

A KINETIC STUDY OF THE VAPOR
PHASE CATALYTIC PARTIAL
OXIDATION OF TOLUENE

BY

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PREFACE

A kinetic study was made of the vapor phase catalytic oxidation of toluene. In this study a flow reactor was used to collect kinetic data in the high toluene concentration regions. These data were used in an attempt to calculate reaction rate constants and orders. The conclusion reached is that the oxidation of toluene is too complex to be given a simple kinetic equation which assumes that the rate is proportional to the products of the concentration of the reactions raised to some power.

I wish to thank the entire staff of the School of Chemical Engineering at Oklahoma State University for their help and guidance. I especially wish to thank Dr. R. N. Maddox and Dr. J. M. Marchello for their advice in making possible this study.

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CHAPTER I

INTRODUCTION

As the chemical industry has increased in complexity, there has been an increasing need for the utilization of more exact methods in the design and operation of equipment. Design and operating problems fall into two general classes. The first is that of the equilibrium processes in which the system is assumed to be at thermodynamic equilibrium. The second type of problems are those in which the system can not be assumed at equilibrium and it is necessary to consider the rate at which the process occurs. One of the most important rate controlled processes in the chemical industry is that of the chemical reaction itself.

Reaction kinetics is the study of the time dependence for chemical reaction. At the present time reliable information on reaction rates is available for comparatively few reactions. Of the reactions which have information available, many are of little practical importance.

Among the important classes of reactions needing study is the catalytic partial oxidation of hydrocarbons. Toluene was selected as a substance which would provide a fruitful field of study in this area. An important characteristic of toluene is that it is the simplest member of the family of aromatic hydrocarbons with asphaltic side chains. A knowledge of the characteristics of toluene oxidation would provide a basis

for the study of the oxidation of more complex compounds such as the xylenes. The study of the oxidation of toluene also offers an important end in itself. This process has been used for years as an important industrial source for benzoic acid and benzaldehyde (5). The reaction is normally carried out over vanadium pentoxide or some similar metallic oxide or combination of metallic oxides. The catalyst which is used in a particular situation is determined by the desired products, by the desired temperature and by economic factors.

With the above factors in mind a study was made of the oxidation of toluene in the presence of vanadium pentoxide. The following were the goals of this study:

1. To measure the rate of oxidation of toluene in the vapor phase in a flow reactor using vanadium pentoxide catalyst.
2. To determine the order and rate constants for the data obtained in part one.
3. To calculate the Arrhenius constants for the rate constants at different temperatures.

CHAPTER II

SURVEY OF REACTION KINETICS

The Basic Rate Equation

The rate of a chemical reaction is expressed as the amount of material produced or consumed per unit time (22). The rate is an extensive property. To eliminate this difficulty it is normally found desirable to define the reaction rate as the extensive reaction rate per unit volume. This can be expressed mathematically in the following manner (26):

$$r_A = -1/V \frac{d\eta_A}{d\theta} \quad (2-1).$$

The negative sign arises because the substance A is disappearing by reaction.

Equation (2-1) may be put in a more useful form with the aid of the law of mass action. This law may be stated as: "The rate of a chemical reaction is proportional to the active masses of the participants" (26). The problem with this statement is the interpretation of the term "active mass." It is common practice when making calculations to assume that active mass means concentration (26). However, some authorities (9) feel that the thermodynamic activity should be regarded as the proper "active mass." This theory has not yet been

verified. One major problem that prevents the application of activity to the solution of chemical rate equations is that in those cases in which the concentration and activity should give different answers the reactions are frequently too complex to conveniently study. Also, kinetic data are normally so poor that in all but the most non-ideal solutions any error due to the use of concentration would be within the error in the kinetic data.

The law of mass action may be expressed in mathematical terms for a reaction of the type:



The mass action rate expression for the above equation is as follows:

$$r_A = k C_A^a C_B^b C_C^c \quad (2-3).$$

The order for a component is defined as the power (a, b, c, etc.) to which the concentration of the component is raised in the rate equation. The order of the reaction is defined as the sum of the orders of each of the components. In the case of a complex reaction, which proceeds through a number of intermediate steps, equation (2-3) normally is not applicable. It is still found that an equation similar to equation (2-3) may often fit the reaction. In this case, the rate depends on the concentration to some power. Thus the rate equation for the reaction in equation (2-2) becomes

$$r_A = k C_A^\delta C_B^\beta C_C^\gamma \quad (2-4)$$

where: δ, β and γ are constants for that particular reaction.

In this case a pseudo order is defined in a similar manner to the order.

The pseudo order with respect to components A, B and C is defined as , and respectively. Likewise the pseudo order of the reaction is defined as the sum of the pseudo orders of each component.

In order to obtain a differential equation one may combine equation (2-1) with (2-3) to obtain the following expression:

$$-1/v \frac{d a}{d\theta} = k C_A C_B C_C \quad (2-5).$$

The Flow System

Two major reasons can be given for the study of reacting systems under flow condition. The first is that the flow system makes possible the study of fast reactions (5). Batch methods require that samples be taken at very short time intervals, while in a flow system it is only necessary to change the flow rates to study the time dependence of the reaction. Perhaps even more important than the time element is the fact that a very large percentage of industrial processes utilize flow systems. While the design engineer may frequently extend batch data to flow systems, the results are at best doubtful (11). Such factors as back mixing and wall effects present problems which are not present in batch systems. The scaling up of flow reactors presents similar problems, but in general it may be done on a much sounder basis than if batch data were utilized.

To completely analyze a flow system, the transitory behavior of the reactor should be considered. However, a steady state may be effected which will permit an analysis of the reactor. When formulating the mathematics for the steady state condition, it is normally

assumed that there is no back mixing and the velocity profile is constant across the diameter of the reactor. Hougen and Watson (10) point out that the above conditions are a good approximation in all but very large diameter reactors. By considering a material balance over a differential volume of the reactor under steady state conditions, the following equations are obtained:

$$r_A dV_R = \text{moles converted in the section}$$

$$F_A dX_A = \text{reduction in the number of moles of A.}$$

By equating these terms the following equation is obtained:

$$r_A dV_R = F_A dX_A$$

or

$$r_A = F_A \frac{dX_A}{dV_R} \quad (2-6).$$

This equation is sometimes seen in another form which may be obtained as follows:

A simple material balance will show that

$$X_A F_A = N_A$$

or

$$X_A = \frac{N_A}{F_A}$$

thus

$$r = \frac{dN_A}{dV_R} \quad (2-7).$$

This expression is frequently used as the defining expression for the reaction rate in a flow system.

Catalytic Systems

In catalytic systems the reaction rate normally will depend on the surface area of the catalyst rather than on the reactor volume. Thus equations (2-6) and (2-7) must be modified. Probably the simplest method of doing this is to follow the system of Hougen and Watson (10) and assume that the surface area is proportional to the mass of catalyst. An equation similar to equation (2-6) may be written as follows:

$$r dW = F_A dX_A \quad (2-8)$$

$$\text{then } r = F_A \frac{dX_A}{dW_A} \quad (2-9).$$

Equation (2-9) may be used to define the reaction rate in a catalytic flow system. In a manner which is similar to the method used to obtain equations (2-7), equation (2-8) may be transformed to

$$r = \frac{dN_A}{dW} \quad (2-10).$$

The above equation may then be combined with equation (2-4) or some other expression for the rate of reaction and used to determine the concentration at any point in the reactor and for flow rate provided a solution to the equation exists.

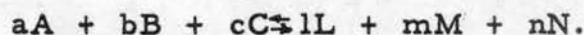
The Effect of Temperature on Reaction Rates

To investigate the effects of temperature on reaction rates, it is convenient to consider certain properties of a chemical reaction at

equilibrium. The equilibrium constant for a chemical reaction, in an ideal solution, may be expressed as follows:

$$K = \frac{C_A^a C_B^b C_C^c}{C_L^l C_M^m C_N^n} \quad (2-11).$$

The above equilibrium constant is for a reaction of the form



It may be noted that a chemical reaction at equilibrium has no reaction rate. For this reason it is necessary that at equilibrium any reaction rate in the forward direction have an equal reaction rate in the reverse direction or

$$r_f = r_R \quad (2-12).$$

Then from equation (2-3)

$$k_f C_A^a C_B^b C_C^c = k_R C_L^l C_M^m C_N^n \quad (2-13)$$

$$\text{or} \quad \frac{k_f}{k_R} = \frac{C_A^a C_B^b C_C^c}{C_L^l C_M^m C_N^n} \quad (2-14)$$

which when combined with equation (2-12) gives

$$\frac{k_f}{k_R} = K \quad (2-15).$$

This shows that the equilibrium constant for the reaction is the forward reaction rate constant divided by the reverse reaction rate constant.

To obtain a relation between the temperature and reaction rate,

Arrhenius considered the variation of the equilibrium constant with temperature. The equation which relates temperature and equilibrium constant is given as follows: (14)

$$\frac{\partial \ln K}{\partial T} = \frac{\Delta H}{RT^2} \quad (2-16).$$

Then by substituting equation (2-15) into (2-16) it is found that:

$$\frac{\partial \ln k_f}{\partial T} - \frac{\partial \ln k_R}{\partial T} = \frac{\Delta H}{RT^2} \quad (2-17).$$

Arrhenius, after examination of equation (2-17), assumed that there was some type of energy term associated with both the forward and reverse reaction rates such that:

$$\frac{\partial \ln k_f}{\partial T} = \frac{E}{RT^2} \quad (2-18).$$

Equation (2-18) may then be integrated assuming E to be constant to obtain:

$$k = Ae^{-E/RT} \quad (2-19)$$

where: A is a constant of integration.

Equation (2-19) has explained with reasonable accuracy the variation of reaction rate with temperature in all cases thus far studied (28).

It is also found to explain fairly well complex kinetic phenomena such as catalytic reaction. This is true although E probably includes the results of several processes such as absorption and desorption.

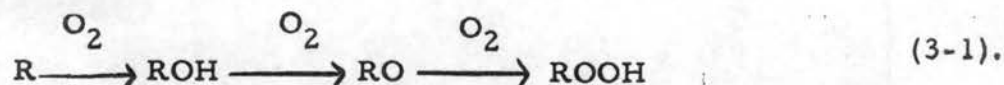
CHAPTER III

OXIDATION REACTIONS

One of the more important types of industrial reactions is the oxidation of hydrocarbons. The study of these reactions may be subdivided into such groups as liquid phase reactions, gas phase reactions, homogeneous reactions and catalytic reactions. While all types of oxidations have caused at least some interest, the catalytic vapor phase oxidation of hydrocarbons seems to be of somewhat more importance to the chemical process industries than the other types. The reason for this importance is that such compounds as aldehydes, ketones and acids are frequently produced by such means (7). The mechanism of these reactions has been investigated, however, the theory has not been completely established and very little kinetic data is available.

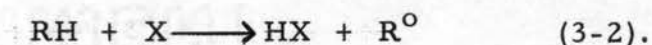
Mechanism for Oxidation

The basic order for the oxidation of hydrocarbons is one consisting of the reaction of the hydrocarbon to an alcohol, to an aldehyde and to an acid. That is,

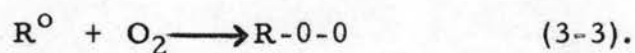


While these steps are in general correct they frequently do not present the complete picture. The method by which the oxygen attacks

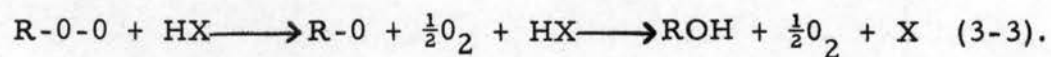
the hydrocarbon is composed of a number of steps, any one of which could easily control the kinetics of the reaction. The initiation of oxidation has been studied extensively without reaching any comprehensive theory which will provide an explanation for all cases (16). It should be noted that the oxidation mechanism frequently is highly dependent on temperature (12). The path which such reactions follow is thought to consist of a series of free radical and peroxide complexes. In catalytic oxidation the catalyst is thought to have the function of providing a free radical as follows:



From this point the free radical normally forms a peroxide by a reaction of the form.



At this point a number of steps are possible. One such step which seems to be fairly probable is an oxygen splitting off the peroxide and the resulting compound combining with the hydrogen catalyst complex to give a half mole of oxygen and a mole of alcohol.



One of the problems involved in the study of such reactions is that it is extremely difficult to fix the concentration of the free radicals. It is also difficult to analyze for the peroxide complexes. Detailed discussions of oxidation reactions may be found in any one of the reference works on the subject (3, 17, 18).

Toluene Oxidation

Toluene has been oxidized with air or oxygen in industry for many years (5). The primary products of this oxidation depend largely on the temperature and the type of catalyst used in the oxidation. With low temperatures, i.e. under about 400 degrees centigrade, and in the presence of vanadium pentoxide catalyst, the yields appear to be largely benzoic acid. However, at higher temperatures a higher percentage of benzaldehyde is produced. In general, vanadium pentoxide will tend to produce benzoic acid while other acceptable catalysts will tend to produce benzaldehyde. In addition to the benzoic acid and benzaldehyde a number of other products have been observed in the oxidation of toluene (8). A list of the observed products is as follows:

- Carbon Dioxide
- Water
- Maleic Anhydride
- Anthroquinone
- Phenol
- Quinone.

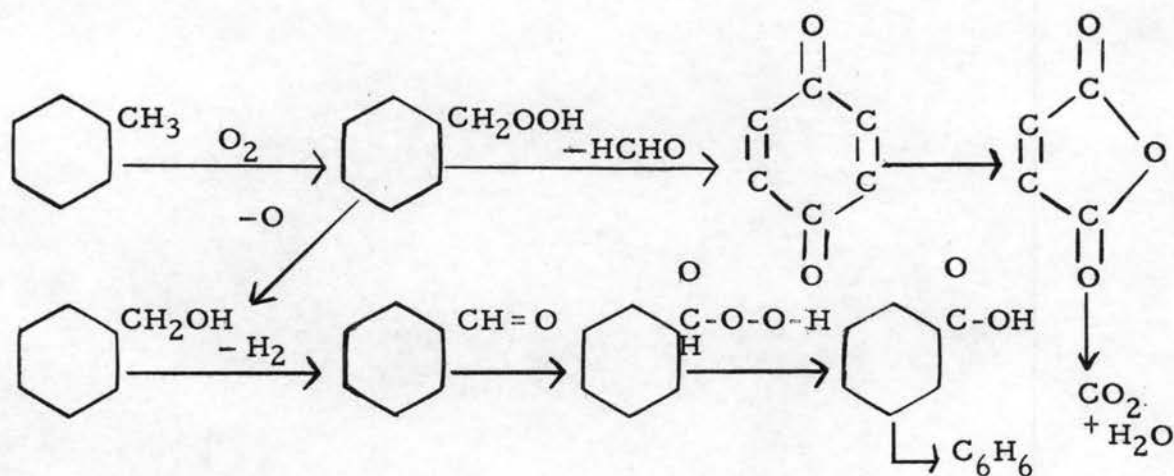
In the experiments which have been made on this oxidation, the air to toluene ratio was rather large. About sixteen percent toluene was found to be the highest with a more typical figure being about five or ten percent (8).

