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Aqueous Phase Oxidation of Organics (Wet-Air, Vapor-Liquid Equilibrium, Synergism, Free Radical, Xylene, Phenol).

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AQUEOUS PHASE OXIDATION OF ORGANICS

The Louisiana State University and Agricultural and Mechanical Col. Ph.D. 1985

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AQUEOUS PHASE OXIDATION OF ORGANICS

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Chemical Engineering

by
Richard Scott Willms
B.S., Louisiana State University, 1980
M.S., Louisiana State University, 1983
December 1985

"Today Glashow's thesis--the product of those two years of thought--sits on his bookcase, stuck in a black spring binder on a neglected top shelf. He has to hunt for it, wading through the stacks of preprints and journals that clutter his office, when he wants to show it to visitors. . . . 'Here it is!' Glashow says, standing on a wobbly stool. He hefts the volume appreciatively. 'These things are always long, to show you have lots of bright ideas, and filled with tons of calculations--student showboating. Mine is a complete parade of crazy digressions. I haven't looked at this in years. But there's one part I'm still proud of. Here, wait--it's in the appendix.'"

--Description of Sheldon L. Glashow
by R. P. Crease and C. C. Mann

DEDICATION

On the outside chance that this is the only book I will ever write, it seems wise to cover everybody this time.

To Patty,
Mom and Dad,
Mike, Chris, and Misty

ACKNOWLEDGEMENTS

Many people have helped, inspired, motivated, financed, and endured this effort. The following individuals and entities have confederated to make my Ph.D. studies enjoyable and worthwhile.

Kelly Serio, Wylie Barrow, Kris Talbot, Kathy Kane, and Ann Hay assisted by running the reactor and/or working on the literature search. During the experimental apparatus building stage of this research Kelly's muscle and mechanical know-how were invaluable.

Anne Balinsky paved the way for this work by supervising the building of the experimental apparatus and performing the first experiments on the unit for her Master's research. Other graduate students, Andreas Constantinides and Ed McFatter, contributed by running experiments and performing data analysis.

Dr. B. J. Miller of the LSU Agronomy Department graciously donated time by preparing and analyzing the soil used in this research. American Cyanamid donated the malathion. Ethyl Corporation provided valuable service by overhauling the reactor agitator and by allowing us to use their library. The U. S. Environmental Protection Agency funded a portion of this research through the administration of Rockwell International. Thanks also go the the Coates fund which assisted in paying for the preparation of this document.

I would like to thank my office mates, Gary Focht and Lian Sa, as well as the other chemical engineering graduate students for adding

"high touch" to "high tech". Special thanks go to the chemical engineering softball team for allowing me to play third base and shortstop. Thanks are also in order to Dr. Don Ristroph for letting us have the graduation party at his house.

David Millican spent this Halloween night collating and checking page numbers. He also provided valuable fellowship throughout the course of my graduate studies.

I have appreciated those in this department that have encouraged and supported efforts to publish this research, especially Dr. Edward McLaughlin.

Three faculty members were most closely associated with this research--Dr. Danny Reible, Dr. David Wetzel, and my advisor Dr. Doug Harrison. I thank Dr. Reible, not only for his guidance throughout this project, but also for his help in getting the model portion of this research published. Ranging from lasers to calligraphy and thermo to quilting, Dr. Wetzel always provides a unique and valuable contribution to those who have the privilege of working with him. I thank him for his extraordinary help during my graduate studies. I consider myself quite fortunate to have studied under Dr. Harrison's advisorship. His skill as an engineer and an administrator are exemplified in his ability to quickly assess a problem and ask the important questions. I thank him for his guidance during this research and especially for his valuable comments during the preparation of this dissertation.

Both Dr. Wetzel and Dr. Harrison served on the Ph.D. examining committee. Also serving were Dr. Frank Groves, Dr. Kerry Dooley, Dr. David Constant, and Dr. Les Butler. I thank them for serving in this capacity.

A very heartfelt thanks go to my wife's parents, Mr. and Mrs. Malcolm L. Hurstell for their patience and support during both my own and my wife's graduate studies.

My own parents, Dr. and Mrs. Richard K. Willms have also patiently encouraged me while pursuing my doctorate. I thank them for teaching me to set my goals high and to have the intestinal fortitude to attain them.

Finally, I thank my wife, Patty, for enduring through these graduate school years. She has always been supportive and helpful as long as I keep working hard.

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ABSTRACT

Fundamental disappearance kinetics parameters have been obtained for four compounds individually subjected to aqueous phase oxidation. These four compounds are m-xylene, phenol, tetrachloroethylene, and malathion. Concentration histories were obtained using a one liter "sampled-batch" reactor. Reaction conditions ranged from 114-290 °C and 1000-2500 psi air. A kinetics model incorporating vapor-liquid equilibrium effects was developed and used to determine reaction rate constants. The reactions were found to be first order in organic and 1/2 order in oxygen. Induction periods were observed for m-xylene and phenol. The durations of these periods were found to be inversely proportional to oxygen concentration. Activation energies were determined for all compounds except malathion which reacted at rates faster than could be measured.

Two reaction rate enhancement techniques were investigated, namely initiation and synergism. The former was explored by adding hydrogen peroxide to m-xylene reactions. It was discovered that small amounts of initiator eliminated the induction period without affecting the subsequent reaction rate. Synergism experiments entailed reacting m-xylene and phenol simultaneously. When starting with equimolar quantities of each, the m-xylene reaction rate was increased by about 1.5 orders of magnitude while phenol rates were only slightly decreased.

A final set of experiments determined that additions of soil to m-xylene reactions dramatically reduced reaction rates. Tetrachloroethylene, however, was unaffected by such additions.

A free radical mechanism involving hydroperoxides and degenerate chain branching was shown to accurately describe the individual m-xylene and phenol reaction results.

CHAPTER 1

OVERVIEW AND OBJECTIVES

OVERVIEW

Aqueous phase oxidation, as the name implies, is the oxidation of chemicals, usually organics, in water solution. This technology is also referred to as wet-air oxidation, wet oxidation, the Wetox process, and the Zimmerman process. These reactions are generally carried out at conditions ranging from 130-350 °C and 500-2000 psi air.

Aqueous phase oxidation is an important subset of a broader area of chemistry entitled liquid phase oxidation which has been researched rather extensively as evidenced in such books as Emanuel et al. (1967), Denisov (1974), Hawkins (1961), Edwards (1962), and Emanuel (1965), as well as numerous journal publications. Essentially every system considered by these authors used an organic for the solvent if a solvent was used. As will be shown later, there are relatively few works which consider the oxidation of organics in water solution.

The interest in aqueous phase oxidation stems largely from its applications in the wastewater treatment and, more recently, the hazardous waste destruction field. Disposal of hazardous wastes has historically meant storage in landfills or similar facilities. Due to widely publicized contamination problems associated with some storage facilities and to the Resource Conservation and Recovery Act, increasing emphasis is being placed on the ultimate destruction of hazardous wastes. At the current time, the most commonly used ultimate disposal method is incineration.

For wastes containing a sufficient concentration of combustible matter (about 30%, Baillod and Faith (1983)), incineration is a relatively economical means of waste disposal. When wastes are more dilute, however, large quantities of energy must be supplied to attain the temperatures necessary for gas phase combustion reactions. In these cases, other waste disposal techniques become favorable.

Figure 1.1, from Baillod and Faith (1983), is a qualitative plot of cost for destruction <u>versus</u> concentration of waste for four hazardous waste disposal methods--chemical oxidation, biological treatment, aqueous phase oxidation, and incineration. It is observed that at the lowest concentrations, wastes can be destroyed by mixing them directly with a chemical oxidizing agent such as hydrogen peroxide, ozone, or bleaches. As wastes become more concentrated, the cost of adding such oxidizing agents becomes prohibitive, but the waste may become a food source for biological organisms which metabolize the waste to innocuous products. As wastes become further concentrated, the waste is likely to become toxic to such organisms. From this point until the waste is concentrated enough to support gas phase oxidation, it is most economical to carry out the oxidation in the aqueous phase, eliminating the need to vaporize large quantities of water. Finally, for the the most concentrated wastes, incineration is the method of choice.

Aqueous phase oxidation is now being utilized in approximately 200 installations worldwide (Dietrich <u>et</u> <u>al.</u> (1984)). It is currently be-

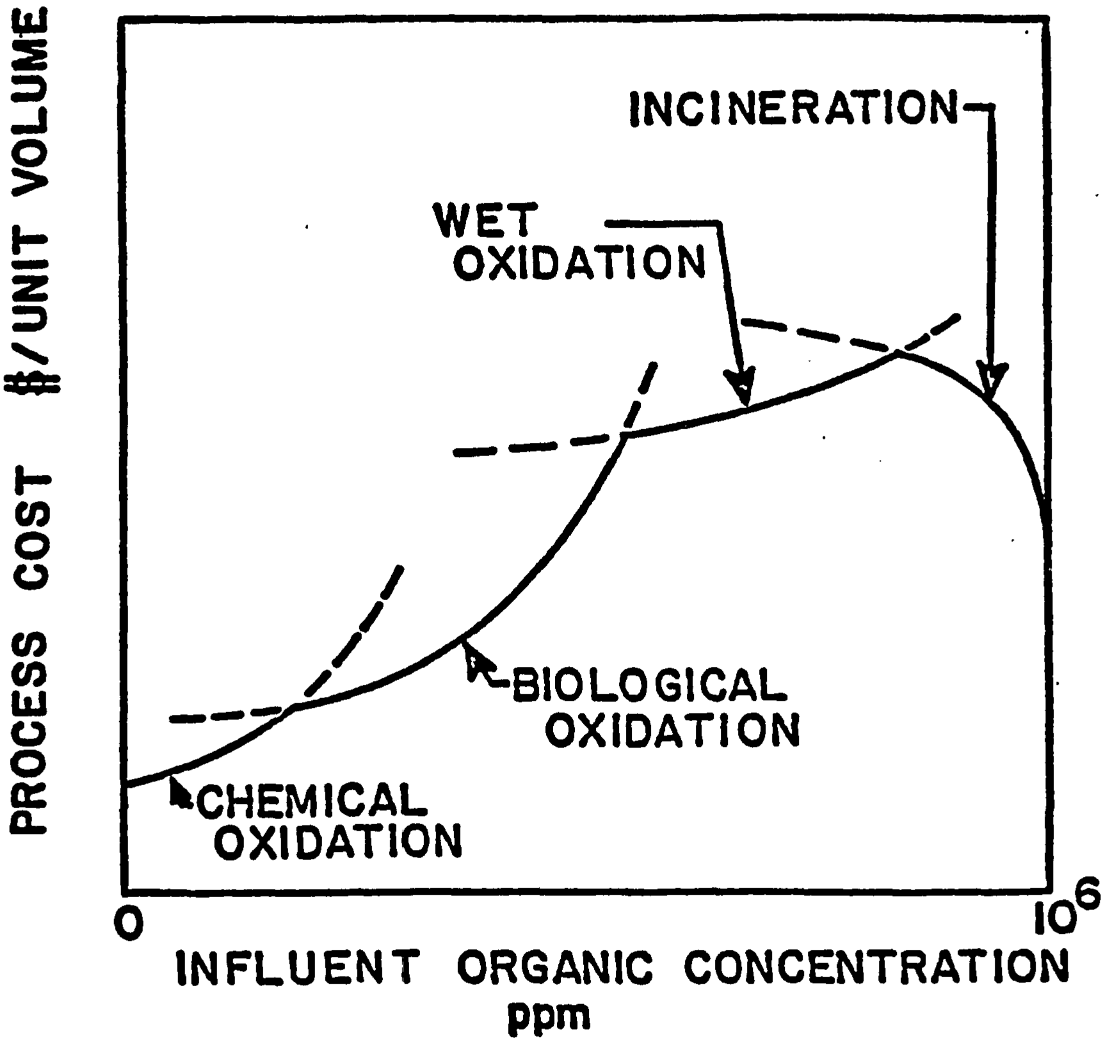


Figure 1.1 Conceptual Relationship Between Process Costs and Influent Organic Concentration (Baillod and Faith (1983))

ing used most extensively in municipal waste treatment facilities, the pulp and paper industry, and chemical processing plants. It is also being used for activated carbon regeneration. Besides these applications, aqueous phase oxidation is presently being considered as a method for detoxifying hazardous waste spill sites.

A typical aqueous phase oxidation installation reported in Baillod and Faith (1983) is shown in Figure 1.2. The central component of the system is a reaction vessel which can be either bubble or impeller agitated. A series of continuous flow stirred tank reactors (CFSTR) has also been proposed. The scheme shown in Figure 1.2 assumes that the oxidizable matter in the waste is sufficiently concentrated so that no net heat need be added to maintain reaction temperatures. In fact, the process shown assumes that excess heat will be available to generate process steam. Thus, the only real energy requirements are those necessary to operate the high pressure liquid feed pump and air compressor. A new design reported by Rappe (1985) even eliminates much of this energy demand by using the large hydrostatic pressures generated at the depths of an oilwell-like reactor.

The origin of the industrial use of aqueous phase oxidation is generally traced to a patent by Strehlenert (1915) which applied this technology to the treatment of pulping liquor. The next patent appears to be that due to Henglein and Niemann (1927) which describes a zinc sulfide oxidation process. The technology did not, however, attract significant attention until the appearance of two patents, one by Cederquist (1958) and the other by Zimmermann (1958, 1959). The former is a process for producing energy by oxidizing peat in the aqueous phase

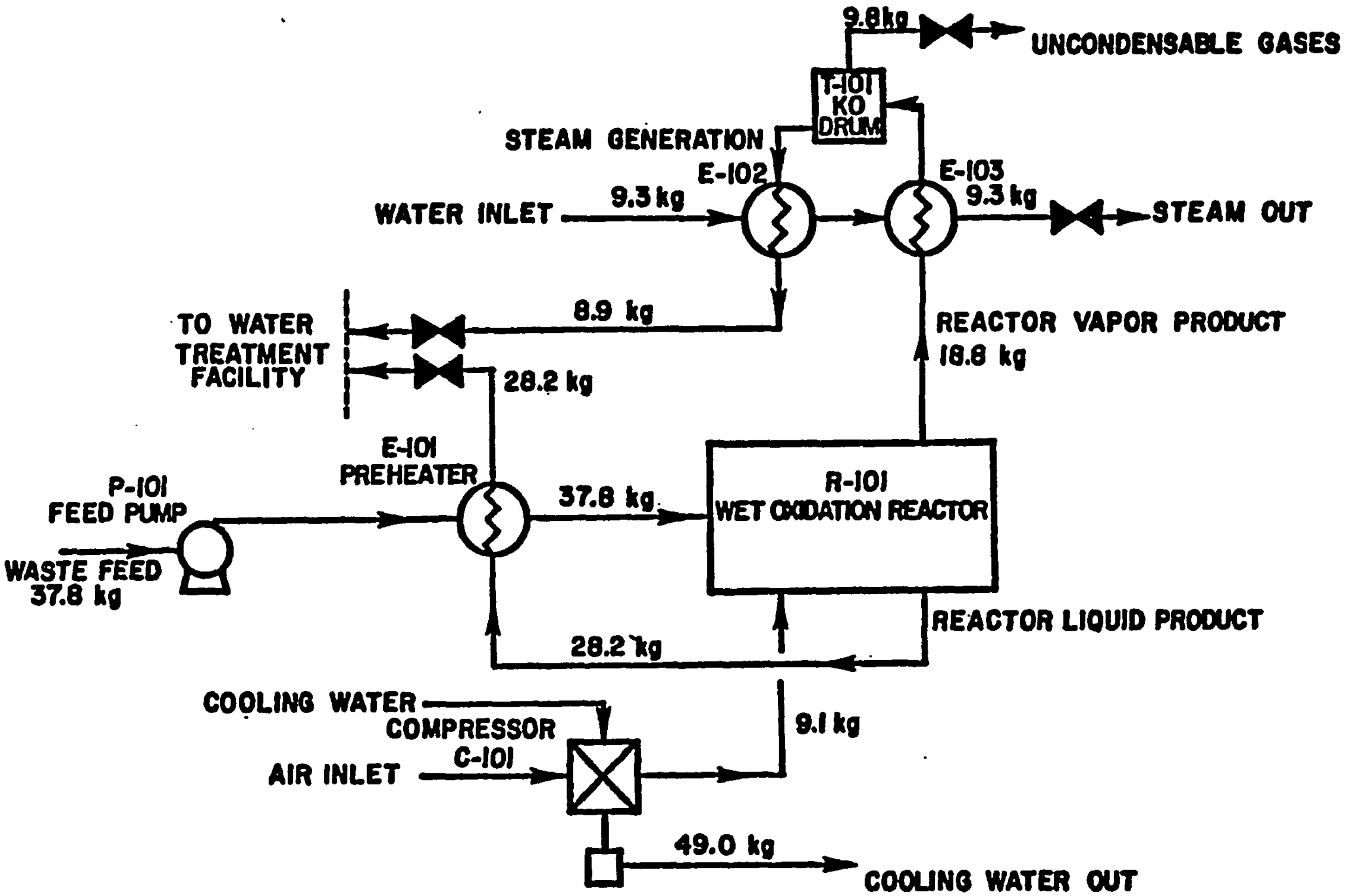


Figure 1.2 Typical Industrial Flowsheet for Aqueous Phase Oxidation

and the latter is a method for oxidizing aqueous wastes containing from 3-4% organic solvents. Following these two patents a variety of studies of aqueous phase oxidation have been conducted. Most of these are listed in chapter three in Tables 3.1 and 3.2. As will be noted there, the majority of these investigations were performed from a very "applied" point of view. Only a few of the studies collected the data necessary to determine fundamental kinetics parameters such as rate constants, reaction orders, and activation energies. Furthermore, of the studies which do collect the necessary data, many were conducted with a surprising lack of both experimental and analytical precision.

As a result, the database of quality information concerning aqueous phase oxidation is left severely wanting. At least in part, this deficiency served as an impetus for the current work.

OBJECTIVES

The first objective of this research was to develop an experimental technique which would provide the information necessary to determine fundamental kinetics information. Once this was accomplished, it was necessary to derive a mathematical model to describe accurately the concentration *versus* time behavior of organics subjected to aqueous phase oxidation conditions in batch reactors. The model developed includes reaction rate constants and reaction orders. By matching experimental data to the model, these constants can be determined and subsequently used to calculate activation energies and preexponentials necessary for the Arrhenius equation. A variety of unexpected complications arise in the development of such a model. Among these problems are vapor-liquid equilibrium effects which, when ignored, lead to artificially low reaction rate constants. Furthermore, drawing samples from the reactor upsets this equilibrium and leads to reductions in liquid phase concentrations which could mistakenly be attributed to chemical reaction. Both the experimental design and mathematical model will be given in chapter two.

The next goal was to collect experimental data on four organic compounds individually subjected to aqueous phase oxidation. These compounds where chosen to represent those on the Environmental Protection Agency's Priority Pollutant list and are m-xylene, phenol, tetrachloroethylene, and malathion. These experiments were conducted not only for the information concerning these compounds alone, but also to establish "base cases" to which future experiments could be compared (described below). It was, furthermore, instructive to consider a reaction mechanism which accounts for the concentration <u>versus</u> time characteristics of the data collected. By comparing mechanism simulation results with experimental results, it was possible to develop some understanding of the underlying reaction mechanism. This information is reported in chapter three.

Further experimentation was designed to develop an understanding of reaction rate enhancement techniques. Three such techniques have been identified--catalysis, free radical initiation, and synergism. Catalysis, having been addressed by a number of other authors, was only treated from a literature review standpoint. Very little information, however, was available on the other two topics. Free radical initiation was investigated by adding hydrogen peroxide to m-xylene reactions, and synergism was explored by reacting m-xylene and phenol simultaneously in one reactor. Utilization of these techniques may make aqueous phase oxidation an even more viable technology for industrial applications. These results are discussed in chapter four.

Finally, information was needed on the effects of soil on aqueous phase oxidation reactions to determine its usefulness as a method for decontaminating hazardous waste spill sites. Soil was individually added to reactions involving m-xylene, tetrachloroethylene, and malathion. These results are compared to "base case" results and mechanistic interpretations are offered in chapter five.

It is hoped that this research will help to alleviate a portion of the paucity of quality aqueous phase oxidation data. It is the purpose of this work not only to contribute to this database, but also to provide a framework of definitions and problem identification which will help direct future investigations.

CHAPTER 2

EXPERIMENTAL METHODS AND MATHEMATICAL MODEL

INTRODUCTION

As will be noted in chapter three, many of the previous studies of aqueous phase oxidation have used the simple "closed-batch" experimental method. This technique is only capable of measuring the concentration at the beginning and end of an experiment. This type of information is usually used to determine percent destruction after a specified amount of time. Though easy to perform, this method does not provide the transient concentration *versus* time information necessary for determining fundamental kinetics parameters such as rate constants, reaction orders, and activation energies. This information is more efficiently obtained using the "sampled-batch" procedure used in this research. Chapter three will site a number of studies that used this technique. In many cases these studies obtain good data, but fail to model the data properly by ignoring vapor-liquid equilibrium effects. As shown below, this neglect can cause significant errors in the determination of kinetics parameters.

The purpose of this chapter is to 1) present the experimental procedures used to obtain data in this research and 2) develop the equations used to model these data. This information has been published previously (Willms et al. (1985)).

EXPERIMENTAL

Equipment

Figure 2.1 shows the experimental apparatus. All materials in contact with reaction fluids were 316 stainless steel. The one liter Autoclave Engineers reactor, fitted with a variable speed "MagneDrive" stirrer and an electric furnace, served as the reaction vessel. It is rated to 343 °C and 5000 psi. An Autoclave Engineers temperature controller generally held the temperature to within +/- 2 °C of setpoint. The agitator was a six-bladed turbine and was operated at 750 RPM.

The Valco, Inc. sampling valve allowed the injection of one µl liquid samples into the gas chromatograph (GC). Its key component is a polymer seal with one µl grooves which, when rotated, vaporized the high pressure liquid reactor sample into the low pressure GC carrier gas stream. The severe duty of high temperature and pressure resulted in rapid erosion of both the high and low temperature polymer materials usually supplied by Valco. The most satisfactory results were realized by using what Valco calls "injection molded Valcon-H" polymer, only obtained on special request. The valve was equipped with a heater and controller to maintain the desired temperature. The tubing leading from reactor to valve and from valve to GC were maintained at the valve temperature with heating tape. A two micron Nupro in-line filter kept solids from reaching the valve.

A Perkin-Elmer model 990 gas chromatograph equipped with dual flame ionization detectors analyzed the reactor samples, with results recorded and processed on a Hewlett Packard Model 3390A integrator. For all GC work the following parameters applied: carrier gas--helium; carrier gas

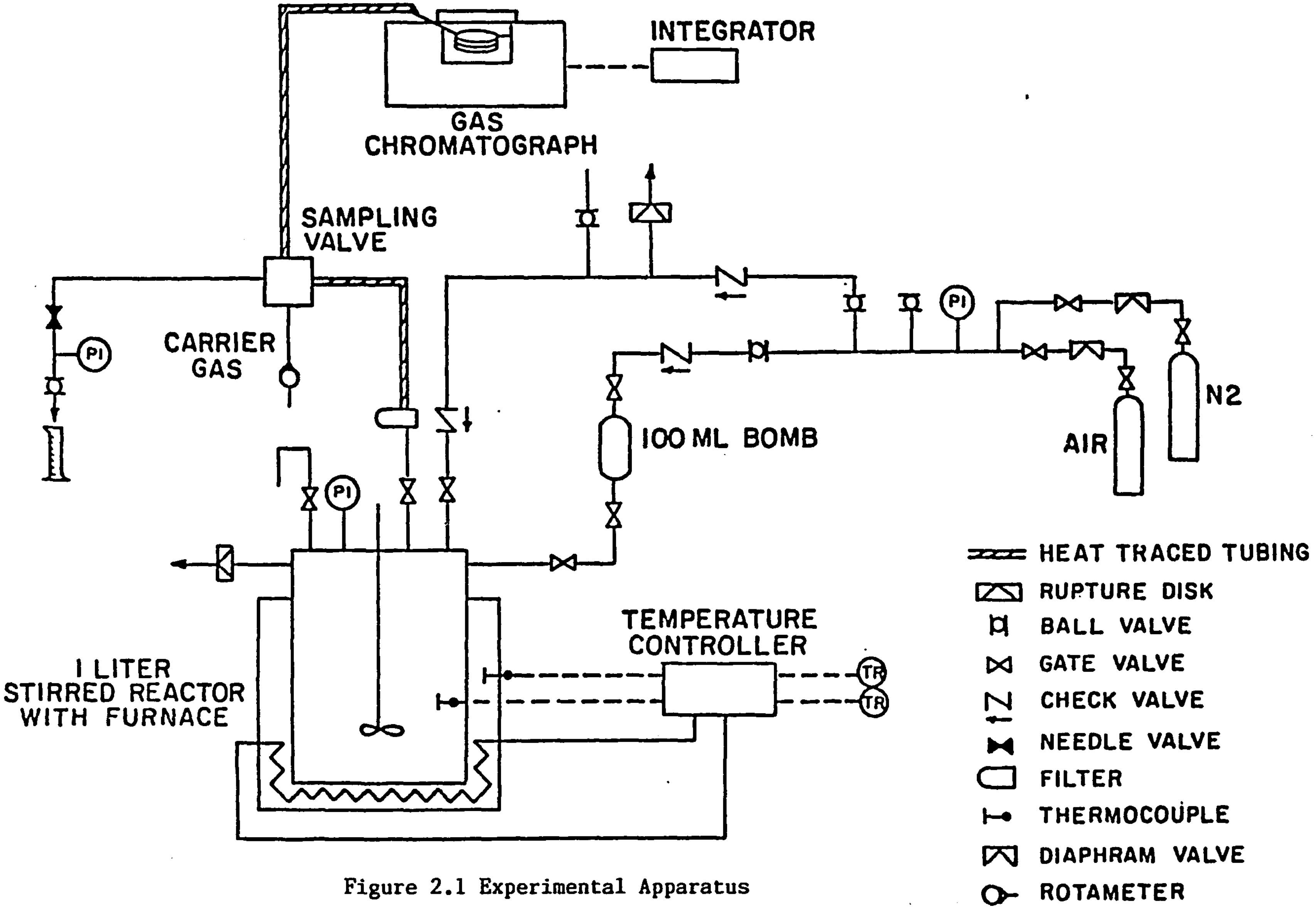


Figure 2.1 Experimental Apparatus

flowrate--30 ml/min; valve temperature--150 °C; column temperature--isothermal at temperatures noted below; manifold temperature--250 °C. The two GC columns used were 6 ft. x 1/4 in. x 2 mm ID and made of glass. For tetrachloroethylene analysis the column was packed with 5% SP-1200 and 1.75% Bentone 34 on 100/120 mesh Supelcoport. For phenol and malathion, a 5% OV-17 on 80/100 mesh Gas Chrom Q packing was used. Both of these columns were utilized in m-xylene experiments. The column temperatures were 110 °C for phenol, 80 °C for tetrachloroethylene, 195 or 210 °C for malathion, 90 °C for m-xylene with the Bentone column, and 110 °C for m-xylene with the OV-17 column.

Procedures

An experimental run to determine the concentration history of an organic subjected to aqueous phase oxidation conditions consisted of the following events. The one liter reactor was filled with 700 ml of distilled water and heated to the run temperature. A measured amount of organic was then flushed into the reactor with 80 ml of preheated water to start the experiment. Concentration was determined periodically by drawing approximately five ml of reactor contents though the valve and subsequently injecting the one µl sample into the GC by actuating the valve.

These and other experimental procedures are presented in greater detail in Appendix E.

MATHEMATICAL MODEL

Introduction

Due to the sampling technique and the inherent nature of the aqueous phase oxidation process, a variety of potential problems with the interpretation and analysis of the raw concentration-time data exist. These include vapor-liquid equilibrium effects, the effects of sample withdrawal from the batch reactor, and density variations between reactor and sample injector. Corrections for each of these effects must be incorporated into the analysis in order to extract fundamental kinetics parameters. The objectives of this section are to identify these complicating factors, indicate their effects, and develop a methodology for the determination of true kinetics parameters from raw data.

Experimental Analysis

Typical aqueous phase oxidation data for m-xylene reacted at 200 °C and 2000 psi air are shown in Figure 2.2. Concentrating attention on the experimental data points, rather than the model curve which will be discussed later, it is observed that the reaction can be divided into two distinct phases. At the beginning of the experiment the concentration of the organic remains approximately constant for the first 340 minutes. This region is referred to as the induction period and is typical of free radical reactions. The scatter associated with the first two or three data points is attributed to the time required to dissolve the organic and establish phase equilibrium. This is followed by a period of rapid reaction during which the concentration decays exponentially. This will be referred to as the active or rapid reaction period.

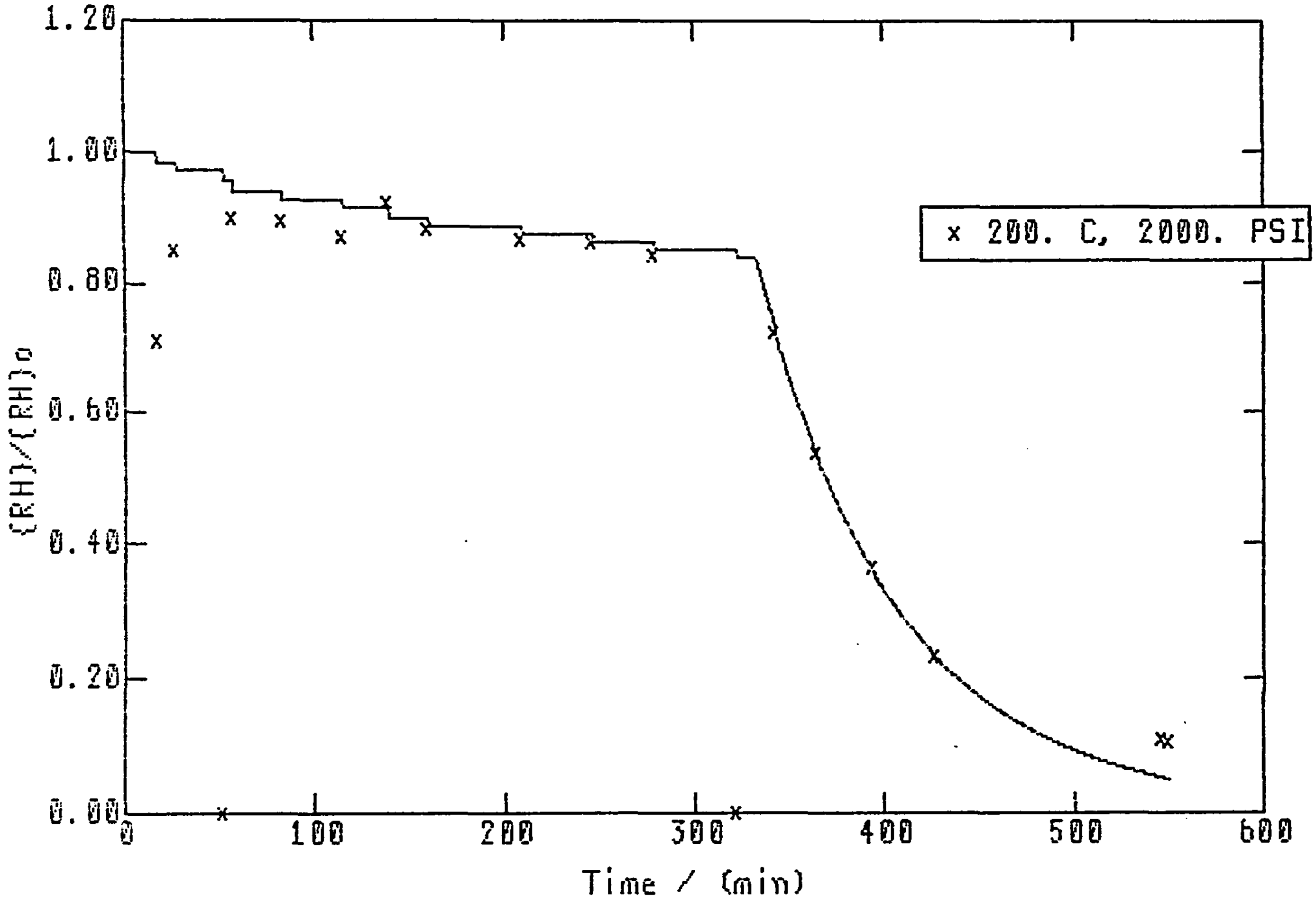


Figure 2.2 Representative Experimental Data and Model Curve for m-Xylene Aqueous Phase Oxidation

The reaction rate of the organic in the active reaction period can be represented, in general, as

$$r = k([O_2]^L)^m([RH]^L)^n \ . \qquad (2.1)$$

The majority of aqueous phase oxidation reactions are believed to be first order in organic, so $n = 1$. Furthermore, when the oxygen concentration is much greater than the organic concentration, it is essentially constant and can be combined with k, resulting in k', the pseudo-first order rate constant. The rate equation now becomes

$$r = k'([RH]^L) \ . \qquad (2.2)$$

A more detailed examination of the induction period indicates a gradual decrease in concentration with time. This was found to be a function of the number of samples collected and not the time since initiation of the experiment. This indicates that the downward trend represents the re-equilibration between vapor and liquid in the reactor after a sample is withdrawn.

