25</td>
<td>1.68</td>
<td>0.064</td>
<td>0.429</td>
<td>0.559</td>
</tr>
<tr>
<td>32</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>718</td>
<td>272.90</td>
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<td>25</td>
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<td>0.054</td>
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<td>-1</td>
<td>728</td>
<td>270.75</td>
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Table 6.9 Constants of Regression Equation in the Optimum Region

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<th>Constants</th>
<th>$Y_B%$</th>
<th>$Y_M%$</th>
<th>$S%$</th>
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<td>$s$</td>
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<td>1.93</td>
<td>1.48</td>
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Multiple Corr. (R) 0.883 0.904 0.971

where $Y$ represented $Y_B$, $Y_M$, or $S$.

The values of $a_i$'s were shown in Table 6.9.

6.4) Determination of the error variance ($s^2$).

Both equations (3.7) and (3.8) were used in determining the error variance. In the first method, $s^2$ was determined as a residual error.
term from the composite design matrix. Thus,

\[ s^2 = \frac{\sum_{j=1}^{n} (y_j - y_j)^2}{(n - k - 1)} \]

where \( y_j \) = observed response of Run No. "j".

\[ y_j = \text{calculated response of Run No. "j", based on eq. (6.4)} \]

\( n = \text{total no. of runs} = 25 \)

\( k+1 = \text{total no. of constants in eq. (6.4)} = 15 \).

The value of the error variance \( s^2 \), was found to be 3.728, and the standard deviation, \( s \), was 1.93, for 10 degrees of freedom.

In the second method, a group of four identical runs were made. These were Runs Nos. 42-45 in Table 6.8. By using eq. (3.8), the error variance was found to be 1.99, with the estimated standard deviation, \( s \), equal to 1.41 (degree of freedom = 3).

The difference in the "s" value between the two methods simply showed that equation (6.4) did not exactly fit the data, as could be seen by the value of 0.904 for the multiple correlation, \( R \). A perfect fit, of course, would give the value of 1.0. In the analysis of error, the value of "s" = 1.41 would be more correct, since this was found directly from an experiment designed for its calculation, whereas, the value of "s" found by the first method was a residual value which might include other unknown effects.
CHAPTER VII

DISCUSSION OF RESULTS

7.1) Optimum Conditions

The constants of the regression equations as tabulated in Table 6.9 do not include any three-or four-factor interactions. This does not mean that no such term existed in the regression equation. Kinetically, there is no ground to eliminate any of these interactions, since each term contributes to the shaping of the contour surface, and in a complex process such as benzene oxidation, it may be presumed that three-and four-factor interactions will occur.

In the statistical sense, while there is no preference for one effect over another, it may be argued that the higher interaction terms could be eliminated from the contour equation. Though the resulting equation would not have as good a fit as would be the case when there were more terms in the equation, the resulting change in the multiple correlation would be small. The advantage would be that the error variance, $s^2$, could be calculated with more degrees of freedom, and hence, would be more reliable. In addition, interpretation of the regression equation could easily be made with an equation of the form of (6.4). It should be mentioned that since the design of the experiment was orthogonal, the calculations of each constant (except the quadratic terms) were independent of each other. Thus, elimination or addition of the three-and four-factor terms to the
regression equation would not change the values of the other constants. Were the design not orthogonal, new values of the constants would have to be calculated, each time another constant was added or dropped from the equation.

For the yield, $Y_M$, of maleic anhydride, the regression equation is:

\[(7.1) \quad Y_M = 28.69 - 0.004 x_1 - 0.146 x_2 - 1.037 x_3 - 1.533 x_4 + 0.084 x_1^2 - 0.758 x_2^2 - 0.824 x_3^2 - 0.621 x_4^2 - 0.147 x_1 x_2 - 0.203 x_1 x_3 + 0.002 x_1 x_4 - 0.073 x_2 x_3 - 0.866 x_2 x_4 + 0.586 x_3 x_4\]

By differentiating eq. (6.1) with respect to $x_1$, $x_2$, $x_3$ and $x_4$, and equating the resulting set of equations to zero, the maximum value of $Y_M$ could be found. The resulting set of equation is:

\[
\begin{align*}
\frac{\partial Y_M}{\partial x_1} &= -0.004 + 0.168 x_1 - 0.147 x_2 - 0.203 x_3 + 0.002 x_4 \\
\frac{\partial Y_M}{\partial x_2} &= -0.146 - 0.147 x_1 - 1.516 x_2 - 0.073 x_3 - 0.866 x_4 \\
\frac{\partial Y_M}{\partial x_3} &= 1.037 - 0.203 x_1 - 0.073 x_2 - 1.648 x_3 + 0.586 x_4 \\
\frac{\partial Y_M}{\partial x_4} &= -1.533 + 0.002 x_1 - 0.866 x_2 + 0.586 x_3 - 1.242 x_4
\end{align*}
\]

The solution of (7.2) would be:

\[
\begin{align*}
x_1 &= +0.668, \text{ corresponding to } T = 726.3^\circ K, \\
x_2 &= +1.019, \text{ corresponding to } R = 269, \\
x_3 &= -0.227, \text{ corresponding to } V = 9.80 \text{ cm./sec.} \\
x_4 &= -2.052, \text{ corresponding to } W = 19.74 \text{ g.}
\end{align*}
\]

The minimum value of $Y_M$ was found to be 30.17%.

If eq. (7.1) is differentiated twice with respect to each $x_i$, it is seen that there is a minimum yield with respect to the temperature
effect, and maxima with respect to all other variables, as could be seen from the signs of the quadratic terms in eq. (7.1). This agrees with Pinchbeck's work (30) on naphthalene oxidation, but not with Yao's work (14) in the fixed bed oxidation of benzene.

The optimal conditions for $Y_M$ corresponded to the value of $(W/F) = 1.395$ g. cat.-hr./mol. The average contact time, $T$, would be around 0.5 sec., and the average value of $\varepsilon$ would be 0.89. The bed would be close to slugging at this $\varepsilon$ value.

7.2) The Canonical Equation

Equation (7.1), though suitable for locating the optimum conditions did not give a clear picture of the contour surface. A better understanding of the contour could be made if eq. (7.1) was changed into its canonical form. This, in effect, meant that the axes of the variables $x_i$'s were rotated to be in line with the axes of the contour surface. The method of reduction to the canonical form is given fully by Davies (36). The resulting equation is:

$$(7.3) \quad Y_M - 30.17 = -1.2098 x_1^2 - 0.8536 x_2^2 - 0.1564 x_3^2 + 0.1008 x_4^2$$

where $x_i$'s were defined as followed:

$$X_1 = -0.997 (x_1 - 0.668) + 0.045 (x_2 - 1.019) + 0.043 (x_3 + 0.227) - 0.041 (x_4 + 2.052)$$

$$X_2 = -0.995 (x_1 - 0.668) + 0.661 (x_2 - 1.019) + 0.048 (x_3 + 0.227) - 0.064 (x_4 + 2.052)$$

$$X_3 = -0.937 (x_1 - 0.668) + 0.208 (x_2 - 1.019) + 0.005 (x_3 + 0.227) - 0.281 (x_4 + 2.052)$$

$$X_4 = -0.503 (x_1 - 0.668) + 0.506 (x_2 - 1.019) - 0.224 (x_3 + 0.227) - 0.664 (x_4 + 2.052)$$
and $x_i = \frac{(U_i - \bar{U}_i)}{\Delta U_i}$ where $\bar{U}_i$ and $\Delta U_i$ were as given in Table 6.7.

Equation (7.3) expresses the change in conversion as one moves away from the center of the system (i.e., the point where $Y_M = 30.17$) to some point whose coordinates were $x_i$'s. In this case, the changes are negative for $x_1$, $x_2$ and $x_3$. Hence, there would be a decrease of yield along those directions from the center. On the other hand, along the axis $X_4$, the change would be positive, denoting an increase in yield.

There could not be any graphical representation for the 4-variable equation. However, in the case where $X_4$ was given a fixed value, the resulting three dimensional contour would be an ellipsoid with a point maximum ($\approx 30.17$ when $X_4=0$) at the center. This is shown in Figure 7.1 a. For other three dimensional spaces involving $X_4$, the contour would be in the shape of Figure 7.1 b. In both of these figures, each surface represents points of equal yields. It should be apparent from equation (7.3) that the contour involving $x_1$, $x_2$, $x_4$ would be of similar form with the contour involving $x_1$, $x_3$, and $x_4$.

In Figure 7.1 b, the yield would be increasing as one moved away from the center along the axis $X_4$, and decreasing along the other two axes. Figure 7.2 shows the cut-sections of the contour in Figure 7.1 b. In these sections, each line represents points of equal yields.

7.3) Catalytic Reactions

As mentioned in Section 4.1, the reactions between benzene and the catalysts could be considered as an equilibrium between the oxidation rate of benzene and the re-oxidation of the reduced catalyst. In the case where both reactions were first-order with respect to benzene and the absorbed oxygen on the catalyst, the resulting kinetic equation
b). *Three-dimensional col*

Arrows indicate directions of increase in yield.

**FIGURE 7.1 — Contours.**
Arrows indicate directions of increase in yield.

**FIGURE 7.2** --- Cross Sections of Three-Dimensional Cöl.
was:

\[
(4.11) \quad \frac{W}{F} = \frac{1}{T} \left[ \frac{1}{k_1} \ln \left( \frac{C_B}{C_B_0} \right) + \frac{1}{k_2} \ln \left( \frac{C_{O2}}{C_{O2_0}} \right) \right]
\]

where \( k_1 \) = reaction rate constant for the oxidation of benzene

\( k_2 \) = reaction rate constant for the oxidation of the reduced catalyst.

To solve for \( k_1 \) and \( k_2 \), eq. (4.11) was changed to:

\[
(7.5) \quad \ln \left[ \left( \frac{C_B}{C_B_0} \right) \right] + \frac{1}{k_2} \ln \left[ \left( \frac{C_{O2}}{C_{O2_0}} \right) \right] = \frac{(W/F)}{T}
\]

A plot of the right-handed term vs. the "In" term on the left side would give a slope equal to \( 1/k_1 \), and an intercept equal to \( 1/k_2 \).

An attempt to plot out eq. (7.5) showed that the data scattered widely. This was to be expected since eq. (4.11), though rigorous, was based on the assumption that there was only one benzene oxidation reaction, whereas, in fact, there were several oxidation reactions on benzene plus other reactions on the products. Figures 7.3 and 7.4 show these plots for 673°K (400°C) and 728°K (455°C) respectively.

The rate constants were found to be:

\[
\begin{align*}
k_1 \text{ (benzene)} & : \\ & 400^\circ C \quad 0.41 \\ & 450^\circ C \quad 1.26 \\

k_2 \text{ (catalyst)} & : \\ & 0.13 \\ & 6.65
\end{align*}
\]

(UNIT of \( k_1 \) and \( k_2 \) was in g mol/hr. (g cat.) atm.)