In general, it is found that the oxides of most transition metals will serve as a catalyst for the oxidation process. Vanadium pentoxide appears to give better yields at lower temperatures than the other compounds. However, it is found that a mixture of vanadium pentoxide and one of the other oxidation catalysts will frequently be more desirable

than the pure vanadium pentoxide (4).

Mechanism of Toluene Oxidation

While studies have been made on the oxidation of toluene, it is not possible to state with certainty what the complete mechanism is. One of the facts that stands out about the mechanism of this reaction is the point of attack of the oxidation. In toluene, as in the oxidation of most aromatics with side chains, it is found that the oxygen will attack the side chain before the benzene ring is involved in the process (3). At present, the only study which proposes any relatively complete mechanism is that by Suvorov, Rakiyov and Anchia (24). These workers established that the following steps exist in the oxidation of toluene over vanadium pentoxide.



This mechanism is not complete because of the obvious omission of the series of steps by which oxidation is initiated. The oxidation initiation mechanism is probably very similar to the free radical steps mentioned previously.

Kinetic Studies

The kinetics of the reaction of toluene and oxygen have not been studied extensively. The first extensive set of experiments on the reaction were made by Maxted (15). These experiments were not truly kinetic studies because not enough data were reported to permit the calculation of orders and rate constants. However, these data are useful in obtaining an idea of quantitative yields at different flow rates. An investigation was made by Sasayama (21) in which he concluded that the rate did not depend on the toluene concentration. However, a later study by Mars and Von Kreleven (14) caused doubt on this conclusion. The latter workers, using a fluidized bed of vanadium pentoxide catalyst, found that the rate should depend on both oxygen and toluene concentrations.

CHAPTER IV

EXPERIMENTAL APPARATUS

A flow reaction system was constructed in order to study the kinetics of the partial oxidation of toluene. The main piece of experimental apparatus was a flow reactor with both preheating and reaction chambers. Inlet and outlet flow meters were provided to measure the flow rates of all pertinent streams. The exit stream from the reactor was also equipped with a condenser, a caustic scrubber and a silica gel adsorber. The inlet stream was provided with a silica gel adsorber and a manometer. Heat for the reactor and preheat system was supplied from heating tapes wound around the system. Both thermocouples and thermometers were provided in order to ascertain the temperature at selected points in the system.

The Reactor

The reactor consisted of a twelve inch long piece of three quarter inch black iron pipe. The catalyst was held in place by spun glass, which in turn was held in place by wire screen. This reaction chamber was wound with heating tape so the temperature could be controlled.

Upstream from the reaction chamber were two preheat sections.

The primary function of the first was to vaporize the liquid toluene which was fed to the reactor. This section was constructed of one quarter inch standard steel pipe thirty inches long. The section was provided two inlets, one for air and the other for toluene. A ten inch long portion of this section was packed with small stainless steel packing. The purpose of this was to provide better heat transfer and thus to improve the vaporization of the toluene. The heat source for this section was a heating tape wound around the pipe. The second preheat section consisted of a thirty-six inch section of one-half inch pipe wound with heating tape. This section was intended to preheat the gaseous mixture before it entered the reaction chamber.

The entire preheat and reaction system is shown in Figure 1. The heater which is shown downstream from the reaction chamber was to prevent any liquid from condensing and collecting in the bottom of the system. This heater consisted of a short piece of heating wire. The entire system was insulated to prevent heat losses.

Flow Streams Before Entering Reactor

There were two flow streams which entered the reactor. The first of these was a toluene line. This line came from a reservoir, passed through a Matheson T 602 rotameter and through a needle valve before entering the reactor. The second flow line passed air through silica gel filter to remove any water which might be present. At this point a manometer filled with carbon tetrachloride was connected to the flow line in order to measure the pressure drop across the system.

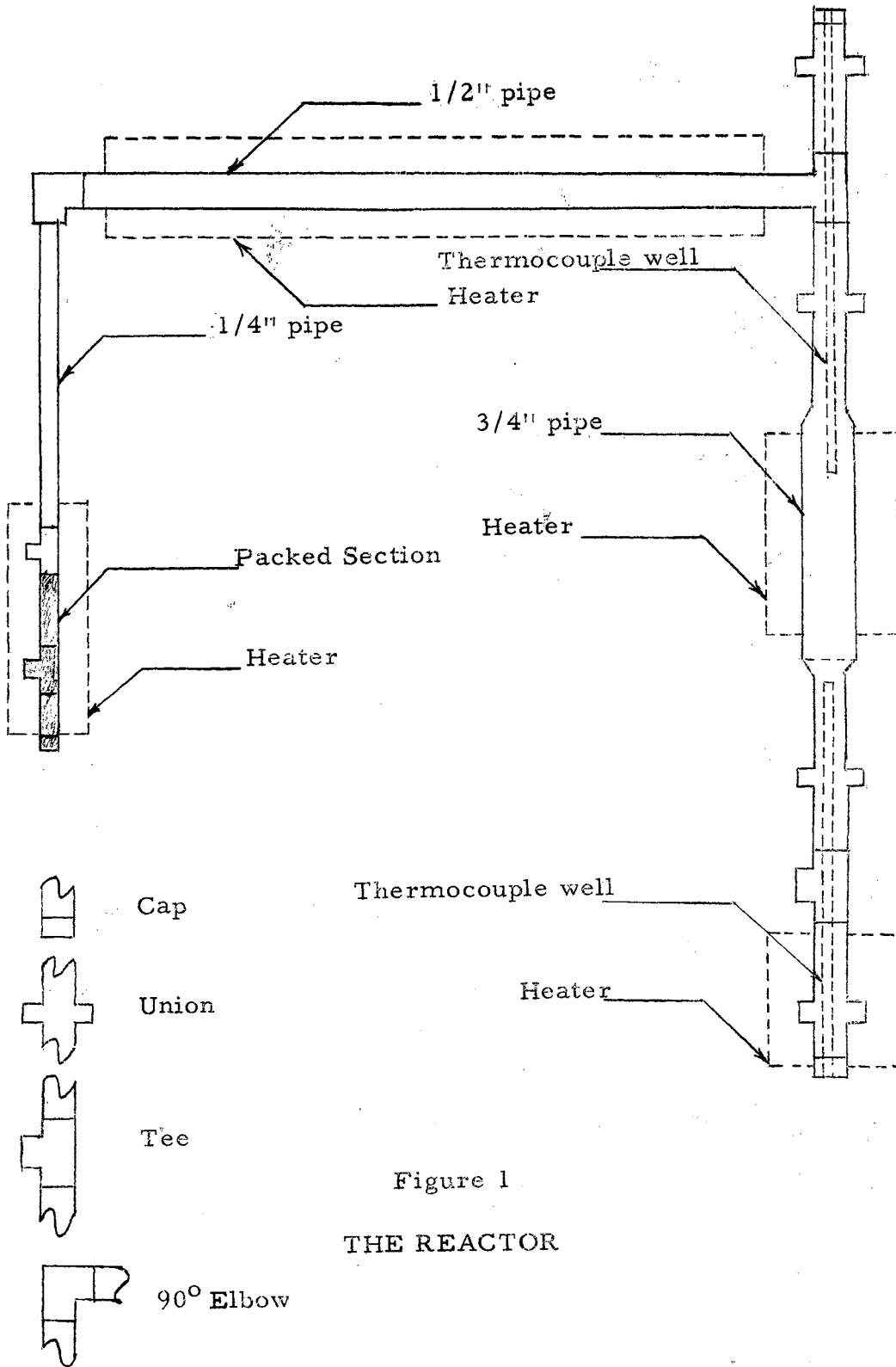


Figure 1
THE REACTOR

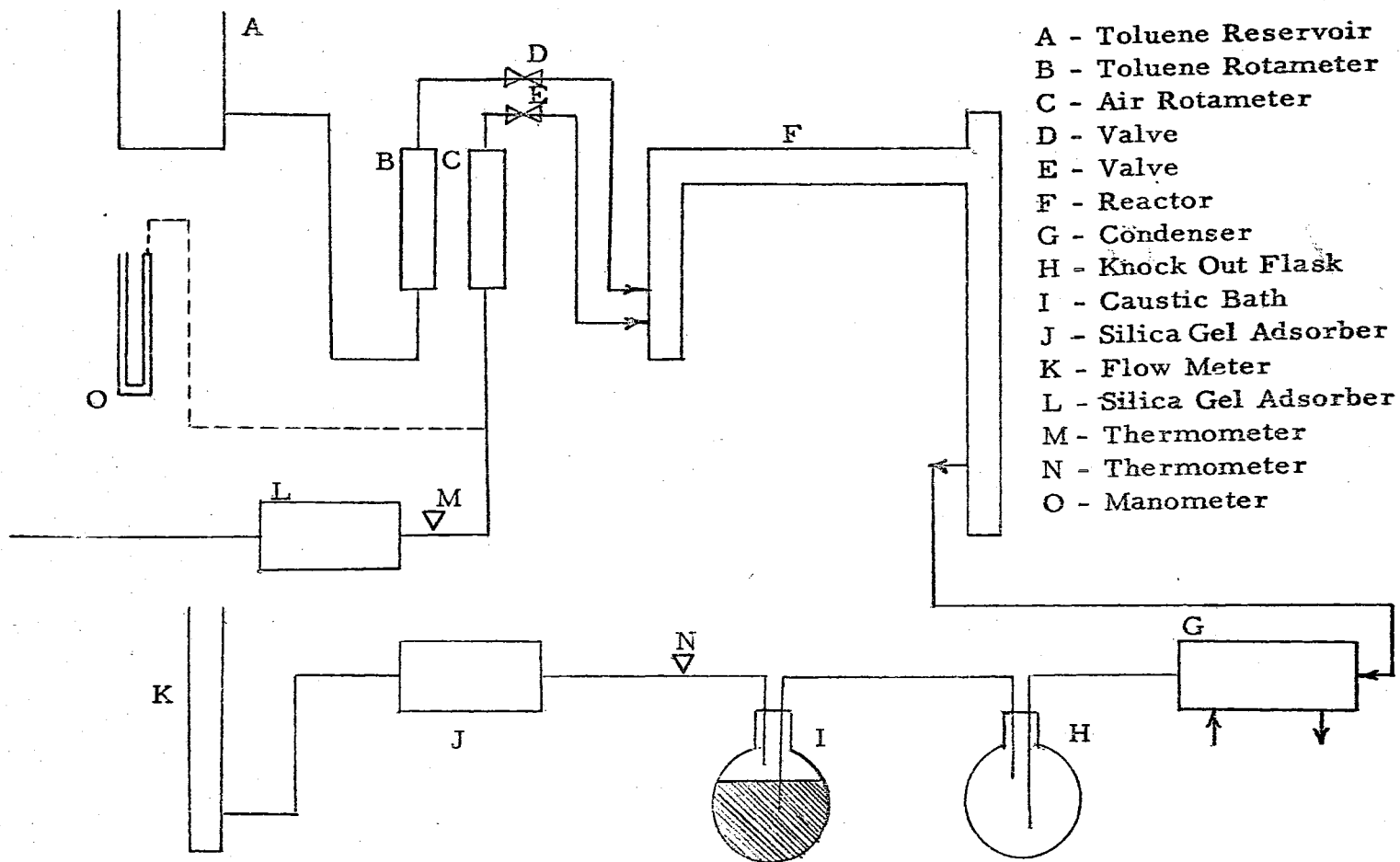
The air was then passed through a Matheson T-601 rotameter, through a needle valve and into the reactor. Figure 2 shows the complete system.

The Flow Stream Leaving the Reactor

After leaving the reactor the flow streams were first passed through a glass condenser to remove the toluene and other condensables. After passing through the condenser the stream was fed to a five liter flask in order to collect the condensate. The gas leaving the collection flask was then passed through a caustic scrubber. This scrubber consisted of a two liter flask packed with Berl saddles and filled with concentrated sodium hydroxide solution. The purpose of this scrubber was to remove any carbon dioxide from the stream, leaving only oxygen and nitrogen. From this point the gas was passed through a silica gel dryer to remove any water or organic material which remained in the stream. The gas then was fed through a soap bubble flow meter and to the atmosphere.

Temperature Measurement

The temperature was measured at five points in the equipment. Two of these measurements were made with mercury in glass thermometers. The other three measurements were made by means of copper constantan thermocouples. Copper constantan was selected as the thermocouple material because of its large voltage-to-temperature ratio. The two glass thermometers were placed so as to note the temperature of the air entering the system and of the gas leaving the system.



- A - Toluene Reservoir
- B - Toluene Rotameter
- C - Air Rotameter
- D - Valve
- E - Valve
- F - Reactor
- G - Condenser
- H - Knock Out Flask
- I - Caustic Bath
- J - Silica Gel Adsorber
- K - Flow Meter
- L - Silica Gel Adsorber
- M - Thermometer
- N - Thermometer
- O - Manometer

Figure 2

FLOW DIAGRAM OF THE SYSTEM

Two of the thermocouples were mounted in wells. One of these wells was in the reaction chamber above the catalyst and the other was below the reaction chamber as shown in Figure 1. The third thermocouple was mounted on the outside of the reaction chamber to measure the wall temperature. The thermocouples were connected as shown in Figure 3. The potentiometer used was manufactured by Leeds and Northrup Company and was sensitive to about two degrees centigrade with the copper constantan thermocouples.

The Electrical System

The only electrical equipment used in the apparatus was the heaters. The heaters were wired to variable voltage transformers as shown in Figure 3. It should be noted that heaters B and C were powered from the same transformer. The resistances of the heaters were as follows:

Heater	Location	Resistance
A	Reactor	26 OHMS
B	Second Preheat Section	13.5 OHMS
C	First Preheat Section	26 OHMS
D	Bottom of System	2.5 OHMS.