A preliminary experiment was made to show that the reduction in concentration during the induction period was indeed due to sampling and not reaction. Nitrogen was substituted for air, while the temperature and pressure were held at 225 °C and 2500 psi. At these conditions the induction period using air would be be about 30 minutes (as will be shown in chapter three). Over a 76 minute period 18 five ml samples were taken. The liquid concentration decreased after each sample, just as it did under air pressure. Only if the stirrer was not turned on between consecutive samples was a constant concentration observed.

The presence of significant quantities of organic in the vapor phase has received little study in previous investigations. Analysis of the concentration decrease with total liquid volume removed during the induction period allows estimation of partition coefficients between the liquid and vapor phases. By assuming that the vapor-liquid equilibrium is rapid compared to the rate of reaction during the active reaction phase, it is possible to decouple the vapor-liquid equilibrium effects from the reaction kinetics in this region. Fitting of the data to kinetics expressions without considering repartitioning between liquid and vapor can lead to significant errors in the evaluation of rate constants as will be shown below.

Model Development

Henry's Law: The first step in modeling these data involves characterizing the vapor-liquid equilibrium behavior. For an organic component whose equilibrium mole fraction is close to zero, such as m-xylene in water, the vapor-liquid equilibrium can be expressed by Henry's law,

$$yP = xH \ . \tag{2.3}$$

When published values of H are available, this equation can be used directly. In their absence the induction period data becomes useful for estimating H, since no appreciable reaction is occurring during this time. Pressure is known, but y and x must be related to other measured variables, specifically liquid phase concentration and liquid volume. A mass balance on organic in the reactor solved for $[RH]^V$ reveals

$$[RH]^V = \frac{m_2^T - V^L[RH]^L}{V^T - V^L} . \qquad (2.4)$$

Thus, if the gas phase is ideal,

$$y_2 = \frac{RT}{P\ MW_2} \left[\frac{m_2^T - V^L[RH]^L}{V^T - V^L} \right] \qquad (2.5)$$

and for a dilute solution

$$x_2 \approx \frac{[RH]^L\ MW_1}{\rho_1^L\ MW_2} . \qquad (2.6)$$

Due to density changes and the vapor pressure of water, the liquid volume is not simply the difference between the initial volume charged into the reactor and the amount removed during sampling. V_L can be computed, neglecting water's compressibility, by simultaneously solving

$$V^L = \frac{(V_0^L - V_{out})\rho_0^L - m_1^V}{\rho^L} \qquad (2.7)$$

and

$$m_1^V = \frac{p^*\ MW_1\ (V^T - V^L)}{RT} . \qquad (2.8)$$

Also, m_2^T, necessary for equation 2.5, is found by

$$m^T_{2,k} = m^T_{2,0} - \sum_{i=1}^{k} \gamma(V_{out,i} - V_{out,i-1})[RH]^L_{i-1} . \qquad (2.9)$$

Thus, given m_2^0 and the induction period liquid phase concentrations and associated liquid volumes, values of x and y can be obtained and used to calculate H. Though H could be calculated from a single datum point, superior results are obtained by calculating the H associated with each point in the induction period and averaging. Alternatively, interactive graphics can be used to plot the experimental data and the model concentrations. Values of H can be guessed until model and experiment match.

The main difficulty with using this method is obtaining reliable values for m_2^0. Injecting a precise quantity of sparingly soluble organic into a high pressure reactor is a difficult task. Thus, for this investigation only literature values of H were used.

Partitioning Mass Between Vapor and Liquid: Once a value for H has been found, $[RH]^L$ can be determined at any m_2^T and V^L. The total mass of organic in the reactor is the sum of that in the liquid and that in the vapor. The mass in the vapor for an ideal gas in equilibrium with the liquid is given by

$$m_2^V = \frac{H\ MW_1}{RT\rho_1^L} (V^T - V^L)[RH]^L . \qquad (2.10)$$

Furthermore, the mass in the liquid is

$$m_2{}^L = V^L[RH]^L \; . \tag{2.11}$$

Adding equations 2.10 and 2.11 reveals

$$m_2{}^T = \left[V^L + \frac{H\ MW_1}{RT\rho_1{}^L}(V^T - V^L) \right] [RH]^L \; . \tag{2.12}$$

Finally, let

$$\phi = V^L + \frac{H\ MW_1}{RT\rho_1{}^L}(V^T - V^L) \tag{2.13}$$

and equation 2.12 becomes

$$m_2{}^T = \phi[RH]^L \; . \tag{2.14}$$

Note that V^L, and therefore ϕ, is constant between reactor samples, resulting in a linear relationship between $m_2{}^T$ and $[RH]^L$. This greatly simplifies the following model.

Two Parameter, Two Region Model: The final task is to expand the model to include the active reaction period. An idealized plot of $[RH]^L$ versus time is shown in Figure 2.3. The solid line shows the actual liquid phase concentration as five samples were withdrawn. The triangles show the concentrations as determined by experimental analysis. Two samples were drawn in the induction period while three were drawn in the active reaction period. The rapid decrease in concen-

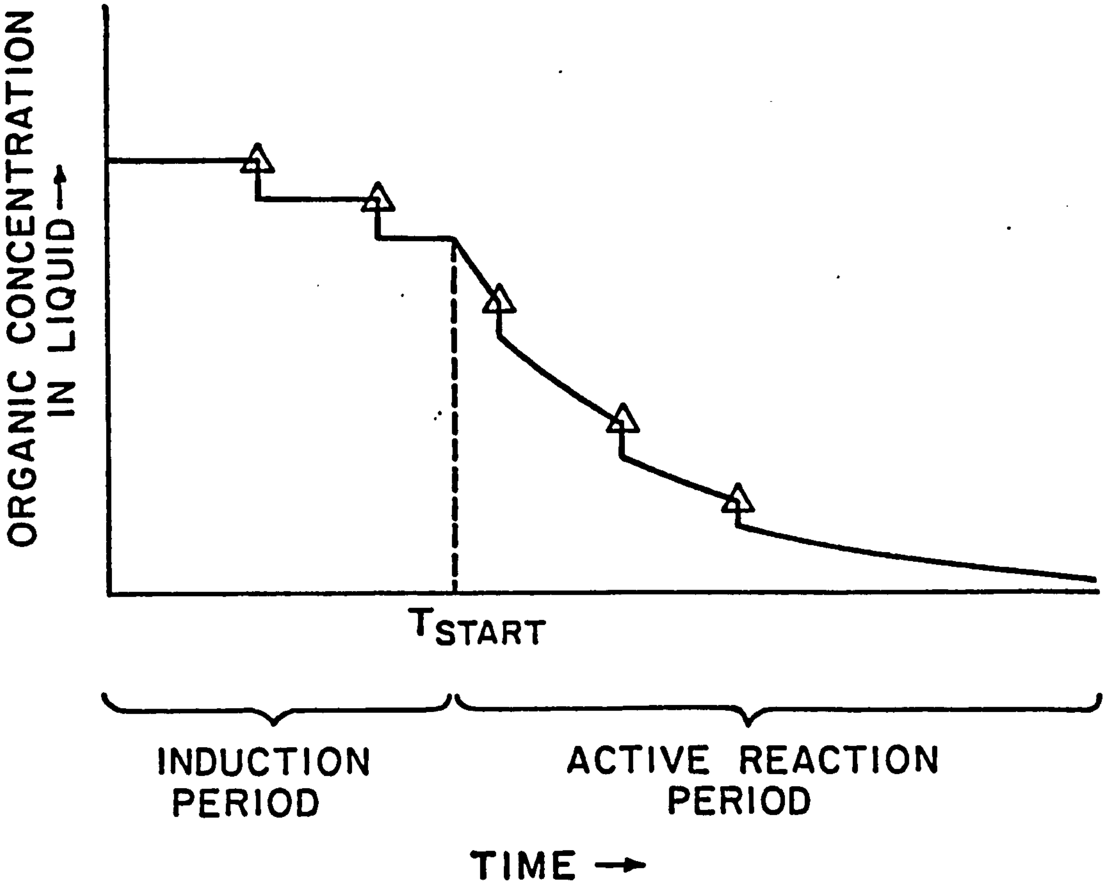


Figure 2.3 Idealized Concentration versus Time Results

tration following each sample is due to mass lost from the liquid to the newly created vapor space. Note, however, that though this process is rapid, it is not fast enough to decrease the sample concentration during the time it is being withdrawn (10 seconds), especially since the stirrer is off at this time. This reflects an assumption about the system, namely, sampling rate ›› liquid-gas mass transfer rate ›› reaction rate. It is also assumed that there is no reaction in the vapor phase.

A general differential mass balance on organic in the reactor is

$$\frac{dm_2^T}{dt} = -q_e[RH]^L - r_2V^L \tag{2.15}$$

with the initial condition

$$m_2^T = m^T_{2,0} \quad \text{at } t = 0 .$$

During the induction period the reaction term is zero, thus

$$dm_2^T = -q_e[RH]^L dt . \tag{2.16}$$

Note that q_e is only non-zero during sampling and, since sampling is too fast to affect $[RH]^L$, it is constant during integration. The integration of $q_e dt$ is, therefore, just the sample volume, V^S. Substituting equation 2.14 for m_2^T, integrating, and solving for $[RH]^L$ gives

$$[RH]^L = \frac{\phi_0 - V^S}{\phi} [RH]_0^L . \tag{2.17}$$

Thus, given the liquid volume before and after sampling (to compute the ϕ's), sample volume, and $[RH]^L$ before sampling, one can calculate $[RH]^L$ after the sample.

Once the induction period is over, the reaction term in equation 2.15 must also be considered. Pseudo-first order kinetics is assumed. Substituting equations 2.2 and 2.14 into equation 2.15, and considering only the time between samples so the sampling term can be ignored

$$\frac{d(\phi[RH]^L)}{[RH]^L} = -k'V^L dt \ . \tag{2.18}$$

Since V^L, and thus ϕ, are constant between samples, integration gives

$$[RH]^L = [RH]_0^L \exp\left[\frac{-k'\ V^L}{\phi}(t - t_0)\right] . \tag{2.19}$$

It is useful to observe that all vapor-liquid equilibrium effects are accounted for in the ratio V^L/ϕ. If Henry's constant is zero (all organic remains in the liquid phase), the ratio is unity, and equation 2.19 reduces to the familiar integrated form of the first order rate equation. On the other hand, if H were infinity, the ratio would become zero and equation 2.19 would reduce to $[RH]^L = [RH]_0^L$. This indicates that all organic is in the vapor phase, and thus, no liquid phase reaction occurs.

During the induction period only equation 2.17 is necessary to predict the liquid phase concentration; however, once reaction starts, $[RH]^L$ is diminished continuously due to reaction (equation 2.19) and discontinuously and instantaneously due to sampling (equation 2.17). These equations can be combined to predict $[RH]^L$ at any time by

$$
\begin{aligned}
[RH]_i^L = {} & \sum_{i=1}^{m} \left[\frac{\phi_{i-1} - V_i^S}{\phi_i} \right] [RH]^L_{i-1} \\
& + \sum_{i=m+1,2}^{n} [RH]^L_{i-1} \exp \left[\frac{-k'V^L_{i-1}}{\phi_{i-1}} (t_i - t_{i-1}) \right] \\
& + \sum_{i=m+2,2}^{n} \left[\frac{\phi_{i-1} - V_i^S}{\phi_i} \right] [RH]^L_{i-1}
\end{aligned}
\qquad (2.20)
$$

with

$$t_m = t_{start} \cdot$$

The first summation term accounts for concentration changes due to sampling prior to the active reaction period. Thereafter, the second and third terms alternately reduce $[RH]^L$ due to reaction and due to sampling, respectively. Realize that the notation for these two terms indicates that the index is incremented by two rather than one since they represent alternating rather than simultaneous processes.

It should be stressed that the model uses only liquid phase properties, eliminating the need for vapor phase sampling and analysis. This single equation provides a complete description of the concentration history of moderate temperature, high pressure, multiphase batch reactor data which follow the assumptions stated in the course of this development.

Computer programs using this model are listed in Appendix F.

Results and Discussion

The three adjustable parameters in the model are m_2^0, k' and t_{start}. At first it was believed that m_2^0 would be known by measuring the amount of organic injected into the reactor inlet line. In reality, it was discovered that as much as 20-30% of the organic could hold-up on the inlet tubing walls. Thus, this quantity is unpredictable and must be considered an adjustable parameter.

The procedure for determining these parameters is dependant on the presence or absence of an induction period. If an induction period occurs, as in Figure 2.2, m_2^0 is fixed by choosing its value so that the model and induction period data coincide. This match can be accomplished either visually using interactive graphics (as in this research) or by a least squares technique. If an induction period does not occur, t_{start} is known to be zero. In either case the number of unknowns has been reduced to two. These remaining values are determined by using an optimization technique (Powell's Method of Conjugate Directions, Powell (1964), for this research) to minimize the sum of the squares of the differences between the model and selected experimental data points. The points selected are those in the fully developed active reaction period. The first one or two points in the transition between the induction and active reaction periods may not be used. Furthermore, data at fractional conversions of over about 0.85 are not used since "tailing" of results may occur in this region (this phenomenon will be discussed in chapter three). Using this two step process, very satisfactory results were obtained. This can be seen by comparing the calculated line and the experimental data in Figure 2.2.

The traditional method of determining first order rate constants is from the slope of a semi-log plot of $[RH]/[RH]_0$ *versus* time. The error associated with using this method for determining k' for volatile compounds is equal to the ratio V^L/ϕ. For m-xylene at 200 °C and 2000 psi (H = 100,000 psi) with a 1025 ml reactor containing 700 ml of liquid, this ratio is 0.37. This means that the traditional methods would give values of k' that are low by a factor of 2.7. The more volatile the organic, the worse the error would be. This discrepancy is due to the fact that the traditional method fails to realize that, as the organic reacts in the liquid phase, it is being replenished from the vapor phase. Thus, the reaction is proceeding faster than the data indicate upon casual inspection.

This comparison suggests an alternate method for determining k' in the absence of time and/or a computer. An average value for the ratio V^L/ϕ can be obtained and divided into the k' obtained by the traditional method. The resulting value of k' should be a good approximation to the value obtained by the more accurate computer technique presented above.

Summary

It has been established that significant errors in estimating reaction rate constants can be caused by neglecting the effects of vapor-liquid equilibrium on batch reactor data. A model which includes these effects has been derived. Excellent results were obtained using this model to predict the liquid phase concentration of sparingly soluble, volatile hydrocarbons subjected to aqueous phase oxidation conditions.

CHAPTER 3

INTRINSIC RATE DATA FOR SELECTED ORGANICS

INTRODUCTION

The previous chapter developed the mathematical model which will be used in this chapter to determine intrinsic rate constants, k, and the duration of induction periods, t_{start}, for four model compounds. These compounds are m-xylene, phenol, tetrachloroethylene, and malathion. The reaction systems reported here are limited to water, air, and one organic. Chapter four will explore rate enhancement by adding either a second organic or an inorganic free radical source (H_2O_2) to the reaction system. Chapter five will deal with the addition of soil to the basic reaction system.

This chapter will 1) review the literature relevant to this study, 2) describe each of the four model compounds, 3) analyze the salient features of their concentration <u>versus</u> time behavior, 4) show that the chapter two model is valid for these systems, 5) report k and t_{start} for each experiment, 6) discuss the effects of temperature and pressure on reaction rates and t_{start}, and 7) propose a reaction mechanism.

RELEVANT LITERATURE

As presented in Table 3.1, a variety of techniques have been used to study the aqueous phase oxidation of organics. The simplest experiment

Table 3.1 Aqueous Phase Oxidation Studies--Compounds Studied and Experimental Methods Used

Investigator(s)	Compound(s) Studied	Experimental Method
Abel *et al.* (1954)	Municipal Sludge	Closed-Batch
Bacher (1976)	Glucose	-
Baillod and Faith (1983), Baillod *et al.* (1982)	Phenol, 2-Chlorophenol, 4-Nitrophenol, 1,2-Dimethylphthalate, 1,2-Dichloroethane, Petrochemical Waste	Sampled-Batch
Bettinger *et al.* (1980)	Coal	Sampled-Batch
Brett and Gurnham (1973)	Glucose	Closed-Batch
Cadotte and Laughlin (1979)	Pulping Liquor, Paper Sludge, Wood Preservative	Closed-Batch, Sampled-Batch, Continuous-Flow
Canney and Schaefer (1983)	Numerous	Closed-Batch
Cantieni (1931)	Formic, Acetic, Propionic, and Butyric Acid	-
Chowdhury and Ross (1975)	Brewery Effluent, Cellobiose Solution, Raw Municipal Wastewater	Sampled-Batch
Day *et al.* (1973)	Propionic Acid	Sampled-Batch
DeAngelo and Wilhelmi (1983)	Spent Caustic Liquor	Closed-Batch
Devlin and Harris (1984)	Phenol	Stopped-Flow
Dietrich *et al.* (1984)	Numerous	Closed-Batch
Hatcher and Hill (1929)	Propionic, n-Butyric, and Isobutyric acid, and Peracids, (Hydrogen Peroxide)	Sampled-Batch
Helling *et al.* (1981)	Phenol	Sampled-Batch
Hurwitz *et al.* (1965)	Municipal Sludge	Pilot Plant, Full Scale
Imamura *et al.* (1981)	Polyethylene Glycol	Sampled-Batch
Katzer *et al.* (1976)	Phenol	Sampled-Batch
McGinnis *et al.* (1983)	Wood	Closed-Batch
Miller *et al.* (1981) Miller and Swientoniewski (1982)	Ethylene Dibromide, Hexachlorobutadiene, Trichloropropane, Atrazine, DDT, Malathion, Mirex, Pentachlorophenol, Di-n-butylphthalate, Chloroanthracene, Diphenyl Hydrazine, Nitrobenzene, o-Xylene	Closed-Batch
Moses and Smith (1954)	Methanol, Formaldehyde, Formic Acid, Acetic Acid, Methyl Acetate, Benzene	Closed-Batch
Olson (1967)	Glucose	Closed-Batch
Ottengraf and Lotens (1978)	Municipal Sludge	Sampled-Batch

Table 3.1 (Continued)

Investigator(s)	Compound(s) Studied	Experimental Method
Ploos van Amstel and Rietema (1970)	Glucose, Lysine	Sampled-Batch
Ploos van Amstel and Rietema (1973), Ploos van Amstel (1971)	Municipal Sludge	Sampled-Batch
Pruden and Ferguson (1973)	Phenol	Continuous-Flow
Pruden and Le (1976)	Phenol, Nitrilotriacetic Acid	Continuous-Flow
Pujol *et al.* (1980)	Pulping Liquor	Sampled-Batch
Randall (1981)	Numerous	Closed-Batch
Randall and Knopp (1980)	Acenaphthene, Acrolein, Acrylonitrile, 2-Chlorophenol, 2,4-Dimethylphenol, 2,4-Dinitrotoluene, 1,2-Diphenylhydrazine, 4-Nitrophenol, Pentachlorophenol, Phenol, Acetic Acid	Closed-Batch
Rieche and Strankmuller (1958)	Phenol	-
Sadana and Katzer (1974)	Phenol	Sampled-Batch
Shibaeva *et al.* (1969b)	Phenol	Sampled-Batch
Shibaeva *et al.* (1969c)	Phenol	Sampled-Batch
Skaates *et al.* (1981)	Glucose	Sampled-Batch
Stepanyan *et al.* (1972)	Methanol, Formaldehyde	-
Sugaya *et al.* (1983)	Municipal Sludge	Closed-Batch
Sundstrom *et al.* (1976)	Nylon 66	Closed-Batch
Takamatsu *et al.* (1970b)	Municipal Sludge	Closed-Batch
Thielen *et al.* (1981)	Numerous	Closed-Batch
Weygandt (1969)	Acetone, Butanone, Cyclopentanone, n-Butyl Alcohol, sec-Butyl Alcohol, Isobutyl Alcohol, tert-Butyl Alcohol	Sampled-Batch
Wilhelmi and Knopp (1979)	Numerous	Closed-Batch
Williams *et al.* (1973)	Propionic Acid, Butyric Acid	Sampled-Batch
Yunis (1967)	Glucose	Closed-Batch

involves loading a reactor with water and a test organic, pressurizing, heating to reaction temperature, and holding for a specified amount of time. The reactor contents are analyzed after quenching to room temperature. This "closed-batch" procedure only provides one data point per experiment and requires numerous runs to sufficiently characterize the concentration versus time behavior at even one set of reaction conditions. It is further limited by the non-isothermal, non-isobaric events of heating and quenching with the test compound in the reactor. This makes "time zero" difficult to define. These efforts are generally more concerned with screening numerous compounds for application purposes than in studying the fundamental nature of aqueous phase oxidation. As such, several of these studies also report pilot plant and full scale operation data.

More fundamental data has been obtained using "sampled-batch" studies. Such experiments heat the reactor and water to reaction temperature, then inject the test compound. Reaction progress is monitored by periodically either collecting samples in vials for subsequent analysis or using a sampling valve to directly inject reactor contents into an analytical device (usually GC, HPLC, or GC/MS). The obvious advantage of this method is that one experiment completely characterizes the concentration history for a particular temperature and pressure. The injection time precisely defines "time zero". Furthermore, samples are collected at reaction conditions so that such phenomenon as vapor-liquid equilibrium also become apparent. This is the technique used in this investigation.

A less frequently used continuous-flow method has also been noted in Table 3.1. This method flows both air and aqueous organic through an agitated reactor. Organic concentration is recorded at various residence times after steady-state has been reached so that the entire concentration history can be constructed.

One study listed in Table 3.1 relates experiments conducted with a stopped-flow reactor. A typical example of this method would entail injecting a small quantity of reactant into a flowing stream of solvent (water). The flow is stopped when the mixture reaches the "reactor", which is actually a flow-through optical cell. The absorption of UV-visible light is usually used to determine concentration. This technique is well suited to mechanistic studies, and in loose terms could be considered the liquid phase equivalent of the shock tube often used in gas phase kinetics experiments.

Though numerous aqueous phase oxidation studies are listed in Table 3.1, only a limited number provide the information necessary to enhance the fundamental understanding of the phenomenon. The predominance of studies of pulping liquor and municipal sludge (often modeled as glucose) reflects the early applications of aqueous phase oxidation in these two industries. The rather nondescript nature of these solutions, however, makes generalization to other systems impossible. A second category of compounds studied is listed simply as "numerous" (e.g. Canney and Schafer (1983)). Though many compounds are included in these investigations, they all use the simple closed-batch experimental method, and thus only report percent destruction after a predetermined amount of time. Again, the basic information necessary to determine reaction orders, rate constants, and activation energies has not been obtained.

The only studies which approach the problem from a fundamental point of view are the sampled-batch, continuous-flow, and stopped-flow experiments which are shown in Table 3.2. Of these seventeen studies, four

Table 3.2 Aqueous Phase Oxidation Studies Which Obtained Fundamental Reaction Kinetics Information

Investigator(s)	Temperature (°C)	Compound	Activation Energy (kcal/gmole)
Baillod and Faith (1983)	204-260	Phenol	7.9
	204-260	2-Chlorophenol	19.3
	204-260	4-Nitrophenol	28.8
	204-260	1,2-Dimethylphthalate	23.9
	204-260	1,2-Dichloroethane	11.6
	204-260	Phenol/Cat	-
	204-232	2-Chlorophenol/Cat	-
	204-232	4-Nitrophenol/Cat	-
	204-260	1,2-Dimethylphthalate/ Cat	-
Bettinger *et al.* (1980)	204-353	Coal	27.
	204-232	Coal/Cat	-
Chowdhury and Ross (1975)	176-232	Brewery Effluent	23.3
	176-232	Brewery Effluent/Cat	17.1
Day *et al.* (1973),	232-288	Propionic Acid	33.
Devlin and Harris (1984)	150-225	Phenol	-
Helling *et al.* (1981)	185-230	Phenol (0.0 order O_2)	4.9
	185-230	Phenol (0.5 order O_2)	2.9
	185-230	Phenol (1.0 order O_2)	1.2
Imamura *et al.* (1981)	160-220	Polyethylene Glycol	23.4
Katzer *et al.* (1976)	114-200	Phenol/Cat (oxidation to Carbon dioxide)	13.7
Olson (1967)	110-140	Glucose	26.7
Ploos van Amstel and Rietema (1973)	180-290	Activated Sludge	23.
Pruden and Le (1976)	200-250	Phenol	10.8
		Nitrilotriacetic Acid	13.0
Pujol *et al.* (1980)	220-290	Pulping Liquor	3.2
	290-320	Pulping Liquor	32.3
Sadana and Katzer (1974)	96-146	Phenol/Sm./Lg. Cat.	42/24
Shibaeva *et al.* (1969b)	180-210	Phenol	25.6
Shibaeva *et al.* (1969c)	130-180	Phenol/H_2O_2	26.3
Skaates *et al.* (1981)	176-260	Glucose	31.0
Weygandt (1969)	200-240	Acetone	16.1
	160-200	Butanone	16.9
	160-200	Cyclopentanone	13.3
	180-200	*n*-Butyl Alcohol	22.2
	180-200	sec-Butyl Alcohol	24.8
	180-200	Isobutyl Alcohol	22.4
	180-200	tert-Butyl Alcohol	25.1

deal with poorly characterized mixtures such as pulping liquor and brewery effluent. Of the remaining thirteen, six deal only with phenol.

One is quickly convinced of the poorly developed state of the art by inspecting values of the activation energies listed in Table 3.2. For uncatalyzed phenol oxidation, values have been reported ranging from 4.9 to 25.6 kcal/mole. One study asserts that the activation energy for pulping liquor oxidation changes from 3.2 to 32.3 kcal/mole at 290 °C (Pujol *et al.* (1980)). Helling *et al.* (1981) used pseudo-first order rate constants rather than intrinsic rate constants to calculate their value of activation energy (pressure was not constant). There is a surprising lack of thoroughness and experimental care apparent in some of these studies. A few, however, are worthy of note and are summarized in the following paragraphs.

C. R. Baillod and his co-workers at the Michigan Technological University have been the most prolific authors on this subject. Their list of publications includes:

a) Baillod *et al.* (1982)- Study of five compounds cited in Table 3.1
b) Baillod and Faith (1983)- EPA project report cited in Table 3.2
c) Baillod *et al.* (1985)- A process economic evaluation
d) Baillod *et al.* (1979)- A paper citing limited results for phenol and 2-chlorophenol (studied more extensively in (b) above)
e) Baillod *et al.* (1983)- A process mathematical model
f) Skaates *et al.* (1981)- Glucose study cited in Table 3.2
g) Bettinger *et al.* (1980)- Coal study cited in Table 3.2.

They account for three of the publications qualifying for Table 3.2 and many of the individual compounds studied. A brief summary of their Table 3.2 papers is in order.

Baillod and Faith (1983) studied five compounds chosen to represent various classes of compounds typical of priority pollutants. The temperature range and activation energies for each compound are listed in Table 3.2. The reported values of E, however, are rather suspect. These are based on slopes of Arrhenius plots of the pseudo-first order rate constant, k', which is the product of the intrinsic rate constant, k, and the oxygen concentration. During these experiments the initial oxygen pressures varied from 288 to 360 psig, and the final oxygen pressures were from 144 to 216 psig. Thus, the pseudo-first order assumption is invalid since the oxygen concentration is reduced during a run to about one half its initial value. This may at least partially explain why the reported values of E, especially for phenol, appear rather small compared to those reported by others. This study also reports concentration *versus* time data for reaction intermediates and products, catalytic results, and ozonation results.

The Skaates *et al.* (1981) work with glucose appears to be a more careful study, holding oxygen partial pressure constant at 334 psi. The activation energy of 31 kcal/mole is more reasonable than those reported in the previous study. In this examination it was also concluded that acetic acid added to the aqueous phase slightly increased the reaction rate. They assume the reaction rates are first order in both glucose and oxygen.

The third Michigan Technological University publication listed in Table 3.2 is Bettinger *et al.* (1980). This study explored the effects of temperature, oxidant, catalyst, and particle size on the oxidation of coal. The activation energy of 27 kcal/gmole is for a high-volatile-A-bituminous coal. Though again this value is based on k' rather than k, it does seem quite reasonable. This report also includes a rather extensive literature survey.

The other Michigan Technological University publications are either repeated in the three papers just outlined or deal with topics beyond the interests of this thesis (economic evaluation and process mathematical model).

Other important papers are summarized as follows.

Day _et al._ (1973) at the University of Waterloo studied the oxidation of propionic acid solutions at 232-288 °C. These more severe conditions are required since low molecular weight acids are generally more stable than higher molecular weight compounds. In fact, these acids are often cited as major reaction products (Baillod and Faith (1983)). Thus, this study is significant in that it examines the last steps in the ultimate hydrocarbon oxidation to carbon dioxide and water. Their activation energy of 33 kcal/gmole is quite believable for this more refractory compound. Their regression analysis shows the reaction order to be 1.42 for organic and 0.41 for oxygen. The confidence limits on these values are rather large, however, showing that the organic order could range from 0.6 to 2.2, and the oxygen order from less than zero to about one. These same investigators have also published a paper which includes sketchy results for butyric acid along with the propionic acid findings (Williams _et al._ (1973)).

The work by Devlin and Harris (1984) is unique as the most detailed attempt at describing the reaction pathways of phenol aqueous phase oxidation. Using data obtained from a stopped-flow reactor plus the oxidation and ozonation data of others, they conclude that the reaction proceeds through either hydroquinone or catechol to the corresponding quinones. Thence, the aromatic ring opens, and oxidation proceeds to smaller and smaller mono- and dicarboxylic acids, ultimately to carbon dioxide and water.

J. R. Katzer and co-workers at the University of Delaware have produced a number of papers on aqueous phase oxidation, most notably Sadana and Katzer (1974) and Katzer _et al._ (1976). Both deal with catalytic aqueous phase oxidation of phenol, the former with partial oxidation at lower temperatures, the latter with complete oxidation at higher temperatures. The more recent paper is unique in than it reports the rate of carbon dioxide production rather that phenol disappearance. They conclude that, in this case, the activation energy is lower due to the effect of a rate limiting step in the oxidation mechanism. In both papers the data are best represented by assuming a first order reaction rate dependance on organic and 1/2 order on oxygen during the rapid reaction phase. During the induction period the first reference finds that the reaction has a first order dependance on oxygen concentration. It is not clear, however, whether the observed decrease in organic concentration during the induction period is actually due to chemical reaction or to the stripping effect of the oxygen flowing through the reactor to the fume hood.

The dissertation by Weygandt (1969) presents concentration _versus_ time data for the seven compounds listed in Table 3.2. Butanone reacted the fastest and acetone the slowest. He concludes that the reaction is first order in both organic and oxygen concentration. Also presented are percent destruction data for 23 compounds subjected to 200-250 °C and 2000 psi air for about 3 hours.

The final papers to be mentioned here are those of Shibaeva et al. (1969b) and (1969c) who examined the aqueous phase oxidation of phenol alone and with hydrogen peroxide, respectively. Their activation energy values are quite reasonable for chemical rather than physical processes. The first paper shows the usual first order rate dependance on organic at neutral pH, but this shifts to zero order under acidic conditions. They purport that the reaction is first order in oxygen concentration, and propose the first steps in the oxidation mechanism. In the follow-up paper all experiments are conducted under acidic conditions (pH 1.5), and the effects of hydrogen peroxide on phenol oxidation is explored under both an argon and an oxygen atmosphere.

EXPERIMENTAL APPARATUS AND PROCEDURES

The experimental apparatus and procedures are described in chapter two and Appendix E.

COMPOUNDS

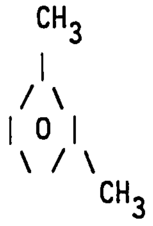
The four compounds chosen for this study represent three classes of organic chemicals: substituted aromatics (m-xylene and phenol), chlorinated aliphatics (tetrachloroethylene), and organophosphates (malathion). Table 3.3 lists some of the physical properties of the four compounds at ambient conditions. In addition to these properties, it was necessary to obtain values for the Henry's law constant for m-xylene at temperatures up to 300 °C. These were not directly available, but can be computed with vapor pressures and solubilities according to the following analysis.

Table 3.3 Physical Properties of Experimental Compounds at Ambient Conditions. (Data obtained from Verschueren (1983) except where noted)

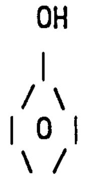
Physical Property	m-Xylene	Phenol	Tetrachloroethylene	Malathion
Molecular Weight:	106.16	94.11	165.83	330.36
Melting Point (°C):	-48	41	-22.7	2.85
Boiling Point (°C):	139	180.0	121.4	156-157
Vapor Pressure (mm Hg)*:	6	0.2	14	.00004
Solubility (mg/l):	160**	82000***	150****	145*

Structure:

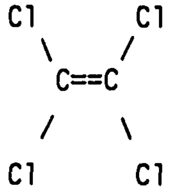
m-Xylene



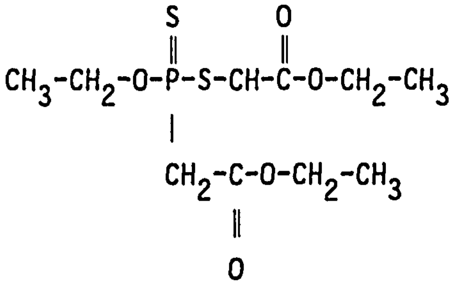
Phenol



Tetrachloroethylene



Malathion



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* at 20 °C

** at 20 °C (Chernoglazova and Simulin (1975))

*** at 15 °C

**** at 25 °C

For a sparingly soluble compound such as m-xylene, Henry's law,

$$y_i P = H_i x_i \ , \tag{3.1}$$

holds over the entire range of solubility. Thus, at the limit of solubility, x_i^*, m-xylene will exert its full, pure component vapor pressure, p_i^*, which is equivalent to $y_i P$. Thus,

$$H_i = p_i^* / x_i^* \ . \tag{3.2}$$

The vapor pressures were found in Vargaftik (1983), and solubilities were obtained from the American Petroleum Institute Technical Data Book (1983). Values of H were computed at various temperatures as shown in Table 3.4. It was found by a nonlinear least squares technique that these data could be correlated between the temperatures of 90 and 300 °C by the following equation

$$\begin{aligned} H = {} & 70177 \sin(0.015250\ T) - 0.025666\ T^3 - 13.153\ T^2 \\ & - 1336.95\ T + 3580.24 \ . \end{aligned} \tag{3.3}$$

This correlated the data quite well as can be seen by comparing the markers representing the values in Table 3.4 with the lower line representing equation 3.3 in Figure 3.1. This equation was useful for obtaining values of H at intermediate temperatures.