The resulting energy of activation for the oxidation of benzene \( (k_1) \) was 21.0 k cal/mol, and for the re-oxidation of the reduced catalyst, it was 29.7 k cal/mol. This was higher than the value that Mars and van Krevelen (20) found (22 k cal/mol) for the second reaction of their catalyst. Other values for the activation energy of the catalysts were: Calderbank (8) -- 26 k cal/mol, Tarama (33) -- 32.4 k cal/mol. The
FIGURE 7.5 --- Calculation of Rate Constants at 400°C. (Equation 7.5).
FIGURE 7.4 — Calculation of Rate Constants at 450°C (Equation 7.5).
result in this study seemed to agree with those of Tararaa who had found that catalysts of the $V_2O_5-MoO_3$ type had higher activation energy than catalysts of pure $V_2O_5$ ($32.4 \text{ vs. } 20 \text{ kcal/mol}$).

Emmett (43) had reported the activation energy for benzene oxidation (first reaction) to be 15-28 kcal/mol, and that of maleic anhydride to be 13-16 kcal/mol. The value of 21.0 kcal/mol found in this study probably was a composite figure reflecting the oxidations of both benzene and maleic anhydride. However, the equations derived here were not the same as those of Emmett's.

The individual values of $k_1$ and $k_2$ probably were not very valid, and could serve as an approximate guideline only. This was due to the large error variance, $s^2$, of the $Y_B$ values which contributed to the scattering of the data.

An attempt was also made to correlate Yao's fixed bed data (14) using eq. (7.5). However, the data scattered widely and the number of points was too small for the correlation to be meaningful. This could be because the percent conversion ($Y_B$) was too low, hence, the ratios $(C_B)_1/(C_B)_0$ and $(C_{O_2})_1/(C_{O_2})_0$ were not accurate. Yao's data are included in Appendix D.

7.4) Oxidation of benzene

The reaction rate constants and activation energy for the disappearance of benzene could best be calculated by assuming the simplified model in Sect. 4.2 as follows:

\[
\begin{align*}
B & \xrightarrow{K_1} M \\
D & \xrightarrow{K_2} D
\end{align*}
\]

$B = \text{benzene}$  \hspace{1cm} $M = \text{maleic anhydride}$  \hspace{1cm} $D = \text{CO + CO}_2$
By using the same set of assumptions as in Sect. 4.2, the %
conversion of benzene, \( Y_B \), could be found from eq. (4.13) to be:

\[
Y_B / 100 = 1 - e^{-K'_o \theta^2 (C_{O2})_{Ave.}(W/F)}
\]

(7.6)

where \( K'_o = K' + K_2' \), and the superscript' was used to indi­
cate that the rate constants were calculated by the fixed-bed equation.
The symbols \( K_o, K_3 \), etc. (without any superscript) will be used to
denote the general terms of the individual rate constants regardless
of the methods of computation.

The use of \( W/F \) in eq. (7.6) is an arbitrary choice assuming that
the fluid voidage, \( \varepsilon \), and the density ratio, \( \rho_f/\rho_p \), are constant.
In the case of the fixed bed process, both \( \varepsilon \) and \( \rho_f/\rho_p \) would be constant.
Hence, the calculations of \( K_o \) and its corresponding activation energy
would be unaffected.

In the case of the fluidized-bed process, the variations of \( \varepsilon \) and
\( \rho_f/\rho_p \) with time could be accounted for by using the modifying term, \( \xi \).
Thus, when the distribution of contact time is considered, eq. (4.13)
becomes:

\[
Y_B / 100 = 1 - \int_0^\infty e^{-K'_o \theta^2 (C_{O2})_{Ave.}(W/F)} h(\xi) \, d\xi
\]

(7.7)

where \( K'_o \) denotes the reaction rate constant based on the contact
time distribution. The derivation of eq. (7.7) is shown in the Appendix.

The distribution function, \( h(\xi) \), has to be determined for each
range of superficial velocity. The function \( h(\xi) \) had been found by
Orcutt (12) for the velocity range of 0.3-0.48 ft./sec., using similar
catalysts as in this study. Thus, Orcutt's findings could be combined
with eq. (7.7) and the reaction rate constant \( K'_o \) calculated. The func­
tion \( h(\xi) \) vs. \( \xi \) is shown in the Appendix.
To solve for $K''$, eq. (7.7) must be rearranged to allow for a numerical integration of the function $h\left(\xi\right)$. The resulting equation is:

$$\frac{Y_B}{100} = 1 - \sum_{j=1}^{n} e^{-K'\pi} (c_{O_2})_{Ave.} \left(\frac{W/F}{F}\right) \xi_j h\left(\xi_j\right) \Delta \xi_j$$

or,

$$(7.8) \quad \frac{Y_B}{100} = 1 - \sum_{j=1}^{n} \left[ 1 - K'' \xi_j \xi_j^2 + \frac{(K'' \xi_j)^3}{2!} - \frac{(K'' \xi_j)^3}{3!} + \ldots \right] h\left(\xi_j\right) \Delta \xi_j$$

where $\xi = \pi (c_{O_2})_{Ave.} \left(\frac{W}{F}\right)$

For the calculation of reaction rate constants in this study, Orcutt's function of $h\left(\xi\right)$ vs. $\xi$ was divided into 50 $\Delta \xi$ intervals of 0.1 each (i.e., $n = 50$). The average values of $\xi$ and $h\left(\xi\right)$ were found for each interval from Orcutt's curve and tabulated in the Appendix. To calculate $K''$, the terms in the summation brackets were extended to the 9th power. By comparing the results from a 9th-power equation and a 7th-power equation, it was seen that the former would give a result sufficiently close to the true value in the exponential equation. The odd number of power was needed to insure at least one real root in the solution of eq. (7.7).

Another calculation could also be made by using the average contact time, $\tau$, as defined in eq. (5.3). This was the same as assuming a plug flow characteristic and a homogeneous process. The final solution is:

$$(7.9) \quad \frac{Y_B}{100} = 1 - e^{-K'' \pi (c_{O_2})_{Ave.} \left(\frac{RT}{\tau}\right)}$$

where $K''$ denotes the reaction rate constant as calculated by this method. The derivation of eq. (7.9) is shown in the Appendix.

The three equations (7.6), (7.8) and (7.9) were used to calculate the reaction rate constants for the disappearance of benzene. The
corresponding activation energies were found by assuming one step for the over-all reaction and applying the Arrhenius equation of the form
\[ k = Ae^{-\frac{\Delta E}{RT}}. \]

As was mentioned earlier in Section 4.2, the reaction rate constant, \( K_3 \), for the disappearance of maleic anhydride could be found only by oxidizing maleic anhydride directly. However, Emmett (43) in tabulating the data for benzene oxidation, had found the ratio of \( K_1/K_o \) (i.e., the ratio of the rate constants for anhydride formation, and for the disappearance of benzene) to be approximately 0.70 for most catalysts. If this value is combined with eq. (4.14), the resulting equation may be solved for \( K_3 \) for the fixed-bed case as follows:

\[ Y_{M/100} = \frac{0.7K''}{K_2-K_0} \left[ 1 - \frac{Y_B}{100} \right] - \frac{K''}{2} \left( \frac{C_{O_2}}{\text{Ave.}} \right) \left( \frac{W/F}{T} \right) \]

\( K_3 \) could also be calculated in the manners similar to those of eqs. (7.8) and (7.9). The corresponding equations for \( K_3 \) for the fluidized-bed case are:

\[ Y_{M/100} = \frac{0.7K''}{K_2-K_0} \left[ 1 - \frac{Y_B}{100} \right] \left[ e^{-K'' \int h(\xi) d\xi} \right] \]

or,

\[ Y_{M/100} = \frac{0.7K''}{K_2-K_0} \left[ 1 - \frac{Y_B}{100} \right] - \frac{K''}{2} \left\{ \sum_{j=1}^{n} \left[ 1 - K'' \xi_j^2 + \frac{(K'' \xi_j)^2}{2!} \right] \right\} h(\xi_j) \Delta \xi_j \]

and, for the plug flow method:

\[ Y_{M/100} = \frac{0.7K''}{K_2-K_0} \left[ 1 - \frac{Y_B}{100} \right] - \frac{K''}{2} \left( \frac{C_{O_2}}{\text{Ave.}} \right) \left( \frac{RT}{T'} \right) \]

In order to find the rate constants and the corresponding activation energies, two hypothetical runs were made from the statistical regression equations (6.2) and (6.4) together with the values in Tables 6.3 and 6.9. The runs were made to correspond to the centers of the preliminary design and the composite design respectively. This was
done to insure that the hypothetical runs were in the regions covered by the regression equations, and to provide sufficient spread in the temperature. The conditions of these two hypothetical runs are shown in Table 7.1.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>T°K</th>
<th>V cm.</th>
<th>W g.</th>
<th>W/F g-hr sec.</th>
<th>T°C</th>
<th>CO₂ per sec.</th>
<th>Y₀ %</th>
<th>Yₙ % per mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) Center</td>
<td>663</td>
<td>76.05</td>
<td>7.24</td>
<td>62.5</td>
<td>6.05</td>
<td>1.11</td>
<td>1.06</td>
<td>0.1795</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>70.66</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>14.34</td>
</tr>
</tbody>
</table>

of preliminary design

2) Center | 723 | 248.4 | 9.88 | 30.0          | 2.11| 0.654       | 1.17 | 0.1990       |
|           |     |       |      |               |     |             |      | 93.60        |
|           |     |       |      |               |     |             |      | 28.69        |

The reaction rate constants for the disappearance of benzene (K₀) and for the disappearance of maleic anhydride (K₄), assuming K₄/K₀ = 0.7 are shown in Table 7.2.

<table>
<thead>
<tr>
<th>Equation No.</th>
<th>(7.6)</th>
<th>(7.10)</th>
<th>(7.8)</th>
<th>(7.11)</th>
<th>(7.9)</th>
<th>(7.12)</th>
<th>K₀</th>
<th>K₃</th>
<th>K₃/K₀</th>
<th>K₀</th>
<th>K₃</th>
<th>K₃/K₀</th>
<th>K₀</th>
<th>K₃</th>
<th>K₃/K₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conditions (1), 390°C</td>
<td>1.01</td>
<td>2.03</td>
<td>2.01</td>
<td>1.19</td>
<td>0.89</td>
<td>0.75</td>
<td>384</td>
<td>286</td>
<td>0.75</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Conditions (2), 450°C</td>
<td>4.78</td>
<td>2.17</td>
<td>0.44</td>
<td>2.78</td>
<td>1.96</td>
<td>0.71</td>
<td>1093</td>
<td>495</td>
<td>0.44</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Unit of rate constant per mol.

<table>
<thead>
<tr>
<th></th>
<th>g mol/hr.g.cat.atm²</th>
<th>g mol/hr.g.cat.atm²</th>
<th>g mol/hr.l.atm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activation energy, kcal per mol.</td>
<td>24</td>
<td>1.0</td>
<td>13.4</td>
</tr>
</tbody>
</table>
Equations (7.6) and (7.10) were also applied to Yao's fixed bed data. However, since no hypothetical run could be calculated from Yao's regression equation, the calculations were made directly on the individual runs. To calculate the activation energy, the values of the rate constants were averaged logarithmically from two groups. The first group included Runs $C_1 - C_4$, and represented the average temperature of 698°K. The second group included Runs $C_5 - C_8$, and represented the average temperature of 725°K. The rate constants, their logarithmic averages and the corresponding activation energies, $\Delta E$, are shown in Tables 7.3 and 7.4.