The heating tapes used for heating tapes A, B and C were rated to operate at temperatures up to 500 degrees centigrade.

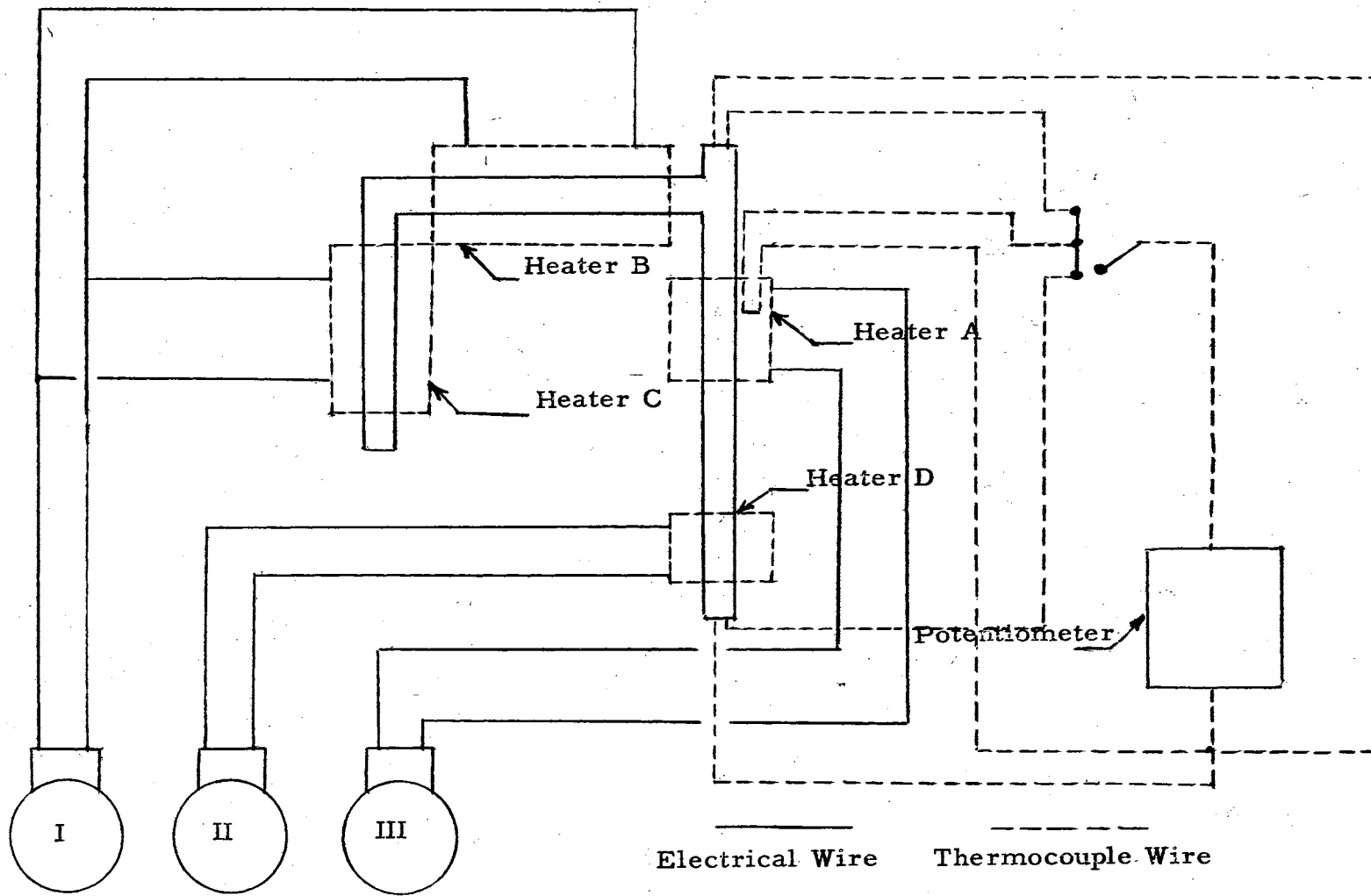


Figure 3

THE ELECTRICAL SYSTEM

CHAPTER V

EXPERIMENTAL PROCEDURE

The experimental apparatus described in Chapter IV was used to collect rate data on the oxidation of toluene. The toluene used in the experiment was technical grade (95 mole percent) toluene manufactured by Phillips Petroleum Company. The composition of the material was checked by a gas phase chromatograph and found to contain approximately 95 percent toluene. No impurities other than ethyl benzene were observed. The air was obtained from a compressed air line. The catalyst was chemically pure vanadium pentoxide manufactured by the Harshaw Chemical Company.

Calibration of Instruments

Before attempting to run the equipment the rotameters and thermocouples were calibrated. The air rotameter was calibrated with the aid of a stop watch and soap bubble flow meter. The toluene rotameter was calibrated by use of a graduated cylinder and stop watch. The calibration curves for these instruments are included in Appendix G. The scale of the potentiometer was marked in degrees Fahrenheit for use with an iron-constantan thermocouple. The copper-constantan thermocouples were checked at the ice point, the boiling point of water

and the melting point of lead with the potentiometer. These checks were then used to verify that the thermocouple calibration charts for iron-constantan (25) and for copper-constantan (23) could be used to convert the temperature to degrees centigrade.

Preparation for the Experiment

Before taking experimental data, the catalyst was weighed into the reaction chamber and the depth measured. Three problems were then solved. The problems were:

1. The system was freed from leaks.
2. The pressure drop across the apparatus was reduced.
3. Uniform flow was produced.

The first problem arose from several small leaks in the system. It was solved by simply pressuring the system, locating the leaks with soap solution, and tightening the fittings. After it appeared that all of the leaks were stopped the system was checked by passing air through it and making a material balance to prove there were no leaks.

The problem of high pressure drop arose from liquid condensing in the bottom of the reactor and blocking the outlet. This problem was solved by simply adding a heater at the bottom of the reactor to prevent condensation before the gas reached the condenser.

Non-uniform flow arose because of a heat transfer problem in the evaporator section of the reactor. The toluene, after being fed, frequently would not immediately vaporize. This problem was solved

by packing a section of the vaporizer. This permitted better heat transfer, more uniform vaporization and thus a reasonably steady flow.

Before making a series of runs it was necessary to take several preparatory steps. The silica gel dryers, having absorbed water from previous runs, were regenerated. This was done in an oven at about 200 to 300° C. This drying lasted for about two hours. After the dryers had been regenerated and cooled, the heaters on the apparatus were adjusted to permit the equipment to come to the proper temperature before operation. One to two hours were allowed for this operation. Shortly after the heaters were turned on, the air line was opened to permit the complete oxidation of any material which might have remained from any previous runs. Finally, the toluene reservoir was filled and the collection flask downstream from the condenser was emptied.

Operation of the Experiment

The first step in the operation of the equipment was to adjust the flow rates to the desired level of operation. The transformers were then adjusted to the proper settings for the desired operation temperature. The range of voltages used on the transformers in order to obtain temperatures from 250 to 500 degrees centigrade were as follows:

TRANSFORMER	VOLTAGES
I	75-120 Volts
II	80- 95 Volts
III	15- 20 Volts.

It was found that the reactor could be controlled at any temperature in the range of interest. Any time the flow rate was changed it was

necessary to readjust the heater so as to compensate for the different rate of heat removal.

In all cases the toluene flow rate was set at 4.80×10^{-4} gram moles per second and the air flow rate was varied. The air flow rates ranged from about $.25 \times 10^{-4}$ gram moles per second to 1.8×10^{-4} gram moles per second. The flow rate out was measured with a soap film flow meter because changes in density would not permit the use of a rotameter. After one run was made, the flow rate of oxygen was changed and the heater readjusted. The process was continued until the entire flow range was covered at that operating temperature. The data recorded from such runs were:

1. Temperature of the gas leaving the reactor.
2. Temperature of the gas in the reactor.
3. Wall temperature of the reactor.
4. Temperature of the air entering the system.
5. Temperature of the gas leaving the system.
6. Feed rate of toluene.
7. Feed rate of air.
8. Gas exit rate from the system.
9. Pressure drop across the system.
10. Atmospheric pressure.

After collecting the data at one temperature, the transformers were re-adjusted so as to permit study at another temperature. In this manner data were collected at reactor temperatures of 237, 309, 364 and 416°C .

Shut Down

After a series of runs were made, the apparatus was shut down. The electricity was turned off and the valve on the toluene flow line was closed. The air was normally left running in order to oxidize any organic materials which might remain in the system.

CHAPTER VI

PRESENTATION AND DISCUSSION OF RESULTS

The methods used in the previous chapter were used to obtain the data which are presented in Tables I through IV. These tables include the ten pieces of information which were recorded, the total volumetric flow rate and the number of moles of oxygen reacted per unit time. The temperature of the reactor was taken to be the temperature above the catalyst head. This was done because the thermocouple that measured this temperature was actually located in the reactor while the thermocouple below the catalyst bead was not. The following were the dimensions of the catalyst bead:

DEPTH	1.70 centimeters
VOLUME	4.74 cubic centimeters
MASS OF V_2O_5	3.3136 grams.

These data were used to attempt to calculate rate constants and orders for the oxidation of toluene.

To compute the rate constants, the work of Sasayama (19) was assumed to be valid, e. g. the rate is independent of the concentration of toluene. Equation (2-10) may then be written

$$r_a = \frac{dN_{O_2}}{dW} = kC_{O_2} \quad (6-1)$$

TABLE I

EXPERIMENTAL DATA FOR TOLUENE OXIDATION AT 238 DEGREES CENTIGRADE

Temp. in Reaction Chamber °C	Temp. Below Reaction Chamber °C	Wall Temp. °C	Enter- ing Air Temp. °C	Exit Air Temp. °C	Atmos- pheric Pressure mm Hg	Pressure Drop mm Hg	Toluene Feed Rate gm. moles sec. x 10 ⁴	Air Feed Rate gm. moles sec. x 10 ⁴	Exit Air Rate gm. moles sec. x 10 ⁴	Oxygen Reacted gm. moles sec. x 10 ⁵	Volume Flow cc/sec.
238	123	311	35.0	37.0	739.2	7.1	4.80	1.457	1.300	1.57	27.0
236	123	310	34.4	37.0	739.2	7.1	4.80	1.187	1.050	1.37	25.7
237	123	309	34.4	36.5	739.2	7.1	4.80	.7980	.6887	1.09	24.0
236	128	309	34.4	36.0	739.2	6.8	4.80	.5139	.4612	.527	22.8
237	128	309	33.9	36.0	739.2	6.8	4.80	.3432	.2715	.417	22.1
237	128	309	33.9	36.0	739.2	7.1	4.80	1.365	1.134	2.31	26.5
237	128	309	33.9	36.0	739.2	7.1	4.80	1.014	.8916	1.17	25.0
235	128	309	33.9	36.0	739.6	7.1	4.80	.6239	.5704	.535	23.2
237	155	319	33.3	36.0	739.6	7.1	4.80	1.732	1.475	2.52	28.1
238	155	310	33.3	36.0	739.6	7.1	4.80	1.564	1.238	3.26	27.4
238	155	310	33.3	36.0	739.6	7.1	4.80	1.251	1.054	1.97	26.1
239	155	310	33.3	36.0	739.6	7.1	4.80	1.385	1.135	2.50	26.7
239	155	310	33.3	36.0	739.6	7.1	4.80	.9815	.8719	1.10	25.0
239	155	312	33.3	36.0	739.6	7.1	4.80	.8213	.7672	.541	24.3
239	155	310	33.3	36.0	739.6	7.1	4.80	.7329	.6778	.461	23.8
239	155	312	33.3	36.0	739.6	7.1	4.80	.6062	.5481	.581	23.3
239	155	310	33.3	36.0	739.6	7.1	4.80	.5672	.5114	.558	23.1
239	155	310	33.3	36.0	739.6	7.1	4.80	.4027	.3836	.191	22.5
239	155	310	33.3	36.0	739.6	7.1	4.80	1.611	1.304	3.07	27.7

TABLE II

EXPERIMENTAL DATA FOR TOLUENE OXIDATION AT 309 DEGREES CENTIGRADE

Temp. in Reaction Chamber °C	Temp. Below Reaction Chamber °C	Wall Temp. °C	Enter- ing Air Temp. °C	Exit Air Temp. °C	Atmos- pheric Pressure mm Hg	Pressure Drop mm Hg	Toluene Feed Rate gm. moles sec. x 10 ⁴	Air Feed Rate gm. moles sec. x 10 ⁴	Exit Air Rate gm. moles sec. x 10 ⁴	Oxygen Reacted gm. moles sec. x 10 ⁵	Volume Flow cc/sec.
310	165	407	33.3	37.5	739.9	7.9	4.80	1.843	1.479	3.64	31.7
310	185	407	31.7	34.0	744.0	7.8	4.80	1.336	1.184	1.52	29.1
310	145	407	32.2	34.0	744.0	7.1	4.80	.8302	.7767	.538	26.7
311	145	404	32.2	34.0	743.0	7.1	4.80	.3641	.3231	.410	24.6
308	150	404	32.2	34.0	744.0	8.0	4.80	1.468	1.367	1.01	29.6
311	170	404	32.2	34.0	744.0	7.7	4.80	1.016	.8824	1.34	27.6
307	190	410	31.6	33.5	743.4	8.0	4.80	1.704	1.437	2.65	30.7
307	192	410	31.6	33.5	743.4	8.0	4.80	1.628	1.397	2.31	30.3
307	193	410	31.6	33.5	743.4	7.6	4.80	.4675	.4517	.158	24.8

TABLE IV

EXPERIMENTAL DATA FOR TOLUENE OXIDATION AT 416 DEGREES CENTIGRADE

Temp. in Reaction Chamber °C	Temp. Below Reaction Chamber °C	Wall Temp. °C	Enter- ing Air Temp. °C	Exit Air Temp. °C	Atmos- pheric Pressure mm Hg	Pressure Drop mm Hg	Toluene Feed Rate gm. moles sec. x 10 ⁴	Air Feed Rate gm. moles sec. x 10 ⁴	Exit Air Rate gm. moles sec. x 10 ⁴	Oxygen Reacted gm. moles sec. x 10 ⁴	Volume Flow cc/sec.
416	152	512	37.8	49.0	740.4	7.1	4.80	1.533	1.271	2.62	36.8
416	168	508	37.8	46.0	740.4	7.1	4.80	.8418	.7290	1.13	32.7
415	152	508	37.8	45.0	740.4	6.5	4.80	.5475	.4493	.982	31.0
416	175	512	37.3	44.0	740.4	6.5	4.80	.2777	.2340	.437	29.5
415	175	510	37.3	44.0	740.4	7.1	4.80	1.699	1.429	2.70	37.7
415	168	508	37.3	43.5	740.4	6.8	4.80	1.003	.8344	1.69	33.6
415	230	508	32.2	36.5	739.2	7.1	4.80	1.706	1.366	3.40	37.8
417	230	512	32.2	36.5	739.2	7.1	4.80	1.177	1.002	1.75	34.8
416	220	512	32.2	36.5	739.2	7.1	4.80	.8708	.7391	1.417	33.0
416	230	510	32.2	36.5	739.2	7.1	4.80	1.616	1.320	2.96	37.3