The Henry's law constants in Table 3.4 were calculated at the vapor pressure of water at the appropriate temperature. Since experiments were conducted at pressures above the vapor pressure of water, the Poynting correction must be employed as given by Heidman et al. (1985)

Table 3.4 Values of H at Various Temperatures for m-Xylene

Temperature (°C)	Solubility (mole frac.)	Vapor Pressure (psi)	Henry's Constant (psi)
10	0.000034	0.0627	1844
37.78	0.000036	0.332	9208
65.56	0.00005	1.24	24770
93.33	0.000087	3.63	41680
121.11	0.00016	8.87	55430
148.89	0.00029	19.0	65580
176.67	0.00054	36.6	67860
204.44	0.00105	64.9	61840
232.22	0.002	107.	53440
260.	0.004	167.	41810
287.78	0.0081	250.	30920
315.56	0.025	361.	14440

$$H_i^{P} = H_i^{Pr} \exp\left[\frac{MW_i\,(P - Pr)}{\rho_i\, R\, T} \right] . \qquad (3.4)$$

Thus, by using equations 3.3 and 3.4, H can be calculated at various pressures as a function of temperature as shown in Figure 3.1.

Henry's constant for phenol was believed to be small enough that it could be assigned a value of zero. The basis for this assumption is that phenol is infinitely soluble in water at temperatures greater than 68 °C. Further support comes from the observation that there was negligible difference between experimentally measured initial liquid phase concentrations and the quotient of the mass of phenol injected and the initial liquid volume.

The Henry's law constant for tetrachloroethylene has also been assumed to be zero in all model calculations. This is admittedly rather

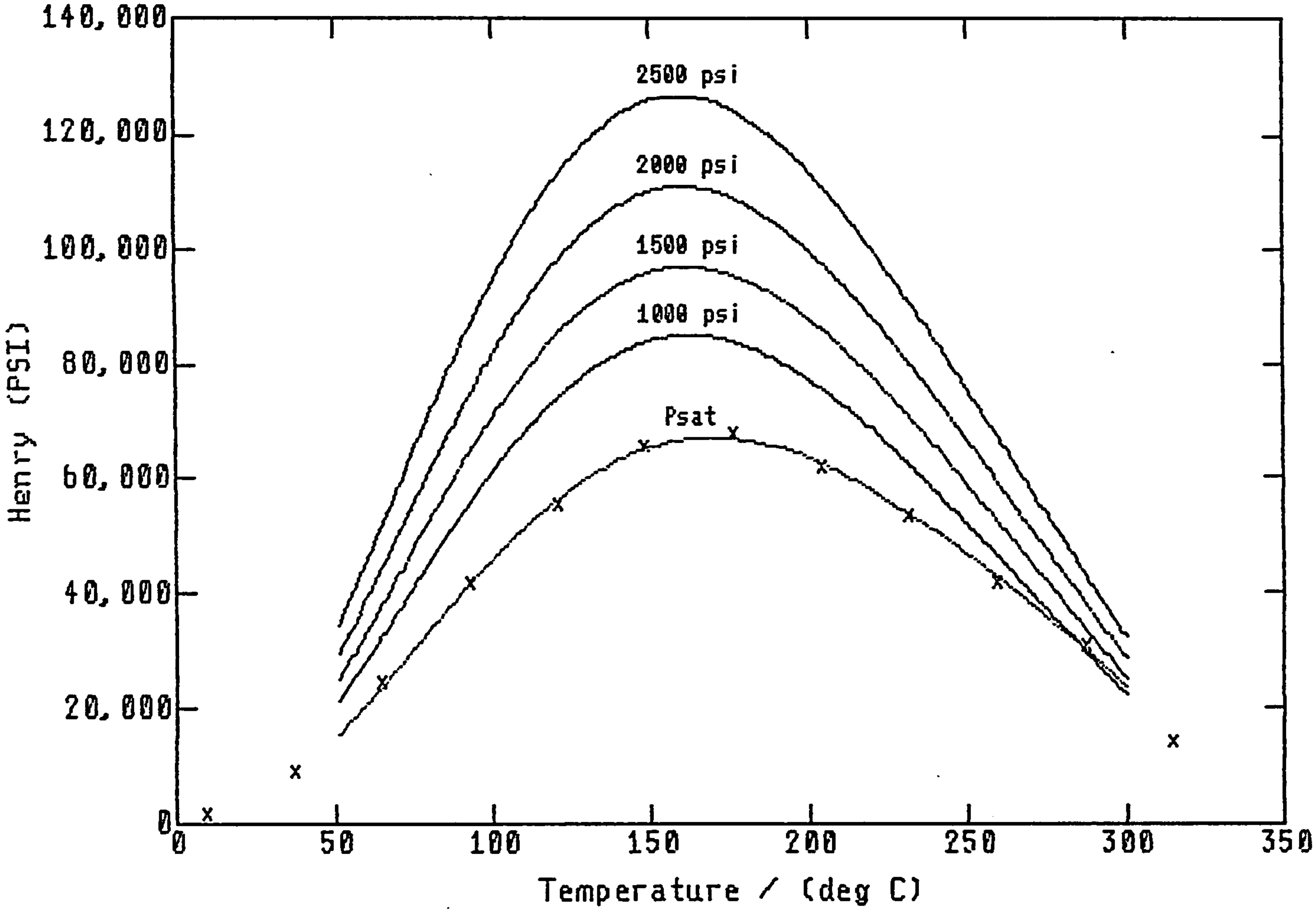


Figure 3.1 Henry's Law Constant for m-Xylene

tenuous as both the solubility and vapor pressure of this compound are comparable to m-xylene which has already been shown to have a very significant Henry's constant. Furthermore, a comparison of the initial experimental concentrations with m_2^0/V^L suggests that H might be greater than zero, but not as high as the m-xylene values. If H for tetrachloroethylene is as large as the m-xylene values, the calculated rate constants could be as much as 25-50% too small. It would not, however, have such a severe effect on the calculated activation energies. This assumption was necessary since a thorough search of the literature failed to provide either H or the values needed to compute it at experimental temperatures.

Lastly, the Henry's constant for malathion was not needed as will be shown in the next section.

CHARACTERIZATION OF REACTIONS

The data collected in this investigation are the concentration <u>versus</u> time histories of the original organic. No attempt was made to identify or monitor the concentrations of intermediate or product compounds. Though this information would be quite useful, it would have required temperature programming of the gas chromatograph which would have increased the time for concentration analysis. The on-line sampling configuration must finish analyzing one sample before the next can be taken. Thus, far fewer samples could be acquired, and in many cases insufficient data would be obtained for subsequent regression calculations.

A complete tabulation of all experimental conditions and concentration <u>versus</u> time data for these runs is presented in Appendix A.

m-Xylene

Fourteen experiments with m-xylene were conducted at temperatures of 200-240 °C and pressures of 1000-2000 psi air. In each case 780 grams of water and about 0.11 grams of m-xylene were used. Typical concentration *versus* time behavior is shown in Figure 3.2. The experimental data points are depicted by the markers, while the lines represent the results of the chapter two model.

The reaction can be divided into two distinct phases, an induction period where negligible reaction occurs and an active or rapid reaction period. It is thought that during the induction period free radicals are being generated by an initiation reaction until some critical free radical concentration is achieved. This initiation is relatively slow and the critical concentration is relatively small, so any consumption of organic is indistinguishable from experimental noise. The slow decrease in organic concentration that is observed is explained entirely by vapor-liquid equilibrium effects which have been outlined in chapter two.

Subsequent to the induction period, concentration decreases exponentially. Through the greater part of this decrease, the model which assumes first order kinetics in organic matches the data quite well. As time progresses, however, the experimental concentrations decrease more slowly than the model predicts. This apparent change in the reaction order has been observed by others, such as Chowdhury and Ross (1975) and Baillod and Faith (1983). This phenomenon can be explained by autoinhibition or a mechanistic interpretation, both of which will be discussed later.

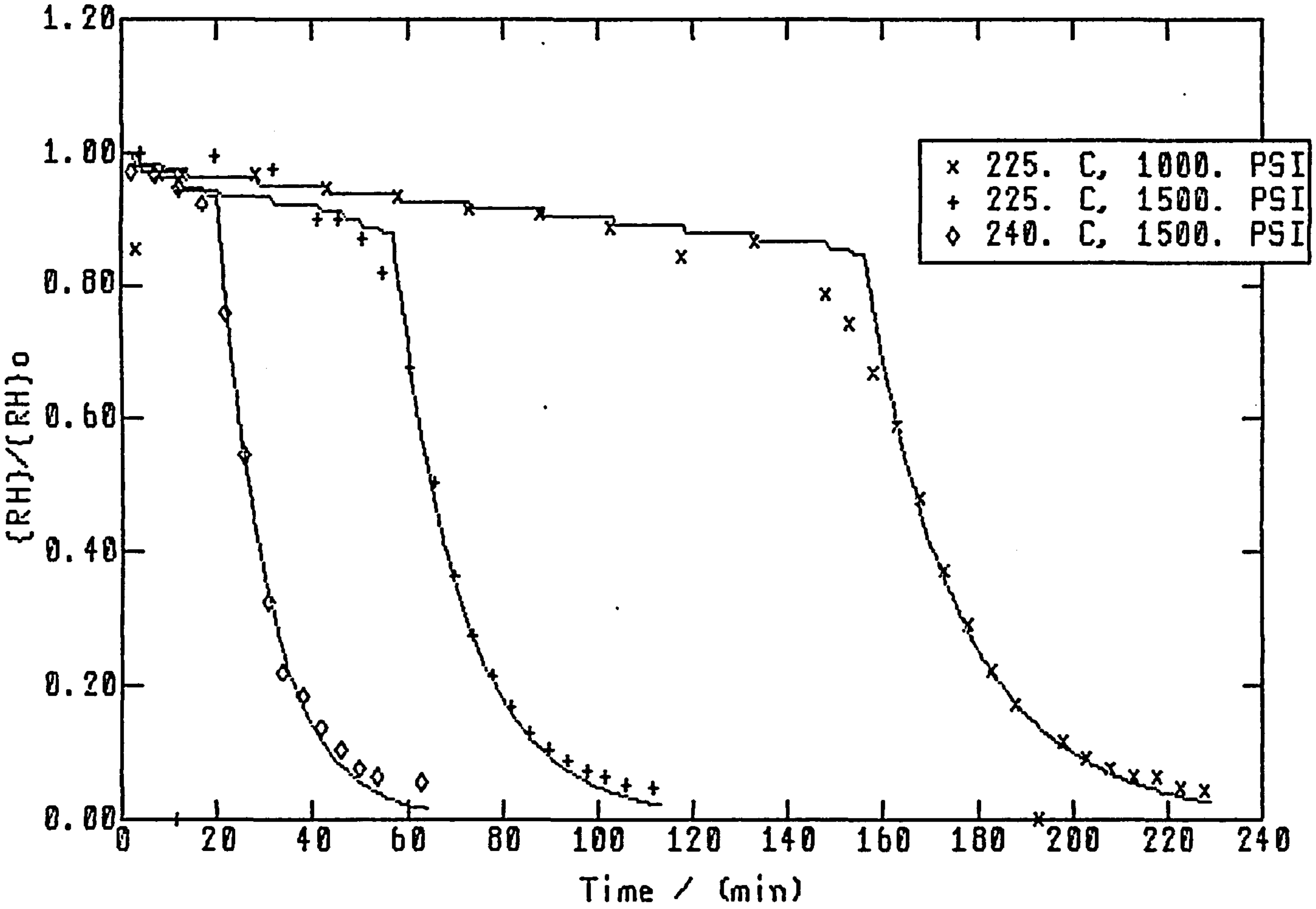


Figure 3.2 Experimental Data and Model Curves for m-Xylene Aqueous Phase Oxidation

Lastly, it is observed that increases in temperature or pressure serve to decrease the induction time and increase the reaction rate in the active reaction period.

Phenol

Six phenol experiments were conducted between 130 °C and 200 °C, all at 2000 psi air. All runs used 780 grams of water and about 0.1 grams of phenol. An examination of Figure 3.3, showing examples of these runs, reveals behavior qualitatively very similar to that of m-xylene though faster reaction rates are observed for phenol. At the higher temperatures the induction period is small, while at lower temperatures it is quite significant. Just as for m-xylene, increasing temperature increases the active phase reaction rate.

Tetrachloroethylene

Two runs with tetrachloroethylene (TCE) were performed, one at 225 °C and 2500 psi air with 0.068 grams of TCE, the other at 275 °C and 2000 psi air with 0.103 grams of TCE. Each utilized 780 grams of water. As shown in Figure 3.4, neither of these two runs shows an induction period. The model which assumes an exponential decay follows both sets of data nicely, though at the lower temperature this functional form is difficult to discern within the time scale of the experiment. It is observed that much slower reaction rates occur even at these more severe temperatures than for either of the two previous compounds.

Malathion

Four experiments were conducted with malathion, two at 130 and two at 160 °C, all at 2000 psi air. The mass of water was 780 grams in all

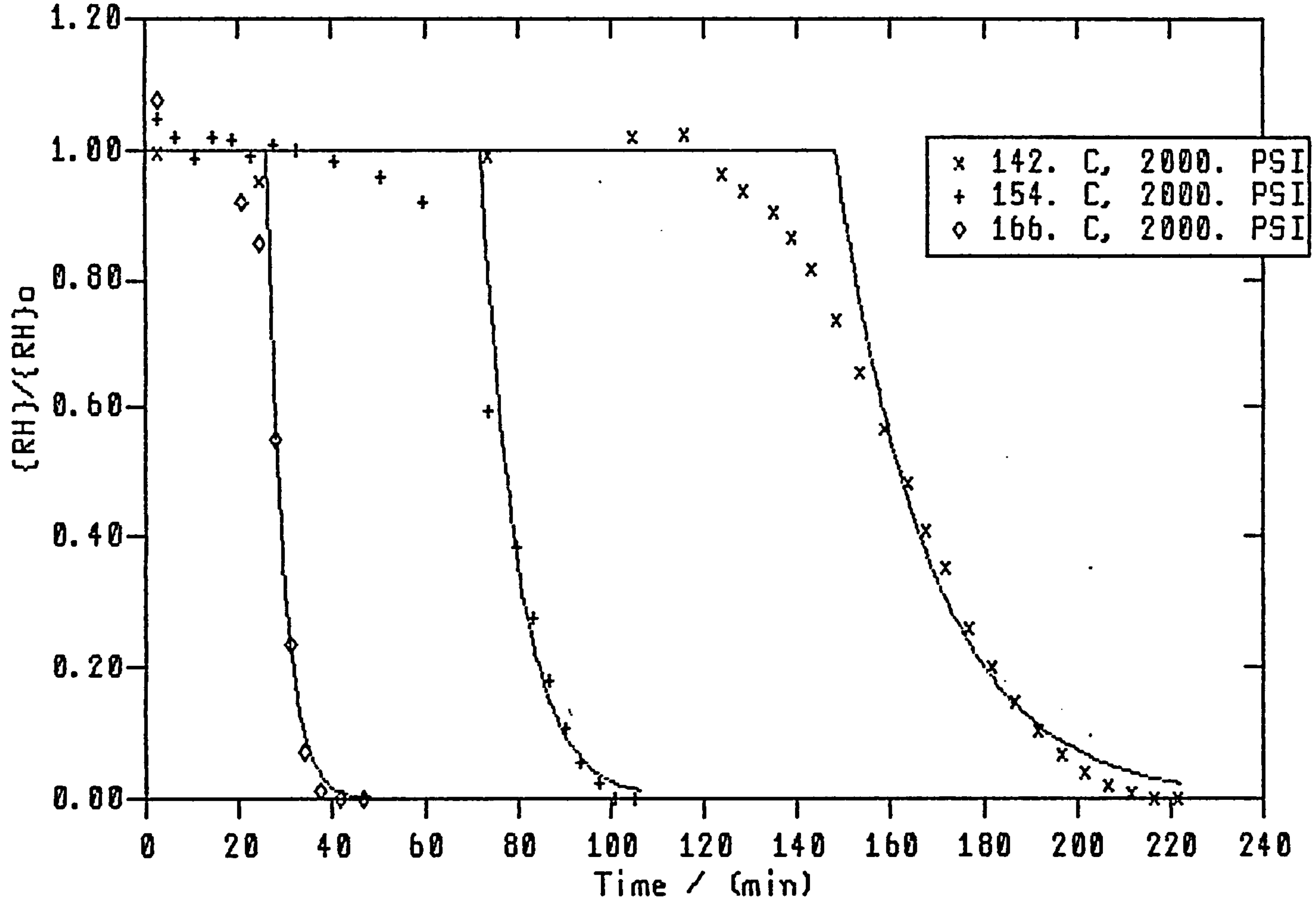


Figure 3.3 Experimental Data and Model Curves for Phenol Aqueous Phase Oxidation

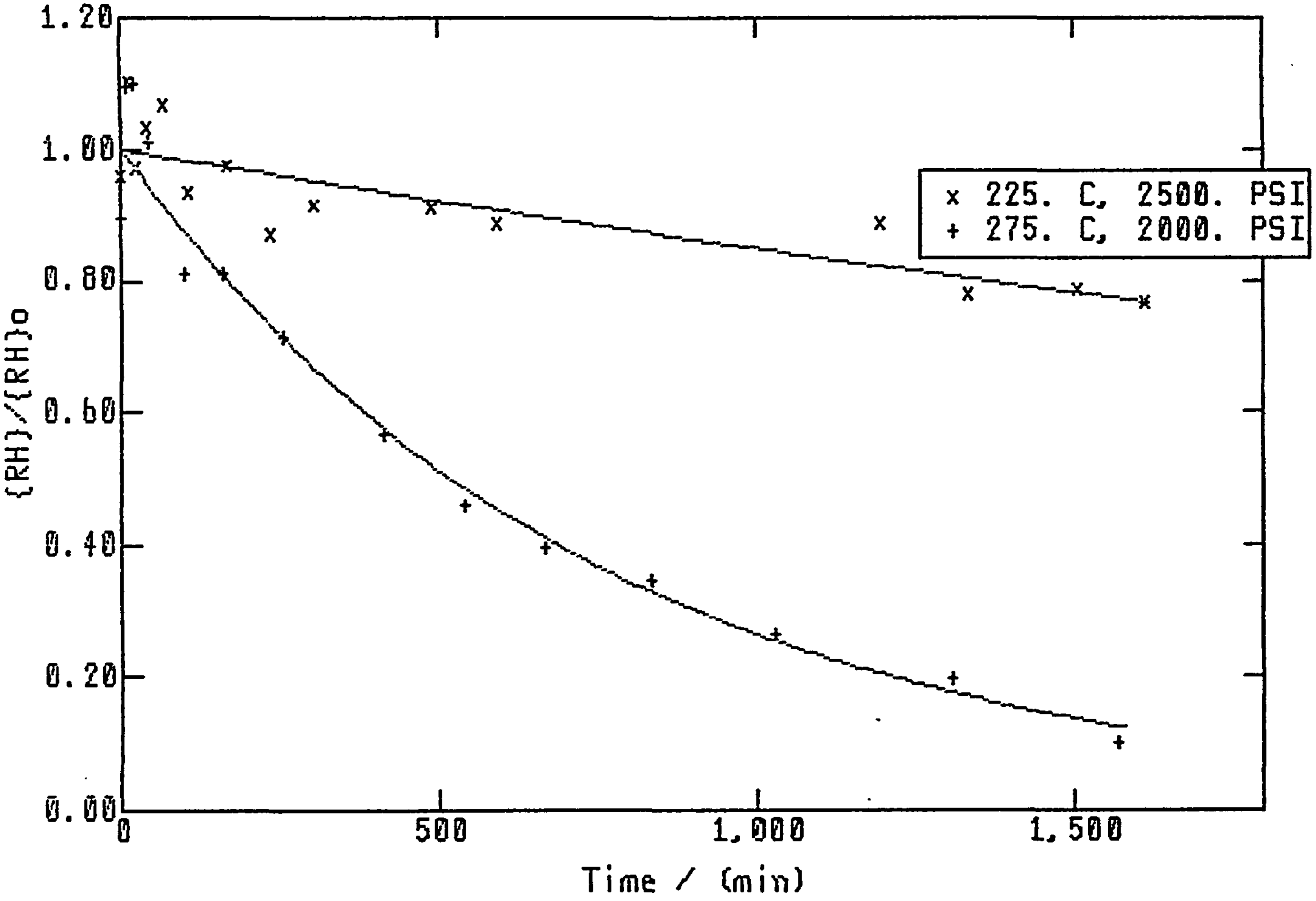


Figure 3.4 Experimental Data and Model Curves for Tetrachloroethylene Aqueous Phase Oxidation

cases, while the initial amount of malathion ranged from 0.07 to 0.18 grams. The results of these runs are radically different from any of the others, as malathion was completely consumed before the first reactor sample could be withdrawn (about two minutes). Only a number of unidentified reaction products were recorded on the chromatograms. Some of these increased in area, then disappeared, while others increased to steady state values after about 20 minutes. This behavior is consistent with the conclusions of others (e.g. Cowart et al. (1971) and Mitchell (1966)) that the predominant reaction is not oxidation but hydrolysis which occurs at appreciable rates even at ambient conditions. As hydrolysis is an effective means of detoxifying organophosphorus compounds (Mitchell (1966)), subjecting malathion to reaction conditions such as those used in this study is much more than sufficient to destroy it.

MODEL

The model used to describe these data was developed in chapter two. Therein, several assumptions were made. The only assumptions in question here are that the gas phase is ideal, there is no mass transfer limitation, and that the oxygen concentration is in such excess that it can be considered constant.

It was established that the gas phase could be considered ideal by comparing molar volumes calculated by the Redlich-Kwong and the ideal gas equations of state. At 200 °C and 2500 psi air it was determined that only 3.1% difference exists between these two calculations, while at 225 °C and 2000 psi air this difference was reduced to 0.1%.

With respect to mass transfer, a number of papers have addressed this issue. Day et al. (1973) varied the agitator speed from 200 to 600 rpm at different temperatures and found that this had no effect on reaction rate. Sadana and Katzer (1974) conclude that their reactions faced no mass transfer limitation with stirrer speeds of 650 rpm due to the characteristics of their data, such as high values of the activation energy. Sadana (1972) includes calculations which indicate no mass transfer limitation. Williams et al. (1973) also found no mass transfer limitation. Pruden and Ferguson (1973) did report mass transfer limiting conversions of phenol at low pressures (800 psi air) in an unstirred, air sparged reactor. At higher pressures (1200-2200 psi air) this effect diminished and presumably would disappear if the reactor was agitated. The reactor in this work was stirred as fast as any of these studies (750 rpm) and pressures were also comparable (1000-2500 psi air).

Furthermore, as an independent check for mass transfer limitation, mass transfer coefficients were calculated according to the correlations presented in Barona (1979). This gave k_L as 0.138 and 0.174 cm/sec at 200 and 250 °C, respectively, for oxygen in water. The rate of oxygen transfer is described by

$$V^L \, d[O_2]/dt = k^L a \, ([O_2]^* - [O_2]) \; . \tag{3.5}$$

This rate is also proportional to the organic reaction rate,

$$d[O_2]/dt = S \, d[RH]/dt = S \, k' \, [RH]^n \; . \tag{3.6}$$

Equating, rearranging, and dividing by $[O_2]^*$ gives

$$\frac{[O_2]}{[O_2]^*} = 1 - \frac{V^L S \; k' \, [RH]}{k_L a \, [O_2]^*} . \qquad (3.7)$$

The ratio, $[O_2]/[O_2]^*$, is a measure of the degree of oxygen depletion in the system, ranging from 1 for no oxygen depletion to 0 for complete oxygen depletion. The maximum conceivable depletion will occur 1) at the beginning of the active reaction period when the organic is reacting at its maximum rate ($[RH] = [RH]_0$), and 2) when each organic molecule is oxidized completely to carbon dioxide and water (resulting in $S = 10.5$ moles of oxygen/mole of m-xylene). Assuming $n = 1$ and using typical values of k' and $[RH]_0$ from experiments reported later, it is now possible to calculate values for $[O_2]/[O_2]^*$. For m-xylene at 200 °C and 2000 psi air this ratio is 0.966, while at 240 °C and 1500 psi air it is 0.886. Thus, at the most extreme conditions, the oxygen concentration would be reduced by about 10%. Since oxidation does not proceed immediately to carbon dioxide and water, and since this maximum rate does not exist throughout the active reaction period, the oxygen depletion is actually less severe than the values just given indicate. This and the findings of others presented above indicate that mass transfer can be considered essentially instantaneous, and thus, the vapor and liquid can be assumed to be in equilibrium at all times. If reactions were much faster than those just considered, however, this would not be true.

With respect to oxygen being in large excess, the amount of oxygen initially present in the water before reactions were started has been calculated. This is expressed as the amount of oxygen present in solution divided by the amount of oxygen required to completely oxidize the organic to carbon dioxide and water. Oxygen solubilities were determined from Himmelblau (1960). For each of the compounds the results are: m-xylene 103-276%, phenol 239-353%, and tetrachloroethylene 3540-5250%. In many cases the reaction does not oxidize completely to CO_2 and water, and it has already been shown that reacted oxygen is quickly replenished from the vapor phase by fast mass transfer. Thus, though the global kinetics of organic oxidation is described by

$$d[RH]/dt = k\,[O_2]^m[RH]^n, \tag{3.8}$$

it is valid to assume

$$d[RH]/dt = k'\,[RH]^n \tag{3.9}$$

for the duration of a single experiment during which the oxygen pressure is held constant. To compare rates between runs at different pressures, however, the intrinsic rate constant, k, must be determined by dividing k' by the oxygen concentration raised to the appropriate power.

RESULTS AND DISCUSSION

m-Xylene

The model has been applied to each of the fourteen m-xylene runs. Figure 3.2 shows that the model line agrees quite well with the experimental data. This confirms the assumption that the reaction is first order in organic. The regression analysis described in chapter two produced values of k' and t_{start} which are reported in Table 3.5.

Also shown in the table are values for m_2^0, the oxygen concentration, and the intrinsic rate constant, k. To determine k the reaction order with respect to oxygen, m, as seen in equation 3.8, is required. This

Table 3.5 Experimental Conditions and Model Results for m-Xylene Phenol, Tetrachloroethylene, and Malathion

T (°C)	P (psi)	m_2^0 (gm)	t_{start} (min)	k' (1/min)	O_2 (gm/ml)	k $(1/min)(ml/gm)^{0.5}$
m-Xylene						
200	2000	0.083	175.6	0.0387	0.000999	1.225
200	2000	0.092	332.1	0.0251	0.000999	0.794
200	2000	0.090	317.8	0.0261	0.000999	0.826
200	2000	0.103	156.8	0.0355	0.000999	1.123
225	1000	0.109	180.8	0.0713	0.000436	3.415
225	1000	0.115	156.7	0.0733	0.000436	3.511
225	1500	0.104	57.6	0.0999	0.000782	3.573
225	1500	0.091	59.6	0.0952	0.000782	3.405
225	2000	0.104	152.2	0.1078	0.001127	3.211
225	2000	0.094	53.7	0.1081	0.001127	3.220
240	1000	0.089	36.3	0.1031	0.000409	5.095
240	1000	0.090	64.7	0.0933	0.000409	4.611
240	1500	0.090	22.7	0.1261	0.000807	4.438
240	1500	0.107	20.3	0.1301	0.000807	4.578
Phenol						
130	2000	0.110	315.3	0.0174	0.000730	0.644
142	2000	0.120	148.7	0.0500	0.000761	1.813
154	2000	0.117	72.9	0.1290	0.000799	4.563
166	2000	0.110	26.2	0.2879	0.000844	9.909
178	2000	0.115	-	-	0.000895	-
200	2000	0.110	-	-	0.000999	-
Tetrachloroethylene						
225	2500	0.068	0	0.000165	0.001473	0.00430
275	2000	0.103	0	0.001330	0.001330	0.03647
Malathion						
130	2000	0.185	<2	-	0.000730	-
130	2000	0.185	<2	-	0.000730	-
160	2000	0.127	<2	-	0.000821	-
160	2000	0.068	<2	-	0.000821	-

was found by constructing two Arrhenius plots, the first assuming m = 0.5 and the other assuming m = 1. These are shown in Figures 3.5 and 3.6, and it is observed that only the plot which assumes m = 0.5 collapses all data onto one line. The Arrhenius plot for m = 1, by contrast, shows a series of lines corresponding to the various pressures. Thus, it was concluded that during the active reaction period, the reaction is 1/2 order with respect to oxygen and the values of k in Table 3.5 were calculated accordingly. From the slope of the least squares line on Figure 3.5, an activation energy of 19.6 +/- 3.1 kcal/gmole is calculated (all confidence limits are at the 95% level). It should be noted that a portion of the uncertainty in values of activation energy is accounted for in the +/- 2 °C variation in temperature. In this case it is estimated that this would result in a +/- 2.0 kcal/mole variation in activation energy. The intercept was used to calculate a preexponential factor, A, of 1.17×10^9 $(1/\text{min})(\text{ml/gm})^{0.5}$.

It should be noted at this point that only two previous studies, those of Day _et al._ (1973) and Sadana and Katzer (1974), have been found which concluded that the reaction order with respect to oxygen was 1/2. All other studies which address this issue (_e.g._ Ploos van Amstel and Rietema (1973), Weygandt (1969), and Shibaeva _et al._ (1969b)) either assume or conclude the reaction is first order in oxygen. It is possible that this discrepancy is due to differing compounds, concentrations, or reaction conditions. Certainly with the two precedents cited and the precision of the data presented herein, there is no cause for doubting the 1/2 order in oxygen conclusion.