Table 7.3 Reaction rate constants in fixed-bed (12)

<table>
<thead>
<tr>
<th>Run No.</th>
<th>$W/F$ g.hr. per mol</th>
<th>$C_{O_2}$</th>
<th>$T$ atm.</th>
<th>$T_0$ K</th>
<th>$Y_H$ %</th>
<th>$Y_M$ %</th>
<th>$K_0'$ g.mol/hr.g.cat.atm$^2$</th>
<th>$K_3'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_1$</td>
<td>13.09</td>
<td>20.45</td>
<td>0.983</td>
<td>700</td>
<td>16.42</td>
<td>8.02</td>
<td>0.078</td>
<td>0.053</td>
</tr>
<tr>
<td>$C_2$</td>
<td>13.13</td>
<td>20.60</td>
<td>0.970</td>
<td>701</td>
<td>12.53</td>
<td>4.20</td>
<td>0.053</td>
<td>0.053</td>
</tr>
<tr>
<td>$C_3$</td>
<td>11.22</td>
<td>20.32</td>
<td>0.978</td>
<td>697</td>
<td>23.86</td>
<td>17.08</td>
<td>0.124</td>
<td>0.119</td>
</tr>
<tr>
<td>$C_4$</td>
<td>11.28</td>
<td>19.73</td>
<td>0.978</td>
<td>696</td>
<td>25.08</td>
<td>15.06</td>
<td>0.135</td>
<td>0.124</td>
</tr>
<tr>
<td>$C_5$</td>
<td>13.10</td>
<td>20.32</td>
<td>0.983</td>
<td>721</td>
<td>22.57</td>
<td>5.10</td>
<td>0.0995</td>
<td>0.097</td>
</tr>
<tr>
<td>$C_6$</td>
<td>13.10</td>
<td>19.73</td>
<td>0.972</td>
<td>726</td>
<td>18.20</td>
<td>4.24</td>
<td>0.082</td>
<td>0.084</td>
</tr>
<tr>
<td>$C_7$</td>
<td>11.29</td>
<td>19.95</td>
<td>0.983</td>
<td>730</td>
<td>41.11</td>
<td>22.83</td>
<td>0.248</td>
<td>0.175</td>
</tr>
<tr>
<td>$C_8$</td>
<td>11.32</td>
<td>19.98</td>
<td>0.977</td>
<td>721</td>
<td>35.56</td>
<td>19.16</td>
<td>0.204</td>
<td>0.185</td>
</tr>
</tbody>
</table>

Table 7.4 Average rate constants and activation energies in fixed bed (12)

<table>
<thead>
<tr>
<th>$K_0'$</th>
<th>$K_3'$</th>
<th>$K_3'/K_0'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.091</td>
<td>0.080</td>
<td>0.88</td>
</tr>
<tr>
<td>0.143</td>
<td>0.127</td>
<td>0.89</td>
</tr>
<tr>
<td>17.35</td>
<td>17.80</td>
<td>----</td>
</tr>
<tr>
<td>(kcal/mol)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
7.5) **Results of the Fixed and Fluidized Operations**

Inspection of Table 7.2 showed that the three different methods of computing the rate constants and activation energies in the fluidized bed gave divergent results in terms of $\Delta E$ and the ratio $K_3/K_0$. On the theoretical basis alone, the second method in which the contact time distribution was incorporated into the rate equation giving rise to $K'_0$ and $K'_3$ should provide the most accurate results. This was borne out by comparison of the $\Delta E$ and $K_3/K_0$ values between the fixed bed results and those obtained from the three methods of analysis in the fluidized bed (Table 7.2 vs. Table 7.4). Since the same type of catalysts were used in both operations, it could be expected that, unless the controlling mechanisms varied widely, the values of $\Delta E$ and the ratio $K_3/K_0$ should be similar in both operations. This condition was more closely met when the contact time distribution in the fluidized bed was taken into account, provided, of course, that the reaction could be assumed to be first-order. For a second-order reaction, the contact time distribution would be of little value. This was because the effect of the timewise variation of concentrations in the fluidized bed was linearly additive only for the first-order reactions.

For the fixed-bed process, the activation energies for both $K_0$ and $K_3$ were found to be about 17-18 kcal/mol. This compared favorably with other values found in the literature. For example, Holsen's data (19) gave the value of $\Delta E$ for $K_0$ to be 19-20 kcal/mol, and for $K_3$, the value was 13-14 kcal/mol. Steger's data as tabulated by Emmett (43) gave the value of $\Delta E$ for both $K_0$ and $K_3$ to be 15-16 kcal/mol.

For the fluidized process, the $\Delta E$ values were somewhat low. This
could be due to the fact that the reaction had proceeded to almost completion, especially at high temperatures. In fact, if one considered the fraction $f_b$ of the gas that bypassed the bed as given by Orcutt (12) to be about 0.05-0.08, in the fluidized operation at 450°C (See condition (2) in Table 7.1), all the reactant that had come into contact with the catalysts had reacted, and the fraction unreacted was equal to the fraction bypassed.

The main difference between the results with fixed and fluidized beds is in the values of the reaction rate constants themselves. By considering only the rate constants $K_0$ and $K_3$ of the fluidized bed (i.e., the rate constants found by taking into account the contact time distribution), the fluidized rate constants were between 10-20 times those of the fixed bed. No satisfactory explanation could be made for this difference.

A rough estimation of the mass transfer coefficients in both the fixed and fluidized reactors was also made using the method given by Hougen and Watson (27). It was found that the mass transfer coefficient, $k_g$, was at least 10 times greater than the corresponding $K_0$ and $K_3$. Hence, it could be assumed that diffusion was not a rate controlling step in these operations.

There seems to be two possible explanations for the difference in the rate constants found in these two reactors. Pinchbeck (29) had found the variation in the effectiveness of $V_2O_5$ catalysts to be related to the apparent densities of the catalysts rather than to the actual chemical compositions. It is then possible that the fixed and fluidized-bed catalysts, though of the same chemical compositions, may have
differed in certain physical properties, such as densities, pore areas, etc. The difference in physical properties could have arisen from the methods of compaction or pelletization of the catalysts into their respective final forms. Thus, the effectiveness factors of the two catalysts would be different.

On the other hand, Tandy (31) had found that the catalyst mixture of $\text{V}_2\text{O}_5:K_2\text{SO}_4$ had a broad melting range from about 400-410°C. This is in the operating temperature range of the benzene process. Thus, it is possible that at this condition, the catalyst would be in the form of viscous liquid coated on the alumina support. In this case, the fluidized catalyst particles would certainly have a much larger surface area per unit weight than the fixed-bed particles, since the pore surface would not be available for reaction. The fixed-bed particles were of a cylindrical shape, 0.5 mm. diameter x 0.5 mm. height, compared to the spheroidal fluidized particle's average diameter of 50 microns. By assuming a smooth surface, the external surface of the fixed-bed catalyst was found to be about 6 cm.$^2$/g., and that of the fluidized bed catalyst was about 600 cm.$^2$/g, giving the ratio of the two surface areas to be about 100. This figure, however, would decrease rapidly with an increase in pore surface. For example, if the residual pore surface is 60 cm.$^2$/g. for both catalysts, the area ratio would be only 10. Thus, it is conceivable that the difference in the reaction rate constants between the two operations may be due to the difference in the surface areas of the two catalysts at high temperatures.

Another interesting point is the similar values of the activation
energies for both the disappearance of benzene ($K_o$), and the disappearance of maleic anhydride ($K_3$). If it could be assumed that the overall reactions of the oxidation of benzene and maleic anhydride are essentially first-order or pseudo first-order, it would then indicate that both of these reactions contain the same rate-controlling step. In this case, the step would be the chemisorption or re-oxidation of oxygen onto the catalyst surface. However, this point still needs to be confirmed by direct oxidation of maleic anhydride to determine the overall mechanisms of this reaction.

7.6) **Comparison of the Fixed and Fluidized Operations**

A comparative study on the yields and selectivity obtained in the fixed and fluidized reactors may be made based on the simplified model shown in Sections (4.2) and (7.4), and the set of equations (7.6), (7.7), (7.10) and (7.11). For convenience, these equations are again listed as follow:

\[
\begin{align*}
\text{Fixed-bed reactor} \\
Y_B/100 &= 1 - e^{-K_0 \gamma} \\
Y_M/100 &= \frac{0.7K_o}{K_3 - K_o} \left[1 - \frac{Y_B}{100} - e^{-K_3 \gamma}\right]
\end{align*}
\]

**Fluidized-bed reactor**

\[
\begin{align*}
Y_B/100 &= 1 - \int e^{-K_3 \gamma} h(\gamma) d\gamma \\
Y_M/100 &= \frac{0.7K_3}{K_3 - K_o} \left[1 - \frac{Y_B}{100} \int e^{-K_3 \gamma} h(\gamma) d\gamma\right]
\end{align*}
\]

where \( \gamma = \frac{1}{\overline{W/F}} (C_{O_2})_{Ave} \)

It should be pointed out that the above four equations are based on first-order reactions with respect to benzene and maleic anhydride, whereas the concentration of oxygen is held constant. Moreover, the ratio of the rate constants between the formation of maleic anhydride
and the disappearance of benzene ($K_1/K_0$) is assumed to be 0.70. The effect of this last assumption is that the equations for $Y_M$ are multiplied by 0.70 as shown in eqs. (7.9) and (7.10). Other values of the ratio $K_1/K_0$ could also be used.

To make a comparison between the fixed-bed and fluidized-bed operations, plots of $Y_B$, $Y_M$ and $S$ (i.e., $Y_M/Y_B$) were made with respect to $\gamma$. These are shown in Figures 7.5 - 7.9, with the ratio $K_3/K_0$ as parameters. For ease of comparison, the values of both $K_0$ in all figures were made equal to 2.8 which was the value of $K^{''}_0$ at 450°C as found in Table 7.2. The values of $K_3'$ and $K_3''$ were then varied to provide different ratios of $K_3/K_0$.

In Figure 7.5 where $K_3 = 0$, i.e., no disappearance of maleic anhydride, the selectivity of both the fixed and the fluidized operations are equal, though the yields $Y_M$, and $Y_B$ are lower for the fluidized case. In Figures 7.6 - 7.9, where the ratio $K_3/K_0$ are increased from 0.1-2.0, the curves for $Y_B$, of course, remain fixed, since $K_0'$ and $K_0''$ are taken as 2.8 throughout. For the fixed bed case, $Y_M$ reaches a maximum then decreases rapidly. Similarly, the $S$ curves for the fixed bed starts at 70% (as fixed by the given value of $K_1/K_0$), then decreases to an asymptote along the $Y_M$ curve. On the other hand, for the fluidized case, the $Y_M$ and $S$ curves reach the maxima then decrease slowly. At higher values of $\gamma$, the fluidized bed gives better yield and selectivity than the fixed bed. However, the maximum performance of the fluidized bed is always lower than that of the fixed bed.

Figure 7.10 shows the comparison between the performance of the fluidized reactor at its optimum conditions versus that of the fixed
FIGURE 7.5 — Comparison between Fixed and Fluidized Operations.

- **Fixed Bed**
- --- **Fluidized Bed**

- $K'_0 = K''_0 = 2.8$
- $K'_3 = K''_3 = 0$
- $K_3 / K_0 = 0$
Figure 7.6 — Comparison between Fixed and Fluidized Operations.
FIGURE 7.7 — Comparison between Fixed and Fluidized Operations.