TABLE III

EXPERIMENTAL DATA FOR TOLUENE OXIDATION AT 364 DEGREES CENTIGRADE

Temp. in Reaction Chamber °C	Temp. Below Reaction Chamber °C	Wall Temp. °C	Enter- ing Air Temp. °C	Exit Air Temp. °C	Atmos- pheric Pressure mm Hg	Pressure Drop mm Hg	Toluene Feed Rate gm. moles sec. x 10 ⁴	Air Feed Rate gm. moles sec. x 10 ⁴	Exit Air Rate gm. moles sec. x 10 ⁴	Oxygen Reacted gm. moles sec. x 10 ⁵	Volume Flow cc/sec.
364	220	458	33.3	36.5	736.5	7.2	4.80	1.809	1.589	2.20	35.6
365	221	458	33.3	36.5	736.5	7.2	4.80	1.645	1.334	3.11	34.8
365	190	458	33.3	37.0	736.5	7.2	4.80	1.576	1.295	2.72	34.4
365	190	458	33.3	37.0	736.5	7.2	4.80	1.412	1.168	2.44	33.6
364	170	458	33.3	37.0	736.5	6.8	4.80	1.147	.9236	2.18	32.1
365	215	458	33.3	38.0	736.5	6.8	4.80	.9216	.8076	1.40	30.9
364	215	458	33.3	37.0	736.5	6.8	4.80	.7507	.6536	.918	29.9
364	215	458	33.3	37.0	736.5	6.8	4.80	.6493	.5855	.638	29.4
364	215	458	32.8	37.0	736.5	6.7	4.80	.4954	.4816	.138	28.6
363	215	458	32.8	37.0	736.5	6.6	4.80	.3171	.2975	.196	27.6
363	215	458	32.8	37.0	736.5	6.6	4.80	.2656	.2266	.390	27.3
363	215	458	32.8	37.0	736.5	7.1	4.80	1.460	1.205	2.55	33.7

The concentration of oxygen may be expressed as the moles of oxygen per second fed less the moles of oxygen per second reacted over the gas volume flow rate. Thus:

$$C_{O_2} = \frac{F_{O_2} - N_{O_2}}{Q} \quad (6-2)$$

This may be combined with equation (6-1) to obtain

$$\frac{dN_{O_2}}{dW} = k \left(\frac{F_{O_2} - N_{O_2}}{Q} \right)^\alpha$$

Depending on the value for α the above equation will have one of the solutions that follow:

$$\frac{dN_{O_2}}{dW} = \frac{k}{Q^\alpha} (F_{O_2} - N_{O_2})^\alpha$$

$$\frac{dN_{O_2}}{(F_{O_2} - N_{O_2})^\alpha} = \frac{k}{Q^\alpha} dW$$

$$\int_0^{N_{O_2}} \frac{k}{Q^\alpha} dW = \int_0^{N_{O_2}} \frac{dN_{O_2}}{(F_{O_2} - N_{O_2})^\alpha}$$

If $\alpha = 1$

$$\frac{k}{Q} W = - \left(\ln (F_{O_2} - N_{O_2}) - \ln F_{O_2} \right)$$

$$\frac{k}{Q} W = \ln \frac{F_{O_2}}{F_{O_2} - N_{O_2}} \quad (6-4)$$

But if $\alpha \neq 1$

$$\frac{k}{Q} W = \int_0^{N_{O_2}} (F_{O_2} - N_{O_2})^{-\alpha} dN_{O_2}$$

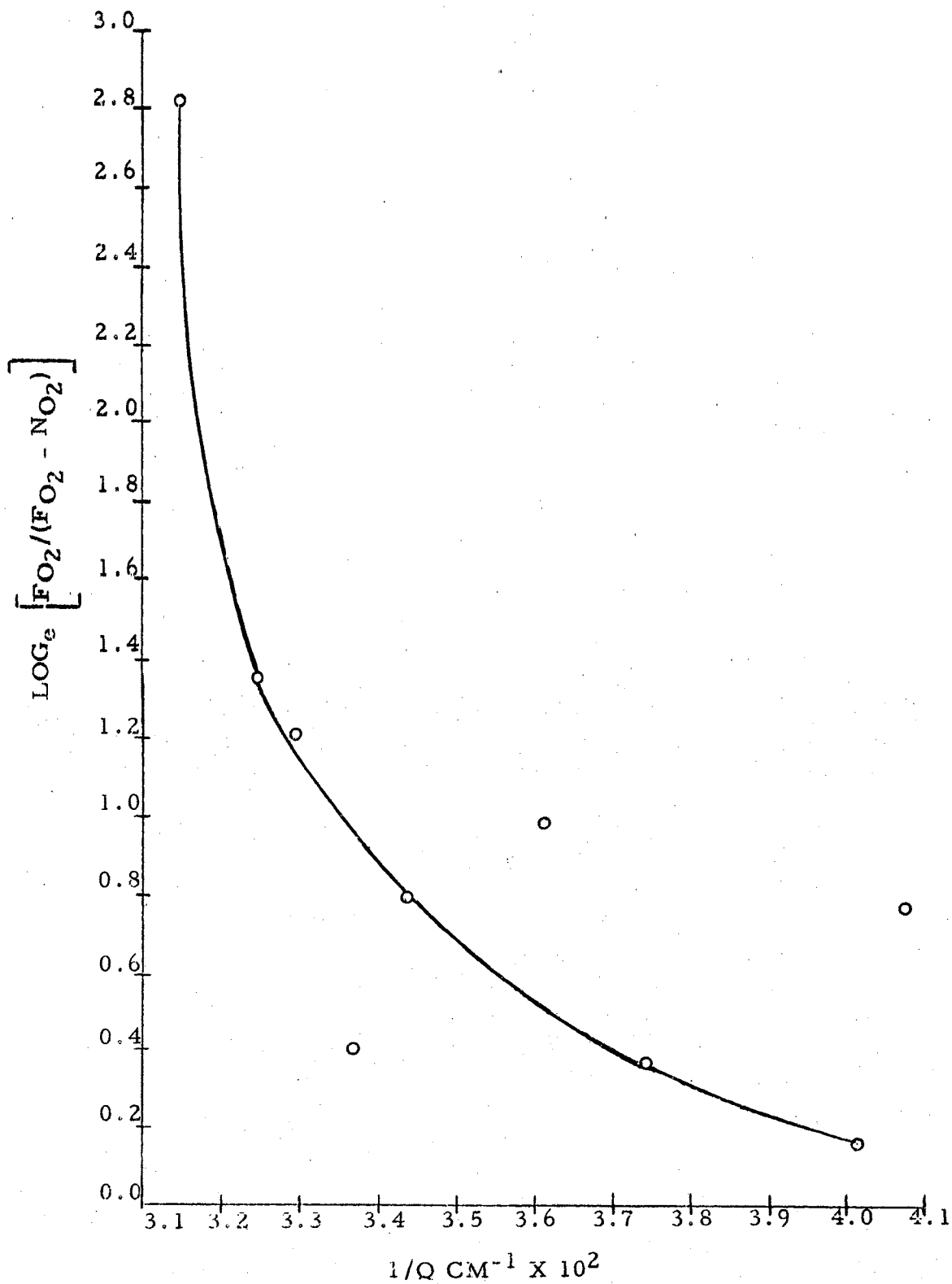


Figure 5
 $\text{LOG}_e \left[\frac{\text{FO}_2}{(\text{FO}_2 - \text{NO}_2)} \right]$ AS A FUNCTION OF $1/Q$
AT A TEMPERATURE OF 309°C

$$\frac{k}{Q^{\alpha}} W = - \left(\frac{1}{1-\alpha} \right) \left[(F_{O_2} - N_{O_2})^{(1-\alpha)} - F_{O_2}^{(1-\alpha)} \right]$$

$$(1-\alpha) \frac{k}{Q^{\alpha}} W = F_{O_2}^{(1-\alpha)} - (F_{O_2} - N_{O_2})^{(1-\alpha)} \quad (6-5)$$

In order to check to see if the reaction is first order, it is only necessary to plot the term $\ln \frac{F_{O_2}}{F_{O_2} - N_{O_2}}$ as a function of the reciprocal of the

volumetric flow rate for each temperature. Should this be the proper order then a straight line with a positive slope through the zero intercept would be obtained.

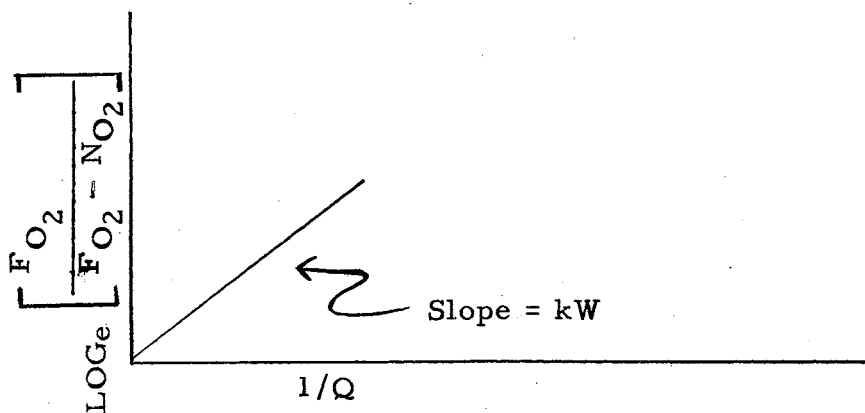


Figure 4

$$\text{LOG}_e \left[\frac{F_{O_2}}{F_{O_2} - N_{O_2}} \right] \text{ AS A FUNCTION OF } 1/Q$$

Figure 5 is this function plotted for data at 309 degrees centigrade. It may be noted that this data clearly does not fit the first order rate expression.

To find the order and rate constants when the order is something other than unity equation (6-5) must be used. One method of using this

expression to find the order and rate constants is to make a least mean square fit of the equation to the experimental data. This approach presents the problem that the form of equation (6-5) does not lend itself to the methods normally used in curve fitting. However, Deming (2) presents a method which enables one to fit, by an iterative procedure, any equation. An outline of this method may be found in Appendix E. This method was programed for the IBM 650 Computer and a fit attempted. Unfortunately, the computer would not converge to an answer. It was then decided to plot the term $F_{O_2}^{(1-\alpha)} - (F_{O_2} - N_{O_2})^{(1-\alpha)}$ as a function of the reciprocal of the volumetric flow rate used to the α power, for various values of α . This plot should be linear and pass through the zero intercept. That is:

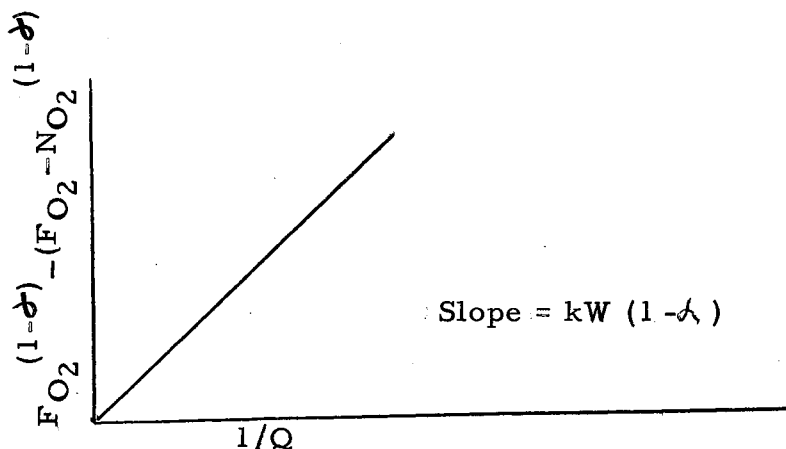


Figure 6

$F_{O_2}^{(1-\alpha)} - (F_{O_2} - N_{O_2})^{(1-\alpha)}$ AS A FUNCTION OF $1/Q^\alpha$

In order to accomplish this the IBM 650 Computer was programed to calculate $(\frac{1}{Q})^\alpha$ and $(F_{O_2} - N_{O_2})^{(1-\alpha)}$ from $\alpha = 0$ to $\alpha = 4$ at intervals of one tenth. Figures 7 through 10 give selected results of such calculations