The next pertinent question is what controls the length of the induction period. As will be shown later, the initiation reaction which

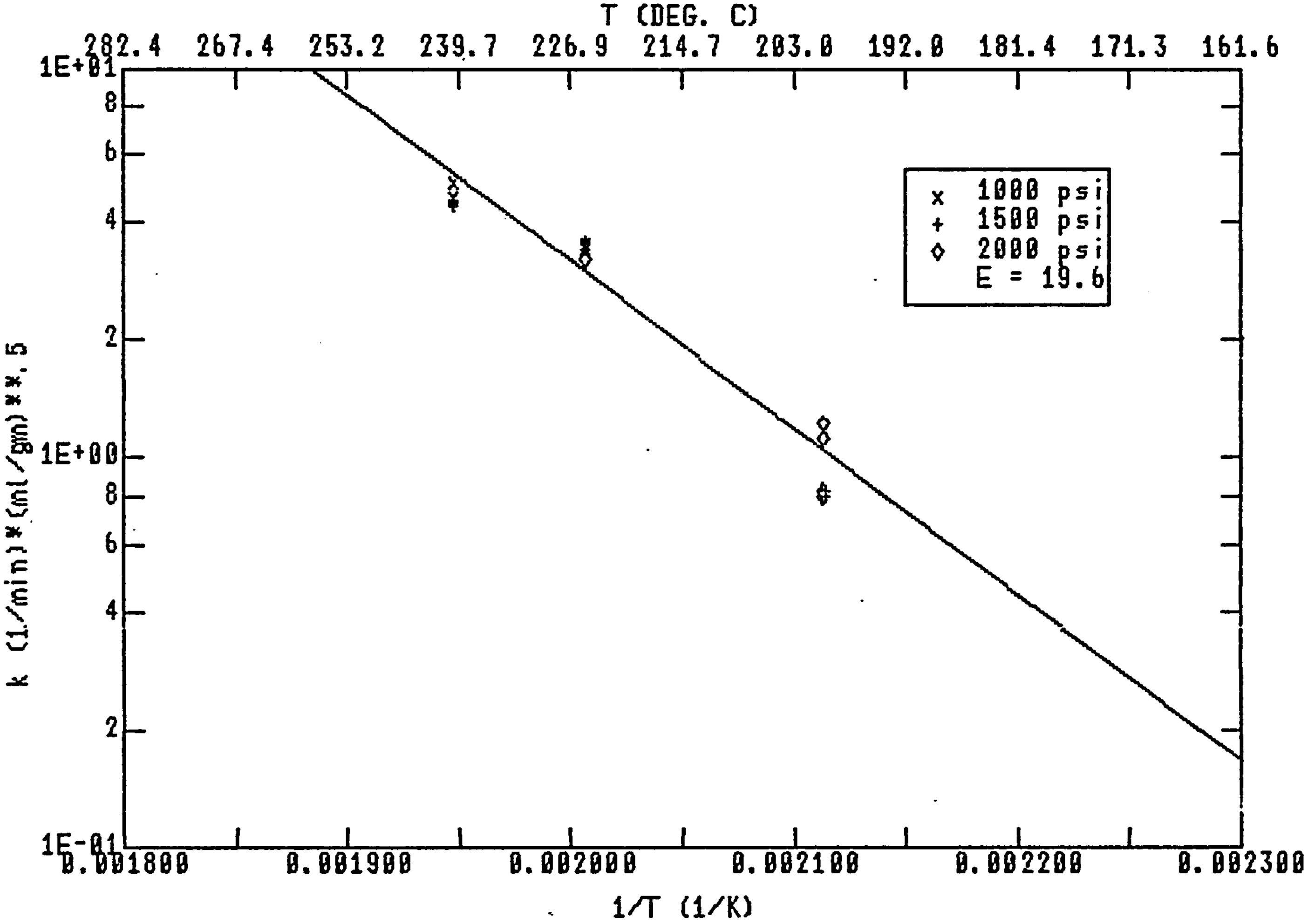


Figure 3.5 Rapid Reaction Arrhenius Plot for m-Xylene, 1/2 Order in Oxygen

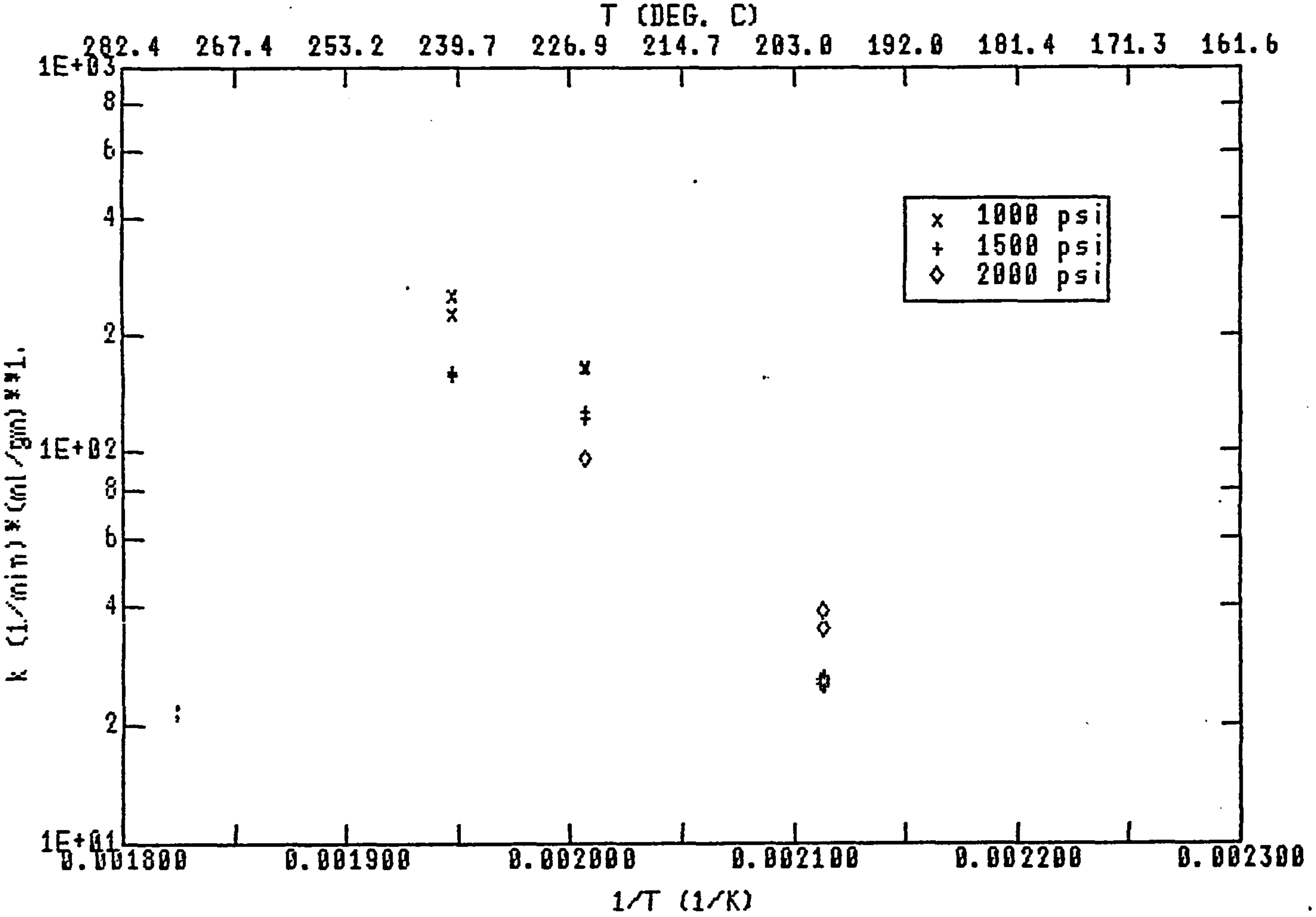


Figure 3.6 Rapid Reaction Arrhenius Plot for m-Xylene, First Order in Oxygen

controls the rate of formation of radicals in the induction period is believed to be first order in both organic and oxygen concentrations and can be expressed as

$$d[R\bullet]/dt = k_0[RH][O_2] \ . \qquad (3.10)$$

Since during the induction period [RH] and $[O_2]$ are essentially constant, the entire RHS is nonvariant. Integration and substitution of the Arrhenius equation reveals

$$R\bullet = A_0 \exp(-E_0/RT)\ [RH]_0[O_2]_0\ t \ . \qquad (3.11)$$

Next, it is conjectured that there is some critical concentration of free radicals, $R\bullet_{crit}$, which results in the onset of the active reaction period at time t_{start}. $R\bullet_{crit}$ is assumed to be independent of temperature over the range of conditions used here. Substituting these values and rearranging gives

$$\ln(t_{start}[O_2]_0) = \ln(R\bullet_{crit}/A_0[RH]_0) + (E_0/R)(1/T) \ . \qquad (3.12)$$

Remember that $[O_2]$ is constant for any particular run, but changes if pressure is altered from run to run. A semi-log plot of $t_{start}[O_2]_0$ <u>versus</u> 1/T should give a straight line with slope E_0/R. Plots were constructed not only with the oxygen concentration raised to the first power as just described, but also raised to the 0.5 and 1.5 power. It was, in fact, found as seen in Figure 3.7 that $[O_2]$ raised to the first power resulted in all data falling on one straight line. It is, therefore, concluded that initiation is first order in oxygen concentration. The slope gives an initiation activation energy of 30.0 +/- 5.7 kcal/gmole and the group of constants, $R\bullet_{crit}/A_0[RH]_0$, is 3.59 x 10^{-15}

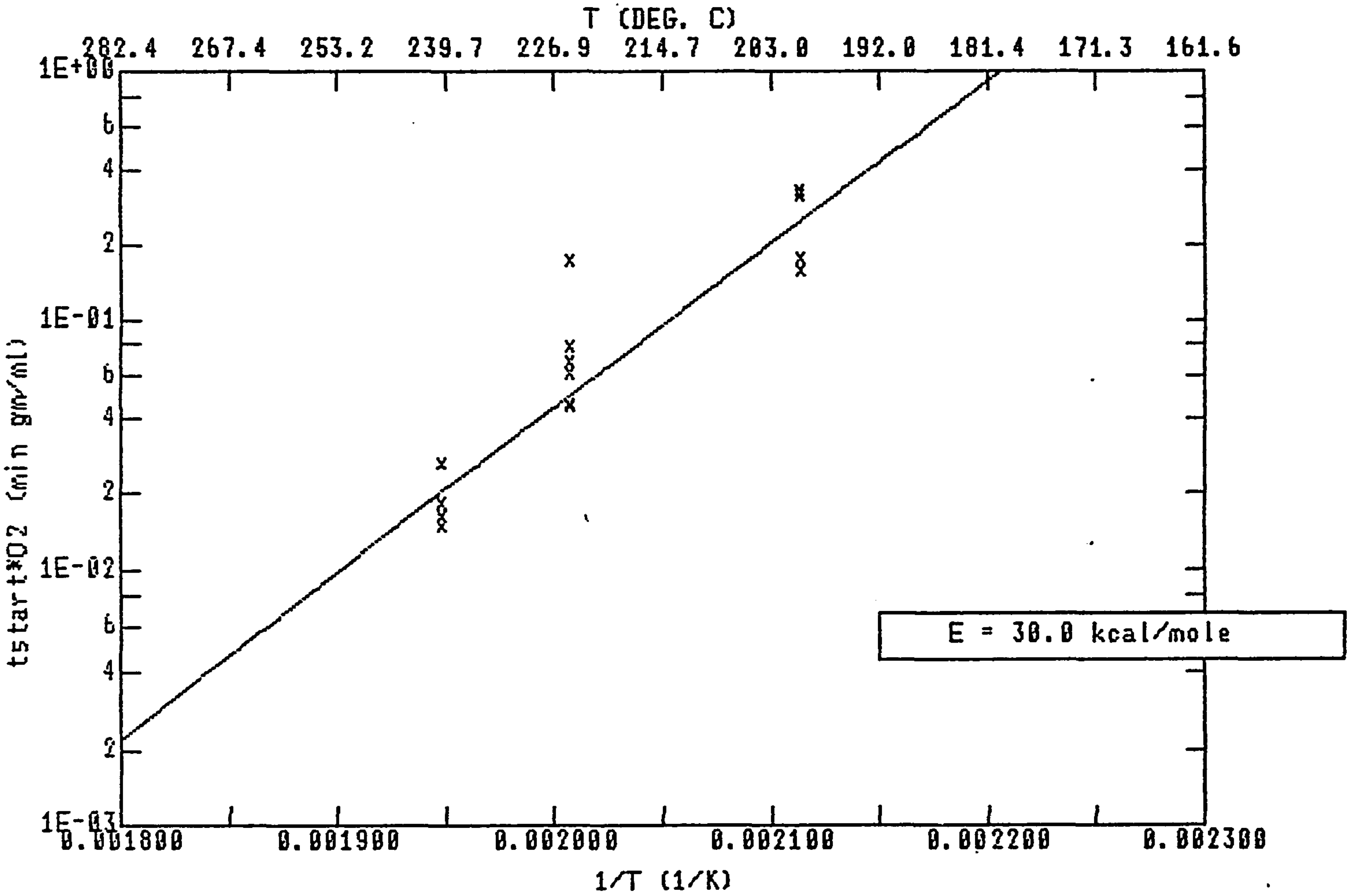


Figure 3.7 Induction Arrhenius Plot for m-Xylene

(min gm/ml). It is observed that this activation energy is in excellent agreement with the value of 31 kcal/gmole reported for o-xylene in benzene solvent by Denisova and Denisov (1969).

It should be noted here that at some time during the induction period other steps in the mechanism (specifically degenerate branching) begin to dominate as the initiation step. This implies that this treatment is not completely accurate, and while the agreement between the experimental data and equation 3.12 lend to its credibility, this could easily be coincidental. Though more data will be required to validate this mechanistic interpretation, it is evident that, at least empirically, this is an effective means of correlating the induction time data.

Phenol

As seen in Figure 3.3, good agreement is observed between the experimental data and the chapter two model which assumes the reaction rate is first order in organic. Note, however, that at the lower temperatures, the reactions appear to be shifting to zero rather than first order. Regression results for the phenol experiments are given in Table 3.5. No oxygen reaction order evaluation could be performed, since all runs are at one pressure. It was, nonetheless, assumed that the reaction was 1/2 order in oxygen as was found in this study for m-xylene and by Sadana and Katzer (1974) for phenol.

Values of k' and t_{start} could not be calculated at the two highest temperatures because the reaction was so fast that sufficient data could not be collected to give meaningful results. Values of k' and t_{start} could, however, be extrapolated from the Arrhenius numbers which will be given in the next paragraph. Using these extrapolated numbers, the model predicted curves which match the experimental data from these two runs as shown in Figure 3.8.

Arrhenius plots for both active and induction period data are shown in Figures 3.9 and 3.10, respectively. The activation energy and preexponential for the active reaction period are 26.8 +/- 3.1 and 2.19 x 10^{14} (1/min)(ml/gm)$^{0.5}$, respectively. This is in excellent agreement with values of 25.6 kcal/mole for phenol and 26.3 kcal/mole for phenol with hydrogen peroxide submitted by Shibaeva et al. (1969b, 1969c). For the induction period the activation energy is 22.5 +/- 7.5 kcal/mole and $R\bullet_{crit}/A_0[RH]_0$ is 1.57 x 10^{-13} (min gm/ml).

Tetrachloroethylene

Table 3.5 gives the model results for the two tetrachloroethylene runs. Figure 3.11 shows the Arrhenius plot for the active reaction period from which an activation energy of 23.2 kcal/gmole was calculated. The confidence limits are not defined for only two data points. The preexponential is calculated as 6.49 x 10^7 (1/min)(ml/gm)$^{0.5}$. No Arrhenius plot for the initiation is shown since these runs showed no detectable induction period.

Malathion

The model was not applied to malathion as only reaction products were present by the time the first sample could be collected.

MECHANISM

Development

A general mechanism for liquid phase oxidation of hydrocarbons has been presented by Emanuel et al. (1967) (essentially the same scheme can

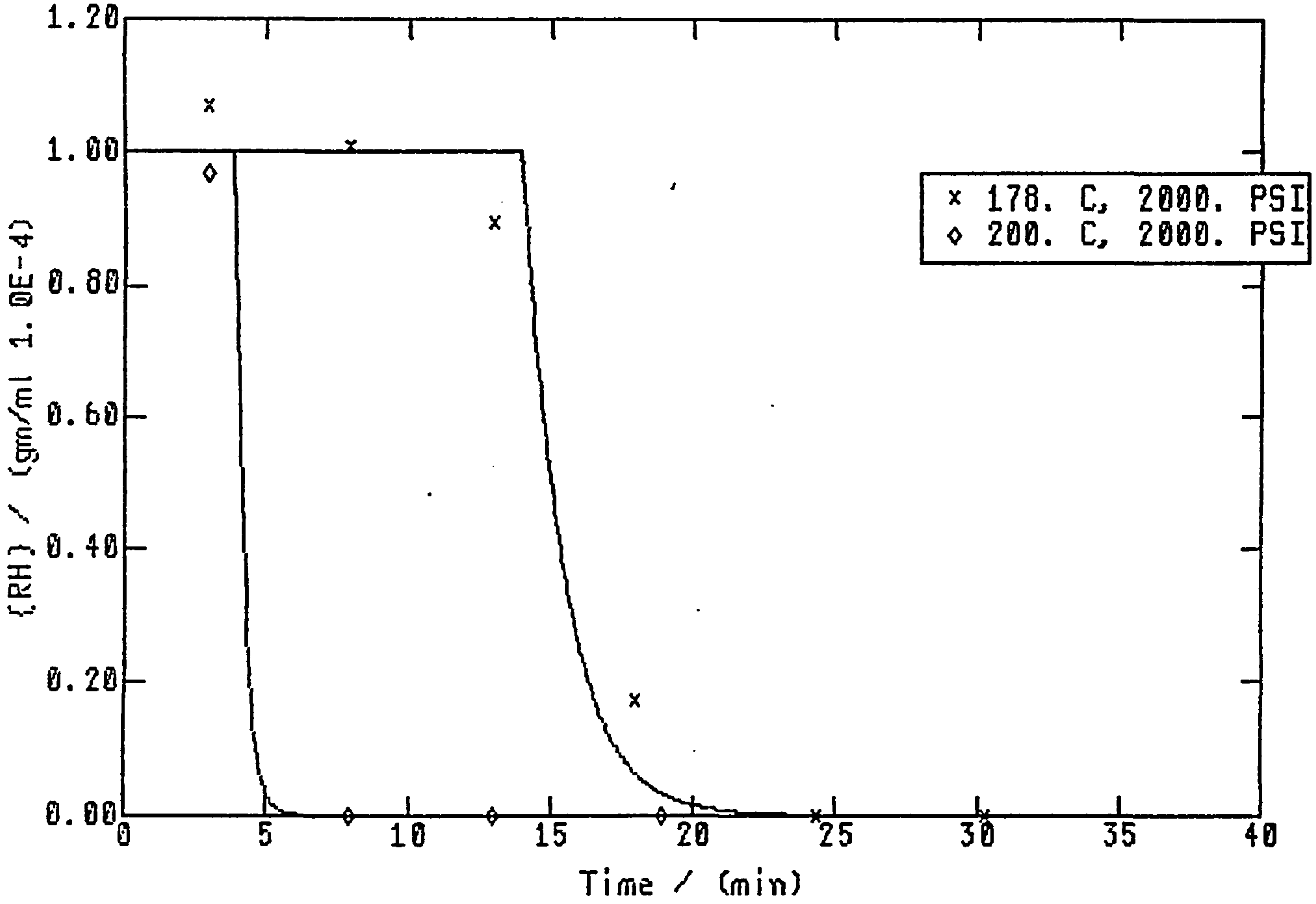


Figure 3.8 Experimental Data and Model Extrapolated Model Curves for the Most Rapidly Reacting Phenol Runs

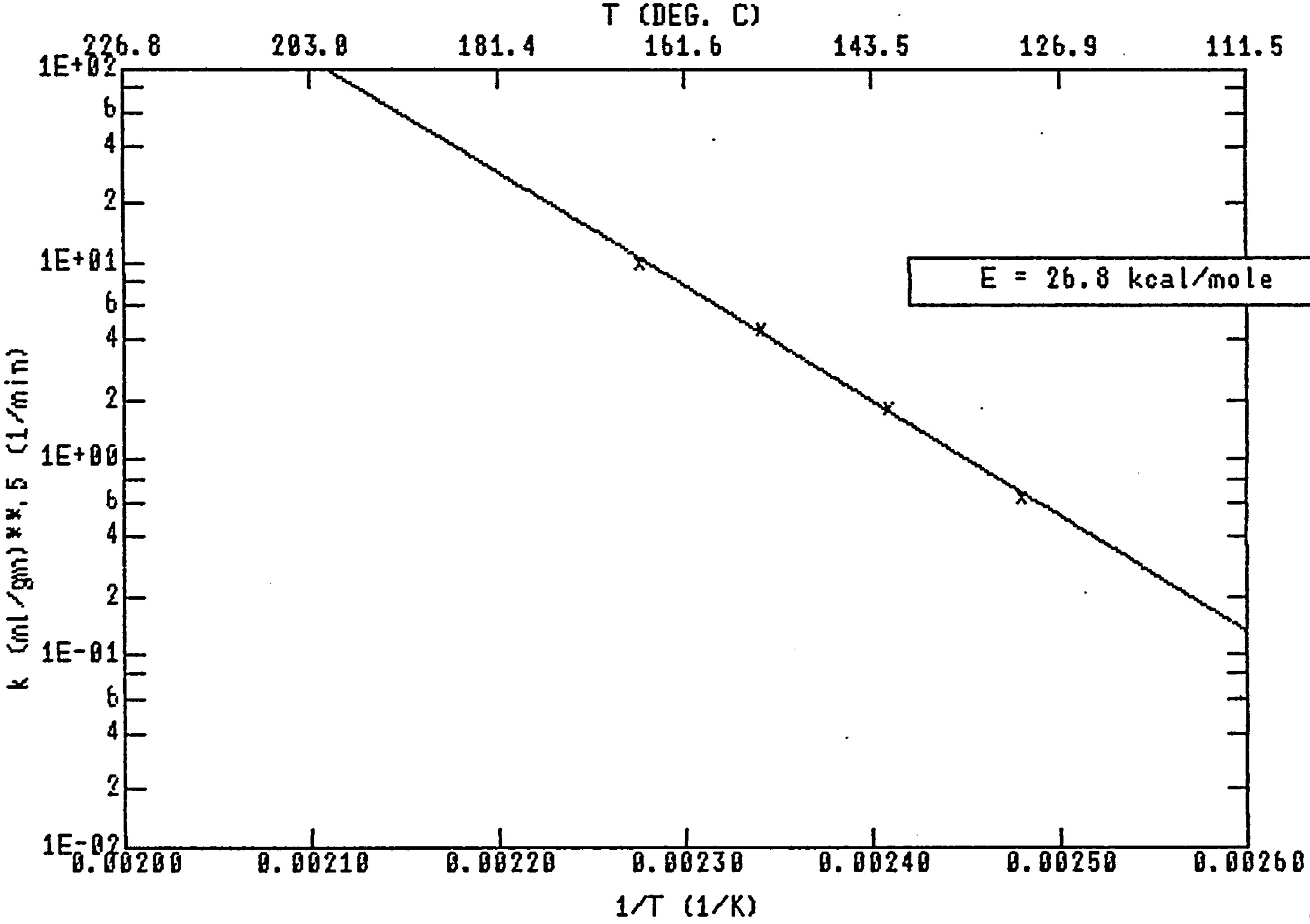


Figure 3.9 Rapid Reaction Arrhenius Plot for Phenol

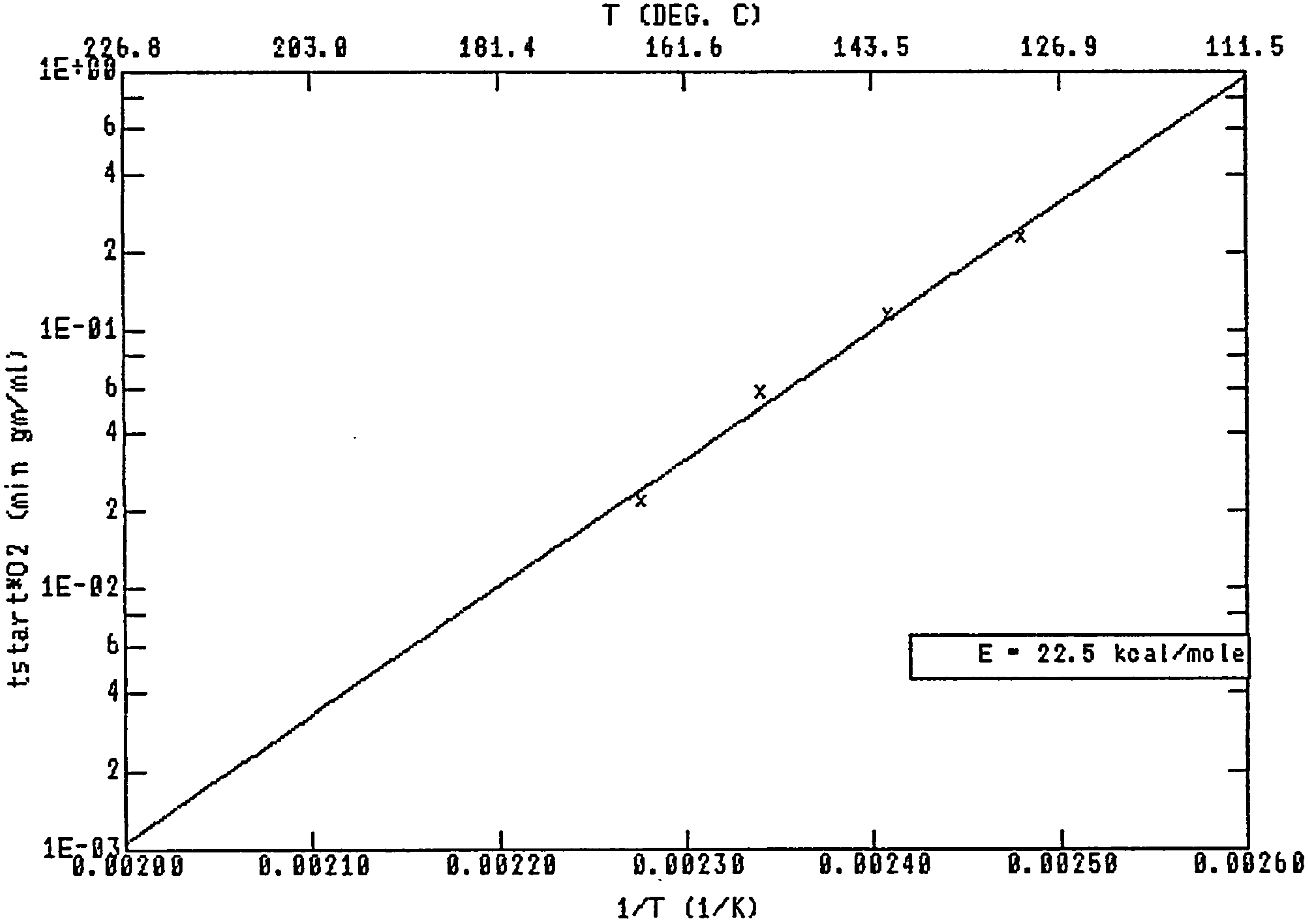


Figure 3.10 Induction Arrhenius Plot for Phenol

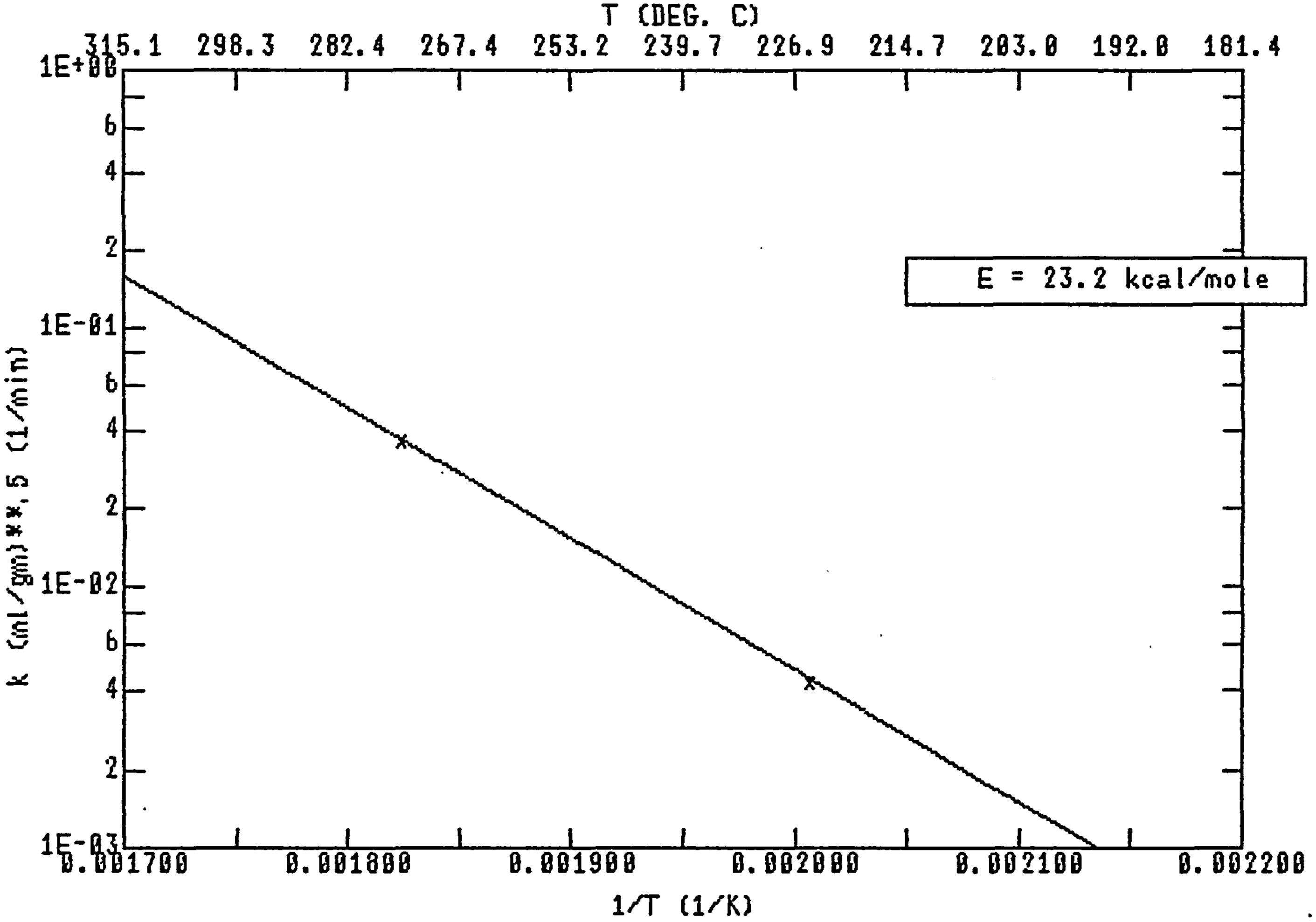


Figure 3.11 Rapid Reaction Arrhenius Plot for Tetrachloroethylene

also be found in Hawkins (1961), Russell (1959), McBurney (1954), Uri (1961), and Chowdhury and Ross (1975)) and is shown as follows

		Reaction
$RH + HR \rightarrow 2R\bullet + H_2$	Initiation	0a
$RH + O_2 \rightarrow R\bullet + HO_2\bullet$		0b
$RH + O_2 + HR \rightarrow 2R\bullet + H_2O_2$		0c
$R\bullet + O_2 \rightarrow RO_2\bullet$	Propagation	1
$RO_2\bullet + RH \rightarrow ROOH + R\bullet$		2
$ROOH \rightarrow RO\bullet + \bullet OH$	Degenerate Branching	3
$R\bullet + R\bullet \rightarrow R\text{-}R$	Termination	4a
$RO_2\bullet + R\bullet \rightarrow ROOR$		4b
$2\ RO_2\bullet \rightarrow ROH + R_1COR_2 + O_2$		4c

The process begins with three possible initiation reactions shown as 0a, 0b, and 0c. According to Emanuel _et al._ (1967) these are the only probable initiation reactions. Other possible initiations such as a simple dissociation of a C-C or C-H bond require too much energy to be significant. Also, a wall catalyzed or organic/water encounter could produce free radicals, but these too are believed to be negligible.

Of the three initiation reactions shown above, 0b is believed to be the only one of significance in these studies. The other two possibilities are rejected, first, because of the dilute solutions used (about 0.001 mole/liter), making the probability of an RH/RH encounter very low. Secondly, the length of the induction period for m-xylene was seen to be dependant on the oxygen partial pressure. Finally, Denisova and Denisov (1969) investigated the formation of radicals with o-xylene in benzene solvent at 100-150 °C. They conclude that reaction 0b is the only significant initiation step and that its reaction rate is described by

$$k_0 = 2.0 \times 10^8 \exp(-31000/RT) \text{ liter/mole sec} . \qquad (3.13)$$

It is therefore assumed here that initiation proceeds according to reaction 0b and that it is slow ($k_0 = 1 \times 10^{-6}$ liter/mole sec from equation 3.13 at 200 °C).

The next two reactions in the general mechanism are the chain propagation steps. Emanuel *et al.* (1967) report that reaction 1 is very fast as long as oxygen is plentiful. This reaction has an activation energy of essentially zero and the rate constant is estimated to be 3×10^7 liter/mole sec for xylene by transition state theory (Emanuel *et al.* (1967)). Reaction 2 has an activation energy of about 7 kcal/mole based on the 2,4,6-trimethylbenzene study reported by Bolland and Gee (1946). Emanuel *et al.* (1967) show that the preexponential of the Arrhenius equation for hydrocarbon reactions involving a secondary C-H bond can be calculated from the activation energy according to

$$\log(A_2) = 2 + 0.5\ E_2 \qquad (3.14)$$

The rate constant for reaction 2 for m-xylene can thus be estimated by

$$k_2 = 3.2 \times 10^5 \exp(-7000/RT) \text{ liter/mole sec} . \qquad (3.15)$$

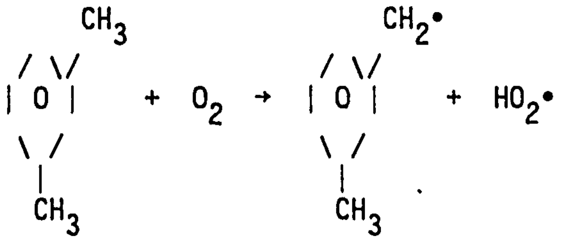
From this equation k_2 is about 200 liter/mole sec at 200 °C. Though slower than reaction 1, it is still orders of magnitude faster than reaction 0b.

Reaction 3 describes a degenerate branching step. Using the hydroperoxide reaction product of the propagation steps, this reaction produces two radicals. Each of these two radicals then initiates another set of propagation chains. At lower temperatures hydroperoxides are stable and do not dissociate. Emanuel _et_ _al._ (1967) report that above 70-80 °C, however, cumyl hydroperoxide dissociates to form two radicals which account for essentially all chain initiations following the induction period. They report similar results for n-butane at 145 °C. Further evidence of the importance of degenerate branching arises from computer simulations of this mechanism with and without reaction 3 present. These will be discussed later. It is, therefore, concluded that at the reaction conditions used in this study, degenerate branching is an important step for m-xylene and phenol oxidation. It is unclear whether this is an important step for tetrachloroethylene.

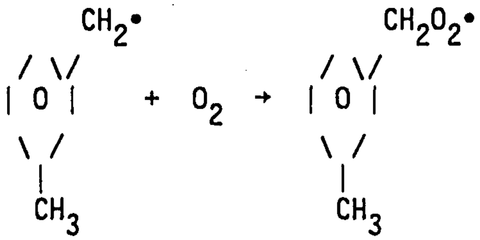
The last reactions in the general mechanism are recombinations of radicals which terminate the chains, shown above as reactions 4a, 4b, and 4c. These reactions have activation energies of 1-2 kcal/mole. To determine which of these reactions predominates, the relative concentrations of radicals must be ascertained. Since k_1 is much faster than k_2, and since the reaction is not starved for oxygen, the concentration of ROO• should be much greater than the concentration of R•. On this basis, reaction 4c should be the only significant termination step. Wall/radical encounters will also result in termination, but the reactor volume to area ratio is believed to be large enough that this can be neglected.