\( \Theta, \text{atm}^2 \cdot \text{g} \cdot \text{cat} \cdot \text{hr} / \text{mol} \)

- **Fixed Bed**
- **Fluidized Bed**

- \( K' = K'' = 2.3 \)
- \( K'_3 = K''_3 = 0.7 \)
- \( K'_3 / K'' = 0.25 \)
**FIGURE 7.8** — Comparison between Fixed and Fluidized Operations.
FIGURE 7.9 --- Comparison between Fixed and Fluidized Operations.

\( Y_b(\text{fix.}) \)

\( Y_b(\text{fluid.}) \)

\( S(\text{fix.}) \)

\( S(\text{fluid.}) \)

\( Y_M(\text{fix.}) \)

\( Y_M(\text{fluid.}) \)

**Fixed Bed**

\( K' = K'' = 2.3 \)

\( K_3 = K_3' = 5.6 \)

\( K_3/K_0 = 2.0 \)

**Fluidized Bed**

\( \bar{\psi} \), atm²·g·cat·hr/mol
Comparison between Fixed and Fluidized Operations
bed reactor. The optimum conditions of the fluidized reactor are as shown in eq. (7.2). The temperature of the reactor is 453°C, the air/benzene ratio is 269, and the value of \( W/F \) is 1.39, with \( W \) being 19.7 g. For the fixed bed reactor, the temperature is 448°C, and the value of \( W/F \) is about 12.1. At this point, the values of \( K'_O \) and \( K'_3 \) are 0.143 and 0.127 respectively (see Table 7.4). As could be seen, the smaller values of \( K'_O \) and \( K'_3 \) decrease the effect of \( \gamma \) on the yields \( Y_B \) and \( Y_M \), and on the selectivity \( S \). Thus, a large change in the value of \( \gamma \), or, in effect, in the value of \( W/F \), does not seriously change \( Y_M \) or \( S \). In fact, the fixed-bed reactor should be operated at a much higher value of \( W/F \) to obtain a maximum yield of \( Y_M \).

On the other hand, for the fluidized bed, due to the large values of \( K''_O \) and \( K''_3 \), the effect of \( \gamma \) on \( Y_M \) and \( S \) is more pronounced. In addition, to achieve the maximum value of \( Y_M \), the reactor had to be operated such that \( Y_B \) was quite high. This explains why in this study, the yield \( Y_M \) was usually higher than in Yao's fixed bed, but the selectivity was much poorer.

It should be mentioned here that in the oxidation of naphthalene to form phthalic anhydride, the activation energies for the disappearance of naphthalene and of phthalic anhydride were also found to be about the same value (26-30 kcal/mol), (23). The higher value of the activation energy could be due to the catalyst compositions (22). Thus, it would seem that the rate-controlling step for the naphthalene process would also be the chemisorption of oxygen to the catalyst surface, and possibly, the naphthalene process could be represented by a simplified first-order model similar to that used in this study.
However, there is a difference between the naphthalene and the benzene oxidation. It is well known that naphthalene could be oxidized economically in a fluidized bed, whereas benzene is oxidized commercially only in a fixed-bed reactor. While the actual basic mechanism of the naphthalene oxidation may not be known, it seems very probable that the ratio between the rate constant for the disappearance of phthalic anhydride to that of the disappearance of naphthalene (i.e., its corresponding $k_2/k_0$) would be low. Thus, the performances of the fluidized and the fixed-bed reactors would be close together (see Figs. 7.5 and 7.6). This may be due to the inherent stability of the benzenoid structure that exists in phthalic anhydride as compared to the vinyl structure of maleic anhydride. In addition, the naphthalene process is usually operated at a lower temperature range (ca. 300 °C) than for benzene. Thus, the disappearance of phthalic anhydride could be expected to be lower than that of maleic anhydride. This is one reason why the fluidized reactor is economically feasible for the naphthalene oxidation process.
Chapter VIII

CONCLUSIONS

Contour equations defining the \% disappearance of benzene, the \% yield and the \% selectivity of maleic anhydride were developed statistically. Of these, the \% yield of maleic anhydride was optimized with respect to temperature, reactant ratio, fluidizing velocity and catalyst weight. The optimum region was found near 450°C, with an air/benzene ratio of about 250, fluidizing velocity of 10 cm./sec., and catalyst weight of 30 g. The resulting W/F ratio was 2.11. In the optimum region, the effect of temperature on the \% yield was small, but the combined effect of fluidizing velocity and catalyst weight, corresponding to the effect of (W/F), was large. The maximum yield of maleic anhydride was found to be about 30\%.

Comparison between the fixed bed process and the fluidized bed process using the same type of catalysts showed that, while the yield of maleic anhydride in the fluidized reactor was generally higher than that of the fixed bed reactor, the \% selectivity was much poorer. The maximum selectivity obtained for the fluidized process was about 36\%; whereas in the fixed bed process, the maximum obtained was 71\%. This was attributed to the larger reaction rate constant ratio of $K_3/K_0$ found in the fluidized reactor.

Both the fluidized bed and the fixed bed data were treated using kinetic rate equations based on pseudo-first-order reaction on benzene
and oxygen. For the fluidized reactor, the rate equation was modified to reflect the contact time distribution in the bed zone. By assuming a simplified model for the reaction paths, the rate constants for the disappearance of benzene and of maleic anhydride were found, and the activation energies calculated.

The activation energies for the disappearance of benzene and of maleic anhydride were found to be 12-13 kcal/mol in the case of the fluidized reactor, and 17-18 kcal/mol in the fixed-bed reactor. The difference was assumed to be partially due to the near-completion of the reactions in the fluidized bed. The activation energy for the re-oxidation of catalyst was also found to be 21.0 kcal/mol in the fluidized bed. The high values of the activation energy would tend to exclude diffusion as a rate controlling step.

The rate constants of the fluidized-bed were found to be 10-20 times higher than those of the fixed-bed. This could be due to the larger surface area per unit weight of the fluidized catalysts at the operating temperature of the reactors, or in the physical difference between the two catalysts.

The equal values for the activation energies for both the disappearance of benzene and of maleic anhydride led to the hypothesis that the controlling mechanism may have been the re-oxidation of the catalyst surface.

Comparison of the yield and selectivity of the two operations indicates that the fluidized reactor would be economical or come close to the performance of the fixed reactor only when the catalysts employed are such that the ratio of the over-all rate constants for the disappearance of maleic anhydride and the disappearance of benzene ($K_3/K_0$)
is low (probably in the range of 0-0.1).

The variation of \((W/F)\) was limited in the fluidized bed by the fluidizing velocity range of the catalyst particles. Since the mean particle diameter of the catalyst particles was low (50 microns), the range of fluidizing velocity was limited to about 6-11 cm./sec. (0.2-0.35 ft./sec.). With such a small range of \((W/F)\), no calculation of the mechanisms by the initial rate method was possible.
Chapter IX

RECOMMENDATIONS

With regards to the possible mechanism of the oxidation process, several recommendations could be made. These are:

1) A study of the oxidation of maleic anhydride directly to find the true value of the rate constant, $K_3$. This, together with the present work, would allow one to calculate all the rate constants in the simplified model. This could be done with pure maleic anhydride or with a mixture of benzene and radioactive maleic anhydride. The former method would be simpler, but may not represent the true conditions in the reactor. In the development of the basic rate-controlling mechanism, the activities of the various gas components are accounted for. However, in the simplified model, some of these activities are assumed to be constant and carried over into the reaction rate constants. If the latter method is used, one will also want to vary the concentration of the radioactive maleic anhydride to make sure that its effect is not carried over into the simplified rate constants.

2) In view of the limitation on the fluidizing velocity encountered in this study, it is suggested that larger-sized particles be used in the fluidization study. This would allow a wider variation of the ratio ($W/F$), and make it possible to calculate the rate mechanism.
by way of the initial rate method. This would provide a mean for confirming the possible mechanisms derived from the integral equations. Along this same line, if several sizes of catalyst particles are used, one may check on the effect of surface area (at the reactor conditions) on the reaction rate constants.

All the catalysts, however, should have the same chemical composition. Different catalysts may produce different values of the activation energies, as indicated by Tarama (22).

3) In order to find the basic kinetic mechanisms of the reaction, a new reactor that could withstand high pressures should be built, so that the reactions could be studied at various pressures. In this case, isotherms of conversion versus (W/F) could be found, and the basic mechanism deduced.

The new reactor should be of the same size and shape as the present one. Whether a straight-tubed fluidized reactor or a tapered one is used, one would still have to find the contact time distribution in the reactor. However, by using reactors of the same size and shape, at least one variable would be eliminated.

The problem of determining the contact time distribution may be more difficult to judge. As mentioned earlier, the contact time distribution has some value only in the case of a first order reaction. In this study, a pseudo-first order reaction was assumed and the contact time distribution seemed to work well. However, the actual basic rate equation may not involve a first-order reaction (particularly with regard to oxygen).

On the other hand, the value of the contact-time distribution lies
in better approximation of the results obtained from a fluidized reactor. Thus, for any fluidized reactor in use, it is imperative that the contact-time distribution be found. This could be done by using benzene alone in the reactor and calculating the distribution by way of Laplace transforms in the same manner as Orcutt's (12). This method necessitates knowing the true value of the rate constant (for the disappearance of benzene) beforehand. As was shown in Sect. VII, the rate constant also varies with the size of the catalyst particles. Thus, the determination of the rate constant must be done with the same sized catalyst as that to be used in the fluidized bed. This could be done either with a fixed bed or a stirred tank reactor.

Another problem involved in using the Laplace transform method was the large variation of the \( \frac{W}{F} \) ratio needed. Thus, the catalyst has to be properly sized to allow for a wide range of fluidizing velocity.

The second method for determining the contact time distribution is to inject inert gas sinusoidally or as a step function into the bed zone. This is a shorter method, but, the resulting distribution will be that of holding time only (i.e., the time a particle of gas stays in the bed zone, but not necessarily contacting the catalysts, however, the discrepancy is only about 5-8%). A third method would be to inject radioactive reactants (benzene or maleic anhydride) into the inlet stream (containing ordinary reactants). This would give the true contact time distribution of the bed. Possibly, both of these last two methods could be used, since one would also obtain the fraction \( f_b \) of the gas by-passing the bed.
4) With regards to the role of oxygen in this process, a set of experiment should be made to determine the effect of oxygen concentrations. In this study, oxygen concentration was held constant, and thus, the assumption of pseudo-first-order with regard to oxygen was justified. Future experiments should be made with oxygen being varied. This would determine whether the rate controlling step is really the chemisorption of oxygen or not. Radioactive oxygen could also be injected into the inlet stream to determine the contact time distribution and fraction by-passed.

Along the same line, one could also vary the size distribution (and the surface area per unit weight) of the catalyst in order to determine the possibility of dissociation of absorbed molecules on the catalysts.

5) In order to compare the naphthalene process with the benzene process, it is necessary to determine the rate constants for the disappearance of both naphthalene and phthalic anhydride. Comparison of the ratios \( \frac{K_3}{K_0} \) for naphthalene and benzene would explain why phthalic anhydride could be produced economically in the fluidized reactor.