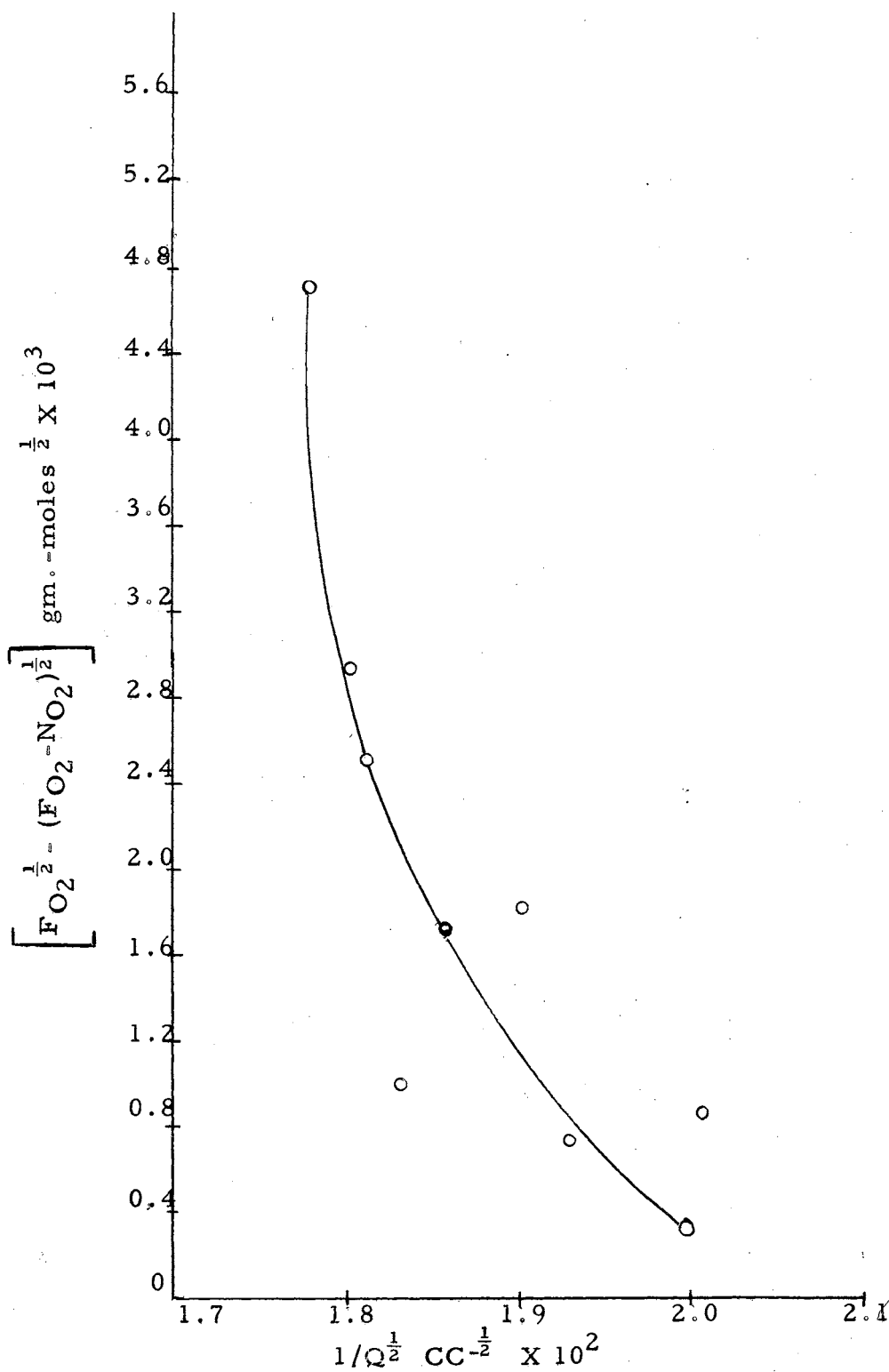


Figure 7
 $[F_{O_2}^{(1-\alpha)} (F_{O_2} - N_{O_2})^{(1-\alpha)}]$ AS A FUNCTION OF $1/Q^\alpha$
 WHEN THE ORDER IS 1/2 AT A TEMPERATURE OF 309°C

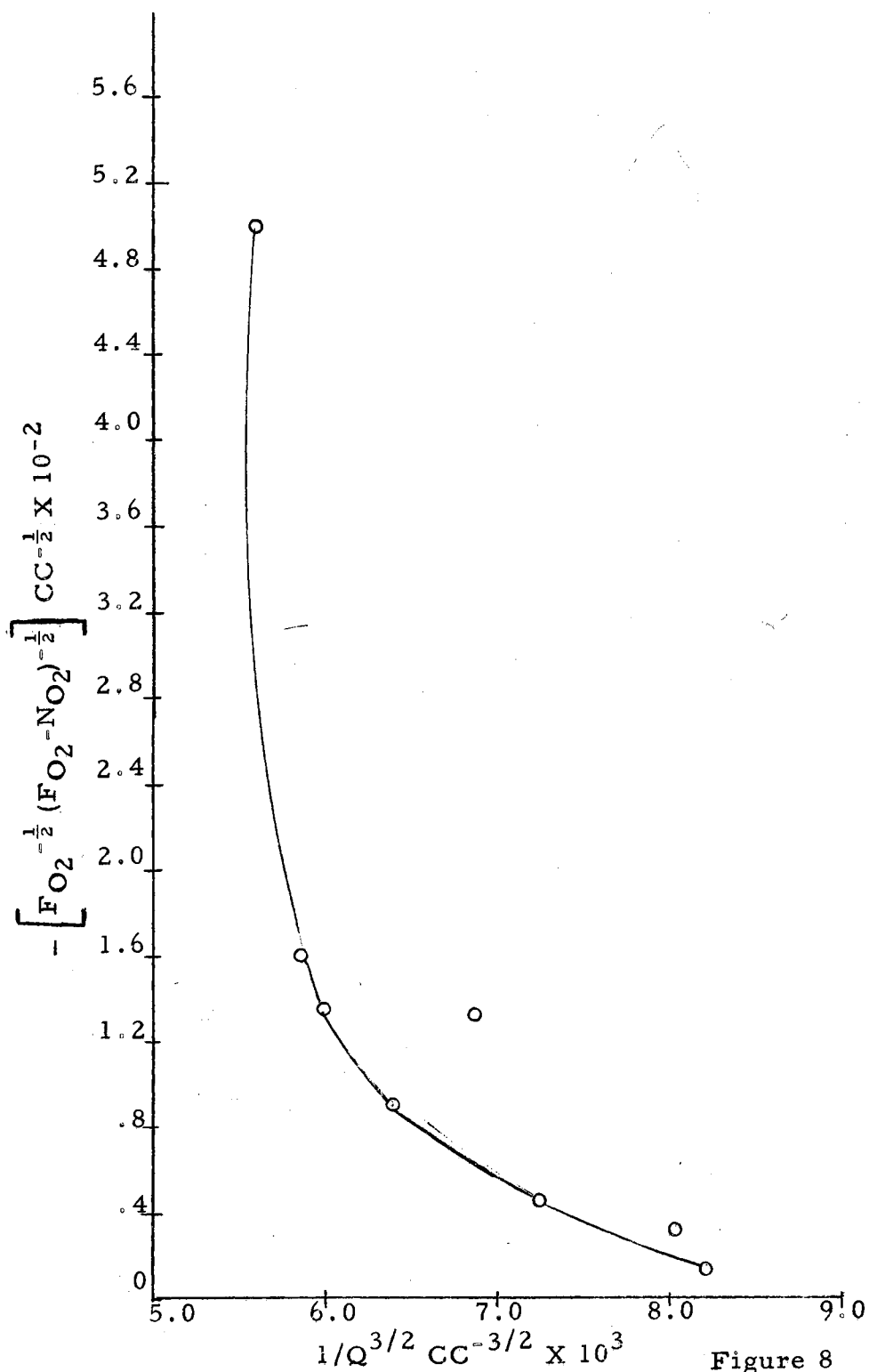


Figure 8
 $\text{FO}_2^{(1-\alpha)} - (\text{FO}_2 - \text{NO}_2)^{(1-\alpha)}$ AS A FUNCTION OF $1/Q^{3/2}$
 WHEN THE ORDER IS 3/2 AT A TEMPERATURE OF 309°C

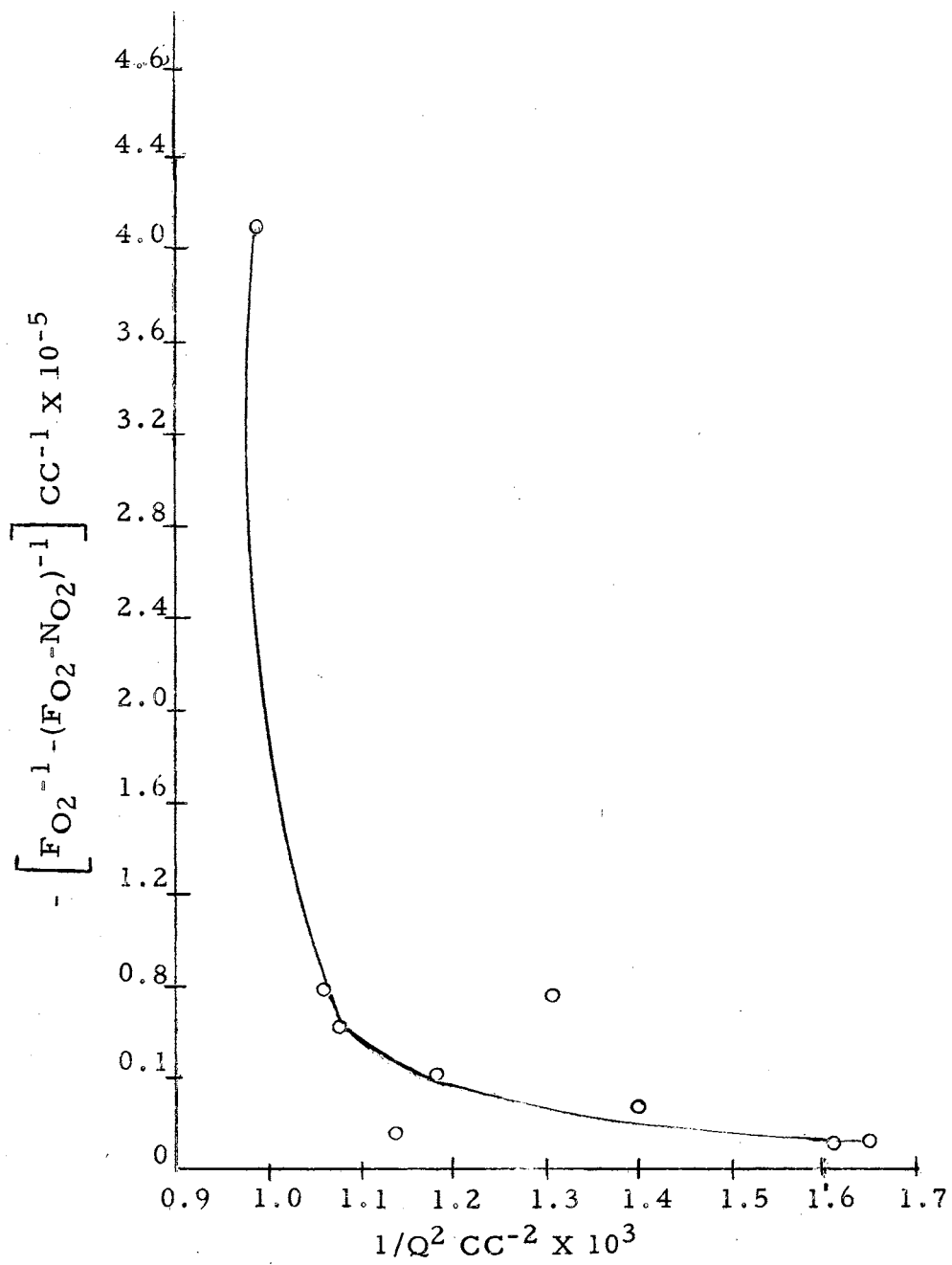


Figure 9

$FO_2^{(1-\alpha)} - (FO_2-NO_2)^{(1-\alpha)}$ AS A FUNCTION OF $1/Q^2$
 WHEN THE ORDER IS 2 AT A TEMPERATURE OF 309°C

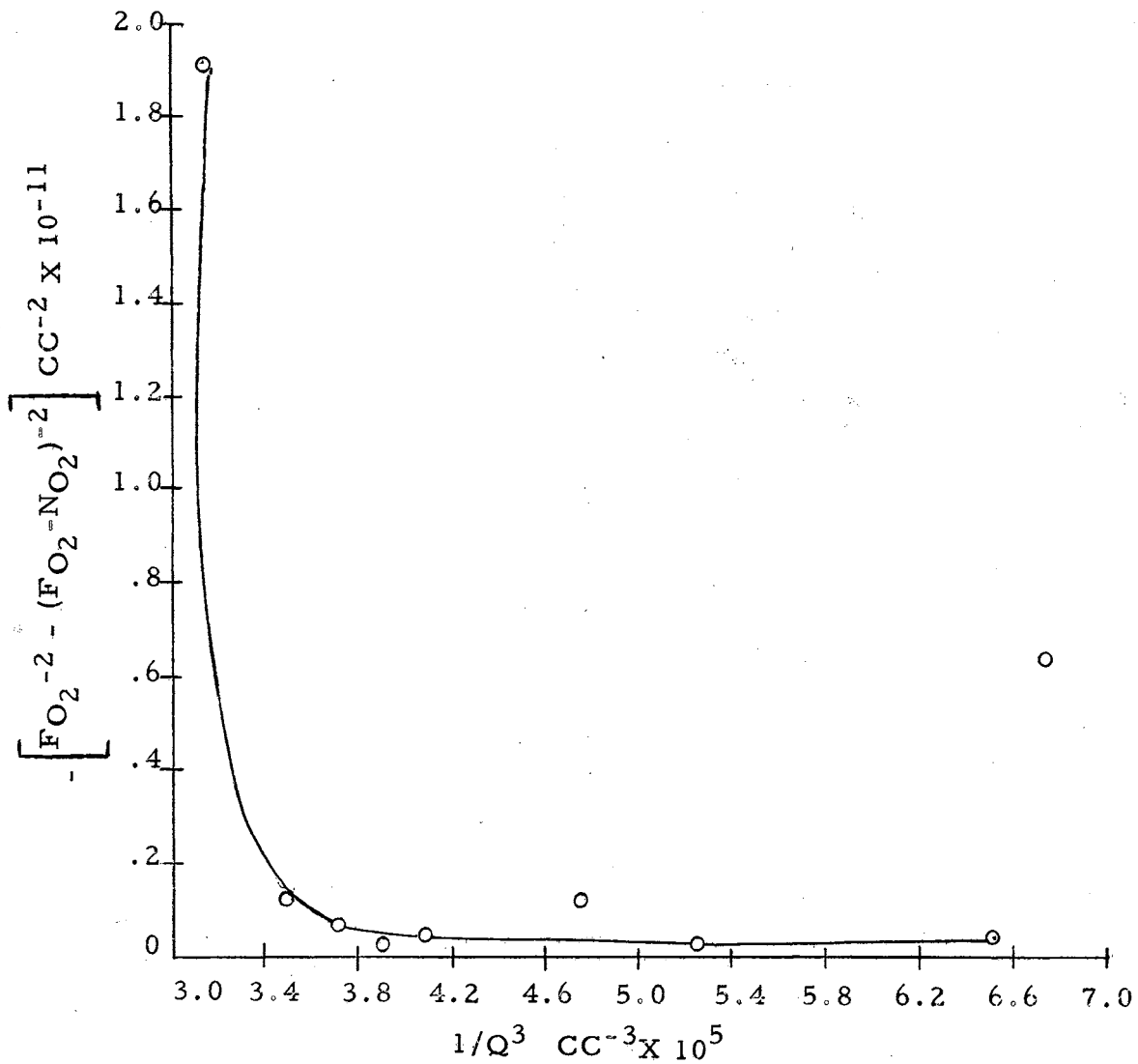


Figure 10

$$\left[F_{O_2}^{(1-\beta)} - (F_{O_2} - NO_2)^{(1-\beta)} \right] \text{ AS A FUNCTION OF } 1/Q^\beta$$
 WHEN THE ORDER IS 3 AT A TEMPERATURE OF 309°C

at a temperature of 309 degrees centigrade. The conclusion to be reached from these plots is that an expression of the form $r_{O_2} = kC_{O_2}^{\alpha}$ will not fit the data. The data for the other three temperatures give very nearly the same results as for 309 degrees centigrade.