Now a mechanism can be postulated specifically for m-xylene.

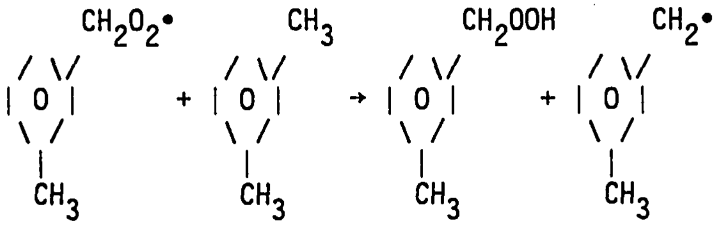
<u>Reaction</u>



0b



1



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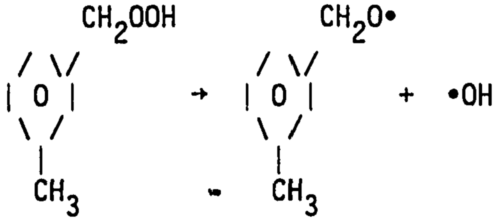

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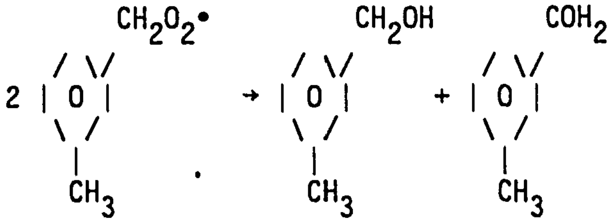
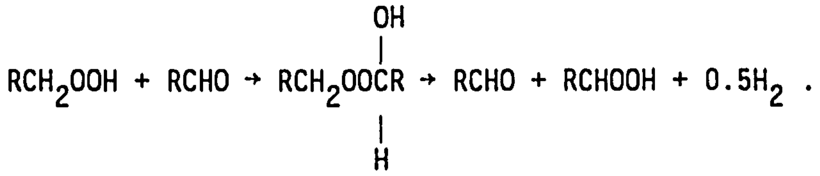


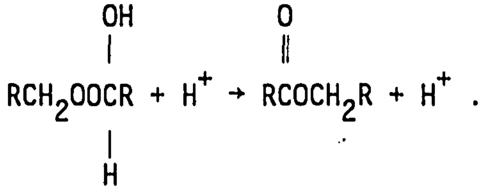
4c

Of course these are not the only reactions which occur. Nothing has been mentioned concerning reactions which produce stable reaction products. These next steps which follow the mechanism shown above appear to be less well known. Emanuel et al. (1967) state that the decomposition of primary hydroperoxides results in an acid, hydrogen, and an ester, with an aldehyde occurring as an intermediate. Though they do not show the source of this aldehyde, Emanuel et al. (1967) present



$$RCH_2OOH + RCHO \rightarrow RCH_2OO\overset{OH}{\underset{H}{C}}R \rightarrow RCHO + RCHOOH + 0.5H_2 .$$

Emanuel et al. (1967) postulate that the ester forms from the ionic reaction shown here simply as



$$RCH_2OO\overset{OH}{\underset{H}{C}}R + H^+ \rightarrow R\overset{O}{\overset{\|}{C}}OCH_2R + H^+ .$$

For secondary hydroperoxides Emanuel et al. (1967) report that alcohols result from

$$RO\bullet + RH \rightarrow ROH + R\bullet .$$

The free valence stabilizing effect of the aromatic ring presumably makes this a possible reaction for xylene even though it contains only a primary carbon. An alcohol could also result from

$$R\bullet + ROOH \rightarrow ROH + RO\bullet$$

which Emanuel et al. (1967) report occurring during cumene oxidation. A similar reaction is also presented,

$$RO\bullet + ROOH \rightarrow ROH + ROO\bullet \ .$$

Russell (1962) shows many of these same reactions. Though not offering any mechanism, Hawkins (1961), reports that Lorand and Edwards (1955) found acids, aldehydes, alcohols, and dimethylbibenzyl (the dimer of $CH_3C_6H_4CH_2\bullet$) resulting from pure p-xylene reacted at 120-130 °C.

These reactions account for the fate of one of the degenerate branching products, namely RO•, but no mention has yet been made of the fate of HO•, the other product. Both Emanuel <u>et al.</u> (1967) and McBurney (1954) show that it continues the free radical chain and produces water by

$$RH + \bullet OH \rightarrow \bullet R + H_2O \ .$$

Once reaction products reach significant concentrations, they may begin to compete for free radicals as they oxidize further, and slow the rate of disappearance of the original organic. This is referred to as autoinhibition. During the induction period and through the first portion of the active reaction period, before significant product concentrations have accumulated, autoinhibition should be negligible.

Computer Simulation

As mentioned previously, computer simulations were performed to gain a qualitative understanding of the relative importance of the various steps presented in the proposed mechanism. Some initial exploratory runs were made and it was confirmed that k_{4a} and k_{4b}, as long as they are not much greater than k_{4c}, have no effect on results as postulated above. They are, therefore, set to zero in all subsequent runs. Furthermore, it was found that when k_1 was set at values in the vicinity of

3.0×10^7 liter/mole sec (the value given above) and k_{0b} was small (also see above), even orders of magnitude of variation in k_1 had no effect on results. Consequently, $k_1 = 3.0 \times 10^7$ liter/mole sec in all the following runs.

To determine the the remaining rate constants in the mechanism, a set of idealized data was generated with an induction period of 120 minutes followed by an active reaction period with a pseudo-first order rate constant of 0.04 1/min (typical of m-xylene at 200 °C and 2000 psi air). The initial organic concentration was 0.0012 mole/liter and the oxygen concentration was held constant at 0.031 mole/liter. A nonlinear least squares regression was applied to determine the rate constants which best match this idealized data.

The first run not only fixed k_1, k_{4a}, and k_{4b} at the values in the penultimate paragraph, but also eliminated degenerate chain branching by setting k_3 to zero. The regression was employed to determine the remaining three rate constants. The results were $k_{0b} = 0.0005$, $k_2 = 1.0$, and $k_{4c} = 0.0$, all in units of liter/mole sec, and a plot of [RH] <u>versus</u> time is given in Figure 3.12. It is observed that there is no abrupt change from an induction to a rapid reaction period. Various other regressions were performed with different starting conditions and it was determined that this was the best match between the idealized and simulation results.

Sensitivity analysis was accomplished by holding all constants at the regression analysis values just presented, save one, which was perturbed through five orders of magnitude. These results are found in Figures 3.13-3.15. The first two figures show that when either k_{0b} or k_2 is increased, the resulting curve retains its same general shape, increasing

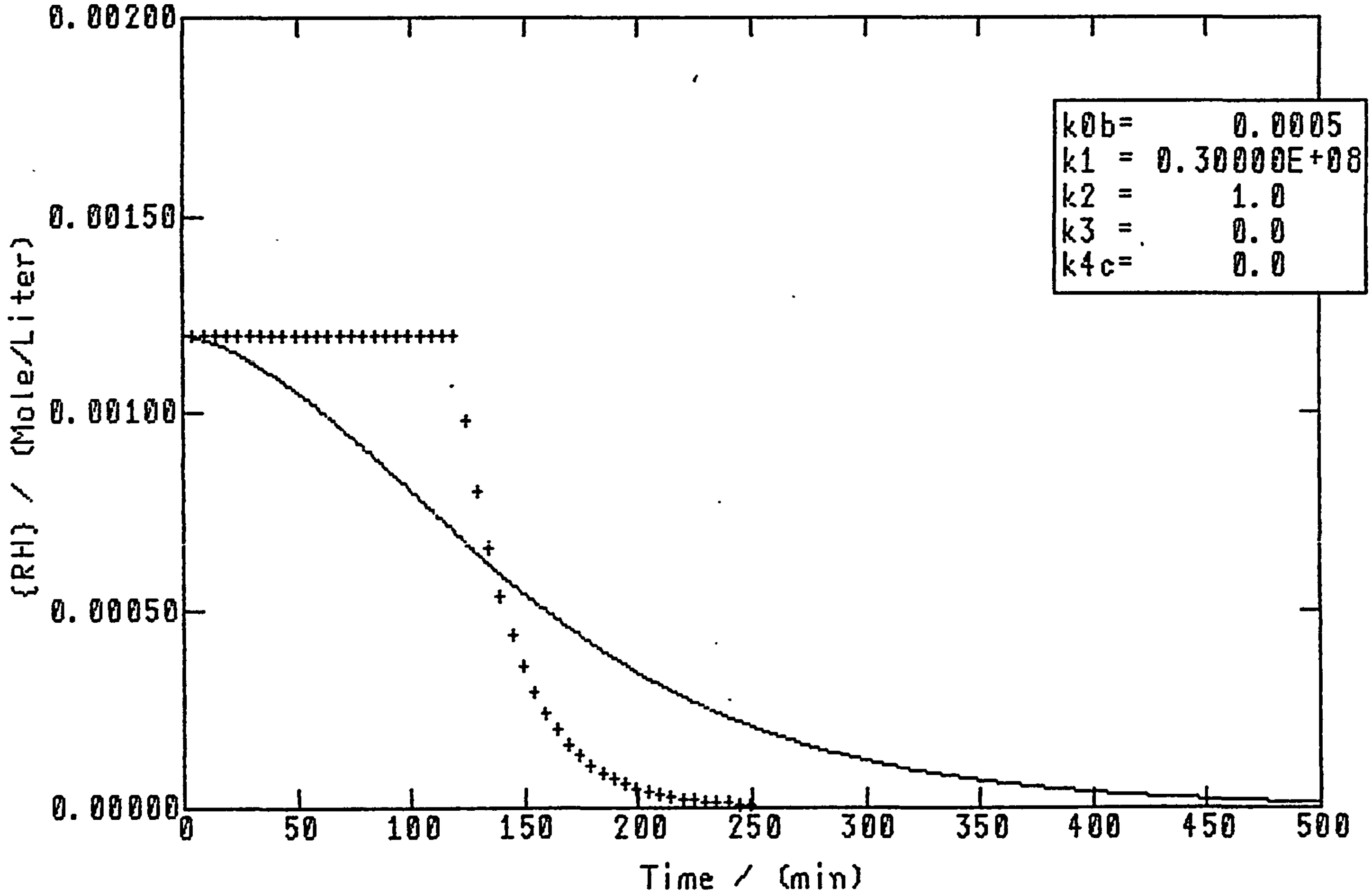


Figure 3.12 Comparison of Idealized Experimental Data and Mechanism Simulation, No Degenerate Branching

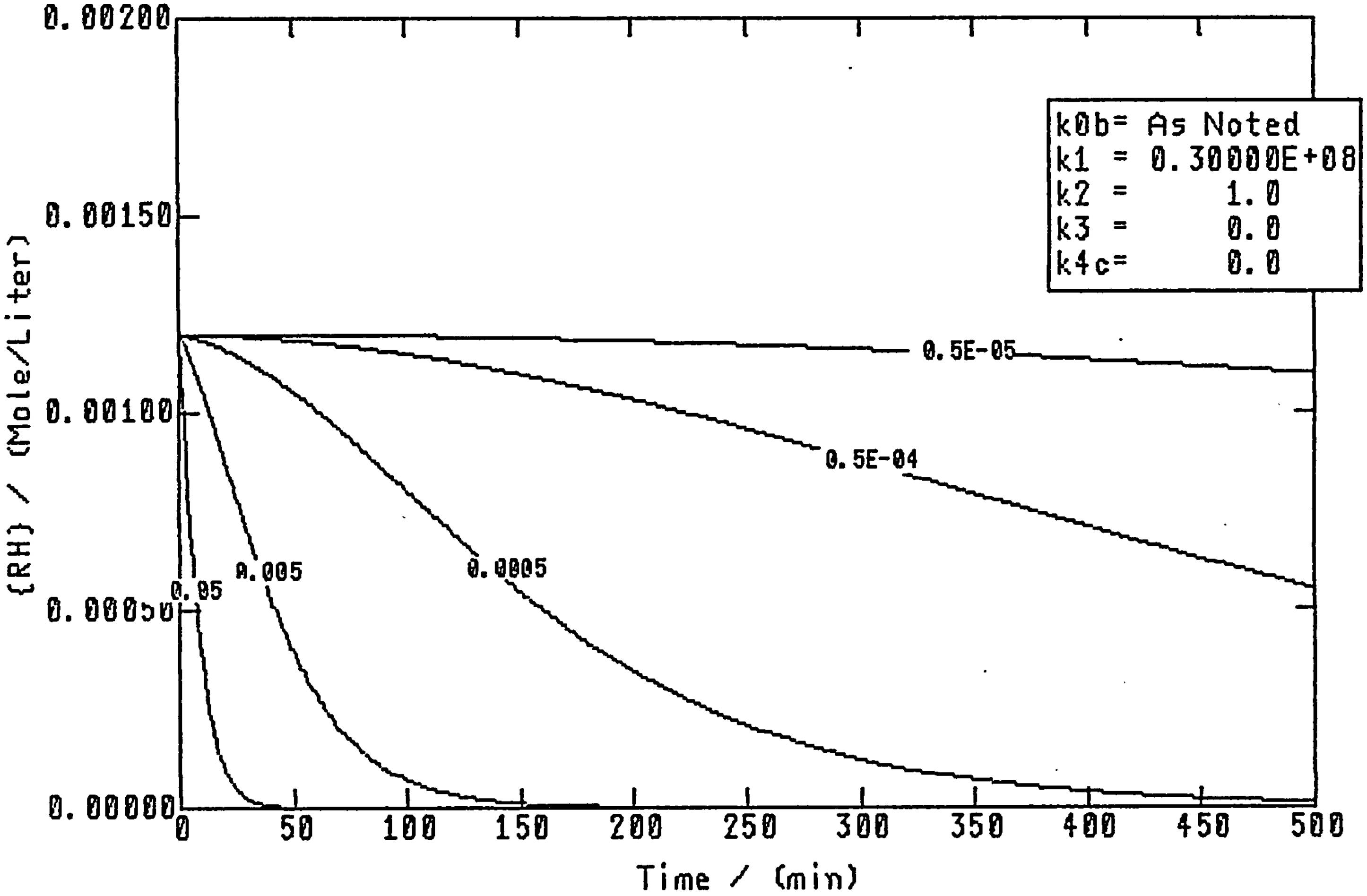


Figure 3.13 Mechanism Simulation Results, No Degenerate Branching, Sensitivity of k0b

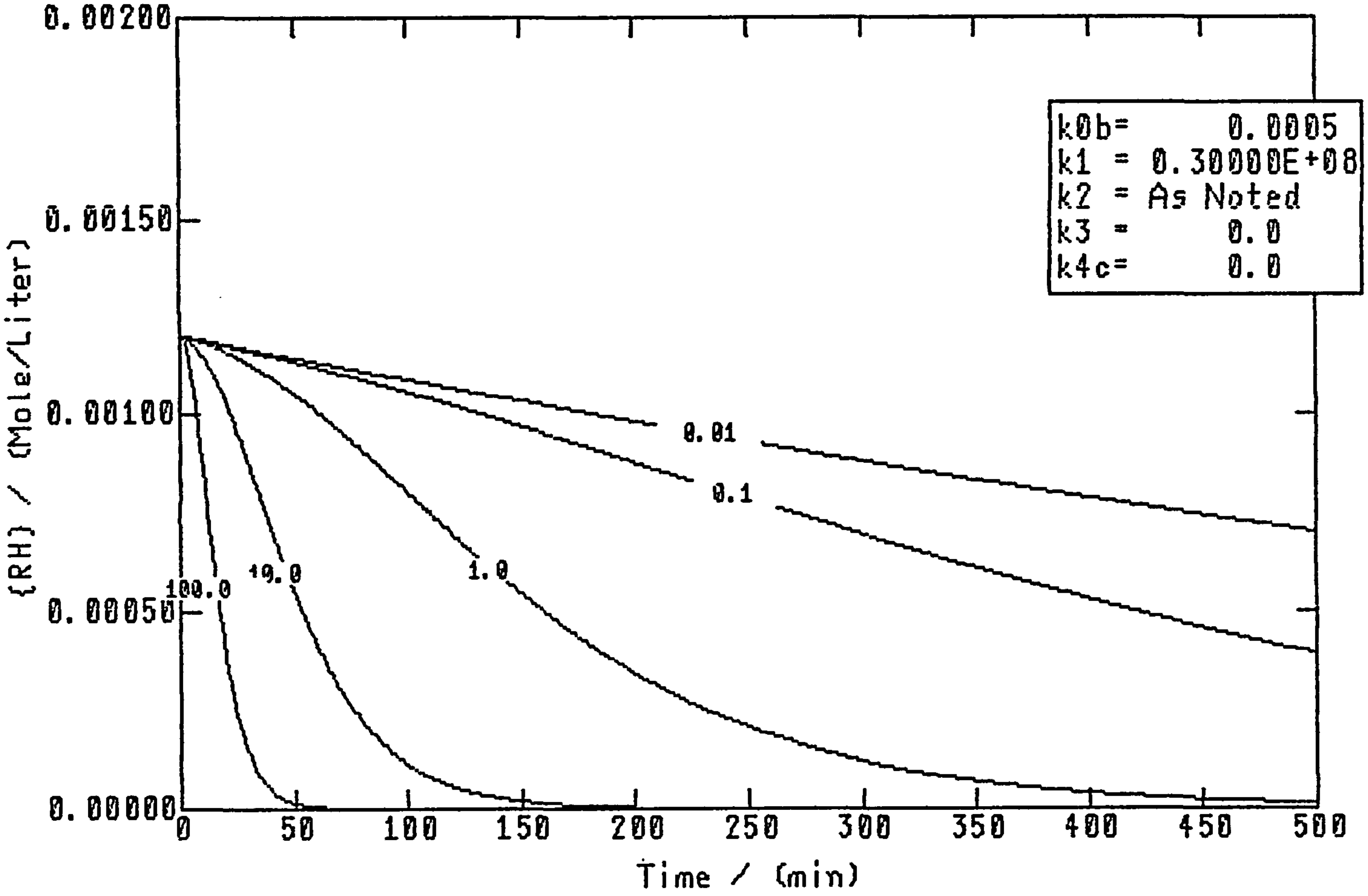


Figure 3.14 Mechanism Simulation Results, No Degenerate Branching,
Sensitivity of k2

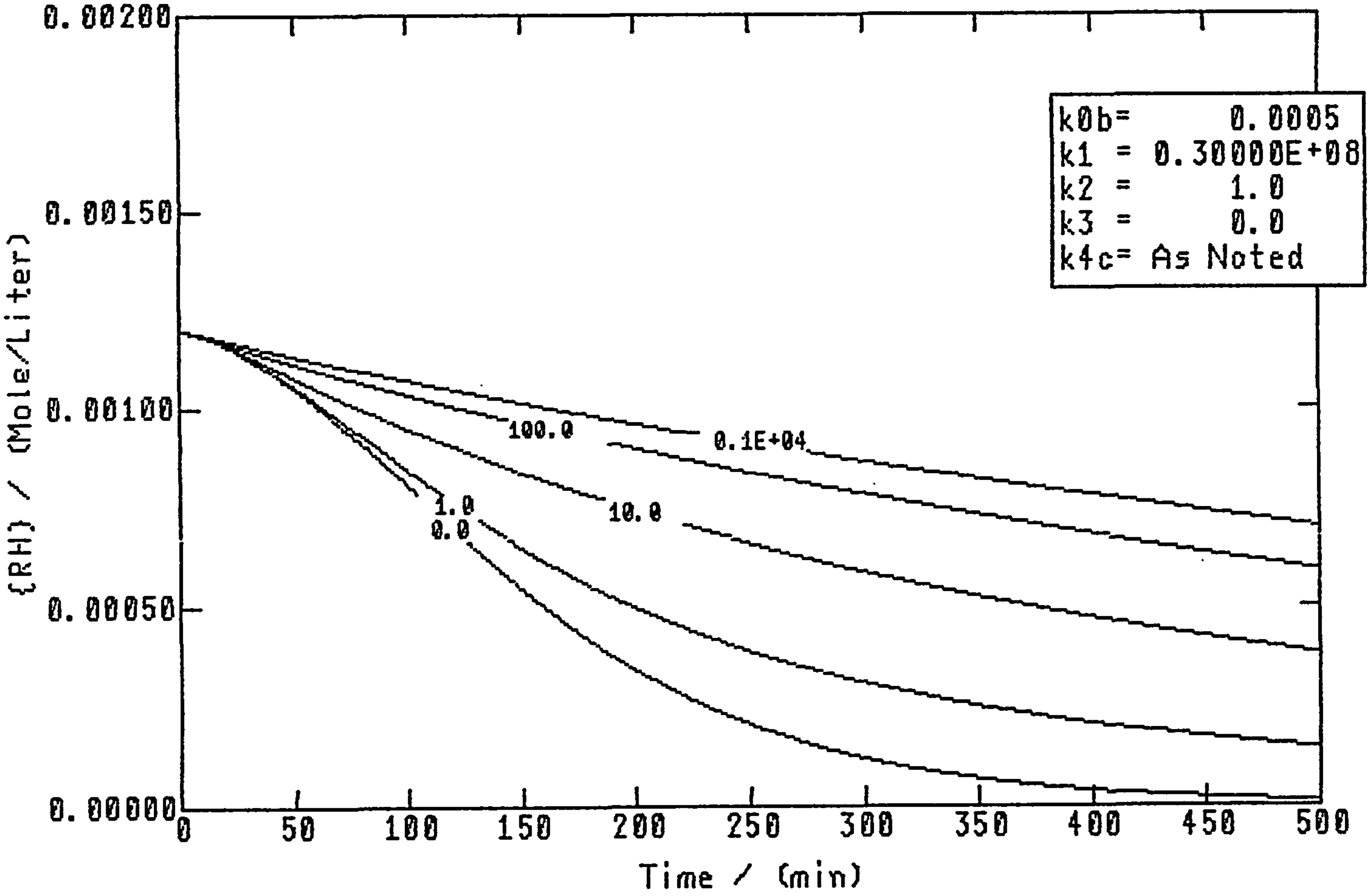


Figure 3.15 Mechanism Simulation Results, No Degenerate Branching, Sensitivity of k4c

only the reaction rate. The third plot indicates that as k_{4c} grows, the curves lose their sigmoid shape, shifting to a simple exponential decay. Presumably this is why the regression chose zero for this value, since it gave the closest approximation to an induction period. Thus, without degenerate branching it was impossible to match the type of results found in m-xylene and phenol experiments.

The second regression analysis modelled the same data as before, but included degenerate branching by using k_3 as one of the regression variables (rather than setting it to zero). k_1, k_{4a}, and k_{4b} were fixed as previously. Furthermore, k_{0b} was fixed at 1.0×10^{-6} liter/mole sec (the experimental value due to Denisova and Denisov (1969)). Thus, it remained for the regression to determine k_2, k_3, and k_{4c}, which it found to be 1.26 liter/mole sec, 0.001 1/sec, and 0.5 liter/mole sec, respectively. As shown in Figure 3.16, this very nicely matches the idealized data, displaying the all-important induction period followed by the rapid exponential decay. In fact, the model would even more accurately match real data which shows a smooth rather than discontinuous transition from the induction phase to the rapid reaction phase.

This was followed by a similar sensitively analysis, the results of which are given in Figures 3.17 - 3.19 and 3.21. Along with the regression variables, k_{0b} was also included in this examination as is shown in the first figure (Figure 3.17). Variation in k_{0b} has negligible influence on the rapid reaction period, but only determines the length of the induction period. The second figure (3.18) shows that the reaction is heavily influenced by the value of k_2, which is only changing by factors of two rather than orders of magnitude as in all other instances. k_2 strongly affects both the length of the induction period

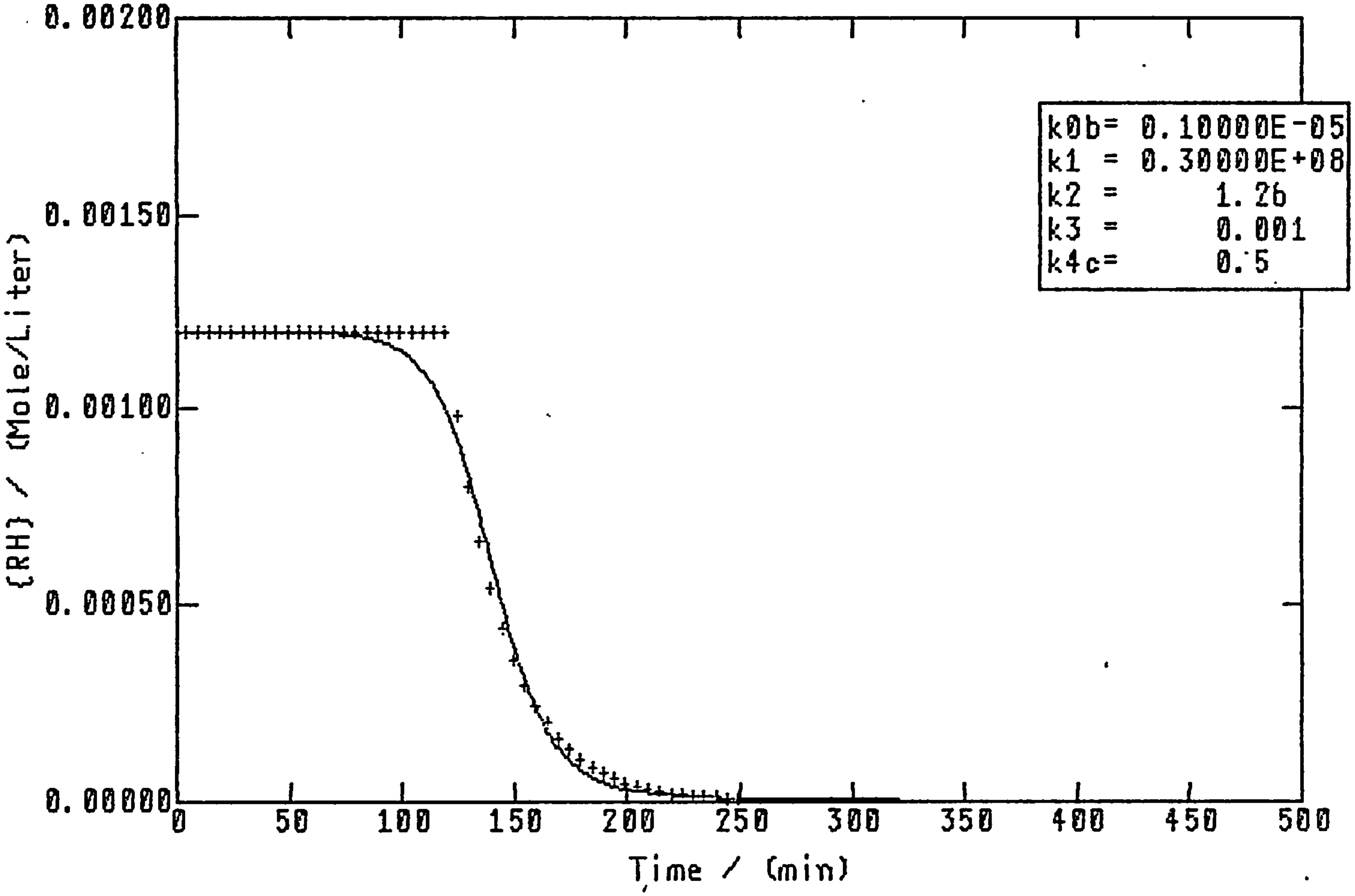


Figure 3.16 Comparison of Idealized Experimental Data and Mechanism Simulation with Degenerate Branching

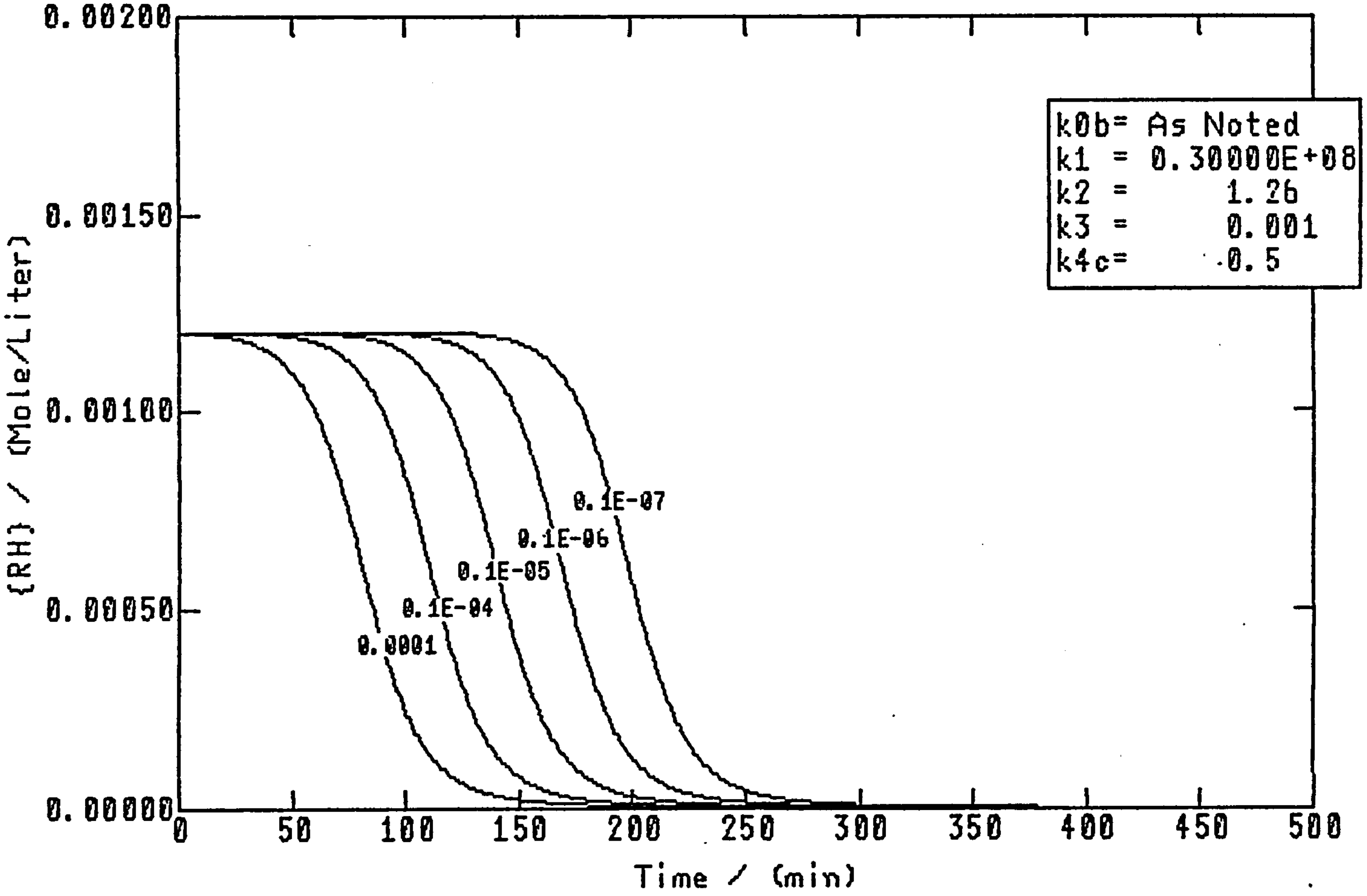


Figure 3.17 Mechanism Simulation Results, With Degenerate Branching, Sensitivity of k0b