As in the case of benzene, separate experiments must be made to determine the rate constants for the disappearance of naphthalene and that of phthalic anhydride. The terms \( K_0 \) and \( K_3 \) could then be calculated independently. Comparison of the values with the benzene process would also provide some informations concerning the possible rate-controlling step. It should be emphasized that the above comparison would be meaningful only if the same type of catalysts were used in both
processes.

6) With regards to the operations of the reactor itself, it is suggested that a more accurate benzene injection system be used. Thus, instead of a pump, a constant pressure control system may be used to inject benzene into the inlet stream. Another method would be to bubble air through benzene in a constant-temperature bath. This would give accurate measurement of benzene when the amount needed is extremely small.

The analytical method ultimately used in this study, though reliable, was time-consuming. The gas analysis should be improved so that the analysis of benzene could be made quicker. Thus, a better hydrogen-flame ionization gas chromatography unit could be used to analyze both benzene and maleic anhydride at the same time, either in the gaseous or liquid forms. Other analytical methods such as mass spectrometer could also be used.

Though the analysis of the gaseous components, namely, CO, CO₂, O₂ and N₂, could be made accurately in the Beckman GC-2 gas chromatography unit, two columns are needed and the method is slow. It may be possible that other analytical equipment such as an infrared spectrometer could be in conjunction with the GC-2 unit. Thus, CO, O₂ and N₂ may be analyzed in the GC-2, whereas CO₂ may be analyzed in the infrared spectrometer.
APPENDIXES
A. Calibrations of Instruments

1. Air Orifice Meter

2. Beckman GC-2 gas chromatograph
   a) for O₂, N₂, CO and CO₂
   b) for benzene

3. Hy-Fi gas chromatograph
   a) for benzene
   b) for maleic anhydride

4. Sample of the titration curve for maleic anhydride.

1) Air Orifice Meter

   The air flow rate was measured by an orifice meter with a 1/16 in. diameter orifice in a ½ in. pipe tube. The orifice meter was calibrated using a wet test meter with a manometer containing a solution of 1:1 glycerin-water (by volume). The following equation was fitted using the least square method.

   \[
   \text{\( W_{\text{Air}} = 0.1543 + 1.6627 (\Delta P \cdot \rho_{\text{Air}})^{1/2} \)}
   \]

   where
   - \( W_{\text{Air}} = \text{gram of air/minute} \)
   - \( \Delta P = \text{pressure drop across the orifice in mm. of the glycerin solution} \)
   - \( \rho_{\text{Air}} = \text{air density at the upstream condition in lb/cu. ft.} \)
The range of the calibration was from 2.5-6.5 g. of air per minute. The average error was ±1%.

2) Beckman GC-2 Gas Chromatograph
   a) Calibration of O₂, N₂, CO and CO₂.

   To calibrate the GC-2 gas chromatograph, gas mixtures of different compositions of O₂, N₂, CO and CO₂ were prepared in a 100 ml. gas burette with a water jacket. The confing liquid was an acidic sodium sulfate solution containing 20% by weight of sodium sulfate and 5% by volume of sulfuric acid. To assure homogeneity, the gas mixtures were stirred with small glass beads which were left in the burette. The mixtures were left overnight before analysis.

   The gas chromatograph was equipped with two 1-cc. sampling valves. Since the two valves were not of identical volumes, each gas component was calibrated in both valves and separate equations fitted by the Least Square method. To correct for the day-to-day variation in atmospheric pressure, a reading of nitrogen in air was taken before any gas mixture was analyzed. The actual gas reading was then corrected to the standard value set at the beginning of the calibration. Table 10.1 contains the pertinent informations of the calibration.

   Table 10.1 --- Calibration of GC-2 Gas Chromatograph for gas analysis

<table>
<thead>
<tr>
<th>Component</th>
<th>Column</th>
<th>Attenuation</th>
<th>Elution time (min.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂</td>
<td>Molecular sieve</td>
<td>20</td>
<td>1:30</td>
</tr>
<tr>
<td>N₂</td>
<td>Molecular sieve</td>
<td>20</td>
<td>2:30</td>
</tr>
<tr>
<td>CO</td>
<td>Molecular sieve</td>
<td>1</td>
<td>9:30</td>
</tr>
<tr>
<td>CO₂</td>
<td>Silica gel</td>
<td>1</td>
<td>2:30</td>
</tr>
</tbody>
</table>
The compositions of the column packing had been shown in Sect. 5.2. The procedure was first to run one gas sample through each valve and analyzed for \( \text{O}_2 \), \( \text{N}_2 \) and \( \text{CO} \) with the molecular sieve column. Next, the silica gel column was then put in place and one more gas sample was sent through each valve to analyze for \( \text{CO}_2 \). Thus, the actual value of the gas composition was an average of two readings. The calibrations for each gas component were summarized in Table 10.2. These are also designated as equations (10.2). Since argon is eluted out at the same time as \( \text{O}_2 \), the mol \% of \( \text{O}_2 \) found in this manner will be too high due to the amount of argon present. The amount of argon is assumed to be constant at 1.0\% in all samples. Thus, it has no effect on the material balance calculation.

<table>
<thead>
<tr>
<th>Valve Position</th>
<th>Gas Component</th>
<th>Equation (10.2)</th>
<th>Range</th>
<th>Max. error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Right</td>
<td>( \text{N}_2 )</td>
<td>( Y = 0.09378X + 0.035 )</td>
<td>75-91%</td>
<td>±1.5%</td>
</tr>
<tr>
<td></td>
<td>( \text{O}_2 )</td>
<td>( Y = 0.09962X - 0.044 )</td>
<td>8-24%</td>
<td>±1.5%</td>
</tr>
<tr>
<td></td>
<td>( \text{CO} )</td>
<td>( Y = 0.004796X - 0.002 )</td>
<td>0.6-6.0%</td>
<td>±1.0%</td>
</tr>
<tr>
<td></td>
<td>( \text{CO}_2 )</td>
<td>( Y = 0.0045915X - 0.048 )</td>
<td>0.6-5.5%</td>
<td>±1.5%</td>
</tr>
<tr>
<td></td>
<td>( \text{N}_2 )</td>
<td>( Y = 0.09569X - 0.100 )</td>
<td>75-91%</td>
<td>±1.5%</td>
</tr>
<tr>
<td></td>
<td>( \text{O}_2 )</td>
<td>( Y = 0.10011X + 0.116 )</td>
<td>8-24%</td>
<td>±1.5%</td>
</tr>
<tr>
<td></td>
<td>( \text{CO} )</td>
<td>( Y = 0.004823X + 0.021 )</td>
<td>0.6-6.0%</td>
<td>±1.0%</td>
</tr>
<tr>
<td></td>
<td>( \text{CO}_2 )</td>
<td>( Y = 0.0047126X - 0.054 )</td>
<td>0.6-5.5%</td>
<td>±1.5%</td>
</tr>
</tbody>
</table>

where \( Y = \% \) of the gas in the mixture.

\[ x = \text{actual integrator rdg.} \times \text{standard value} \]

Integrator value for \( \text{N}_2 \) in an air sample

Standard value for the right valve = 832

Standard value for the left valve = 818

b) **Calibrations of Benzene**

Benzene-air mixtures were prepared from a saturated solution of
benzene in air. A small amount of benzene was put in a 150 cc. glass tube with a rubber disk. After shaking vigorously and then letting the tube come to rest overnight, small amounts of the benzene-saturated air in the tube were drawn out through the rubber disk with a small gas syringe. These small amounts were then diluted with air in other glass tubes to the desired concentrations. The mixing tubes whose volumes were known were connected to a mercury reservoir so that the pressure inside the tube could be adjusted to equal to the atmospheric pressure. After shaking with glass beads, the mixed solutions were allowed to come to equilibrium overnight before being used for calibration.

The column used was an Anachrom ABS column described in Sect. 5.2. To correct for the day-to-day variation, readings of nitrogen in air were taken and used for correction in the same manner as in the gas analysis. The necessary informations were as followed:

- Temperature of column: 80°C
- Attenuation: 200
- Column pressure: 20 psig.
- Current: 250 milliampere
- Range of concentrations: 0.008 - 0.09%
- Average error: ±3%

The fitted equation was found to be:

\[(10.3) \quad Y = 0.584 \times 10^{-3}X + 0.739 \times 10^{-5}X^2\]

where \(Y\) = % benzene in the sample

\[X = \frac{\text{ave. integrator rdg. from both valves} \times 200}{\text{integrator value for } N_2 \text{ in an air sample}}\]
3) **Hy-Fi Gas Chromatograph**

The Hy-Fi gas chromatograph has a hydrogen-flame ionization detector to detect the amounts of vaporized organic materials. The operating data were as followed:-

- **Column temperature**: 135°C
- **Injection point temperature**: 200°C
- **Hydrogen flow rate**: 25 ml./min.
- **Nitrogen flow rate**: 25 ml./min.
- **Input impedance**: For maleic anhydride solution, $10^7$ ohms
  
  For benzene in gas $10^9$ ohms.
- **Output sensitivity**: 1X
- **Signal attenuation**: For maleic anhydride: 16
  
  For benzene: 128
- **Elution time**:–
  
  - **Acetone**: 0.9 min.
  - **Maleic anhydride**: 5.2 min.
  - **Benzene**: 2.7 min.

For benzene, the procedure was to inject several 50-ul gaseous samples into the column. This could be done while the reactor was being run, since the gas samples could be taken from the outlet stream. For maleic anhydride, the collected solids were rinsed out of the cold traps with acetone after the run was completed. The acetone solution of maleic anhydride was then injected into the Chromatograph.

The sample size was 1ul. Figures 10.1 and 10.2 represented the calibrations for benzene and maleic anhydride respectively.

4) **Titration of maleic anhydride**

Ten cc. of the acetone solution of maleic anhydride were diluted
with water to about 50 cc. This was then titrated with a standard 0.25 N NaOH in a Fisher titrimeter. Platinum and calomel electrodes were used. The titrimeter was first standardized with a pH-8 buffer solution of boric acid. Readings were taken of the amounts of base used and the corresponding pH values. These were then plotted to determine the equivalent point. There were two equivalent points; the first one occurred at around pH5 and was discarded. The second one was the true equivalent point and occurred at about pH9.3. The accuracy of the method was checked by titrating a known solution of maleic anhydride. The probable error was ±1%. Figure 10.3 showed a sample of the titration curve.
FIGURE 10-1 — Calibration Curve for Benzene in Air Mixture.
FIGURE 10-2 — Calibration Curve for Maleic Anhydride.
FIGURE 10.3 --- Sample Titration Curve.