It was then assumed that the rate was also influenced by the concentration of toluene. Mathematically, this is expressed as follows:

$$r_{O_2} = \frac{dN_{O_2}}{dW} = k C_{O_2}^{\alpha} C_{tol}^{\beta} \quad (6-6)$$

The concentration may be expressed as follows:

$$C_{O_2} = \frac{F_{O_2} - N_{O_2}}{Q} \quad (6-7)$$

$$C_{tol} = \frac{F_{tol} - N_{tol}}{Q}$$

Equation (6-6) then reduced to

$$\begin{aligned} \frac{dN_{O_2}}{dW} &= k \left[\frac{F_{O_2} - N_{O_2}}{Q} \right]^{\alpha} \left[\frac{F_{tol} - N_{tol}}{Q} \right]^{\beta} \\ \frac{dN_{O_2}}{dW} &= k \left(\frac{1}{Q} \right)^{\alpha+\beta} (F_{O_2} - N_{O_2})^{\alpha} (F_{tol} - N_{tol})^{\beta} \\ \frac{dN_{O_2}}{(F_{O_2} - N_{O_2})^{\alpha} (F_{tol} - N_{tol})^{\beta}} &= k \left(\frac{1}{Q} \right)^{\alpha+\beta} dW \end{aligned}$$

$$k \left(\frac{1}{Q} \right)^{\alpha+\beta} W = \int_0^{N_{O_2}} \frac{dN_{O_2}}{(F_{O_2} - N_{O_2})^{\alpha} (F_{tol} - N_{tol})^{\beta}}$$

Since, in general, the oxygen concentration is not great when compared with the toluene concentration, it is probably valid to assume

that the term $(F_{\text{tol}} - N_{\text{tol}})$ may be replaced by a term $(F_{\text{tol}} - AN_{\text{O}_2})$, where A is a constant. This is equivalent to assuming that the toluene reacted is proportional to the oxygen reacted regardless of their individual concentrations. Again, since the oxygen concentration was small when compared to the toluene concentration, it was assumed that the term $(F_{\text{tol}} - AN_{\text{O}_2})$ should not be too sensitive to the value of A so long as it is not far from the proper value. For this reason, complete oxidation to benzoic acid was assumed and the value for A was selected as 2/3. Thus equation (6-8), reduced to an equation of the form

$$k \left(\frac{1}{Q}\right)^{\alpha + \beta} W = \int_0^{N_{\text{O}_2}} \frac{dN_{\text{O}_2}}{(F_{\text{O}_2} - N_{\text{O}_2})^{\alpha} (F_{\text{tol}} - 2/3 \cdot N_{\text{O}_2})^{\beta}} \quad (6-9)$$

The above equation presents the difficulty that it may not be integrated unless values for α and β are known and even if they are known the equation may be integrated only for special cases. It was decided that it would be well to attempt to make a least-mean-square-fit of equation (6-9) to determine α , β and k. To do this, it was necessary to resort to the methods of Deming (2) to obtain a fit. In addition, the usual problems equation (6-9) must also be integrated and differentiated by numerical methods. These techniques are discussed in such sources as Salvatore and Baron (19, 20). A program to make this fit on the IBM 650 Computer was written. This program is included in Appendix D. This program would not converge to an answer for the experimental data.

At this point it was again noted that if the toluene concentration was large when compared with the oxygen concentration, the term

$(F_{\text{tol}} - 2/3 N_{\text{tol}})$ could be set equal to the toluene feed rate. Then equation (6-9) may be written as follows:

$$k \left(\frac{1}{Q}\right)^{\alpha+\beta} W = \left(\frac{1}{F_{\text{tol}}}\right)^{\beta} \int_0^{N_{\text{O}_2}} \frac{dN_{\text{O}_2}}{(F_{\text{O}_2} - N_{\text{O}_2})}$$

This equation may be integrated to obtain

$$(1-\alpha) k \left(\frac{1}{Q}\right)^{\alpha+\beta} W = \left(\frac{1}{F_{\text{tol}}}\right)^{\beta} \left[F_{\text{O}_2}^{(1-\alpha)} - (F_{\text{O}_2} - N_{\text{O}_2})^{(1-\alpha)} \right]$$

when:

$$\alpha \neq 1$$

or

$$k \frac{1}{Q} W = \left(\frac{1}{F_{\text{tol}}}\right)^{\beta} \ln \left(\frac{F_{\text{O}_2}}{F_{\text{O}_2} - N_{\text{O}_2}} \right)$$

when

$$\alpha = 1$$

By use of the tables for $\left(\frac{1}{Q}\right)^{\alpha}$ and $F_{\text{O}_2}^{(1-\alpha)} - (F_{\text{O}_2} - N_{\text{O}_2})^{(1-\alpha)}$ previously prepared, plots of $F_{\text{O}_2}^{(1-\alpha)} - (F_{\text{O}_2} - N_{\text{O}_2})^{(1-\alpha)}$ as a function of $\left(\frac{1}{Q}\right)^{\alpha+\beta}$ may be obtained. This was investigated and the results were very similar to those obtained when it was assumed that the rate depended only on the oxygen concentration. The plots of $F_{\text{O}_2}^{(1-\alpha)} - (F_{\text{O}_2} - N_{\text{O}_2})^{(1-\alpha)}$ as a function of $\left(\frac{1}{Q}\right)^{\alpha+\beta}$ were essentially the same as Figures 7 through 10. This would seem to imply that the rate of reaction may not be expressed as proportional products of the concentrations raised to some power.

As shown in equations (3-3) and (3-5), the oxidation reaction is very complex. It is, therefore, very possible that the rate could actually

depend on any number of steps. This would provide a very plausible explanation why the data could not be fitted to a kinetic equation of the usual form.

CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

Restatement of Thesis Goals

The study of the oxidation of toluene was started with several goals in mind. These goals were met with varying degrees of success.

The original goals were:

1. To measure the rate of oxidation of toluene in the vapor phase in a flow reactor using vanadium pentoxide catalyst.
2. To determine the order and rate constants for the data obtained in part one.
3. To calculate the Arrhenius constants for the rate constants at different temperatures.

The first of these goals was met by taking experimental data on the apparatus described in Chapter IV. These data consisted of inlet flow rates for toluene and air and the outlet flow rate for air. By material balance, it was possible to convert the information into a form which would give the rate of reaction. These data displayed some scatter but they were sufficiently smooth to permit plotting for the purpose of obtaining orders and rate constants.

The second goal was not met. The analysis of the data which was presented in Chapter VI showed that the data could not be fit to the form

$$r_{O_2} = k C_{O_2} C_{tol}.$$

While the equation is normally assumed to apply to chemical reactions, it is not too surprising that it is not sufficient to predict the rate of oxidation of toluene. The peroxide and free radical mechanism as presented in Chapter III presents a number of complex steps which could easily complicate the reaction to such a degree that a very complex rate equation would be needed. In addition to the steps in the oxidation, equation (3-5) also presents a reaction of sufficient complexity to give an extremely difficult rate expression.

The final thesis goal could not be reached for the same reasons that the second goal was not attained. The calculation of activation energies requires rate constants and they could not be calculated for this reaction.

Conclusions

It is possible to reach three conclusions from this study. They are:

1. The equation $r_{O_2} = k C_{O_2}^{\alpha} C_{tol}^{\beta}$, which is usually assumed to apply in chemical kinetics, will not agree with the data for the catalytic oxidation of toluene in the vapor phase.
2. The kinetics of the catalytic oxidation of toluene in the vapor phase is controlled by a complex mechan-

ism such as free radical and peroxide formation.

3. The reaction of oxygen and toluene in the vapor phase will require considerably more study before any kinetic expression is written.

Recommendations

The following recommendations are made for the study of catalytic oxidation of toluene in the vapor phase. It is recommended

1. That more extensive studies be made of the reaction of toluene and oxygen.
2. That any future studies attempt to establish the concentration of the intermediate reactants.

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APPENDIX A

Table of Nomenclature

A_O	=	Area of annular opening of rotameter tube at its largest cross-section.
A_I	=	The cross-sectional area of rotameter tube just below the rotameter float.
A_f	=	Cross-sectional area of rotameter float.
A, B, C	=	Chemical compounds on the right side of a chemical equation.
a, b, c	=	Moles of compounds A, B and C.
C_A	=	Concentration of Component A.
C_R	=	Rotameter constant.
E	=	Activation Energy.
F_A	=	Molar flow rate of Component A.
g	=	Gravitational constant.
H	=	Enthalpy.
K	=	Equilibrium constant for a reaction.
L, M, N	=	Chemical compounds on the left side of a reaction equation.
l, m, n	=	Moles of compound L, M and N.
M	=	Mass flow rate.
N_A	=	Moles of Component A reacted per unit time.

- P = Pressure.
- Q = Volume flow rate.
- R = Universal gas constant.
- R = A chemical radical.
- R^o = A free radical.
- r_A = Rate of reaction of Component A.
- T = Absolute temperature.
- V = Volume.
- V_f = Volume of rotameter float.
- V_R = Reactor volume.
- W = Mass of catalyst.
- X = Catalyst.
- X_A = Moles of Component A reacted per mole of Component A.
- Z = The value for $\int_0^{N_{O_2}} \frac{d N_{O_2}}{(F_{O_2} - N_{O_2})^\alpha (F_{O_2} - 2/3 N_{O_2})^\beta}$
- α, β, γ = Orders with respect to various components.
- η_A = Moles of Component A at time Θ .
- Θ = Time.
- ρ = Density.
- ρ_f = Density of rotameter float.
- ψ = Molecular weight.

APPENDIX B

Outline of Calculations

1. Convert the pressure drop across the apparatus from millimeters of carbon tetrachloride to millimeters of mercury.
2. Find the pressure at the inlet to the reactor by adding the pressure drop across the apparatus to the atmospheric pressure.
3. Find the flow rates corresponding to the rotameter readings from the graphs in Appendix G.
4. Calculate the inlet molar flow rate for air at the temperature and pressure at which the rotameter was calibrated.
5. Correct the above flow rate for temperature and pressure by the method outlined in Appendix E.
6. Calculate the outlet molar flow rate from the volume flow rate, which was obtained from the soap bubble flow meter, by use of the ideal gas law.
7. Convert all thermocouple readings to degrees centigrade by use of the emf-temperature tables (23, 25).
8. Calculate the total moles entering the reactor by adding the entering air flow rate to the entering toluene flow rate.
9. Calculate, by the ideal gas law, the volume rate of flow through the reactor.

10. Calculate the moles of oxygen consumed in the reactor per unit time by subtracting the effluent air rate from the entering air rate.
11. Calculate the feed rate of oxygen from the feed rate of air (air is 20.99 percent oxygen).
12. Calculate $1/Q$ and $\ln \frac{F_{O_2}}{F_{O_2} - N_{O_2}}$ for the purpose of making plots similar to Figure 5.
13. Enter the data in the computer programs.

APPENDIX C

A Computer Program to Calculate $\frac{1}{Q}$ and

$$F_{O_2}^{(1-\alpha)} - (F_{O_2} - N_{O_2})^{(1-\alpha)}$$

This program was written to calculate the values for $(\frac{1}{Q})$ and $[F_{O_2}^{(1-\alpha)} - (F_{O_2} - N_{O_2})^{(1-\alpha)}]$ for every data point at various values for α . The purpose of these calculations was to compare the various values for α in order to determine if any order would provide a solution to the rate equation $r_{O_2} = k C_{O_2}^\alpha$. The values of α were varied from zero to four at intervals of 0.1. The program was written for use with the IBM 650 Computer in fortran language.

Data Input

All data must be placed on a standard data card with a 12 punch in card column 73. The data for the program must be placed in the following form:

FIRST CARD

Card Columns 1-10

The number of pieces of data to be analyzed in 10 x 0 fixed point notation.

Card Columns 11-20

The number 0000000001.

The Data Cards

One card must be included for each piece of data.

Card Column 1-10

The flow rate of air into the reactor in gram moles per second, in IBM floating point notation.

Card Columns 11-20

The moles of oxygen reacted per unit time measured in gram moles per second, in IBM floating point notation.

Card Columns 21-30

The volume flow rate measured in cubic centimeters per second, in IBM floating point notation.

Program Operation

The program uses the standard fortran board, program decks and console settings. If it is desired to process more than one set of data, then it is only necessary to place the additional data behind the original information. Any such data should be in the same form as above. Not more than fifty pieces of data should be processed in any one set of data.

Program Output

The output from this program consists of one card giving the value for λ and then a card for each piece of input data. The output is in the following form:

First Card

Card Columns 1-10

The value for reaction order in IBM floating point notation.

Data Cards

One card is punched for each piece of input data.

Card Columns 1-10

The value for $1/Q$ in IBM floating point notation.

Card Columns 11-20

The value for $-(F^{(1-\alpha)} - (F - N)^{(1-\alpha)})$ in IBM floating point notation.

This information will be produced for each value for α starting with 4.0 and going to 0.0.