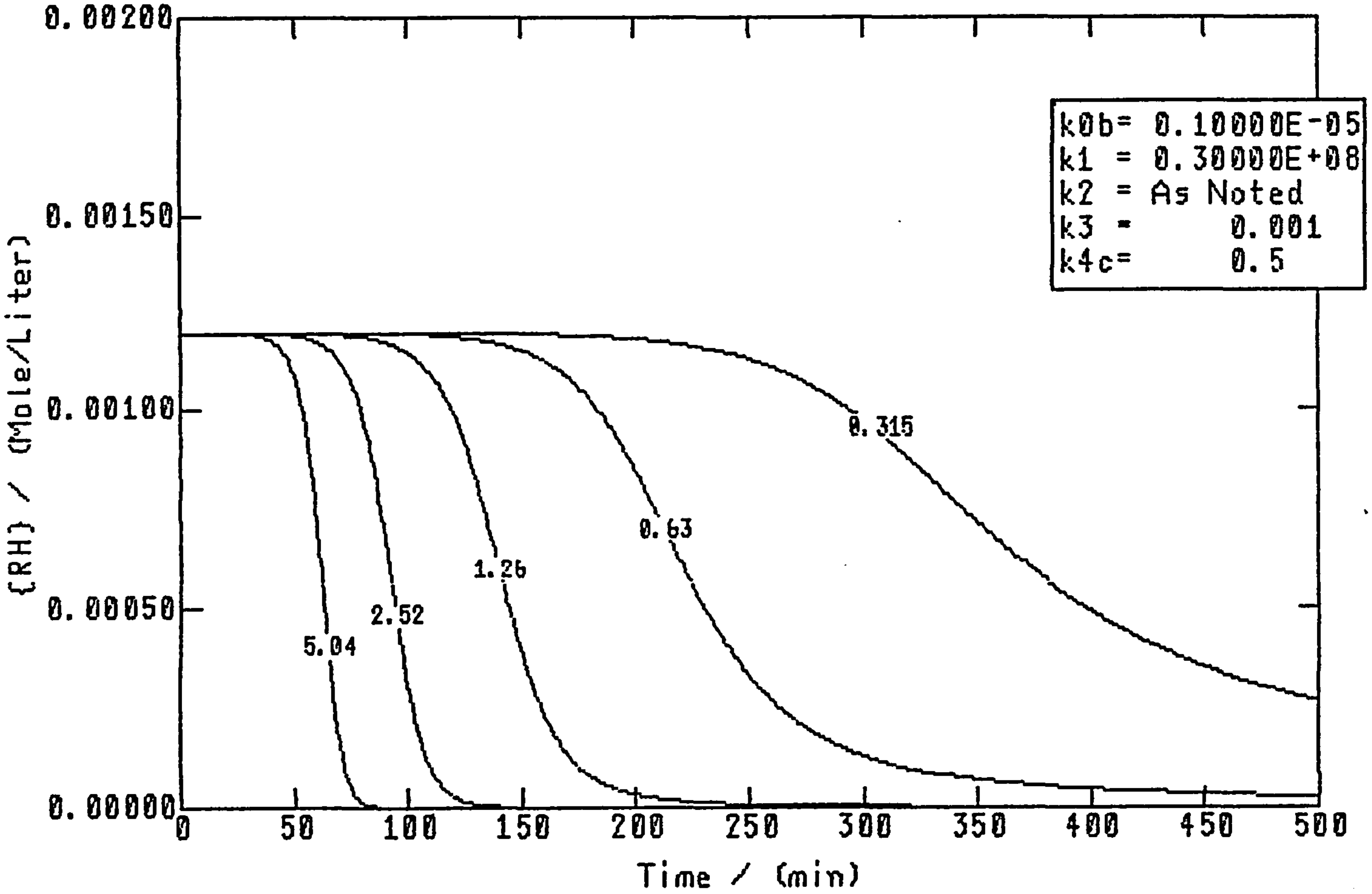


Figure 3.10 Mechanism Simulation Results, With Degenerate Branching, Sensitivity of k2

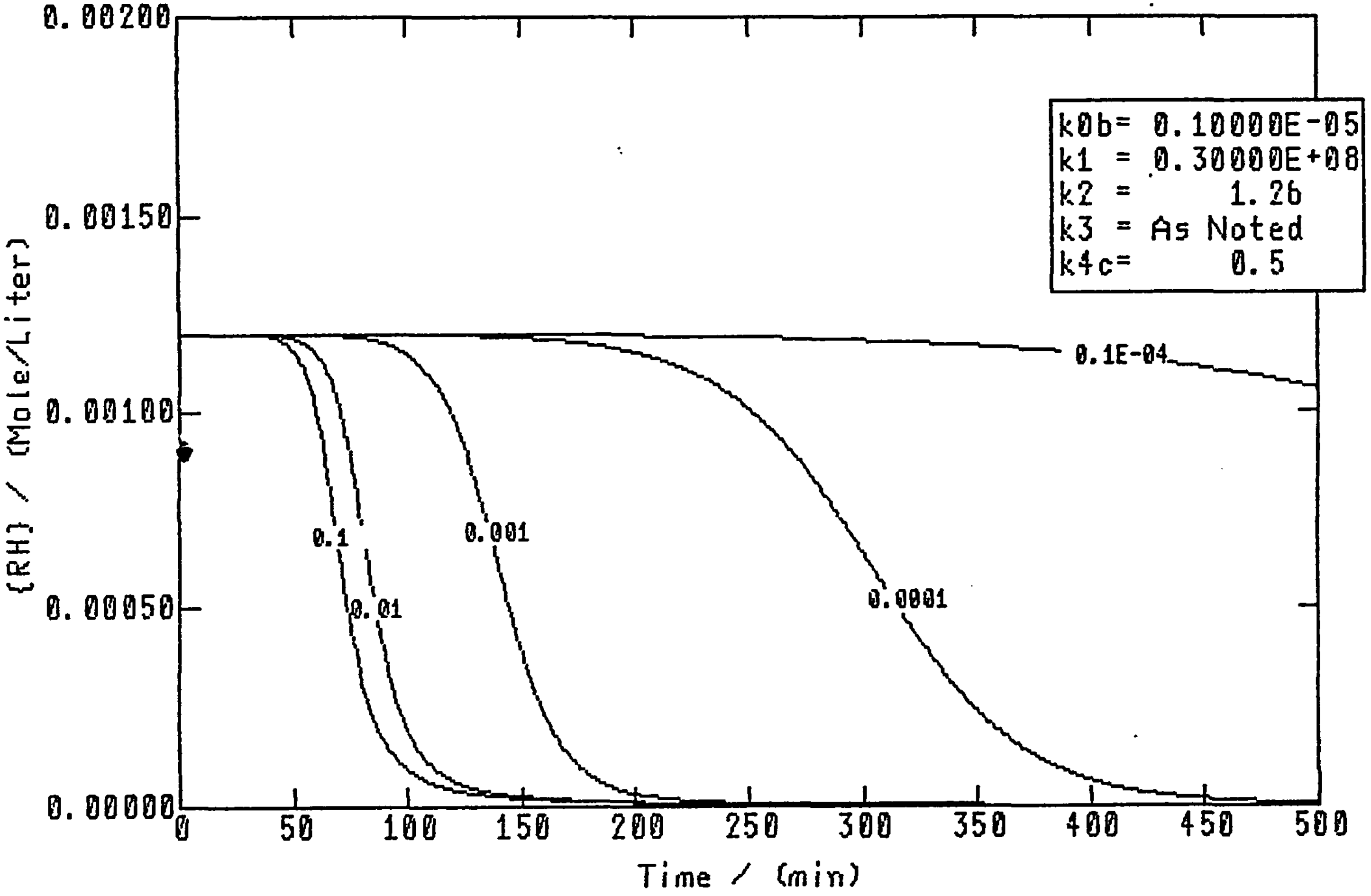


Figure 3.19 Mechanism Simulation Results, With Degenerate Branching, Sensitivity of k3

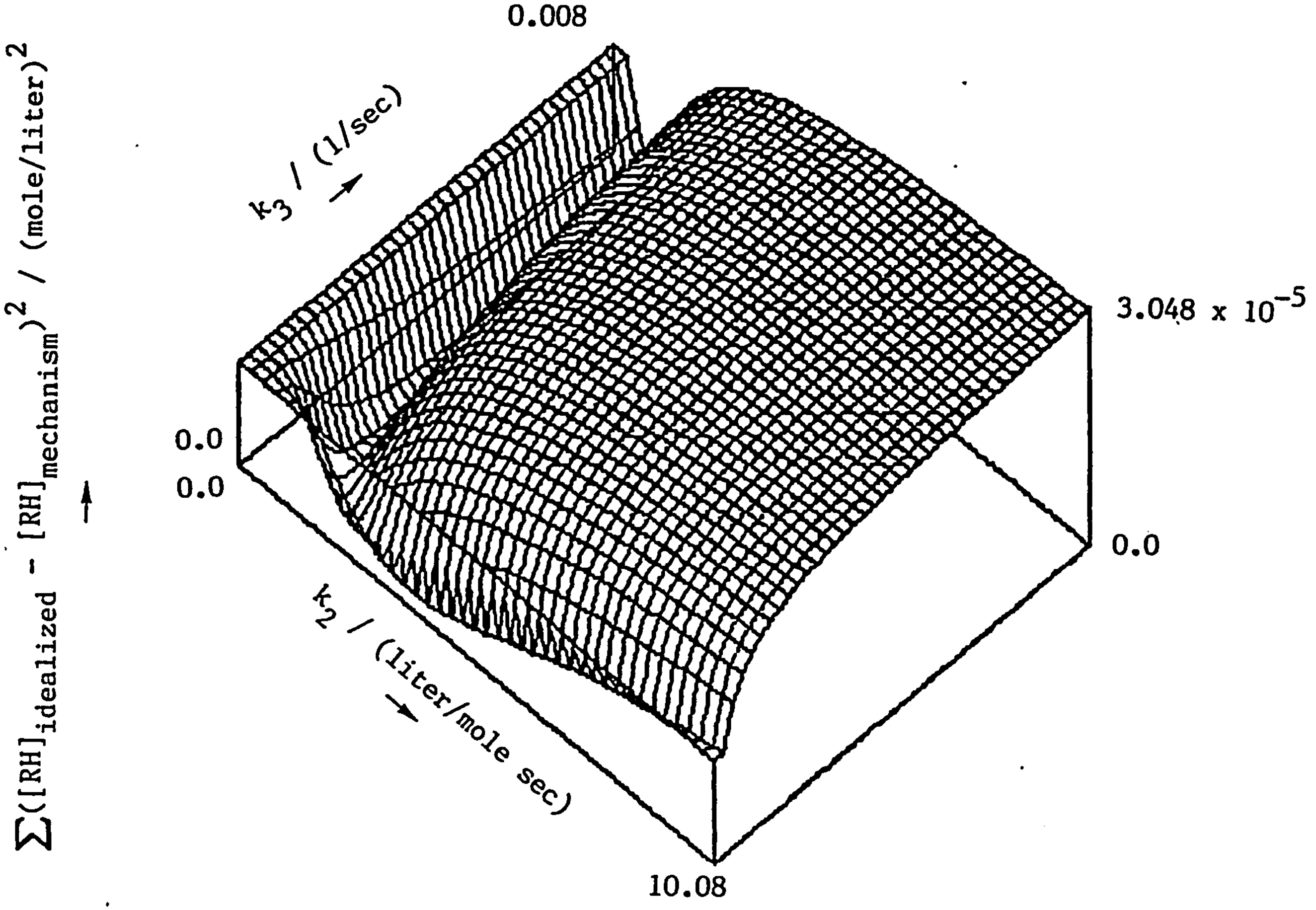


Figure 3.20 Mechanism Simulation Results, With Degenerate Branching, $\sum([RH]_{idealized} - [RH]_{mechanism})^2$ versus k_2 and k_3

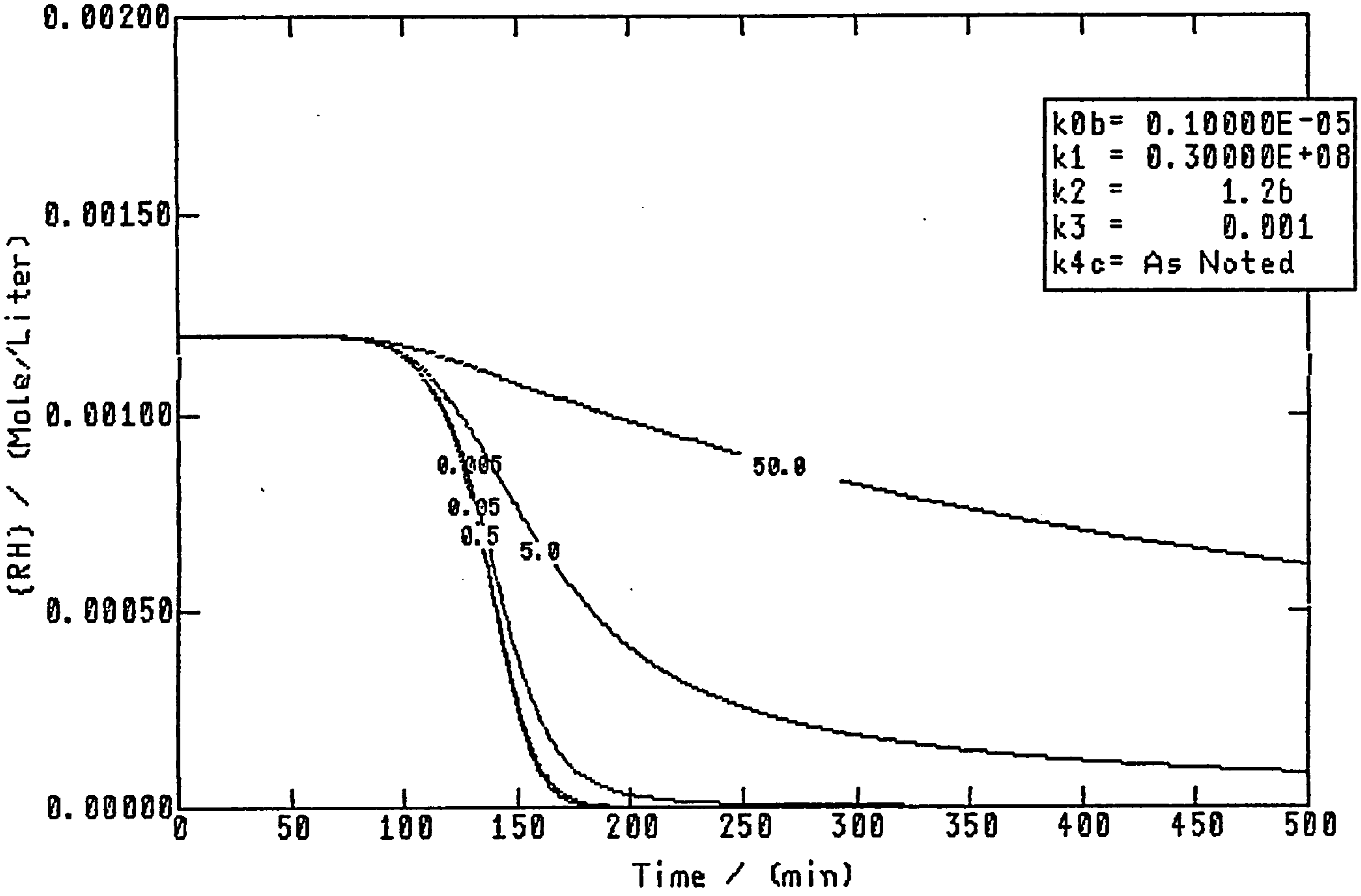


Figure 3.21 Mechanism Simulation Results, With Degenerate Branching, Sensitivity of k4c

as well as the reaction rate. The effects of changing k_3 are given in the third plot, Figure 3.19. These curves have shapes very similar to those of the previous figure, indicating that both k_2 and k_3 have similar influences on organic disappearance. It appears that some mathematical combination of k_2 and k_3 rather than their individual values is important (reminiscent of the relationship between k_{0b} and k_2 in the non-degenerately branched case). This relationship is illustrated in Figure 3.20. This three dimensional plot shows the sum of the squares of the differences of the idealized and model results as the height. The two horizontal axes are k_2 and k_3. The valley running parallel to each of these axes shows that there are, in fact, various combinations of k_2 and k_3 which give good approximations to the idealized data. Thus, there is no guarantee that the values assigned to them by the regression are the "best values". Finally, the fourth figure (3.21) shows that the induction period is independent of the rate of termination. Furthermore, at values near 0.05 liter/mole sec the rapid reaction rate is not affected by k_{4c}, though at higher values k_{4c} begins to impede the reaction rate.

This latter simulation also provides a second explanation for the deviation between experimental and model results observed for m-xylene toward the end of an experiment. The sensitivity analyses in which k_2, k_3, and k_{4c} were varied each show instances which display this behavior. Both this and autoinhibition which was discussed earlier are offered as possible explanations of this phenomenon.

m-Xylene and phenol, showing both induction and active reaction periods, display behavior quite consistent with the degenerately branched free radical mechanism proposed. Tetrachloroethylene, on the other hand, shows markedly different behavior. Much slower reaction rates are expected since initiation requires the rupture of the C=C or C-Cl bonds which are stronger than the C-H bond. The absence of an induction period suggests that degenerate branching either does not occur or is accompanied by faster termination. Furthermore, reaction 2 presupposes the existence of a C-H bond. If chain propagation does occur, it is not as shown above. In short, while tetrachloroethylene may oxidize according to a free radical mechanism, it must be quite different from the scheme just presented.

SUMMARY

Experimental results have been shown for the aqueous phase oxidation of m-xylene, phenol, tetrachloroethylene, and malathion. A mechanism is presented which satisfactorily explains the m-xylene and phenol results. The markedly different results and chemistry of tetrachloroethylene suggest that it follows another mechanism. The very rapid disappearance of malathion is consistent with the belief that it hydrolyzes, rather than oxidizes.

It has been shown that during the induction period the global kinetics of m-xylene is first order in oxygen. During the active reaction period the reaction shifts to 1/2 order in oxygen concentration and is first order in organic. This first order dependance on organic concentration during the active reaction period was also observed for phenol and tetrachloroethylene. For phenol this dependency shifts toward zero order at lower temperatures. The intrinsic rate constants and lengths of induction periods are described by the following equations.

m-Xylene

Induction Phase

$t_{start} = (3.59 \times 10^{-15} / [O_2]_0) \exp(30000/RT)$ (min)

Reaction order in organic unknown
First order in oxygen shown

Active Phase

$d[RH]/dt = k \, [O_2]^{0.5}[RH]^1$

$k = 1.17 \times 10^9 \exp(-19600/RT)$ $(1/min)(ml/gm)^{0.5}$

First order in organic shown
Half order in oxygen shown

Phenol

Induction Phase

$t_{start} = (1.57 \times 10^{-13} / [O_2]_0) \exp(22500/RT)$ (min)

Reaction order in organic unknown
First order in oxygen assumed

Active Phase

$d[RH]/dt = k \, [O_2]^{0.5}[RH]^1$

$k = 2.19 \times 10^{14} \exp(-26800/RT)$ $(1/min)(ml/gm)^{0.5}$

First order in organic shown, shifting to zero order at lower temperatures
First order in oxygen assumed

Tetrachloroethylene

Induction Phase

None

Active Phase

$d[RH]/dt = k\ [O_2]^{0.5}[RH]^1$

$k = 6.49 \times 10^7 \exp(-23200/RT)$ $(1/min)(ml/gm)^{0.5}$

First order in organic shown
First order in oxygen assumed

Malathion

Induction Phase

None

Active Phase

Hydrolyzes completely in less than two minutes

CHAPTER 4

REACTION RATE ENHANCEMENT OF AQUEOUS PHASE OXIDATION

INTRODUCTION

The previous chapter established the disappearance kinetics of three compounds individually subjected to aqueous phase oxidation conditions. Though proceeding at appreciable rates, these reactions would be more economically favorable for hazardous waste detoxification if the rates could be increased. Obviously, elevating either temperature or pressure would accomplish this, albeit at a costly energy penalty. Other methods proposed for this purpose include catalysis, addition of free radical initiators, and synergism.

The objective of this chapter is to determine fundamental kinetics parameters for two of these rate enhancement techniques, namely initiation and synergism. Initiation was explored by adding hydrogen peroxide to the basic reaction system used in chapter three (water, air, and one organic) with m-xylene used as the organic. Synergism was investigated by using two organics, m-xylene and phenol, rather than one in the basic reaction system.

So that all three rate enhancement techniques can be considered in one document, this chapter will begin by presenting literature relevant to catalytic aqueous phase oxidation. This will be followed first by a characterization and discussion of the initiation results, and then a similar section for the synergism experiments. The initiation and synergism findings are summarized at the end of their respective sections.

Before continuing, however, it is prudent to define some terminology. Careful definitions are needed because some have erroneously referred to hydrogen peroxide as a catalyst. At elevated temperatures, hydrogen peroxide dissociates into two radicals which are subsequently consumed in reactions with either oxygen or organic. Being consumed in the reaction, it clearly fits the definition of an initiator rather than a catalyst. Failure to make this distinction will confuse the results of some of the following authors.

CATALYSIS

As this research did not use catalysts in any experiments, the purpose of this section is simply to mention it in the broader context of reaction rate enhancement techniques. A number of the studies listed in Table 3.1 used catalysts in part or all of their experiments. The following paragraphs provide synopses of the more informative catalytic studies.

The work by Chowdhury and Ross (1975) examined the influence of a wide range of heterogeneous and homogeneous catalysts on the aqueous phase oxidation of "strong waste water". This is interpreted as being high COD wastes such as brewery effluent. Their catalysts included two metals, seven metal oxides, mercuric and ferric acetate, and ceric and chromic sulfate. They determined that the addition of certain catalysts, most notably $CuSO_4$ and $Fe_2(SO_4)_3$ could increase reaction rates by factors of two to three over uncatalyzed results. Conversely, the presence of other catalysts retarded reaction rates. They also found that the activation energy was reduced from 23 to 17 kcal/mole for certain catalytic experiments. These findings are somewhat clouded, however, by the addition of hydrogen peroxide in most of the reaction systems. As discussed in the introduction, it is unclear whether this served only to initiate the reaction, being quickly consumed in the first moments of each experiment, or whether it had a continuing effect throughout the course of each run. They further conclude that pressure and pH, which are important variables in uncatalyzed reactions, have negligible effects on catalyzed experiments.

Similar findings were reported by Baillod and Faith (1983). The addition of a copper catalyst to reactions involving phenol, 2-chlorophenol, or 4-nitrophenol increased reaction rates by factors of two to three. The catalyst appeared to have a less dramatic effect on the oxidation of 1,2-dimethylphthalate. They determined that increasing catalyst concentrations further increased reaction rates. Finally, reaction product concentrations were influenced by catalysis.

Brett and Gurnham (1973) studied the catalytic oxidation of glucose. In their first set of experiments they used metal salts (Cr(VI), Co, Zn, Pb, Hg, Mn(VII), and pumice coated with potassium permanganate and potassium dichromate) as catalysts. This was followed by a second set of experiments which included hydrogen peroxide along with each of the metal salt catalysts. For comparison, runs were conducted with no metal salt or hydrogen peroxide present. Their experiments determined percent destruction of COD after 15 minutes at 170 °C and 754 psi air. In the absence of hydrogen peroxide, Pb effected the largest reduction in COD, while most of the other catalysts caused less or no reaction. In each case the addition of hydrogen peroxide increased the COD reduction, with Cr(VI) having the largest effect. Since no concentration versus time data were collected, however, it is unclear when the hydrogen peroxide activity occurred. As was noted above, it may all react at the beginning, or influence reaction rate throughout the run.

Miller and Swientoniewski (1982) studied the aqueous phase oxidation of 15 organics in the presence of a bromide, nitrate, and manganese catalyst in acidic solution. Their reaction conditions ranged from 165-275 °C, 150-1000 psi, and reaction times of 5-420 minutes. They claim that this patented catalyst effectively destroyed most of the organics examined. These conclusions are confusing, however, since they list reaction products such as bromoxylene and dibromoxylene from the "catalytic" oxidation of o-xylene. If the bromide is being consumed in the reaction then, in actuality, it is not a catalyst.

As was discussed in the previous chapter, Sadana and Katzer (1974) present results for the catalyzed aqueous phase oxidation of phenol. Their catalysts included copper oxide supported on alumina, MnO_2 on the same support, and unsupported cupric and cuprous oxide. Though not presenting any uncatalyzed results for comparison, they claim that the catalysts greatly enhanced the reaction rate and affected the product distribution.

The evidence is clear that both homogeneous and heterogeneous catalysts will increase reaction rates and thus decrease the time necessary for the oxidation of organics. The difficulty with homogeneous catalysts is that they must be recovered from waste streams owing to both environmental and economic reasons. Heterogeneous catalysts are often prone to deactivation, especially in "dirty" waste streams. Still, the degree of rate enhancement attainable with certain catalysts may more than offset these concerns.

INITIATION

Introduction

An initiator in this context is any material which serves as an initial free radical source. As explained in the previous chapter, propagation reactions account for essentially all of the consumption of organic. For each chain propagation to originate, however, a free radical must be available. In the systems discussed in chapter three, all free radicals were generated by the slow reaction between organic and oxygen. Because this initiation reaction is slow, long induction periods resulted. These long induction periods can be reduced by adding a free radical source to the reaction medium. In general, only small amounts of initiator need be added, since the majority of organic consumption is not with the initiator itself, but through the chain propagation steps spawned by the initiator. Some of the most popular initiators include peroxides and azo compounds (Emanuel _et_ _al._ (1967)). Other possible initiators include ozone, corona discharge, and nuclear radiation (Brett and Gurnham (1973)). Hydrogen peroxide is the initiator used in the experiments which will be presented later in this chapter.

Though there are numerous studies of initiators in liquid phase oxidation (organic solvents), only one paper could be located which dealt with initiators in aqueous phase oxidation (other than the "catalytic" studies which included hydrogen peroxide results presented above). This is the study due to Shibaeva et al. (1969c) of aqueous phase phenol oxidation with hydrogen peroxide as the initiator. Even these results, however, are difficult to interpret since all experiments were at a pH of 1.5. Under these acidic conditions they show that the dissociation of hydrogen peroxide is much slower than in a neutral pH environment. Thus, they found that intrinsic rate constants were enhanced by factors of one to two orders of magnitude by the presence of hydrogen peroxide. This is markedly different from the neutral pH results of this investigation as will be shown in the following section.

Characterization of Reactions

As established in the previous chapter, the unenhanced aqueous phase oxidation of m-xylene is characterized by a substantial induction period followed by a rapid reaction phase. The initiation experiments which will be described below were performed to determine the effects of the initiator hydrogen peroxide on both the induction and rapid reaction phases.

The experimental procedures used to obtain this information were essentially identical to those used in chapter three. The only deviation for the initiation experiments was that a quantity of hydrogen peroxide was added to the water which was used to flush the organic sample into the reactor. For these experiments this flush water was not preheated before injection into the reactor so that no degradation of the hydrogen peroxide would occur before "time zero". Before presenting these results, however, some terminology must be established.

If hydrogen peroxide were responsible for oxidizing m-xylene completely to carbon dioxide and water, the stoichiometry would be

$$C_8H_{10} + 21\ H_2O_2 \rightarrow 8\ CO_2 + 26\ H_2O\ .$$

Thus, 21 moles of hydrogen peroxide would be required to completely oxidize one mole of m-xylene (or 6.7358 grams of hydrogen peroxide per gram of m-xylene). The amount of hydrogen peroxide added to the reactor in each experiment will be expressed as a percentage of the stoichiometric amount needed to completely oxidize the organic (i.e. (100 * grams hydrogen peroxide) / (6.7358 * grams m-xylene)).

A total of 16 initiation experiments were performed. All runs used 780 grams of water and about 0.11 grams of m-xylene. The first nine experiments, performed at 200 °C and 2000 psi air, examined the effects of varying the amount of H_2O_2 from 0.025% to 25% of stoichiometric. Subsequently, runs were conducted to explore the effects of temperature on H_2O_2 initiated reactions. One run was made with 0.5% stoichiometric H_2O_2 at 175 °C and 2000 psi air. This was followed by five runs using 2.5% stoichiometric H_2O_2, 2000 psi air, and temperatures ranging from 163-193 °C. One last run used 200 °C, 2.5% stoichiometric H_2O_2, and a lower pressure--1500 psi air. A complete tabulation of all experimental conditions and concentration *versus* time data for these initiation runs are compiled in Appendix B.

Effects of Hydrogen Peroxide Concentration: Typical concentration histories for the first set of experiments are given in Figure 4.1. It is observed that the addition of 0.025% stoichiometric hydrogen peroxide had no detectable effect on the oxidation of m-xylene (see Table 3.5

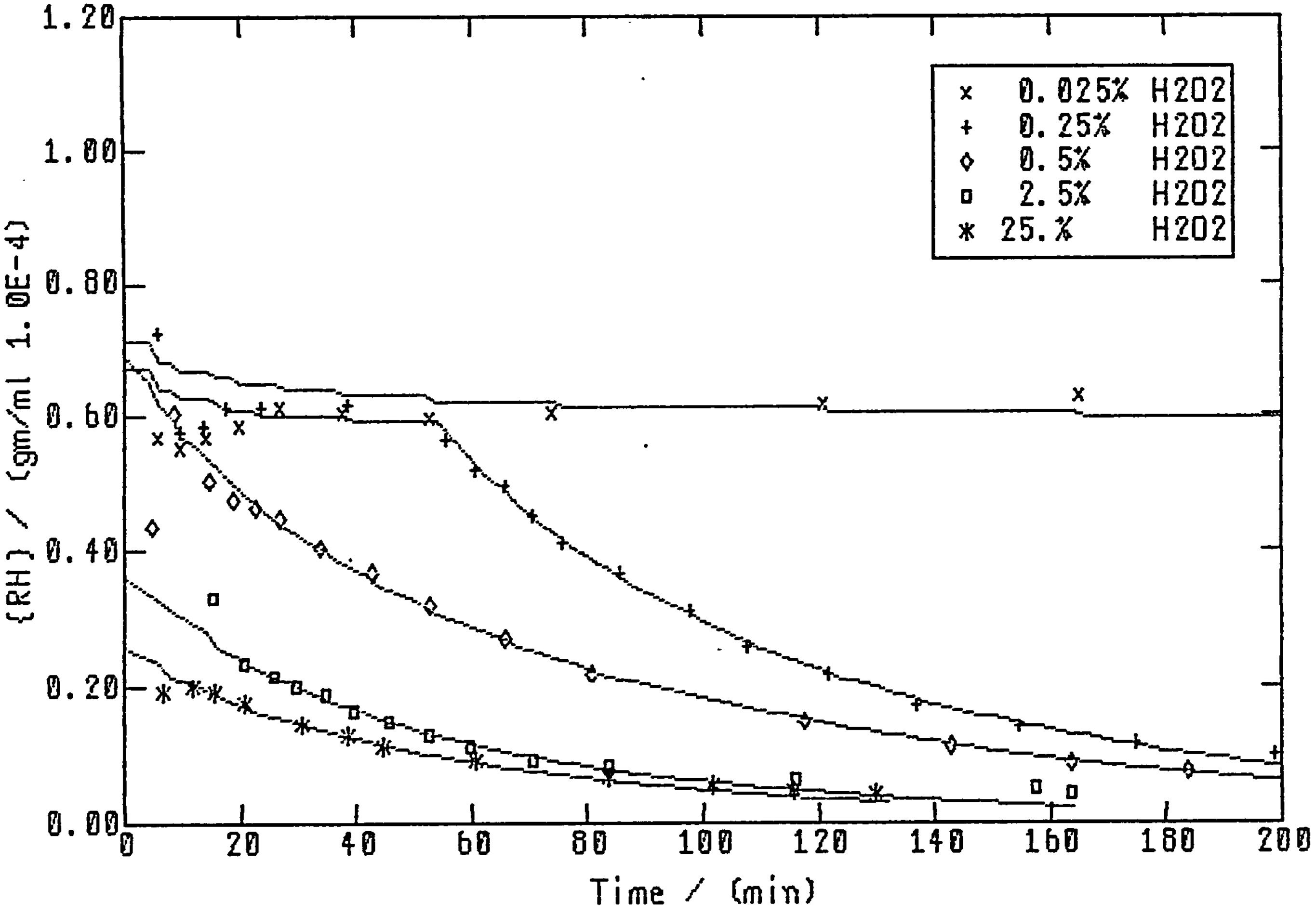


Figure 4.1 Experimental Data and Model Curves for m-Xylene at 200° C and 2000 psi with Various Amounts of H2O2

where induction times of 175-330 minutes were reported at comparable reaction conditions). Raising the amount of hydrogen peroxide to 0.25% of stoichiometric, however, clearly shortens the induction time. Increasing the hydrogen peroxide level further to 0.5% provides the critical or minimum amount which eliminates the induction period without producing any additional oxidation. This translates into a concentration of 4.11 x 10^{-6} gm hydrogen peroxide/ml or, assuming each hydrogen peroxide molecule dissociates into two HO• radicals, 2.42 x 10^{-4} mole HO•/liter. Finally, increasing the hydrogen peroxide addition to 2.5 and 25% not only eliminates the induction period, but a portion of the organic as well.

This behavior can be qualitatively described by comparing it to results found in Emanuel <u>et al.</u> (1967) and reproduced in Figure 4.2. This is a plot of Π <u>versus</u> τ, where Π is [ROOH]/[RH], and τ is a dimensionless time coordinate. It is observed that when no ROOH is initially added to the system (case 1), its concentration grows from zero to an equilibrium value. When more than this equilibrium concentration is added initially (cases 5, 6, and 7), its concentration decays back to equilibrium. A similar phenomenon must be occurring when hydrogen peroxide is added to the system. When 2.5 and 25% stoichiometric hydrogen peroxide is added, more than the equilibrium concentration of radicals is temporarily produced as in Emanuel's cases 5-7. During this time the rate of oxidation of organic is greatly accelerated and an almost instantaneous decrease in organic concentration is observed. Due to termination reactions, however, the radical concentration decreases back to the normal equilibrium value and organic destruction returns to

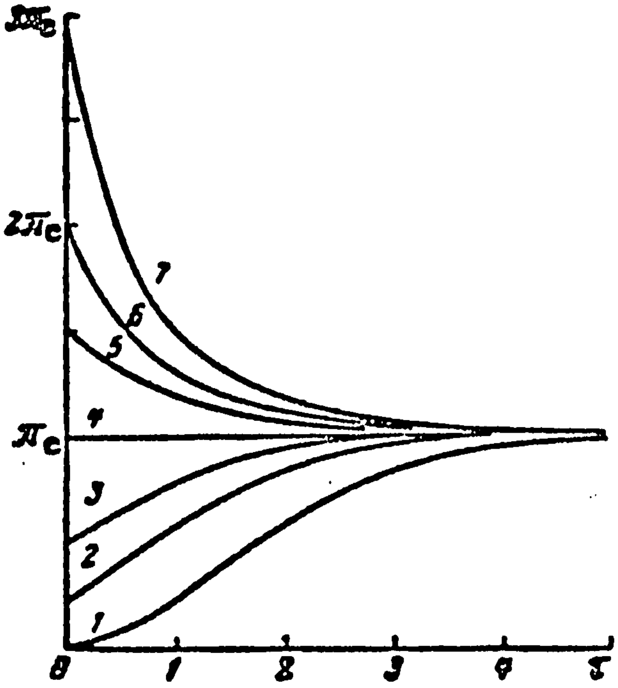


Figure 4.2 Effects of Hydroperoxide Additions to a Liquid Phase Oxidation System, Additions Ranging from Case 1 (No Addition) to Case 7 (Maximum Addition) (Emanuel et al. (1967))

its unenhanced rate. When 0.5% hydrogen peroxide is added, this is analogous to Emanuel's case 4, and 0.25 and 0.025% correspond to cases 1-3.