Equivalent point for maleic anhydride
B. Summary of the Analysis of Variance

The formulas used in the regression analysis are presented below:

\( x_1, x_2, \ldots, x_k \) - observable independent variables (total no. = k)

\( y \) - observable independent variable

\( y_j, x_{ij} \) - \( j^{th} \) observations of the dependent variable and the \( i^{th} \) independent variable (i.e., "j" denotes the number of the set of observations where the total no. = n).

a) Sample means:

\[
\bar{x}_i = \frac{1}{n} \sum_{j=1}^{n} x_{ij}
\]

\( \bar{y} = \frac{1}{n} \sum_{i=1}^{n} y_i \)

b) Unbiased standard deviation:

\[
s_i = \sqrt{\frac{1}{n-1} \sum_{i=1}^{n} (x_{ij} - \bar{x}_i)^2}
\]

\( s_y = \sqrt{\frac{1}{n-1} \left[ \sum_{j=1}^{n} (y_j - \bar{y})^2 \right]} \)

c) Unbiased covariance:

\[
s_{iy} = \frac{1}{n-1} \sum_{j=1}^{n} (x_{ij} - \bar{x}_i)(y_j - \bar{y})
\]

d) Correlation coefficient:

\[
r_{iy} = \frac{s_{iy}}{s_i \cdot s_y}
\]

The array of \( r_{iy} \) includes \( i = 1, 2, \ldots, k \). Elements of the inverse correlation matrix are denoted by \( r_{iy} \).

\[
b_i = r_{iy} \cdot r_{iy}, \quad i = 0.
\]

\[
b_0 = \left( \sum_{j=1}^{n} y_j \right) / s_y
\]

e) Regression coefficients:

\[
a = s_y \cdot b_i / s_i, \quad i = 0.
\]

\[
a_o = y - \sum_{i=1}^{k} a_i \bar{x}_i
\]

f) Square of multiple correlation:

\[
R^2 = \sum_{i=1}^{k} b_i r_{iy}
\]
C. Fluidization

1. Fluidization correlation based on Zenz's method (13).
2. Holding time distribution by Romano (46).
3. Contact time distribution by Orcutt (12).

1. Fluidization correlation based on Zenz's method (13)

In attempting to compute the fluidization curve for an aggregate fluidization system, Zenz based his calculation on the terminal or free velocity of the average particle in the bed of solids. By assuming an isolated solid sphere moving in an infinite expanse of fluid, the drag coefficient may be expressed as:-

\[(10.11) \quad C_d = \frac{4}{3} \frac{D_p}{D_p} \frac{\left(\frac{\epsilon_p}{\epsilon_f} - \frac{\epsilon_f}{\epsilon_f}\right)}{V^2}\]

\(D_p\), the particle diameter is taken to be the geometric mean diameter of the particles' size distribution.

Similarly, the particle's Reynolds' number is calculated by:-

\[(10.12) \quad Re = \frac{D_p}{\epsilon_f} V / u_f\]

A simplified plot is made, if, instead of plotting \(C_d\) vs. \(Re\), one plots the function \((C_d Re^2)^{1/3}\) vs. \((Re C_d)^{1/3}\), whereby:-

\[(10.13) \quad (C_d Re^2)^{1/3} = \frac{D_p}{\epsilon_f^2} \left[ \frac{(\epsilon_p) u_f^2}{\epsilon_f (\epsilon_p - \epsilon_f)} \right]^{1/3}\]

and,

\[(R e^2 C_d)^{1/3} = \frac{V}{\epsilon_f} \left[ \frac{\epsilon_p}{\epsilon_f^2} \frac{(\epsilon_p - \epsilon_f) \epsilon_p}{\epsilon_f} \right]^{1/3}\]

Thus, in effect, this becomes a plot of \(V\) vs. \(D_p\) with the bracketed denominators of the abscissa and ordinate as constants on the physical properties of fluid and particles. Figure 10.4 shows Zenz's correlation in which the fluid void fraction, \(\epsilon\), is a parameter. Thus, given a
FIGURE 10.4 — Zenz's Fluidization Correlation (13).
FIGURE 10.5 — Fluidization with Air, Zenz’s Method (13).

* Note: To convert ft./sec. to cm./sec., multiply by 30.5.
FIGURE 10.6 --- Fluidization with Helium, Zenz's Method (13).

Superficial Velocity, ft./sec.*

* Note: To convert ft./sec. to cm./sec., multiply by 30.5
set of the physical properties of fluid and particles, one may, then construct a plot of $\varepsilon$ vs. $V$. These are shown in Figures 5.7 and 5.8 for the fluidization of the catalyst particles in air and helium. Figures 5.7 and 5.8 are reproduced again in this Appendix as Figures 10.5 and 10.6 respectively.

To verify Zenz's correlation, the catalyst particles were fluidized in a mock reactor at room temperature. This reactor has the same dimensions as the actual one, but is made of clear Lucite. Air and helium were used as fluidizing media. Visual observations were made of the bed heights. The fluid voidage, $\varepsilon$, is found by:

$$\varepsilon = \frac{R_b}{R_b} + \frac{\varepsilon_{mf}-1}{R_b}$$  \hspace{1cm} (10.14)

where the bed height ratio, $R_b$, $= \frac{L_f}{L_{mf}}$.

The bed height, $L_f$, was measured for each fluidizing velocity, but the bed height at minimum fluidization, $L_{mf}$, was taken to be the bed height immediately after fluidization was stopped. The value of $\varepsilon_{mf}$, the fluid voidage at minimum fluidization was calculated from the $L_{mf}$ and $\rho_p$ values and was found to be 0.592. Three different weights of catalysts, namely, 50, 100 and 200 g. were used in the fluidization tests. The experimental results are compared with Zenz's correlations in Figures 10.5 and 10.6.

Table 10.3 shows the approximate values of the physical properties of the three fluidizing media used in this study. The density of the catalyst particles, $\rho_p$ was 1.98 g./ml.
Table 10.3 Values of physical properties of the fluidizing gases

<table>
<thead>
<tr>
<th>Properties</th>
<th>Type of Gas</th>
<th>Reactor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ave. temp., °C</td>
<td>Air</td>
<td>Helium</td>
</tr>
<tr>
<td>Ave. press., mm. Hg.</td>
<td>27</td>
<td>27</td>
</tr>
<tr>
<td>Ave. density, lb./cu.ft.</td>
<td>0.074</td>
<td>0.010</td>
</tr>
<tr>
<td>Ave. viscosity, cp.</td>
<td>0.018</td>
<td>0.018</td>
</tr>
</tbody>
</table>

As could be seen from Figures 10.5 and 10.6, the experimental relationship between $\varepsilon$ and $V$ does not agree with Zenz's correlation for both air and helium. However, the discrepancy is approximately constant in all cases. To correlate the experimental data so that it would agree with Zenz's correlation, a shape factor, $J$, was introduced for the coordinates of Figure 10.4. Thus, equation (10.13) is now changed to:

$$ (C_d R_e)^{2/3} = \frac{D_p}{J} \left[ \frac{\mu_p^2}{\mu_f} \left( \frac{\rho_p - \rho_f}{\rho_f} \right) g \right]^{1/3} $$

and, $$(R_e C_d)^{1/3} = \left[ \frac{\mu_p^2}{\mu_f} \left( \frac{\rho_p - \rho_f}{\rho_f} \right) g \right]^{1/3}$$

For Zenz's curve, the $J$ value was taken to be 1. For the experimental data, the $J$ value was found by trial and error so that the resulting values of $(C_d R_e)^{2/3}$ and $(R_e C_d)^{1/3}$ from eq. (10.14) would give a value of the fluid voidage, $\varepsilon$, equal to the experimental one as shown in Figures 10.5 and 10.6. Table 10.4 gives the values of the shape factor, $J$, as found in this manner.
The average value of $J$ for each weight of catalyst was then used in equation (10.14) in connection with Figure 10.4 to estimate the relationship between $\epsilon$ and $V$ in the case of the reactor gas. This is shown in Figure 5.9 which also includes the relationship between $\epsilon$ and $V$ found without using the shape factor. Figure 5.9 is reproduced in this Appendix as Figure 10.7.

<table>
<thead>
<tr>
<th>Weight of catalyst</th>
<th>Air</th>
<th>Helium</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 g.</td>
<td>0.77</td>
<td>0.74</td>
<td>0.755</td>
</tr>
<tr>
<td>100</td>
<td>0.76</td>
<td>0.69</td>
<td>0.725</td>
</tr>
<tr>
<td>200</td>
<td>0.70</td>
<td>0.66</td>
<td>0.680</td>
</tr>
</tbody>
</table>
Void Fraction

1.0

Zenz's curve

0.9

0.8

0.7

0.6

0.01

0.1

1.0

Superficial Velocity, ft./sec.*

* Note: To convert ft./sec. to cm./sec., multiply by 30.5.

FIGURE 10.7 --- Fluidization with Reactor Gas
FIGURE 10.8 --- Holding Time Distribution
by Romano (46).
4 in. diameter tube

Gas velocity -- 0.30-0.48 ft./sec.

\( f_b = 0.078 \)

**FIGURE 10.9** --- Contact Time Distribution

by Orcutt (12).
D. **Data**

1. Data from the fluidized reactor.
2. Partial data of the fixed bed process (14).
3. Sample calculation of material balance.
### Table 10.5 Data from the fluidized reactor, Preliminary Experiment

<table>
<thead>
<tr>
<th>Run No.</th>
<th>$T_{oK}$</th>
<th>$R$</th>
<th>$V$ cm/s</th>
<th>$W$ g</th>
<th>$W/F$</th>
<th>$T$ atm</th>
<th>$T^*$ sec</th>
<th>$(C_{O2})$ ave</th>
<th>$Y_B%$</th>
<th>$Y_{H_2}%$</th>
<th>$S_%$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>653</td>
<td>47.90</td>
<td>6.52</td>
<td>75</td>
<td>8.18</td>
<td>1.03</td>
<td>1.278</td>
<td>0.1751</td>
<td>54.82</td>
<td>8.81</td>
<td>16.07</td>
</tr>
<tr>
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<th>$T'$ sec.</th>
<th>$(C_{O2})_{ave}$</th>
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<th>Y\textsubscript{B} %</th>
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<td>1.81</td>
<td>2.29</td>
<td>0.19</td>
<td>3.638</td>
<td>0.0055</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10A</td>
<td>78.18</td>
<td>17.54</td>
<td>1.74</td>
<td>2.42</td>
<td>0.18</td>
<td>4.134</td>
<td>0.0062</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>78.06</td>
<td>13.54</td>
<td>3.25</td>
<td>4.52</td>
<td>0.60</td>
<td>3.165</td>
<td>0.0064</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>78.09</td>
<td>18.56</td>
<td>1.34</td>
<td>1.92</td>
<td>0.34</td>
<td>2.705</td>
<td>0.0038</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>78.32</td>
<td>12.69</td>
<td>3.65</td>
<td>4.90</td>
<td>0.43</td>
<td>2.241</td>
<td>0.0069</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14B</td>
<td>78.18</td>
<td>17.59</td>
<td>1.73</td>
<td>2.29</td>
<td>0.21</td>
<td>2.457</td>
<td>0.0034</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15C</td>
<td>78.07</td>
<td>14.47</td>
<td>2.78</td>
<td>3.93</td>
<td>0.77</td>
<td>3.047</td>
<td>0.0079</td>
<td></td>
<td></td>
</tr>
<tr>
<td>16C</td>
<td>78.34</td>
<td>17.59</td>
<td>1.70</td>
<td>2.21</td>
<td>0.20</td>
<td>5.324</td>
<td>0.0081</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 10.9 Analytical results from the fluidized reactor, path of steepest ascent