The Program

Card Number	Statement
1	000000 DIMENSION X(50), Y(50), Z(50)
2	000001 Q(50)
3	000010 READ 1, N, I
4	000000 J = 1
5	000020 READ 2, X(J), Y(J), Q(J)
6	000000 Z(J) = 0.2099* (S(J))
7	000000 IF (J - N) 3, 4, 4
8	000030 J = J + 1
9	000000 GO TO 2
10	000040 A = 4.0
11	000150 CONTINUE
12	000000 PUNCH 1, A
13	000000 J = 1


```
14      000050 B = (1.0/Q(J))**A
15      000000 C = ((Z(J) - Y(J))**
16      000001 (1.0 - A) - Z(J)**(1.0 - A))
17      000000 PUNCH 2, B, C
18      000000 IF (J - N) 6, 7, 7
19      000060 J = J + 1
20      000000 GO TO 5
21      000070 CONTINUE
22      000000 IF (A) 10, 10, 9
23      000090 A = A - 0.1
24      000000 GO TO 15
25      000100 IF(I) 14, 14, 1
26      000140 END
```

APPENDIX D

A Computer Program to Make a Least Mean Square Fit of the Rate Equation

A program was written to make a least mean square fit of equation (6-9). This program was written using the methods of Deming (2) which are described in Appendix F. This required that Equation (6-9) be set in the form:

$$\phi = (X, A_1, A_2 \dots A_n) + y.$$

If the independent variable is the reciprocal of the volume flow rate, then the equation may be treated as follows:

$$k \left(\frac{1}{Q}\right)^{\lambda+\beta} W = \int_0^{N_{O_2}} \frac{d N_{O_2}}{(F_{O_2} - N_{O_2}) (F_{O_2} - \frac{2}{3} N_{O_2})} \quad (D-1)$$

$$\frac{1}{Q} = \left(\frac{1}{kW}\right) Z^{(1/(\lambda+\beta))}$$

$$\text{where: } Z = \int_0^{N_{O_2}} \frac{d N_{O_2}}{(F_{O_2} - N_{O_2}) (F_{O_2} - \frac{2}{3} N_{O_2})}$$

Thus
$$\phi = \left(\frac{1}{kW}\right) Z^{(1/(\lambda+\beta))} - \frac{1}{Q} \quad (D-2).$$

It is then necessary to calculate the derivatives $\partial \phi / \partial \lambda$, $\partial \phi / \partial \beta$ and $\partial \phi / \partial k$ in order to use the method of Deming. The partial, with respect to the reaction rate constant, presents no problem and may easily be shown to be:

$$\partial \Phi / \partial k = \left(\frac{1}{kW} Z \right)^{\left[\left(\frac{1}{k+\beta} \right) - 1 \right]} \left(\frac{Z}{kW} \right) \quad (D-3).$$

The derivatives with respect to α and β present a more complex problem. In this case, it is necessary to find $\partial (U)^V / \partial X$ where both U and V are functions of X . The result of the differentiation is not usually found in differential calculus tables. However, it may be found as follows:

$$\begin{aligned} \ln U^V &= V \ln U \\ d \ln U^V &= V \frac{d \ln U}{dX} + \ln U \frac{dV}{dX} \\ 1/U^V d U^V / dX &= \frac{V}{U} \frac{dU}{dX} + \ln U \frac{dV}{dX} \end{aligned}$$

$$d U^V / dX = V U^{(V-1)} \frac{dU}{dX} + U^V \ln U \frac{dV}{dX}$$

If equation (D-4) is used to find $\partial \Phi / \partial \alpha$ and $\partial \Phi / \partial \beta$ from equation (D-2) the following results will be obtained.

$$\frac{\partial \Phi}{\partial \alpha} = \left(\frac{1}{\alpha + \beta} \right) \left(\frac{1}{kW} Z \right)^{\left(\frac{1}{\alpha + \beta} - 1 \right)} \left(\frac{1}{kW} \frac{\partial Z}{\partial \alpha} \right) - \left(\frac{1}{\alpha + \beta} \right)^2 \left(\frac{Z}{kW} \right)^{\left(\frac{1}{\alpha + \beta} \right)} \ln \left(\frac{Z}{kW} \right) \quad (D-5)$$

$$\frac{\partial \Phi}{\partial \beta} = \left(\frac{1}{\alpha + \beta} \right) \left(\frac{1}{kW} Z \right)^{\left(\frac{1}{\alpha + \beta} - 1 \right)} \left(\frac{1}{kW} \frac{\partial Z}{\partial \beta} \right) - \left(\frac{1}{\alpha + \beta} \right)^2 \left(\frac{Z}{kW} \right)^{\left(\frac{1}{\alpha + \beta} \right)} \ln \left(\frac{Z}{kW} \right) \quad (D-6)$$

The problem of calculating the quantity Z and its derivatives $\partial Z / \partial \alpha$ and $\partial Z / \partial \beta$ arise at this point. Unless the values of α and β are known, the function may not be integrated. In fact, it may be integrated only for specific values for α and β . The solution to this problem is that only numerical values for the function and its derivatives are required. This enables the use of Simpson's Rule (19) to find the values for Z . To find the values for α and β , it is necessary to resort to other numerical methods. Salvadori and Baron (20) show that:

$$\frac{\partial \phi}{\partial X} = \frac{1}{2h} (3 \phi_i - 4 \phi_1 + \phi_{11}) \quad (D-7)$$

where: ϕ_i is the value of the function
at a point X

ϕ_1 is the value of the function
at the point (X-h)

ϕ_{11} is the value of the function
at the point (X-2h)

h is any number.

The error in such a calculation is of the order of h squared. The value of the derivatives may now be evaluated by calculating, by Simpson's Rule, the values of Z at (α, β) , $(\alpha, \beta - h)$ and $(\alpha, \beta - 2h)$ to find $\frac{\partial Z}{\partial \beta}$ and at the points (α, β) , $(\alpha - h)$ and $(\alpha - 2h)$ to find $\frac{\partial Z}{\partial \alpha}$.

Data Input

All data must be placed on standard data cards with 12" punches in card column 73. The data for the program must be placed in the following form:

First Card

Card Columns 1-10

The number of pieces of data to be processed in 10 x 0 fixed point notation.

Card Columns 11-20

The mass of the catalyst in grams using IBM floating point notation.

Card Columns 21-30

The number of subdivisions to be used in the application of Simpson's Rule. This must be an even number greater than four and entered in IBM floating point notation.

Card Columns 31-40

An initial guess as to the order with respect to oxygen (α). This must be entered in IBM floating point notation.

Card Columns 41-50

An initial guess for the order with respect to toluene (β). This must be in IBM floating point notation.

Card Columns 51-60

An initial guess for the reaction rate constant (k). This must be in IBM floating point notation.

Card Columns 61-70

The ratio of the moles of toluene consumed in the reaction to moles of oxygen consumed in the reaction. This number is normally assumed to be $2/3$. IBM floating point notation must be used to enter this quantity.

Second Card

Card Columns 1-10

This position should contain one of three 10×0 fixed point numbers depending on whether it is desired to process any other data than the set which is originally fed.

Option A

If the set of data being fed is all that will be processed then

enter the value 0000000000.

Option B

If it is desired to enter another set of data after the initial values have been fed without changing any of the information on the first card except the number of pieces of data. Enter the number 0000000001.

Option C

If it is desired to enter another set of data after the initial values have been fed and it is desired to change any or all of the information on the first card, then enter the number - 0000000001.

Data Cards

One card must be made for every point that it is desired to include in the fit.

Data Cards

Card Columns 1-10

The feed rate of air in gram moles per second using IBM floating point notation.

Card Columns 11-20

The rate of consumption of air measured in gram moles per second using IBM floating point notation.

Card Columns 21-30

The volume flow rate through the reactor in cubic centimeters per second, using IBM floating point notation.

Card Columns 30-31

The toluene feed rate measured in gram moles per second using

10 x 0 fixed point notation.

Should Option C be used on the second card, then both the first and second cards of the new data should be the same as above.

Should Option B be used on the second card, then a card with the following information should be placed ahead of the data cards.

Card Columns 1-10

The number of data points in the second set of data in 10 x 0 fixed point notation.

Card Columns 11-20

A fixed point number which gives Options A, B, or C in the same manner as above.

Operation of Program

This program uses the usual fortran boards, decks and console settings.

Program Output

The program output is in two sections. The first simply gives the quantities Δ , β , and k at the end of each iteration. This continues until the values for all quantities agree within one-half of one percent. The second group of cards prints the quantities $1/Q^{2+\beta}$, $kW 1/Q^{2+\beta}$ and Z for each piece of data fed.

The Program

Card Number	Statement
1	C00000 CURVE FIT FOR ORDERS AND
2	C00000 RATE CONSTANTS
3	000000 DIMENSION Y(35), Z(35), Q(35)

```
4          000001 T(35, GI(6))
5          000010 READ 1, N, W, AA, A, B, C, AAA, I
6          000000 J = 1
7          000020 READ 2, Z(J), Y (J), Q(J), T(J)
8          000000 Z(J) = 0.2099*Z(J)
9          000000 IF(J-N)3, 4, 4
10         000030 J = J+1
11         000000 GO TO 2
12         000040 PUNCH 1, A, B, C
13         000540 SAA = 0.0
14         000000 SAB = 0.0
15         000000 SAC = 0.0
16         000000 SAO = 0.0
17         000000 SBB = 0.0
18         000000 SBC = 0.0
19         000000 SBO = 0.0
20         000000 SCC = 0.0
21         000000 SCO = 0.0
22         000000 J = 1
23         000440 AL = A
24         000000 BL = B
25         000000 K = 1
26         000050 CONTINUE
27         000000 AX = 0.0
```



```
28      000000 E = Y(J) (3.0) *AA)
29      000000 XX = 0.0
30      000060 XXX = (1.0/((Z(J)-XX)**AL*
31      000061 (T(J)-AAA*XX)**BL))
32      000000 AX = AX + E*XXX
33      000000 XX = XX + E* 3.0
34      000070 XXX = (1.0/((Z(J) - XX)**AL*
35      000071 (T(J)-AAA*XX)**BL))*4.0
36      000000 AX = AX + E *XXX
37      000000 XX = XX + E* 3.0
38      000080 XXX = (1.0/((Z(J)-XX)**AL*
39      000081 (T(J)-AAA**XX)**BL))*2.0
40      000000 AX = AX + E*XXX
41      000000 XX = XX + E*3.0
42      000090 XXX = (1.0/((Z(J)-XX)**AL*
43      000091 (T(J)-AAA*XX)**BL))*4.0
44      000000 AX = AX + E *XXX
45      000000 XX = XX + E*3.0
46      000000 IF (XX/Y(J)+0.3*E-1.0)10, 11, 11
47      000100 CONTINUE
48      000000 GO TO 8
49      000110 XXX = (1.0/((Z(J)-XX)**AL*
50      000111 (T(J)-AAA*XX)**BL))
51      000000 AX = AX + E *XXX
52      000000 GI(K) = AX
```

```

53      000000 IF (K-3) 12, 13, 13
54      000120 K = K+1
55      000000 AL = AL - 0.1
56      000000 GO TO 5
57      000130 K = K + 1
58      000000 AL = A
59      000000 BL - BL - 0.1
60      000000 IF (K-5) 14, 15, 15
61      000140 CONTINUE
62      000000 GO TO 5
63      000150 DIA = (5.0*(3.0*GI(1))-4.0*GI(2)
64      000151 +GI(3)))
65      000000 DIB = (5.0*(3.0*GI(1))-4.0*GI(4)
66      000001 +GI(5)))
67      000180 RO = (1.)/Q(J) - ((1.0/(C*W))*GI(1)
68      000181 ))**(1.0/(A + B)))
69      000000 RAA=- (1.0/(A+B))*((1.0/(C*W))*
70      000001 (GI(1)))*((1.0/(A+B))-1.0)*
71      000002 ((1.0/(C*W))*DIA)
72      000000 RAB = LOGEF ((1.0/(C*W))*GI(1))
73      000001 *((1.0/(C*W))*GI(1)**)1.0/(
74      000002 A + B))*1.0/((A+B)**2))
75      000000 RA = RAA + RAB
76      000000 RBA = (RAA/DIA)*DIB
77      000000 RB = RBA + RAB

```

78 000000 RC = (1.0/(A+B))*((1.0/C*W))
79 000001 *(GI(
80 000002 1))*((1.0/(A+B))-1.0)*((1.0/
81 000003 (C**2*W))*GI(1)0
82 000000 SAA = SAA = RA**2
83 000000 SAB = SAB = RA*RB
84 000000 SAC = SAC = RA*RC
85 000000 SAO = SAO + RA*RO
86 000000 SBB = SBB + RB**2
87 000000 SBC = SBC = RB*RC
88 000000 SBO = SBO + RB*RO
89 000000 SCC = SCC = RC**2
90 000000 SCO = SCO + RC*RO
91 000000 IF (J-N) 19, 20, 20
92 000190 CONTINUE
93 000000 J = J + 1
94 000000 GO TO 44
95 000200 DELT = SAA*SBB*SCC+SAB*SBC*SAC
96 000201 - SAB*SAB*SCC - SAA*SBC*SBC
97 000202 + SAB*SBC*SAC - SAC*SBB*SAC
98 000000 AELT = SAO*SBB*SCC + SBO*SBC*SAC
99 000001 +SAB*SBC*SCO - SCO*SBB*SAC*SAO*
100 000002 SBC*SBC - SBC*SAB*SCC
101 000000 BELT = SAA*SBO*SCC + SAB*SCO*SAC

102 000001 = SAO*SBC*SAC - SAC*SBO*SAC*SCO*
103 000002 SBC**SAA - SAB*SAO*SAC
104 000000 AO = AELT/DELT
105 000000 BO = BELT/DELT
106 000000 CO =(SCO - SBC*BO - SAC*AO)/SCC
107 000210 A = A - AO
108 000000 B = B - BO
109 000000 C = C-CO
110 000000 PUNCH 2, A, B, C
111 000000 IF (ABSF(CO/C)-0.005)22, 24, 24
112 000220 CONTINUE
113 000000 IF (ABSF(BO/B)-0.005)23, 24, 24
114 000230 CONTINUE
115 000000 IF(ABSF(AO/A)-0.005)25, 24, 24
116 000240 J = 1
117 000000 GO TO 54
118 000000 AL = A
119 000250 J = 1
120 000000 AL = A
121 000000 BL = B
122 000260 CONTINUE
123 000000 BUD = (1.0/Q(J))**(A + B)
124 000270 AX = 0.0
125 000000 E = Y(J) / (3.0*AA)
126 000280 XXX = (1.0/((Z(J)))

127 000280 XXX = (1.0/((Z(J))
128 000281 (T(J)-AAA*XX)**BL))
129 000000 AX = AX + E*XXX
130 000000 XX = XX + E*3.0
131 000290 XXX = (1.0/((Z(J)-XX)**AL*
132 000291 (T(J) - AAA*XX)*BL))*4.0
133 000000 AX = AX + E*XXX
134 000000 XX = XX + E*3.0
135 000300 XXX = (1.0/(Z(J)-XX)**AL*
136 000301 (T(J)-AAA*XX)**BL))*2.0
137 000000 AX = AX + E*XXX
138 000000 XX = XX + E*3.0
139 000310 XXX = (1.0/((Z(J)-XX)**AL*
140 000311 (T(J)-AAA*XX)**BL))*4.0
141 000000 XX = XX + E*3.0
142 000000 IF(XX/Y(J)+0.3*E-1.0)32, 33, 33
143 000320 CONTINUE
144 000000 GO TO 30
145 000330 XXX = (1.0/((Z(J)-XX)**AL*
146 000331 (T(J)-AAA*XX)**BL))
147 000000 AX = AX + E*XXX
148 000000 AUD = ((1.0/Q(J))**((A + B))*W*C
149 000000 PUNCH 3, BUD, AX, AUD
150 000000 IF(J - N)34, 35, 35

```
151          000340 J = J + 1
152          000000 GO TO 26
153          000350 CONTINUE
154          000000 IF(I)37, 38, 36
155          000360 READ 3, N, I
156          000000 J = 1
157          000000 GO TO 2
158          000320 CONTINUE
159          000000 GO TO 1
160          000380 END
```

APPENDIX E

Description of the Least Mean Square Method of Deming (2)

The method of Deming will provide a least-mean-square-fit for any function of the form.

$$\phi(X, Y, a_1, a_2, \dots, a_n) = 0 \quad (\text{E-1})$$

where: a_1, a_2, \dots, a_n are constants.