Effects of Temperature: The next experiments were directed toward understanding the effects of temperature on these reactions. The first experiment reduced the temperature to 175 °C, maintained the pressure at 2000 psi air, and utilized 0.5% stoichiometric hydrogen peroxide. Rather than beginning the active reaction period at "time zero", however, an induction period of over 150 minutes resulted. This implies that the critical quantity of hydrogen peroxide is a function of temperature, increasing as temperature is lowered. The next five experiments, shown in Figure 4.3, used 2.5% stoichiometric hydrogen peroxide. At the temperatures shown (163, 170, 177, 185, and 192 °C) this is greater than the "critical" quantity. As expected, reaction rate is more rapid at the higher temperatures. Induction times were effectively zero in all cases.

Effects of Pressure: One experiment was performed at a reduced pressure, 1500 psi air, and 200 °C. This was useful for confirming the reaction order with respect to oxygen as will be discussed in the following section.

Results and Discussion

The mathematical model presented in chapter two was applied to the data from each of these runs. For experiments which displayed an induction period, the regression determined the values of k' and t_{start}. In the absence of an induction period, k' and m_2^0 were chosen by the re-

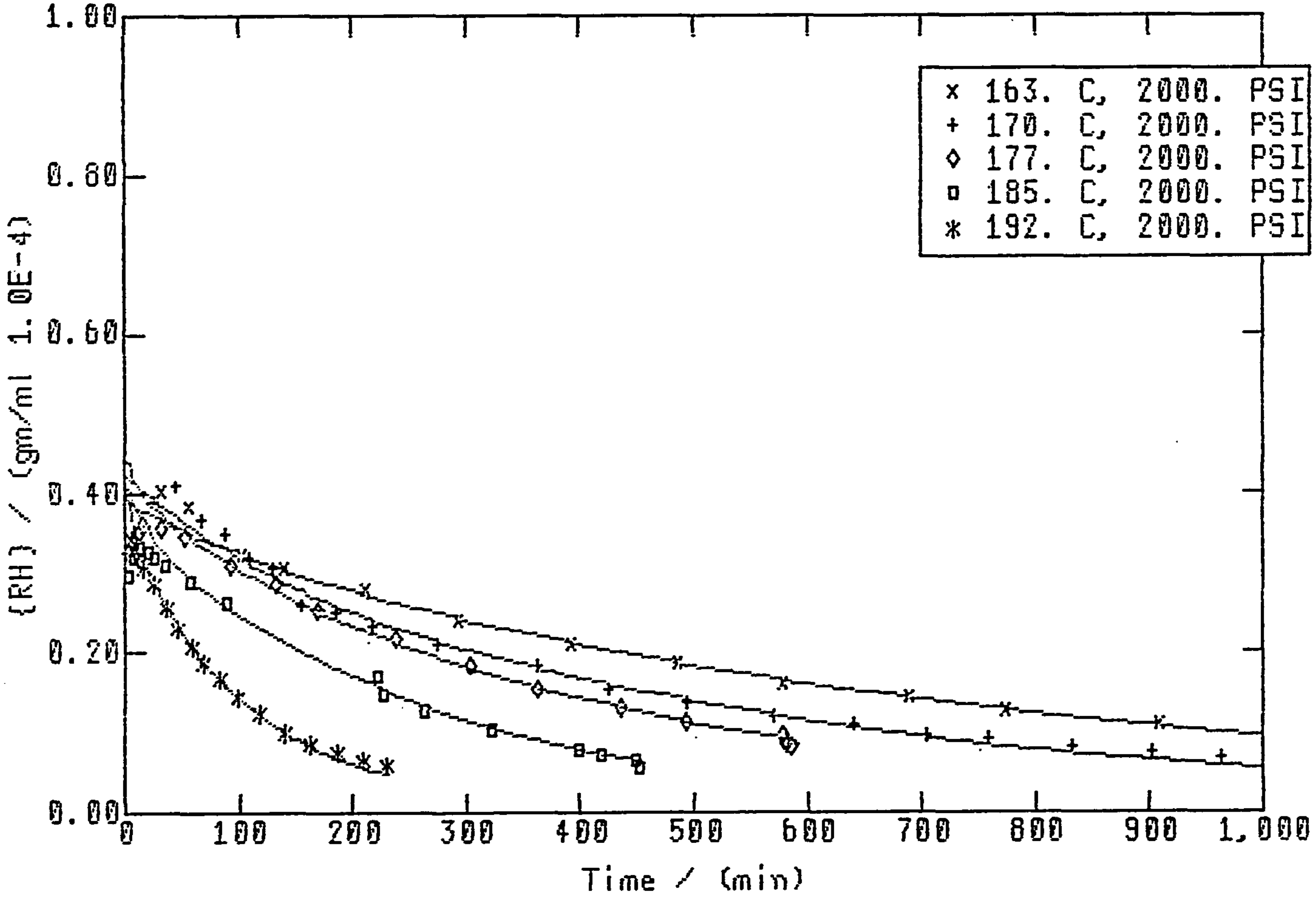


Figure 4.3 Experimental Data and Model Curves for m-Xylene with 2.5% H2O2 at 2000 psi and Various Temperatures

gression. These values and k are given in Table 4.1. In chapter three it was shown that the reaction kinetics in the rapid reaction phase were first order in organic and 1/2 order in oxygen. Again, for these initiated data the rates were first order in organic as demonstrated by the agreement between the model (which assumes pseudo-first order kinetics) and experimental data in Figures 4.1 and 4.3. The 1/2 order dependance on oxygen concentration was confirmed by observing no significant difference between the k obtained in the last experiment listed in Table 4.1 at 1500 psi air and 200 °C, and the values obtained at 2000 psi air and 200 °C. Thus, each k was determined by dividing k' by $[O_2]^{0.5}$.

A comparison of the values of k at 200 °C with the corresponding uninitiated values reported in Table 3.5 in the previous chapter indicates that there is no significant difference between the two. This appears to indicate that hydrogen peroxide, regardless of how much is added, dissociates essentially immediately and reacts with either organic or oxygen. Subsequently, the disappearance of organic proceeds as though there had never been any hydrogen peroxide added. This is in agreement with the qualitative argument concerning an equilibrium concentration of radicals based on Figure 4.2 given above.

This conclusion is further confirmed by observing Figure 4.4, an Arrhenius plot of both the initiated and uninitiated rate constants. The least squares line through the combined data represents an activation energy of 24.2 +/- 2.0 kcal/mole (all confidence limits are at the 95% level), only slightly higher than the value of 19.6 +/- 3.1 kcal/mole reported for uninitiated data in the previous chapter. The preexponential is calculated as 1.26×10^{11} (1/min)$(ml/gm)^{0.5}$. The hy-

Table 4.1 Experimental Conditions and Model Results for Hydrogen Peroxide Initiated m-Xylene

T (°C)	P (psi)	$[H_2O_2]$ (% stoi.)	m_2^0 (gm)	t_{start} (min)	k' (1/min)	O_2 (gm/ml)	k $(1/min)(ml/gm)^{0.5}$
Runs varying amount of H_2O_2							
200	2000	.025	0.100	>500.0	-	0.000999	-
200	2000	.025	0.098	>500.0	-	0.000999	-
200	2000	.25	0.078	43.24	0.0315	0.000999	0.997
200	2000	.25	0.032	67.92	0.0322	0.000999	1.019
200	2000	.25	0.093	54.61	0.0245	0.000999	0.775
200	2000	.5	0.095	0.0	0.0200	0.000999	0.633
200	2000	2.5	0.055	0.0	0.0349	0.000999	1.104
200	2000	2.5	0.049	0.0	0.0270	0.000999	0.854
200	2000	25.	0.036	0.0	0.0260	0.000999	0.823
Runs varying Temperature							
175	2000	0.5	0.090	>150	-	0.000882	-
163	2000	2.5	0.061	0.0	0.00256	0.000832	0.148
170	2000	2.5	0.065	0.0	0.00381	0.000860	0.219
178	2000	2.5	0.067	0.0	0.0048	0.000895	0.160
185	2000	2.5	0.060	0.0	0.00695	0.000926	0.228
193	2000	2.5	0.057	0.0	0.0155	0.000964	0.499
Run varying Pressure							
200	1500	2.5	0.052	0.0	0.0246	0.000717	0.919

drogen peroxide initiated data do have a slightly higher slope than the uninitiated data, but this difference is not outside statistically significant limits. It is, therefore, believed that the combined data provide Arrhenius parameters which are superior to either of the individual findings.

Possibly the most striking feature of these variable temperature data may simply be the fact that reactions occur at these lower temperatures.

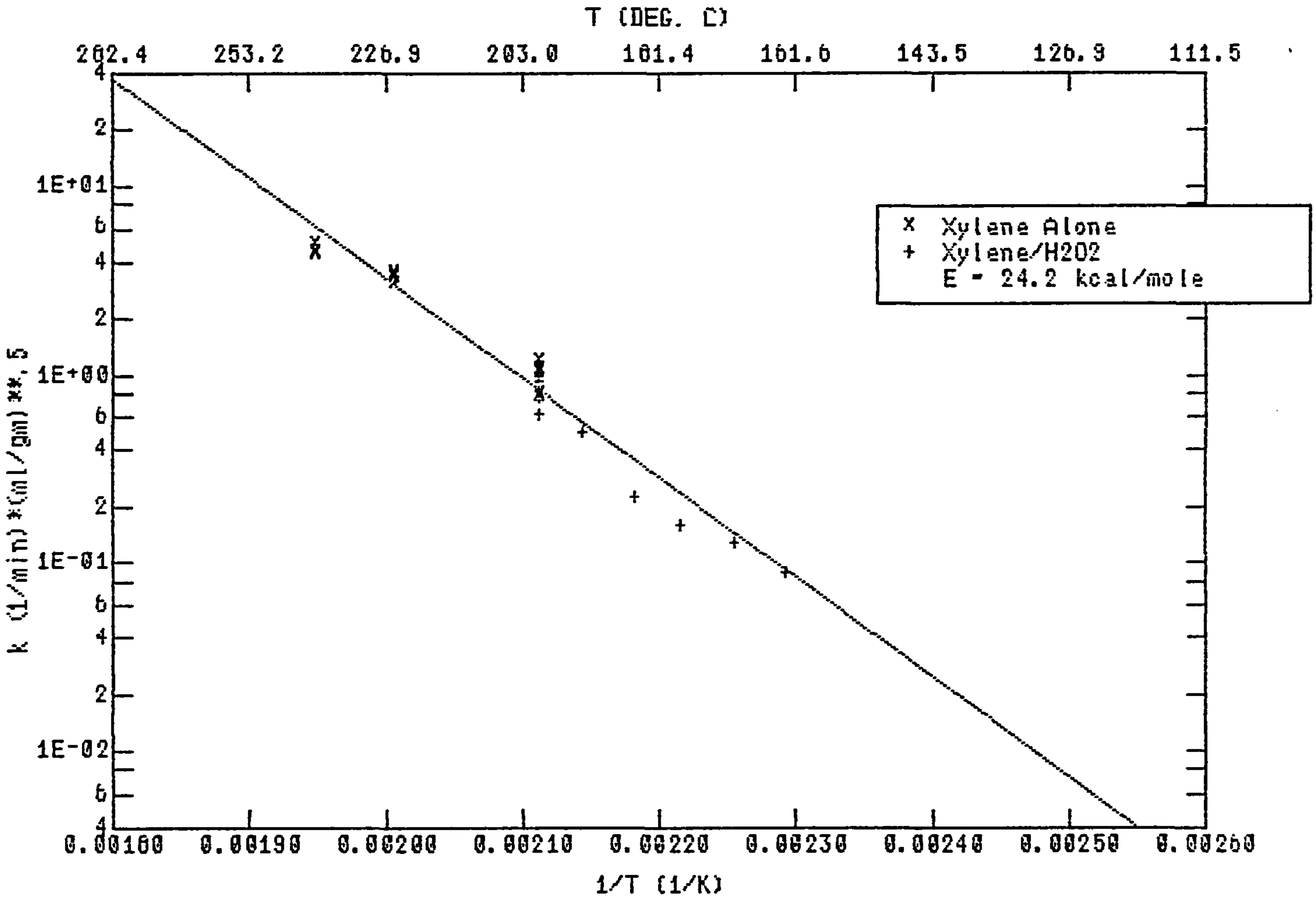


Figure 4.4 Rapid Reaction Arrhenius Plot for m-Xylene Alone and with Various Amounts of H2O2

Without an initiator, induction times at 163 °C and 2000 psi air are estimated to be 3.2 days from the Arrhenius results of chapter three. Once initiated with a small amount of hydrogen peroxide, however, the propagation reactions are sustainable at these reduced temperatures.

Summary

The induction time for hydrogen peroxide initiated m-xylene reactions has been shown to be strongly dependant on the amount of hydrogen peroxide added. The "critical" amount of H_2O_2 which provides the minimum concentration of free radicals necessary for rapid reaction to begin at "time zero" at 200 °C and 2000 psi air is approximately 0.5% of stoichiometric. This critical amount was found to be a function of temperature. The reaction rate constants for initiated experiments were not significantly different than those for uninitiated runs. Thus, these combined data give improved Arrhenius parameters which are summarized below. A qualitative mechanistic interpretation of these initiator results was also offered.

Induction Phase

Eliminated when more than the "critical" quantity of hydrogen peroxide is added to the reactor.

Active Phase

$$d[RH]/dt = k\,[O_2]^{0.5}[RH]^1$$

$$k = 1.26 \times 10^{11}\exp(-24200/RT) \quad (1/\text{min})(\text{ml}/\text{gm})^{0.5}$$

First order in organic shown
Half order in oxygen shown

SYNERGISM

Introduction

Synergism has been defined as a "cooperative action of discrete agencies such that the total effect is greater than the sum of the effects taken independently," (Webster's New Collegiate Dictionary (1974)). With respect to reaction kinetics it is possible that when two or more compounds react at the same time in the same reactor, the overall reaction rate (moles of all organics/volume time) will be greater than the sum of the individual reaction rates. When this behavior is observed it is referred to as synergism.

In reality, synergism is one of four possible interactions which compounds may have on one another. First, all components could be oblivious to one another and react at their pure component rates. Secondly, the individual reaction rates may be altered from their pure component values, but the overall multicomponent reaction rate remains equal to the sum of the pure component reaction rates. The last two possibilities are that the individual reaction rates become altered in such a fashion that the overall multicomponent reaction rate is greater than or less than the sum of the pure component rates. These four cases will be referred to as "no interaction", "rate neutral interaction", "synergistic interaction", and "negative synergistic interaction". They are expressed mathematically as follows.

1) No Interaction

$En_i = 1$ and $Sy = 1$

2) Rate Neutral Interaction

$En_i \neq 1$ and $Sy = 1$

3) Synergistic Interaction

$En_i \neq 1$ and $Sy > 1$

4) Negative Synergistic Interaction

$En_i \neq 1$ and $Sy < 1$

where En is the enhancement number and Sy is the synergism number. They are defined as

$$En_i = k_i^s / k_i \tag{4.1}$$

and

$$\begin{aligned} Sy &= \Sigma\, r_i^s / \Sigma\, r_i \\ &= \Sigma(k_i^s[O_2]^m[RH_i]^n) / \Sigma(k_i[O_2]^m[RH_i]^n) \ . \end{aligned} \tag{4.2}$$

It should be emphasized that the enhancement number and not the synergism number is of greater interest from a practical reactor design standpoint. As an example, consider a reactor which is used to reduce the concentration of organic from $[RH]_0$ to $[RH]_f$. The reactor residence time required for each compound is determined by

$$t_{rt,i} = \int_{[RH_i]_0}^{[RH_i]_f} (En_i\ k_i\ [O_2]^m[RH_i]^n)^{-1}\, d[RH_i] \ . \tag{4.3}$$

The overall residence time must be equal to $t_{rt,i}^{max}$. Any interaction which decreases the maximum t_{rt} is favorable when, as in this thesis, organic destruction is the objective.

It should be mentioned that in other applications the objective is to prevent oxidation (e.g., motor oil additives, "anti-knock" compounds for gasoline, edible oil preservatives). From this point of view interactions which increase t_{rt} are the most desirable. A discussion of these types of compounds can be found in Emanuel et al. (1967).

The interest in synergistic interactions arises primarily from mechanistic rather than economic considerations. For free radical reactions it is common for cross-initiation to occur (Emanuel et al. (1967)). This refers to the situation when a radical generated by one compound is used to initiate the chain propagation steps of another compound. To illustrate, imagine two compounds, "A" and "B". When reacted separately "A" reacts faster than "B". When combined in a reactor, both compounds will generate radicals with "A" generating the majority. Assuming that both parent compounds have similar reactivities with each other's radicals, "A" will share its radicals with "B". The result will be an increase in the reaction rate of "B" since more radicals are available than when "B" is reacted alone, and a decrease in the reaction rate of "A" since "B" has consumed some of the "A" radicals. If the same number of net propagation chains are initiated and they have the same net length as when each compound reacts separately, the increase in the reaction rate of "B" should equal the decrease in the reaction rate of "A". In the terminology defined above this would be a rate neutral interaction. If, however, chain lengths were increased and/or more net chains were initiated, a synergistic interaction would be observed. Shorter and/or fewer chains would lead to negative synergism. Differentiation between these various interactions may not be important from a design engineering point of view, but will provide valuable information to a fundamental researcher.

As was true for initiation, there are limited literature references to synergism in aqueous phase oxidation. Usually one of the two extremes is considered--the simple individual organic or a complicated mixture, such as pulping liquor.

One paper by Shibaeva _et al._ (1969a) does consider the aqueous phase oxidation of benzene and phenol simultaneously. They determined that the benzene reaction rate was enhanced by the presence of phenol in experiments conducted at 180-240 °C.

Characterization of Reactions

The reaction characteristics of m-xylene and phenol reacted individually were given in the previous chapter. The following experiments were conducted to explore the synergistic effects of reacting these two compounds in the presence of one another. The same experimental procedures as in chapter three were followed except that two organics, m-xylene and phenol, rather than one were placed in the inlet line and subsequently flushed together into the reactor. Each experiment utilized 780 grams of water and about 0.11 grams of m-xylene.

The runs were divided into three sets. The first set used equimolar quantities of phenol and m-xylene. The second and third sets reduced the amount of phenol to 50 and 15% of equimolar, respectively. These sets will henceforth be referred to as cases "a", "b", and "c", respectively. Nine runs were conducted for case "a" using temperatures ranging from 130-200 °C. The same temperature range was covered with four experiments in case "b", and case "c" consisted of three runs at temperatures of 154-200 °C. All runs were at 2000 psi air. A complete listing of all experimental conditions and tabular results is provided in Appendix C.

As an example of the type of data obtained in these experiments, refer to Figure 4.5. This shows both the m-xylene and phenol concentration histories during one run at 170 °C and 2000 psi air using equimolar quantities of each (case "a"). It is observed that the initial mass concentration of phenol is higher than that for m-xylene even though their molecular weights are not very different. Most of this difference is attributable to the fact that m-xylene has a rather large Henry's law constant and a significant portion of this compound resides in the vapor phase. Phenol's Henry's law constant is close to zero and essentially all of it remains in the liquid phase. Additional m-xylene reduction may be attributed to its lower water solubility, and, thus, greater tendency to holdup on the reactor inlet tubing walls. Though equimolar quantities were injected, less than equimolar m-xylene may actually enter the reactor.

Figures 4.6-4.8 show representative concentration histories for m-xylene for cases "a", "b", and "c", respectively. The corresponding phenol concentration histories are given in Figures 4.9-4.11. These reactions are characterized by the familiar induction period followed by an exponential decay. As expected, increasing temperature both shortens the induction period and increases the reaction rate.

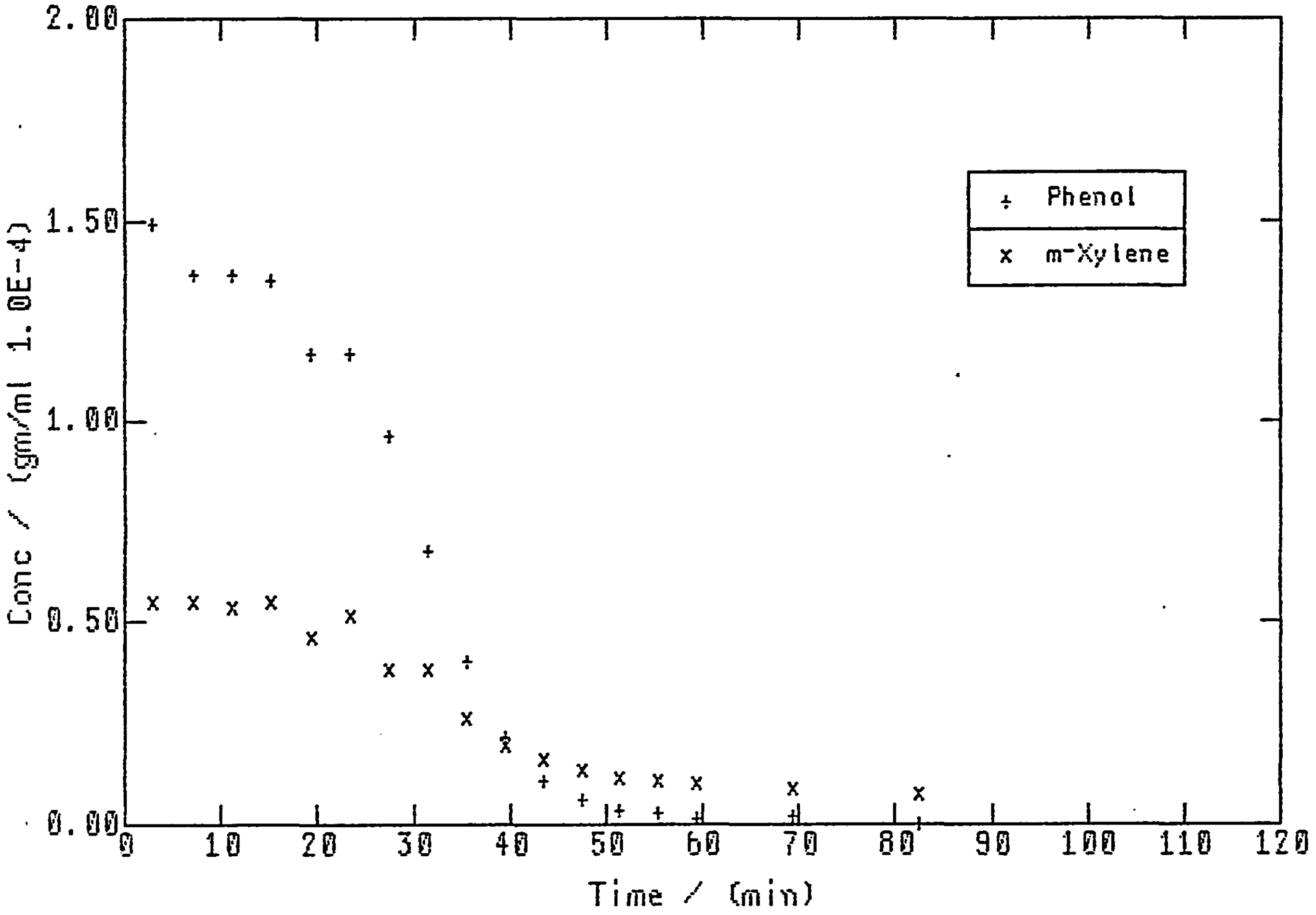


Figure 4.5 Experimental Data for Equimolar m-Xylene/Phenol Synergism
Run at 170 deg C and 2000 psi

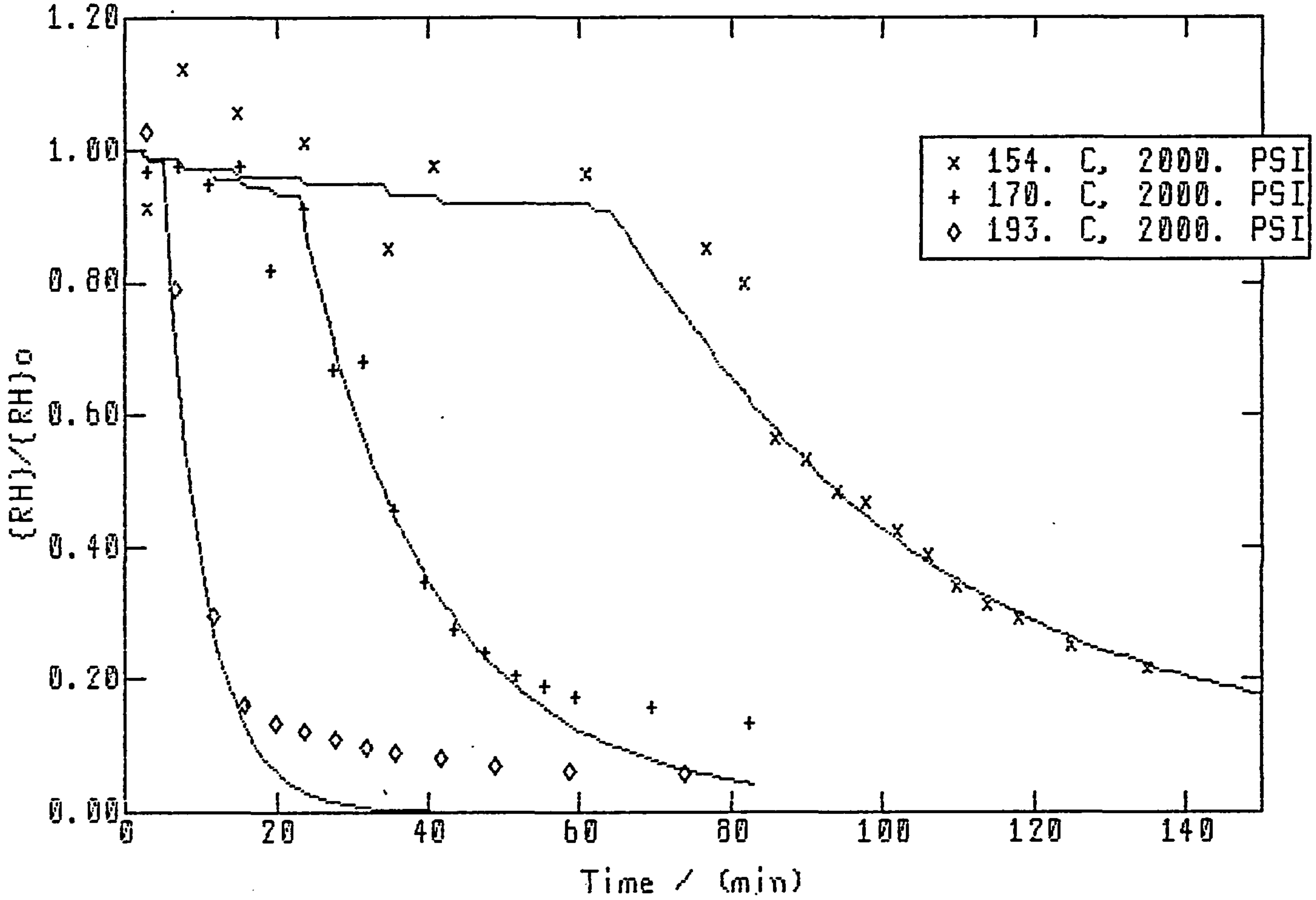


Figure 4.6 Experimental Data and Model Curves for m-Xylene with Phenol (Case "a")

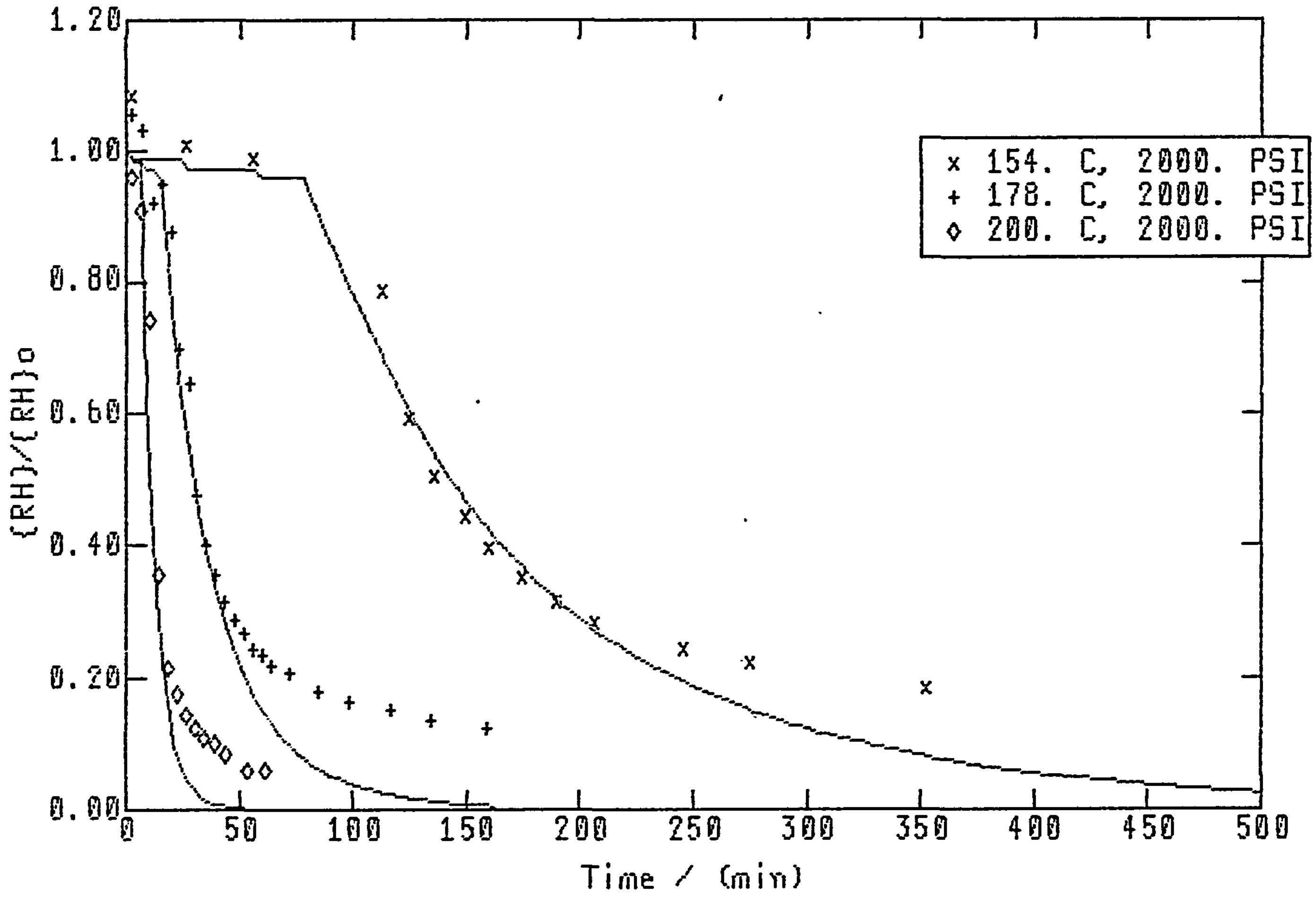


Figure 4.7 Experimental Data and Model Curves for m-Xylene with Phenol (Case "b")