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Mole % of gases in the outlet</th>
<th>Amt of gas collected, g mol</th>
<th>Amt. of anhydride collected, g mol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$N_2$</td>
<td>$O_2$</td>
<td>CO</td>
</tr>
<tr>
<td>17</td>
<td>78.47</td>
<td>19.92</td>
<td>0.48</td>
</tr>
<tr>
<td>18</td>
<td>78.52</td>
<td>19.55</td>
<td>0.58</td>
</tr>
<tr>
<td>19</td>
<td>78.37</td>
<td>19.91</td>
<td>0.53</td>
</tr>
<tr>
<td>20</td>
<td>78.24</td>
<td>19.94</td>
<td>0.61</td>
</tr>
<tr>
<td>21C</td>
<td>78.18</td>
<td>20.17</td>
<td>0.74</td>
</tr>
<tr>
<td>22</td>
<td>78.07</td>
<td>20.53</td>
<td>0.63</td>
</tr>
<tr>
<td>23</td>
<td>78.07</td>
<td>20.52</td>
<td>0.63</td>
</tr>
<tr>
<td>24</td>
<td>78.13</td>
<td>20.56</td>
<td>0.59</td>
</tr>
<tr>
<td>25</td>
<td>78.15</td>
<td>20.22</td>
<td>0.75</td>
</tr>
</tbody>
</table>
Table 10.10 Analytical results from the fluidized reactor, composite design

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Mole % of gases in the outlet</th>
<th>Amt. of gas collected</th>
<th>Amt. of anhydride collected, g mol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N₂</td>
<td>O₂</td>
<td>CO</td>
</tr>
<tr>
<td>26</td>
<td>78.14</td>
<td>19.93</td>
<td>0.88</td>
</tr>
<tr>
<td>27</td>
<td>78.15</td>
<td>19.93</td>
<td>0.88</td>
</tr>
<tr>
<td>28</td>
<td>78.07</td>
<td>20.33</td>
<td>0.71</td>
</tr>
<tr>
<td>29</td>
<td>78.06</td>
<td>20.36</td>
<td>0.72</td>
</tr>
<tr>
<td>30</td>
<td>78.25</td>
<td>19.75</td>
<td>0.91</td>
</tr>
<tr>
<td>31</td>
<td>78.22</td>
<td>19.92</td>
<td>0.85</td>
</tr>
<tr>
<td>32</td>
<td>78.09</td>
<td>20.49</td>
<td>0.65</td>
</tr>
<tr>
<td>33</td>
<td>78.10</td>
<td>20.45</td>
<td>0.67</td>
</tr>
<tr>
<td>34</td>
<td>78.15</td>
<td>19.97</td>
<td>0.84</td>
</tr>
<tr>
<td>35</td>
<td>78.10</td>
<td>19.96</td>
<td>0.87</td>
</tr>
<tr>
<td>36</td>
<td>78.06</td>
<td>20.26</td>
<td>0.76</td>
</tr>
<tr>
<td>37</td>
<td>78.07</td>
<td>20.40</td>
<td>0.68</td>
</tr>
<tr>
<td>38</td>
<td>78.16</td>
<td>20.22</td>
<td>0.74</td>
</tr>
<tr>
<td>39</td>
<td>78.24</td>
<td>19.80</td>
<td>0.88</td>
</tr>
<tr>
<td>40</td>
<td>78.09</td>
<td>20.40</td>
<td>0.68</td>
</tr>
<tr>
<td>41</td>
<td>78.23</td>
<td>19.93</td>
<td>0.82</td>
</tr>
<tr>
<td>42</td>
<td>78.21</td>
<td>20.29</td>
<td>0.68</td>
</tr>
<tr>
<td>43</td>
<td>78.20</td>
<td>20.28</td>
<td>0.68</td>
</tr>
<tr>
<td>44</td>
<td>78.17</td>
<td>20.26</td>
<td>0.71</td>
</tr>
<tr>
<td>45</td>
<td>78.25</td>
<td>20.16</td>
<td>0.73</td>
</tr>
<tr>
<td>46</td>
<td>78.17</td>
<td>20.05</td>
<td>0.80</td>
</tr>
<tr>
<td>47</td>
<td>78.16</td>
<td>20.48</td>
<td>0.58</td>
</tr>
<tr>
<td>48</td>
<td>78.09</td>
<td>20.05</td>
<td>0.82</td>
</tr>
<tr>
<td>49</td>
<td>78.00</td>
<td>20.09</td>
<td>0.86</td>
</tr>
<tr>
<td>50</td>
<td>78.42</td>
<td>20.35</td>
<td>0.54</td>
</tr>
<tr>
<td>51</td>
<td>78.03</td>
<td>19.91</td>
<td>0.92</td>
</tr>
<tr>
<td>52</td>
<td>78.13</td>
<td>20.63</td>
<td>0.57</td>
</tr>
<tr>
<td>53</td>
<td>78.20</td>
<td>19.96</td>
<td>0.83</td>
</tr>
<tr>
<td>Run No.</td>
<td>$T_{oK}$</td>
<td>$R$ cm./sec.</td>
<td>$V$ g.</td>
</tr>
<tr>
<td>--------</td>
<td>----------</td>
<td>-------------</td>
<td>--------</td>
</tr>
<tr>
<td>C-1</td>
<td>700</td>
<td>98.11</td>
<td>30.60</td>
</tr>
<tr>
<td>C-2</td>
<td>701</td>
<td>62.25</td>
<td>30.78</td>
</tr>
<tr>
<td>C-3</td>
<td>697</td>
<td>92.02</td>
<td>34.98</td>
</tr>
<tr>
<td>C-4</td>
<td>696</td>
<td>59.02</td>
<td>26.18</td>
</tr>
<tr>
<td>C-5</td>
<td>721</td>
<td>99.50</td>
<td>31.40</td>
</tr>
<tr>
<td>C-6</td>
<td>726</td>
<td>63.10</td>
<td>31.88</td>
</tr>
<tr>
<td>C-7</td>
<td>730</td>
<td>102.09</td>
<td>36.20</td>
</tr>
<tr>
<td>C-8</td>
<td>728</td>
<td>65.60</td>
<td>26.70</td>
</tr>
</tbody>
</table>
3) **Sample calculation of material balance**

From the percentage of each gas component found in the gas analysis, and the measured volume of gas sample, the amounts of benzene and air inputs corresponding to the gas sample could be calculated (based on the amount of nitrogen and the inlet air/benzene ratio). Together with the known amount of maleic anhydride in the sample, all the components of the reactant and product streams are then known quantitatively. If one disregards the negligible amounts of phenol and naphthoquinone, the oxidation equation would be:

\[
(10.15) \quad x \text{ + y} \text{O}_2 \rightarrow a \text{CO} + b\text{CO} + c\text{CO}_2 + d\text{H}_2\text{O}
\]

where \( x, y, a, b, c, d \) signify the number of moles of each component accordingly.

Thus, the carbon balance would be:

\[
(10.16) \quad 6x = 4a + b + c
\]

The hydrogen balance would be:

\[
(10.17) \quad 6x = 2a + 2d
\]

The oxygen balance would be:

\[
(10.18) \quad 2y = 3a + b + 2c + d
\]

By substituting equations (10.16) and (10.17) into (10.18) and eliminating the term "d", the final equation for oxygen balance is:

\[
(10.19) \quad y = 2a + \frac{3}{4}b + \frac{5}{4}c
\]

Both equations (10.16) and (10.19) were used in checking material balance.
In Run 53, the following analyses were made:

<table>
<thead>
<tr>
<th></th>
<th>Percentage</th>
<th>No. of mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total gas sample</td>
<td>----</td>
<td>5.842</td>
</tr>
<tr>
<td>Maleic anhydride</td>
<td>----</td>
<td>0.0069</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.019</td>
<td>0.00111</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>78.20</td>
<td>4.569</td>
</tr>
<tr>
<td>Oxygen (+ Argon)</td>
<td>19.96</td>
<td>1.166</td>
</tr>
<tr>
<td>CO</td>
<td>0.83</td>
<td>0.048</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.99</td>
<td>0.058</td>
</tr>
</tbody>
</table>

The composition of the inlet air as given in Ref. 47 is as follows:

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>78.04 %</td>
<td></td>
</tr>
<tr>
<td>Oxygen (+ Argon)</td>
<td>21.93 %</td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>0.03 %</td>
<td></td>
</tr>
</tbody>
</table>

By using the no. of moles of nitrogen in the gas sample as reference, the amount of each gas component in the inlet corresponding to the gas sample could be calculated. Also, since the mol ratio of air/benzene in the input was known to be 252.4 in this case, the amount of benzene input could be found. The inlet conditions were:

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Total mol. of air</td>
<td>5.855</td>
<td></td>
</tr>
<tr>
<td>mol. of N₂</td>
<td>4.569</td>
<td></td>
</tr>
<tr>
<td>mol. of O₂</td>
<td>1.284</td>
<td></td>
</tr>
<tr>
<td>mol. of CO₂</td>
<td>0.002</td>
<td></td>
</tr>
<tr>
<td>mol. of benzene</td>
<td>0.023</td>
<td></td>
</tr>
</tbody>
</table>

There was, of course, no CO or maleic anhydride in the inlet stream.

The amounts of oxygen and benzene used, and the amounts of CO, CO₂ and maleic anhydride generated were then found by comparing the inlet and the outlet conditions. These are as follow:

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>x, moles of benzene used</td>
<td>0.022</td>
<td></td>
</tr>
<tr>
<td>y, moles of oxygen used</td>
<td>0.118</td>
<td></td>
</tr>
<tr>
<td>a, moles of maleic anhydride formed</td>
<td>0.0069</td>
<td></td>
</tr>
<tr>
<td>b, moles of CO formed</td>
<td>0.048</td>
<td></td>
</tr>
<tr>
<td>c, moles of CO₂ formed</td>
<td>0.056</td>
<td></td>
</tr>
</tbody>
</table>
The material balance could then be calculated using equations (10.16) and (10.19). Similarly, the various conversion terms, $Y_B$, $Y_M$ and $S$ could also be found.
E. Derivation of Rate Equations

Consider the following model for the oxidation of benzene:

\[ B \xrightarrow{K_1} M \]  
\[ B \xrightarrow{K_2} D \]

\( B \equiv \text{benzene} \)
\( M \equiv \text{malonic anhydride} \)
\( D \equiv \text{CO} + \text{CO}_2 \)

The following assumptions are made:

a. first order reaction with regard to oxygen and benzene
b. irreversible reactions
c. ideal gas conditions
d. the total no. of moles before and after the reactions are constant. This assumption, though not rigorous, is proven out from the experimental data.

1. Disappearance of benzene

Consider a catalytic system in which --

\[ \Pi \] = total pressure in the system
\[ T \] = temperature of the system
\( v \) = a small arbitrary volume of the reactor
\( \varepsilon \) = void fraction in the bed zone
\( \rho_p \) = particle density of the solids in the bed.