In this method, the experimental error may be weighted between X and Y. That is, it is possible to assume what the error in X was when compared with the error in Y. This is not done in the usual methods of curve fitting. The usual assumption is that one variable is free from error.

While the general least-mean-square-fit is of interest, it is sufficient for the purpose of fitting the kinetic equations to consider the method of fitting an equation of the form.

$$Y = \theta(X, a_1, a_2, \dots, a_n) \quad (\text{E-2})$$

It is also sufficient to assume that the observed values of X are correct or that all error lies in the observed value of Y.

The basic technique for the fitting of equation (E-2) involves several steps. The steps are:

1. Set equation (E-2) in the form

$$\phi = \theta(X, a_1, a_2, \dots, a_n) - Y$$

2. Find the derivatives $\partial \phi / \partial a_1, \partial \phi / \partial a_2, \dots, \partial \phi / \partial a_n$
3. Assume values for a_1, a_2, \dots, a_n
4. For each set of (X, Y) in the data calculate the following: $\phi, \partial \phi / \partial a_1, \partial \phi / \partial a_2, \dots, \frac{\partial \phi}{\partial a_n}$
5. Form system of linear equations

$$\begin{array}{r}
 A_1 \sum \frac{\partial \phi}{\partial a_1} \frac{\partial \phi}{\partial a_1} + A_2 \sum \frac{\partial \phi}{\partial a_1} \frac{\partial \phi}{\partial a_2} + \dots + A_n \sum \frac{\partial \phi}{\partial a_1} \frac{\partial \phi}{\partial a_n} = \sum \phi \frac{\partial \phi}{\partial a_1} \\
 A_1 \sum \frac{\partial \phi}{\partial a_2} \frac{\partial \phi}{\partial a_1} + A_2 \sum \frac{\partial \phi}{\partial a_2} \frac{\partial \phi}{\partial a_2} + \dots + A_n \sum \frac{\partial \phi}{\partial a_2} \frac{\partial \phi}{\partial a_n} = \sum \phi \frac{\partial \phi}{\partial a_2} \\
 \vdots \qquad \qquad \qquad \vdots \qquad \qquad \qquad \vdots \qquad \qquad \qquad \vdots \\
 A_1 \sum \frac{\partial \phi}{\partial a_n} \frac{\partial \phi}{\partial a_1} + A_2 \sum \frac{\partial \phi}{\partial a_n} \frac{\partial \phi}{\partial a_2} + \dots + A_n \sum \frac{\partial \phi}{\partial a_n} \frac{\partial \phi}{\partial a_n} = \sum \phi \frac{\partial \phi}{\partial a_n}
 \end{array}$$

6. Solve the system of equations in step 5 for

$$A_1, A_2, \dots, A_n$$

7. Calculate a second approximation for the values a_1, a_2, \dots, a_n with the equation:

$$a'_J = a_J - A_J$$

8. If all a'_J are sufficiently close to a_J , then the least-mean-square-fit to equation (E-2) has been obtained.

If not, then with the adjusted values of a_J return to step 4 and repeat the process until sufficient agreement is obtained.

APPENDIX F

Equation for Correction of a Rotameter for Temperature and Pressure

$$M = C_r A_o \sqrt{\frac{2g (\rho_f - \rho) V_f}{A_f (1 - (A_o/A_1)^2)}} \quad (\text{F-1})$$

Then at any given rotameter reading g , A_o , A_1 , V_f are constant. The ratio of the flow rates of two materials at the same rotameter reading is as follows:

$$\frac{M_1}{M_2} = \frac{C_{R1} A_o \sqrt{\frac{2g \rho_1 (\rho_f - \rho_1) V_f}{A_f (1 - \frac{(A_o)^2}{A_1^2})}}}{C_{R2} A_o \sqrt{\frac{2g \rho_2 (\rho_f - \rho_2) V_f}{A_f (1 - \frac{(A_o)^2}{A_1^2})}}} \quad (\text{F-2})$$

$$\frac{M_1}{M_2} = \frac{C_{R1}}{C_{R2}} \sqrt{\frac{\rho_1 (\rho_f - \rho_1)}{\rho_2 (\rho_f - \rho_2)}} \quad (\text{F-3}).$$

In the case of a gas, the density is very small when compared with the density of a glass or steel float. It may thus be assumed that

Thus

$$\frac{M_1}{M_2} = \frac{C_{R1}}{C_{R2}} \sqrt{\frac{\rho_1 \rho_f}{\rho_2 \rho_f}} = \frac{C_{R1}}{C_{R2}} \sqrt{\frac{\rho_1}{\rho_2}} \quad (\text{F-4}).$$

It may now be noted that small changes in flow rate make little

difference in the value of the rotameter coefficient then it may be assumed that $C_{R_1} = C_{R_2}$. This leads to the result:

$$\frac{M_1}{M_2} = \sqrt{\frac{P_1}{P_2}} \quad (\text{F-5}).$$

If the ideal gas law is assumed to apply the density of a gas is found to be:

$$\rho = \frac{p\psi}{RT} \quad (\text{F-6}).$$

Since the gas for both flow rates are the same, the following relations hold:

$$\frac{F_1}{F_2} = \left[\frac{P_1 T_2}{P_2 T_1} \right]^{\frac{1}{2}} \quad (\text{F-8}).$$

It should be remembered that the above equation is only valid for gases when the flow rates are very nearly the same because of the assumption that the coefficients are equal.

APPENDIX G
CALIBRATION CURVES FOR ROTAMETERS

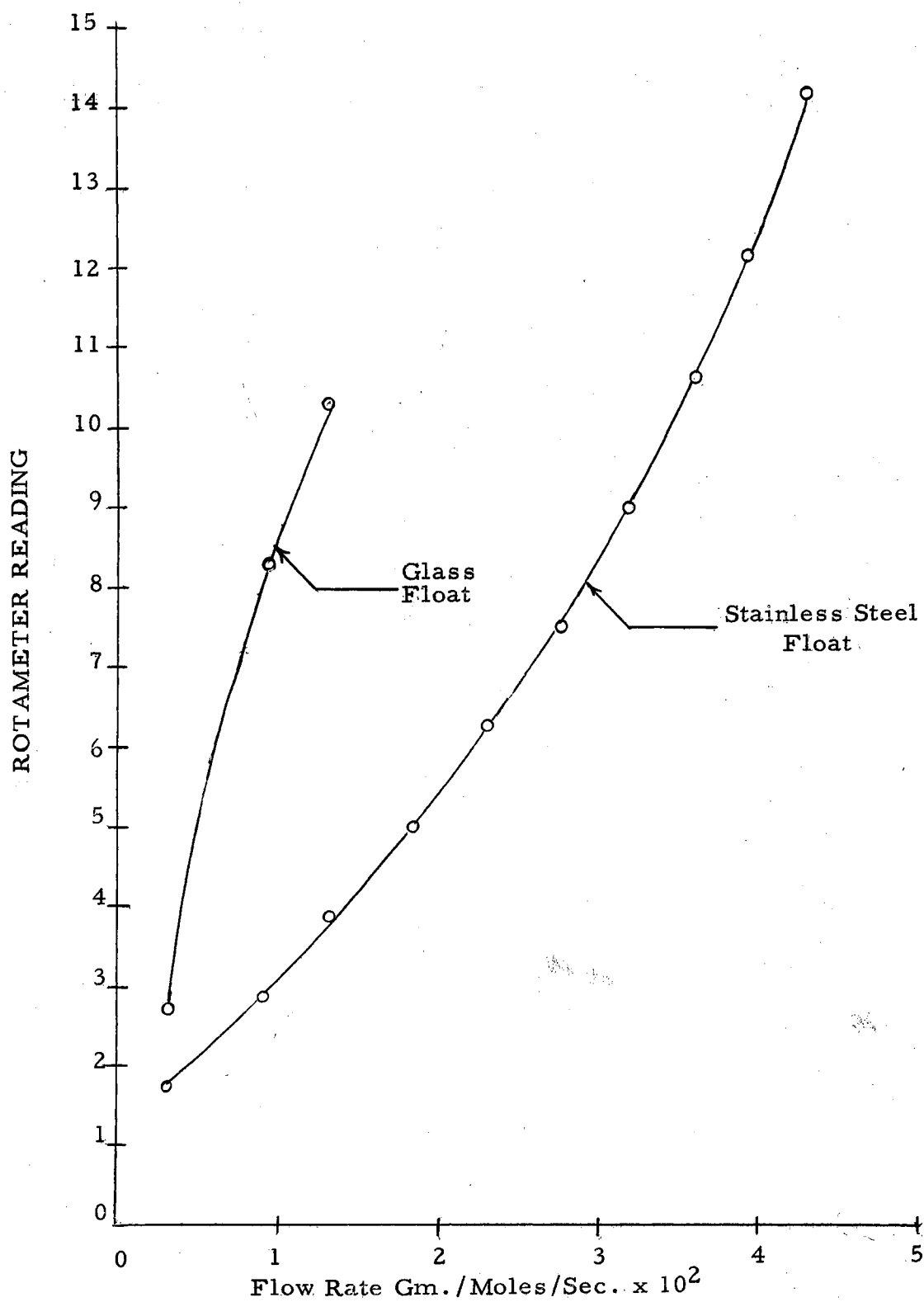


Figure 11

CALIBRATION CURVE FOR MATHESON T-602
ROTAMETER FOR TOLUENE

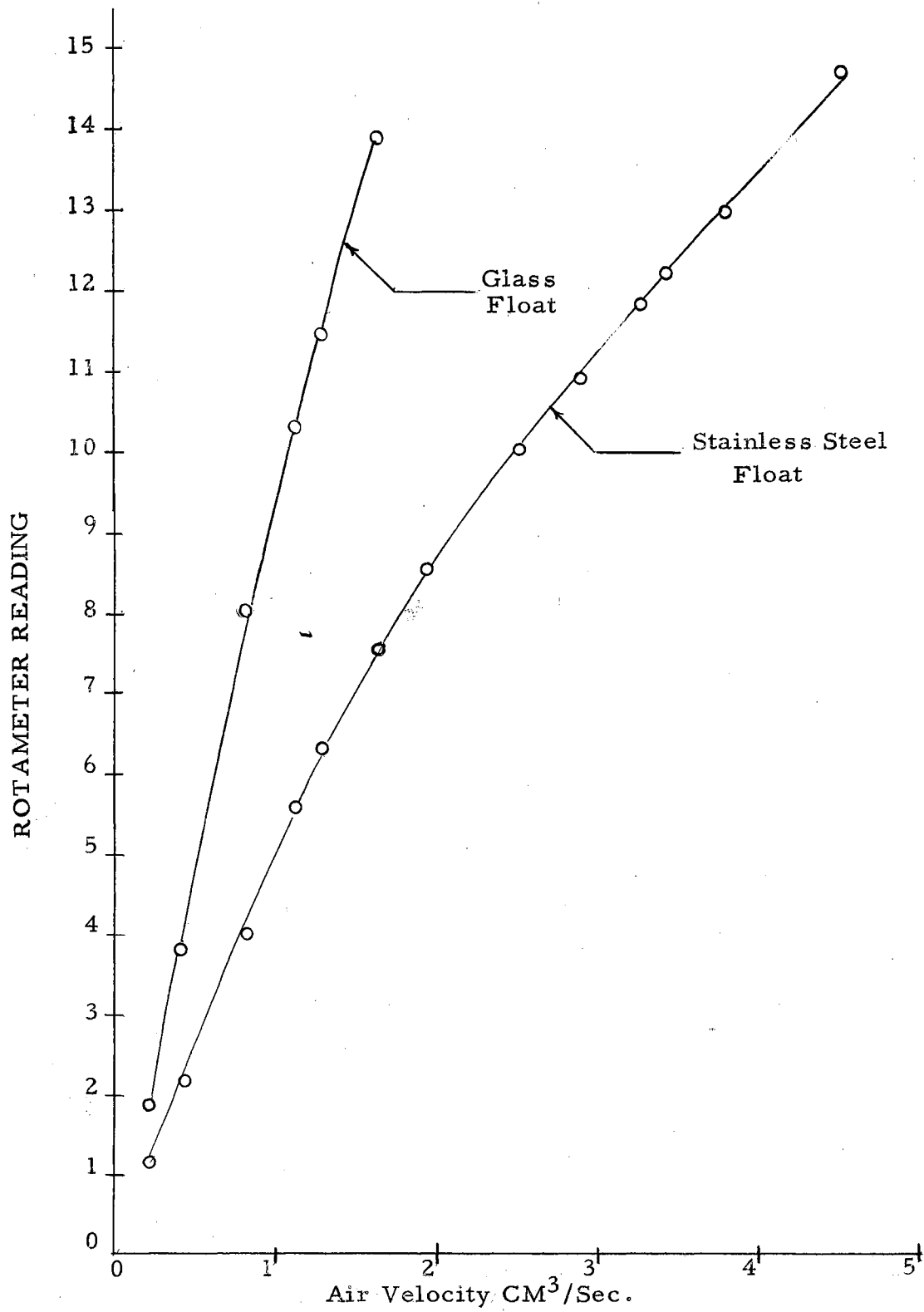


Figure 12

CALIBRATION CURVE FOR MATHESON T-601
ROTAMETER WITH AIR AT A PRESSURE OF
740 MM HG. AND A TEMPERATURE OF 28°C

VITA

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