By assuming that the rate of reaction/mass of catalyst is proportional to the partial pressures of benzene and oxygen, the rate of disappearance of benzene in the volume "v" is:

\[
(10.20) \quad - \frac{dN_B}{d\Theta} = K_0 \rho_B \rho_{O_2} (1-\varepsilon) \rho_p v
\]

where \( N_B \equiv \text{no. of mol of benzene in "v"} \)
\[ \theta = \text{time unit} \]

\[ K_0 = K_1 + K_2 \]

\[ P_B = \text{partial pressure of benzene} \]

\[ P_{o_2} = \text{partial pressure of oxygen} \]

By assuming ideal gas conditions, \( P_B \) may be replaced by

\[ \frac{\Pi(N_B/N_T)}{N_T} = \text{total no. of moles in the volume "v"}. \]

Hence,

\[ -\frac{dN_B}{d\theta} = K_0 \cdot P_{o_2} \cdot \frac{N_B}{N_T} \Pi (1-\epsilon) \frac{C_p}{\epsilon} \nu \]

Replacing \( N_T \) with \( \frac{\Pi \nu \epsilon}{RT} \), one finds-

\[ -\frac{dN_B}{d\theta} = K_0 \cdot P_{o_2} \cdot N_B \cdot RT \cdot \frac{C_p}{\epsilon} \frac{(1-\epsilon)}{\epsilon} \]

or,

\[ -\frac{dN_B}{N_B} = K_0 \cdot P_{o_2} \cdot RT \cdot \frac{C_p}{C_f} \frac{(1-\epsilon)}{\epsilon} d\theta \]

The term "RT" may be replaced by an expression including the gas density, \( C_f \), i.e., \( RT = \frac{\Pi}{C_f} \).

Hence:

\[ (10.21) \quad -\frac{dN_B}{N_B} = K_0 \cdot P_{o_2} \cdot \frac{\Pi}{C_f} \left[ \frac{C_p}{C_f} \frac{(1-\epsilon)}{\epsilon} \right] d\theta \]

A new term, \( Y_B \), is now introduced where \( Y_B \) represents the \% conversion of benzene, or,

\[ (10.22) \quad \frac{Y_B}{100} = 1 - \left( \frac{N_B}{N_B_1} \right) \]

where \( N_B_1 \) = moles of benzene in the input stream.

Equation (10.21) is now changed to:

\[ (10.23) \quad \frac{d\left( \frac{Y_B}{100} \right)}{(1-Y_B/100)} = K_0 \cdot P_{o_2} \cdot \frac{\Pi}{C_f} \frac{C_p}{C_f} \frac{(1-\epsilon)}{\epsilon} d\theta \]

Since the partial pressure of oxygen is large compared to that of benzene, it may be replaced by the average value in term of the
oxygen concentration, i.e.,

\[
\frac{d(Y_B/100)}{(1-Y_B/100)} = K_o \cdot \mathcal{T}^2 \cdot (C_{O_2}^2) \cdot \frac{C_p}{C_f} \cdot \frac{1-\varepsilon}{\varepsilon} \cdot d\theta
\]

In the case of the fixed bed, \( \varepsilon \) may be assumed to be constant.

Hence, eq. (10.24) will be reduced to:

\[
\frac{d(Y_B/100)}{(1-Y_B/100)} = K'_o \cdot \mathcal{T}'^2 \cdot (C_{O_2}^2) \cdot d \left( \frac{W}{F} \right)
\]

where \( K'_o \) signifies the rate constant in the fixed bed. Also,

\[
(10.25) \quad \frac{d(Y_B/100)}{(1-Y_B/100)} = K'_o \cdot \mathcal{V}
\]

where \( \mathcal{V} = \mathcal{T}^2 \cdot (C_{O_2}^2) \cdot \frac{W}{F} \).

In this case, the resulting integration will be:

\[
(10.26) \quad Y_B/100 = 1 - e^{\mathcal{K}' \mathcal{V}}
\]

In the case of the fluidized bed, \( \varepsilon \) may not be assumed to be constant, but is a function of time. Hence, the rate of reaction will depend on \( \frac{1-\varepsilon}{\varepsilon} \cdot t \), where \( t \) = time that the small volume "\( v \)" stays in the bed zone. Equation (10.24) is then changed to:

\[
(10.27) \quad \frac{d(Y_B/100)}{(1-Y_B/100)} = K''_o \cdot \mathcal{T}^2 \cdot (C_{O_2}^2) \cdot \frac{C_p}{C_f} \cdot \int_0^t \frac{1-\varepsilon}{\varepsilon} \cdot d\theta
\]

where \( K''_o \) signifies the rate constant in the fluidized bed.

A new term, \( \mathcal{G} \), is now introduced such that

\[
(10.28) \quad \mathcal{G} = \frac{[C_p/C_f] \cdot \int_0^t \frac{1-\varepsilon}{\varepsilon} \cdot d\theta}{W/F}
\]

Thus, eq. (10.27) will become:

\[
(10.29) \quad \frac{d(Y_B/100)}{(1-Y_B/100)} = K''_o \cdot \mathcal{T}^2 \cdot (C_{O_2}^2) \cdot \frac{W}{F} \cdot \mathcal{G}
\]

It must be assumed that each small volume "\( v \)" will have its
own time "t" of staying in the bed zone. Hence, the term "y" will not be constant. By assuming that the term "y" has a distribution \( h(y) \), equation (10.29) will become:

\[
Y_B/100 = 1 - \int_0^\infty e^{-K_0 y} \cdot h(y) \, dy
\]

Thus, for the fluidized bed, the contact time distribution, \( h(y) \), must be known before \( Y_B \) may be calculated.

2. Formation of maleic anhydride

By following the same assumptions used in the development of the rate equation for the disappearance of benzene, the rate of formation of maleic anhydride is found to be:

\[
dN_M/d\theta = \left[ K_1 \cdot P_{o_2} \cdot P_B - K_3 \cdot P_{o_2} \cdot P_M \right] \cdot (1 - \epsilon) \cdot \frac{P_p}{P_f} \nu
\]

where the subscript "M" signifies properties of maleic anhydride.

Following the same transformation as in the case of benzene, one finds that:

\[
dN_M/d\theta = \left[ k_0 \cdot N_B - K_3 \cdot N_M \right] \cdot P_{o_2} \nu \cdot \frac{P_p}{P_f} \cdot (1 - \epsilon)
\]

A new term \( Y_M \) is now introduced in which \( Y_M \) represents the % conversion to maleic anhydride, i.e.,

\[
Y_M/100 = N_M/N_{B_1}
\]

Equation (10.32) is now changed to:

\[
d(Y_M/100)/d\theta = \left[ K_1 \left( 1 - \frac{Y_B}{100} \right) - K_3 \frac{Y_M}{100} \right] \nu^2 \cdot (C_{o_2})_{av} \cdot \frac{P_p}{P_f} \cdot (1 - \epsilon)
\]

In the case of the fixed bed in which \( \epsilon \) is constant, equation (10.34) may be combined with equation (10.26), integrated and reduced to be:
Similarly, in the case of fluidized bed, equation (10.34) may be combined with (10.30), integrated and reduced to:

\[
(10.35) \quad \frac{Y_M}{100} = \frac{K_1'}{K_3 - K_0} \left[ e^{-K_0 Y} - e^{-K_3 Y} \right]
\]

\[
(10.36) \quad \frac{Y_M}{100} = \frac{K_1''}{K_3 - K_0} \left[ 1 - \frac{Y_B}{100} - \int_0^{\infty} e^{-K_3 Y} h(y) dy \right].
\]
F. List of Symbols

1) Statistical Symbols

a  estimated value of the regression constant
b  constant for the linear estimate of a.
c  constant in the array of Normal equations for the estimate of a.
o  random error in observation
k  number of independent variables
n  total number of runs or sets of observations
nc  total number of runs in a 2-level factorial design
R  multiple correlation
s  unbiased estimate of the standard of error, \( \delta \).
U  actual independent variable
\( \Delta U \)  unit value, i.e., conversion factor between the independent variable \( U \), and its coded term \( x \).
X  canonical independent variable
x  independent variable coded for the regression equation
Y  estimate of the dependent variable in the regression equation
y  observed value of the dependent variable

Greek symbol
\( \alpha \)  true value of the regression constant
\( \eta \)  true value of the dependent variable
\( \sigma \)  true value of the standard of error

Subscript
i  associated with the \( i^{th} \) independent variable
j  associated with the \( j^{th} \) run or set of observation

Superscript
\( \bar{\text{a}} \)  average value
first position in space or contour
second position in space or contour

2) Chemical Engineering Symbols

a no. of moles of maleic anhydride formed
b no. of moles of CO formed
C concentration in mol fraction

C_d drag coefficient
c no. of moles of CO_2 formed
D reactor diameter

D_p particle diameter
d no. of moles of water formed

ΔE activation energy, kcal/mol.
F total mol flow rate of the input stream, mol/hr
F_B benzene mol flow rate (input), mol/hr
f_b fraction of gas bypassing in the fluidized bed

f (g) holding time distribution
g gravitational constant

h (g) contact time distribution
J shape factor

K_0 rate constant for the disappearance of benzene
K_1 rate constant for the formation of maleic anhydride
K_2 rate constant for the formation of CO and CO_2 from benzene
K_3 rate constant for the disappearance of maleic anhydride
k reaction rate constant (general)

k_g mass transfer rate constant

k_1 rate constant for the reaction between benzene and re-oxidized catalyst
$k_2$ rate constant for the reaction between oxygen and reduced catalyst

$L$ bed height (general)

$L_f$ bed height during fluidization

$m,n,p,q$ constants in the rate equation based on the catalyst's reaction model

$N$ no. of moles of reacting component (used only with proper subscript)

$p$ partial pressure (used only with proper subscript)

$R$ mol ratio air/benzene

$R_b$ bed height ratio

$R_c$ Reynolds number

$r$ rate of reaction

$S$ % selectivity, $100 \times \frac{\text{mol of maleic anhydride formed}}{\text{mol of benzene reacted}}$

$T$ temperature, °K

$t$ residence time

$V$ superficial gas velocity

$W$ weight of the catalyst, g.

$W_f$ mass flow rate of the fluidizing gas

$Y_B$ % benzene disappeared, $100 \times \frac{\text{mol of benzene reacted}}{\text{mol of benzene input}}$

$Y_D$ % yield of the gases (CO and CO$_2$), $100 \times \frac{\text{mol of gas formed}}{(6 \times \text{mol of benzene input})}$

$Y_M$ % yield of maleic anhydride, $100 \times \frac{\text{mol of maleic anhydride formed}}{\text{mol of benzene input}}$
Greek symbol

α number of oxygen molecules required for one molecule of benzene
β degree of occupation of oxygen on the catalyst's surface
γ \( \gamma^2(C_O) \) \( \infty \) modifying factor for rate constant
ε void fraction
θ time variable
μ gas viscosity
Π total pressure of gas mixture, atm.
ρ density (general)
ɛ_\text{a} absolute density of catalyst
ɛ_\text{b} bulk density of catalyst
ɛ_\text{f} gas density
ɛ_\text{p} apparent particle density
η modified term for W/F to signify contact time distribution, dimensionless
\( \bar{\tau} \) average contact time, second.
\( \phi(K) \) fraction of reactant remaining

Subscript

B benzene
D gaseous products (CO and CO_2)
f gas mixture (reactants)
i initial conditions
M maleic anhydride
mf loose-bed conditions of a fluidized bed
O_2 oxygen
o outlet conditions
T  total no. of moles in the system

Superscript
// (on rate constants) denoting constants which are calculated by considering the fixed bed rate equation
// (on rate constants) denoting constants which are calculated based on the contact time distribution for fluidized bed
/// (on rate constants) denoting constants which are calculated based on the average contact time
1. Weiss, J. M., and Downs, C. R., IEC, 12, 228, 1920
14. Yao, B. C., M. S. Thesis, The Ohio State University, 1964, also personal correspondence.


44. Ibid., ch. 3.