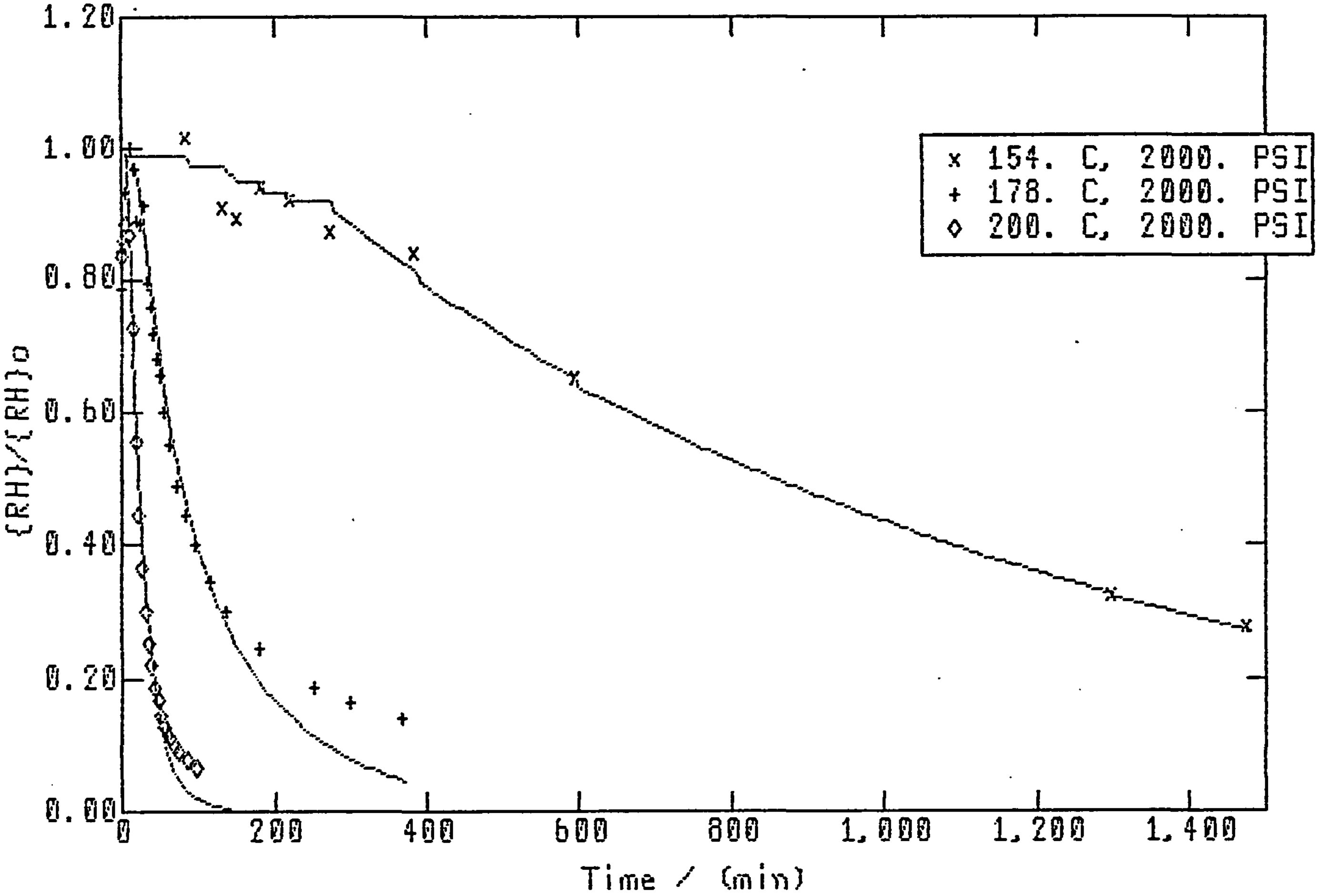


Figure 4.8 Experimental Data and Model Curves for m-Xylene with Phenol (Case "c")

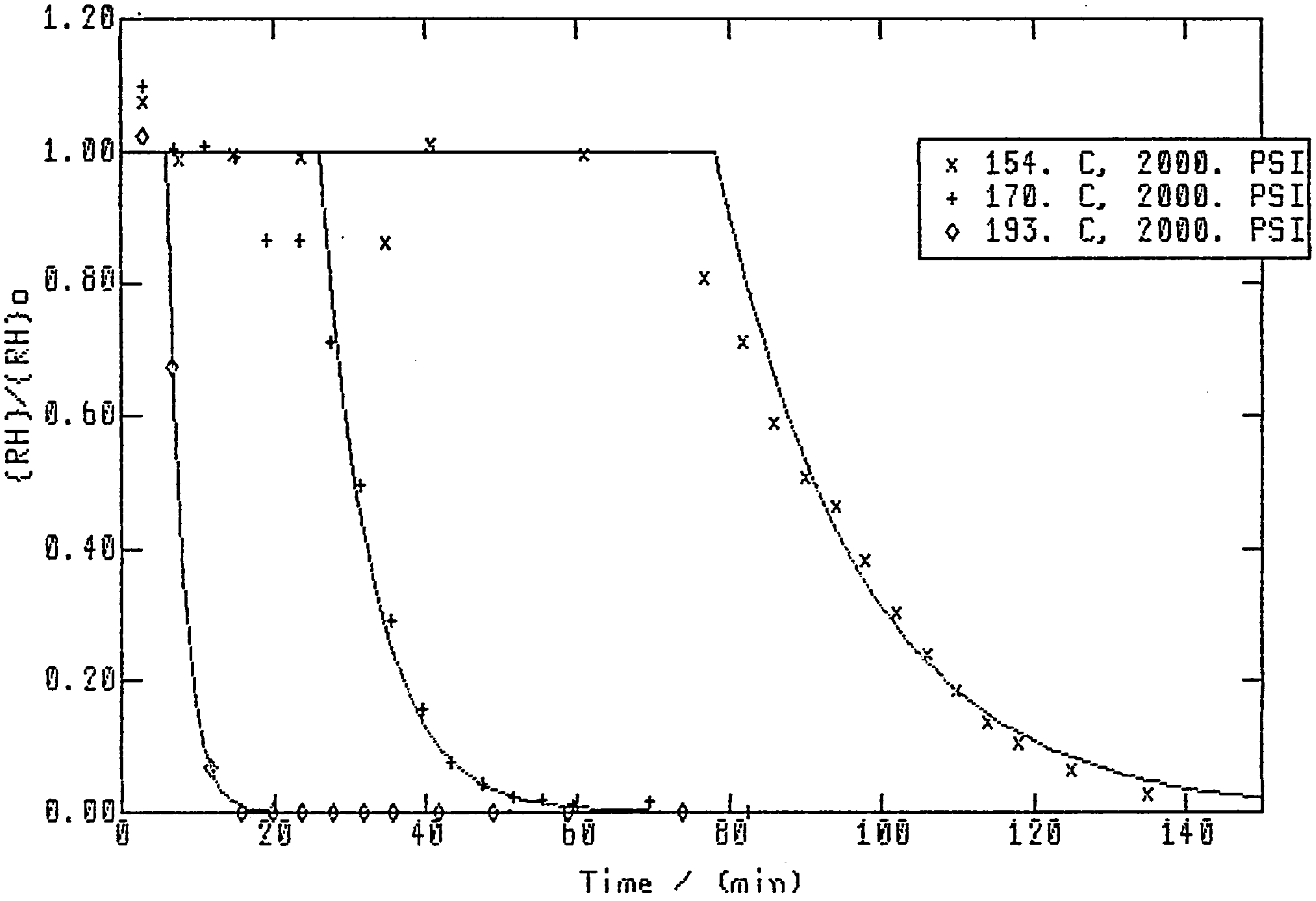


Figure 4.9 Experimental Data and Model Curves for Phenol with
m-Xylene (Case "a")

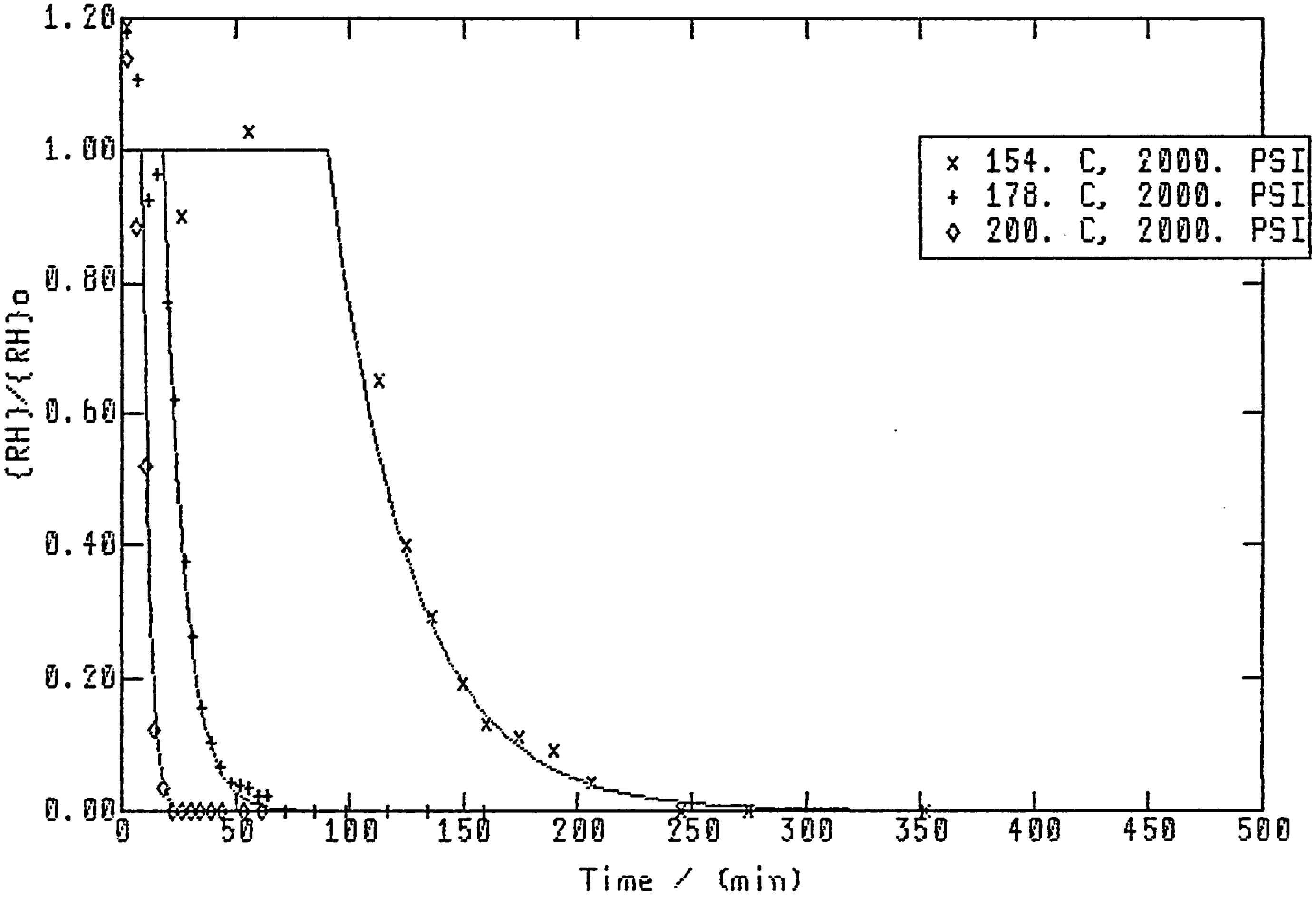


Figure 4.10 Experimental Data and Model Curves for Phenol with m-Xylene (Case "b")

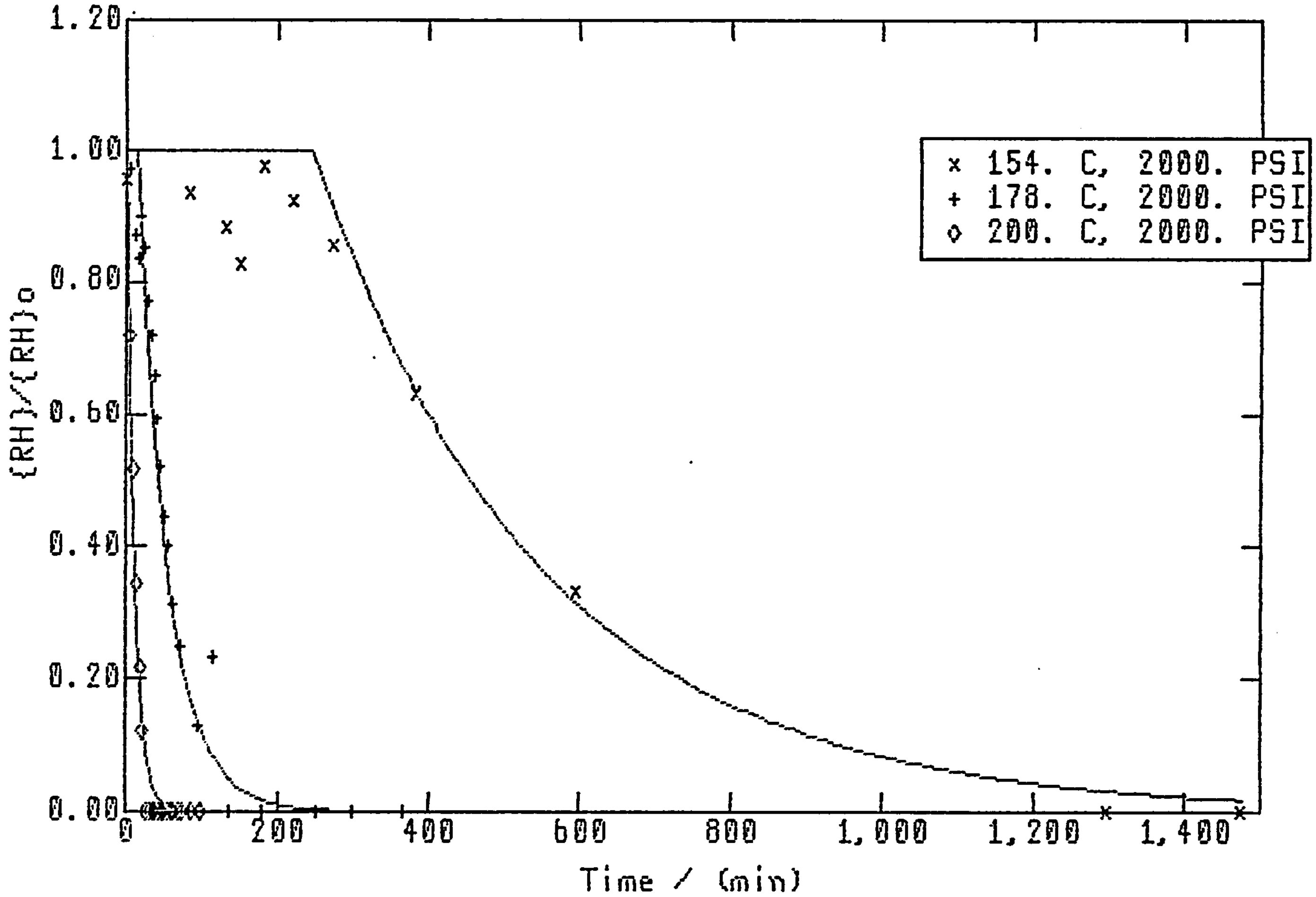


Figure 4.11 Experimental Data and Model Curves for Phenol with m-Xylene (Case "c")

Results and Discussion

The mathematical model presented in chapter two was applied to these data and the resulting values of k', t_{start} and k for m-xylene are given in Table 4.2, and the corresponding values for phenol are listed in Table 4.3. Values could not be determined at the highest temperature run (200 °C) for either m-xylene or phenol in case "a" because reaction rates were so fast that insufficient data could be collected to facilitate a meaningful regression. As was the case for pure component and initiated data, it was assumed that reaction rates are 1/2 order with respect to oxygen to calculate k from k'. This assumption was not verified since all runs were at one pressure. The good agreement between the model line and experimental points in Figures 4.6-4.11 confirms the model's assumption of first order kinetics with respect to organic. Toward the end of some of the m-xylene reactions, however, the concentration does not decrease as rapidly as the model predicts. Explanations were offered for this type of behavior in chapter three for unsynergized m-xylene oxidation. For these synergism experiments, however, this "tailing" appears to coincide with the time at which the faster reacting compound, phenol, has largely disappeared. This can be observed in Figure 4.5-4.11 presented earlier. The cessation of phenol cross-initiating m-xylene propagation chains could contribute to the observed decrease in reaction rate. Certainly, it would be expected that in the limit as [phenol] → 0, m-xylene should return to its slower, unsynergized reaction rate.

Further analysis of results is divided into two sections, first the m-xylene findings followed by those for phenol.

Table 4.2 Experimental Conditions and Model Results for m-Xylene Synergism (m-Xylene/Phenol System)

T	P	m_2^0	t_{start}	k'	O_2	k
(°C)	(psi)	(gm)	(min)	(1/min)	(gm/ml)	$(1/min)(ml/gm)^{0.5}$
Case "a"						
114	2000	0.080	>550.	-	0.000702	-
130	2000	0.088	357.3	0.0122	0.000730	0.452
138	2000	0.088	175.5	0.0201	0.000750	0.734
154	2000	0.092	64.1	0.0407	0.000799	1.44
162	2000	0.078	37.0	0.0757	0.000829	2.63
170	2000	0.086	23.6	0.107	0.000860	3.65
178	2000	0.090	11.9	0.182	0.000895	6.09
185	2000	0.090	10.2	0.225	0.000926	7.39
193	2000	0.085	5.8	0.305	0.000964	9.82
200	2000	0.080	-	-	0.000999	-
Case "b"						
130	2000	0.120	599.6	0.00301	0.000730	0.111
154	2000	0.091	80.0	0.0186	0.000799	0.658
178	2000	0.090	17.7	0.0742	0.000895	2.48
200	2000	0.090	9.0	0.228	0.000999	7.21
Case "c"						
154	2000	0.100	279.9	0.0021	0.000799	0.074
178	2000	0.085	22.5	0.0182	0.000895	0.608
200	2000	0.090	8.5	0.0712	0.000999	2.259

m-Xylene: Figure 4.12 is an Arrhenius plot of k *versus* 1/T for synergized m-xylene. To facilitate comparison, the unenhanced and H_2O_2 initiated values of k are also shown. It is apparent that the m-xylene reaction rate can be enhanced by as much as 1.5 orders of magnitude by adding equimolar quantities of phenol to the reactor. As less phenol is added, the values of k become closer to the unsynergized values. The

Table 4.3 Experimental Conditions and Model Results for Phenol Synergism (m-Xylene/Phenol System)

T (°C)	P (psi)	m_2^0 (gm)	t_{start} (min)	k' (1/min)	O_2 (gm/ml)	k $(1/min)(ml/gm)^{0.5}$
			Case "a"			
114	2000	0.120	>550.	-	0.000702	-
130	2000	0.110	373.3	0.0158	0.000730	0.585
138	2000	0.110	203.2	0.0203	0.000750	0.741
154	2000	0.120	78.6	0.0529	0.000799	1.87
162	2000	0.105	41.1	0.0895	0.000829	3.11
170	2000	0.117	26.9	0.146	0.000860	4.97
178	2000	0.110	14.1	0.207	0.000895	6.90
185	2000	0.110	12.0	0.370	0.000926	12.2
193	2000	0.120	6.2	0.474	0.000964	15.3
200	2000	0.105	-	-	0.000999	-
			Case "b"			
130	2000	0.065	642.6	0.0052	0.000730	0.192
154	2000	0.055	92.0	0.0276	0.000799	0.976
178	2000	0.060	19.8	0.110	0.000895	3.68
200	2000	0.055	9.1	0.355	0.000999	11.2
			Case "c"			
154	2000	0.014	249.6	0.0033	0.000799	0.117
178	2000	0.015	20.9	0.0248	0.000895	0.832
200	2000	0.015	3.9	0.0940	0.000999	2.98

lines though the case "a", "b" and "c" data represent activation energies of 18.7 +/- 1.4, 22.5 +/- 3.6, and 30.0 +/- 30.2 kcal/mole, respectively. The corresponding preexponentials are 6.01 x 10^9, 1.96 x 10^{11}, and 1.68 x 10^{14} $(1/min)(ml/gm)^{0.5}$. The exorbitant confidence limits on the case "c" activation energy are due to the fact that only three data points were available for least squares regression. Furthermore, the

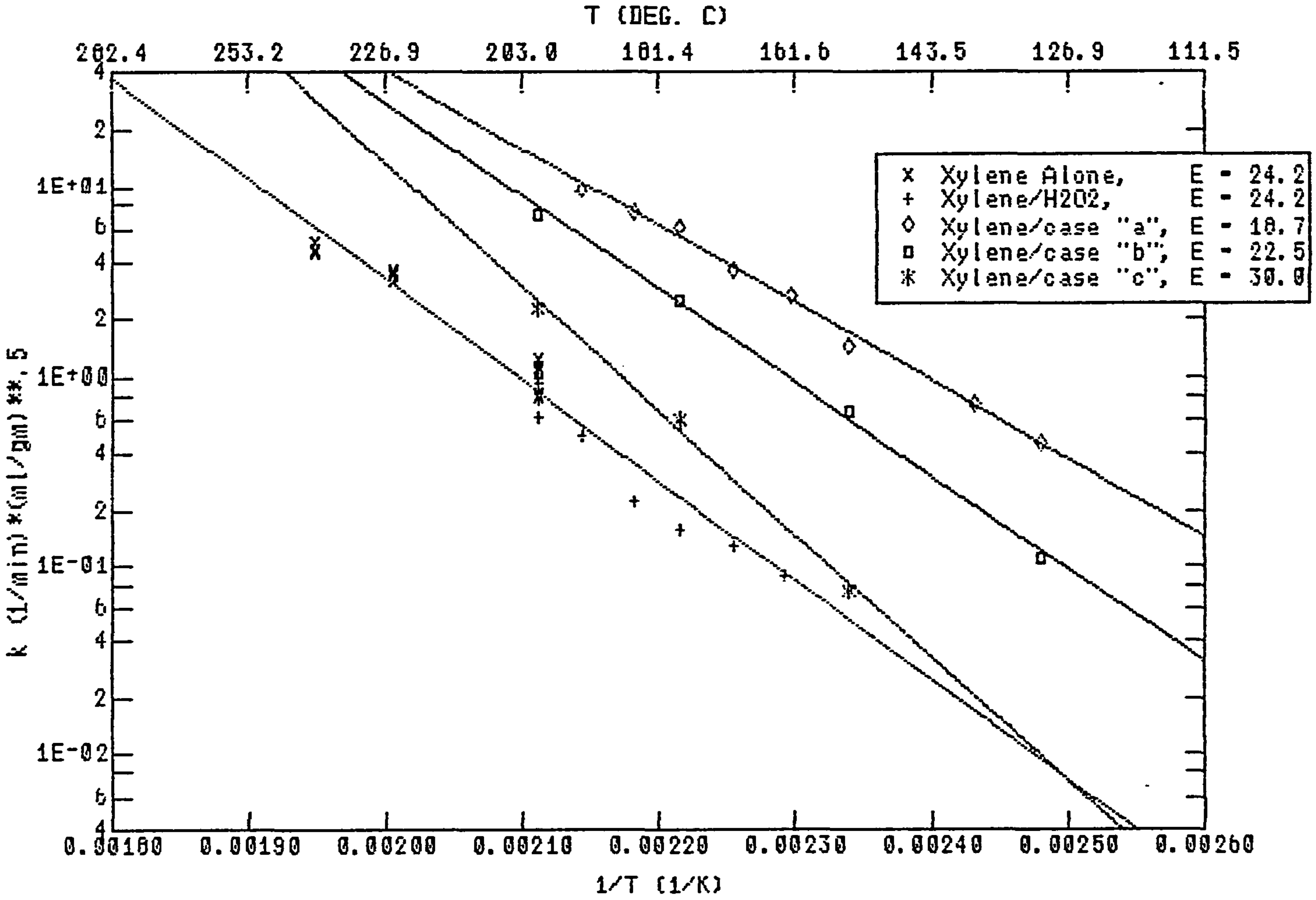


Figure 4.12 Rapid Reaction Arrhenius Plot for m-Xylene with H2O2 and Various Amounts of Phenol

154 °C run results are questionable due to a limited number of concentration measurements.

Recall that the unsynergized m-xylene activation energy reported above was 24.2 +/- 2.0 kcal/mole. The synergized activation energies are not significantly different from the unsynergized value. While the addition of phenol strongly affects the reaction rate, it has little, if any, effect on the activation energy.

A quantitative measure of the degree of rate enhancement for each of the three cases can be obtained by calculating the enhancement number, En. When this ratio is unity, no rate enhancement occurs. Values greater than unity indicate rate enhancement and values less than unity result from rate retardation. Figure 4.13 presents a semi-log plot of En *versus* 1/T. These lines were determined by calculating the quotient of the appropriate Arrhenius expressions. It is observed that adding 15% phenol to the reactor increases the reaction rate by factors of one to four, adding 50% phenol augments reaction rate by about an order of magnitude, and 100% phenol additions give greater than an order of magnitude of rate enhancement.

In chapter three it was shown that the length of the induction period, t_{start}, could be correlated quite well by equation 3.12. Thus, semi-log plots of (t_{start} * $[O_2]$) *versus* 1/T should produce straight lines with a slope of E/R and an intercept of $R\bullet_{crit}/A_0[RH]_0$. While this linearity is maintained in the synergism runs, values of t_{start} are greatly reduced as seen in Figure 4.14. The synergized experiments have induction periods which are approximately 2 orders of magnitude shorter than the unsynergized runs with slightly longer times resulting from

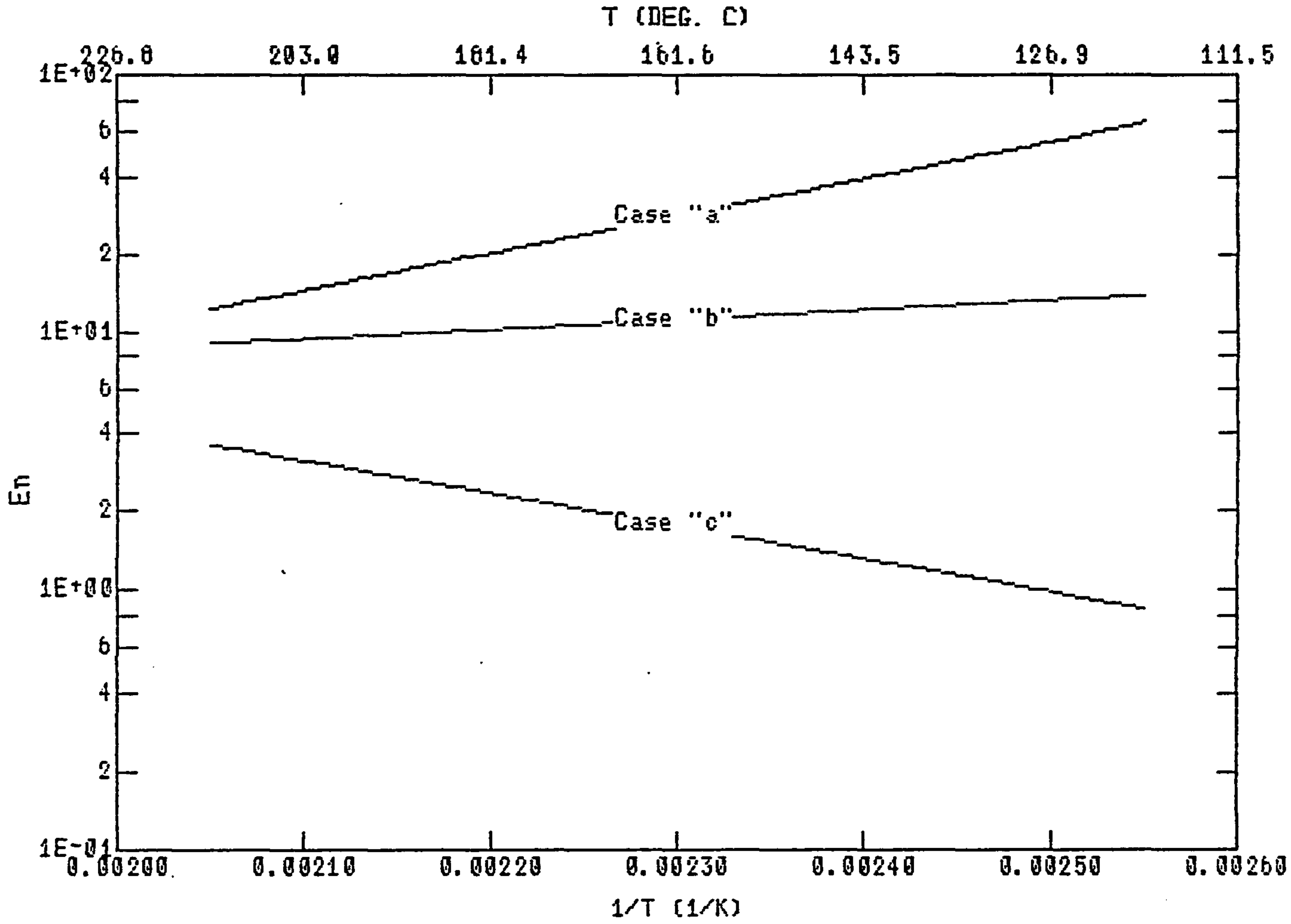


Figure 4.13 Enhancement Number Versus Temperature for m-Xylene

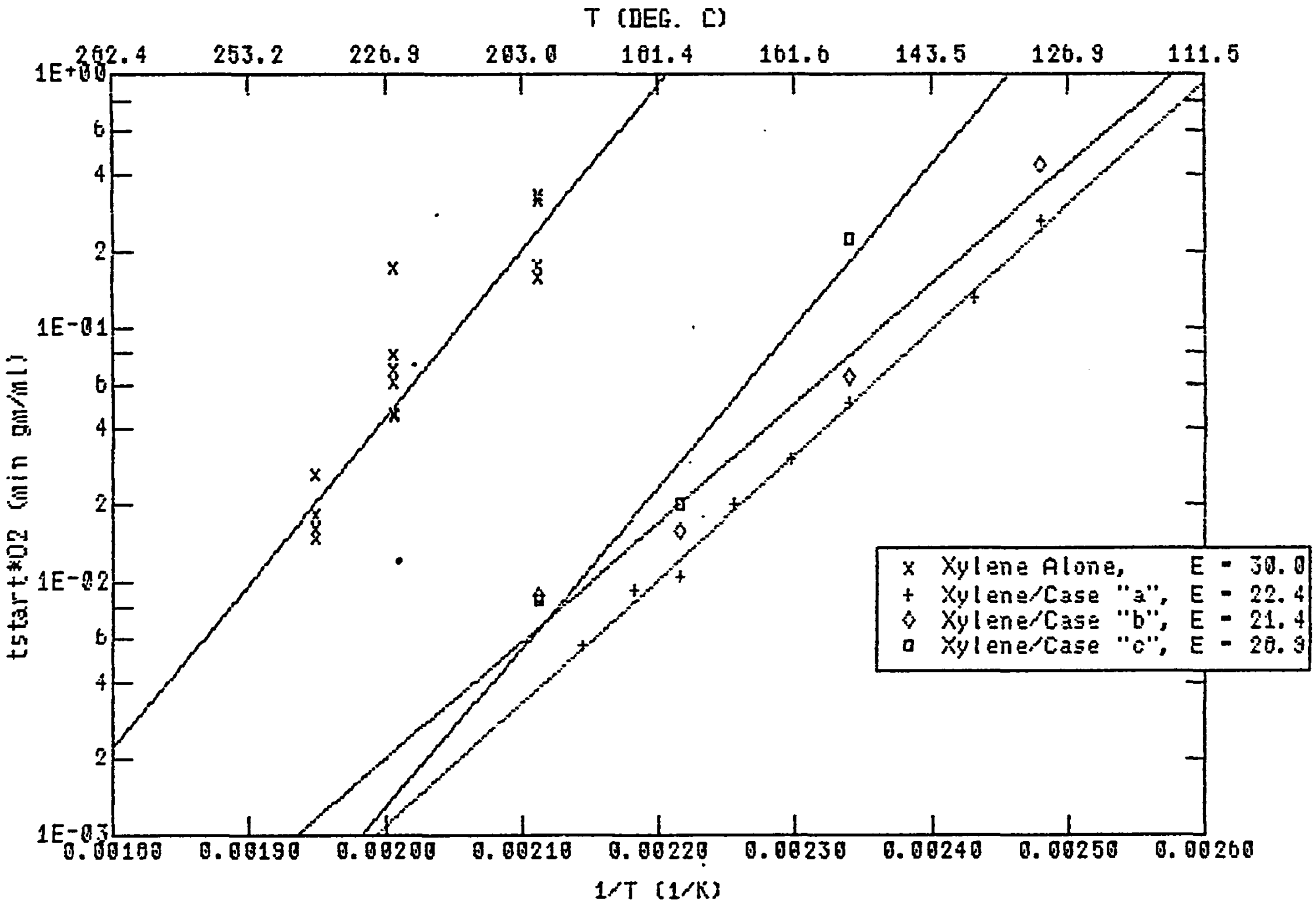


Figure 4.14 Induction Arrhenius Plot for m-Xylene Alone and with Various Amounts of Phenol

lower concentrations of phenol. The lengths of these induction times are roughly equal to the values given for unsynergized phenol in Table 3.5.

This equality is further emphasized by observing the slopes of the case "a", "b", and "c" lines. From these it is determined that the initiation activation energies are 22.4 +/- 1.4, 21.4 +/- 10.7, and 28.9 +/- 79.0 kcal/mole, respectively. The intercepts gave values of 1.75 x 10^{-13}, 8.82 x 10^{-13}, and 3.14 x 10^{-16} (min gm/ml), respectively for the group of constants, $R\bullet_{crit}/A_0[RH]_0$. The initiation activation energy for unsynergized phenol induction was 22.5 kcal/mole. None of the synergism initiation activation energies are significantly different from the pure phenol value. Thus, when m-xylene is reacted in the presence of phenol, the m-xylene induction times become nearly equal to the phenol induction times, and furthermore the activation energies become essentially identical. It appears that phenol cross-initiates m-xylene reactions to such an extent that measurements of m-xylene t_{start}'s are really an indirect measure of phenol induction times.

<u>Phenol</u>: An Arrhenius plot for the phenol rate constants during the rapid reaction phase is given in Figure 4.15 which shows both the three sets of synergized phenol results and the unsynergized findings of chapter three. The slopes of these lines indicate that the phenol in cases "a", "b", and "c" has activation energies of 20.3 +/- 1.7, 22.0 +/- 1.4, and 28.4 +/- 24.4 kcal/mole, respectively. The preexponentials were calculated as 5.09 x 10^{10}, 1.61 x 10^{11}, and 3.99 x 10^{13} $(1/min)(ml/gm)^{0.5}$. The activation energies are slightly lower than the unsynergized value of 26.8 +/- 3.1 kcal/mole (except for the case "c"

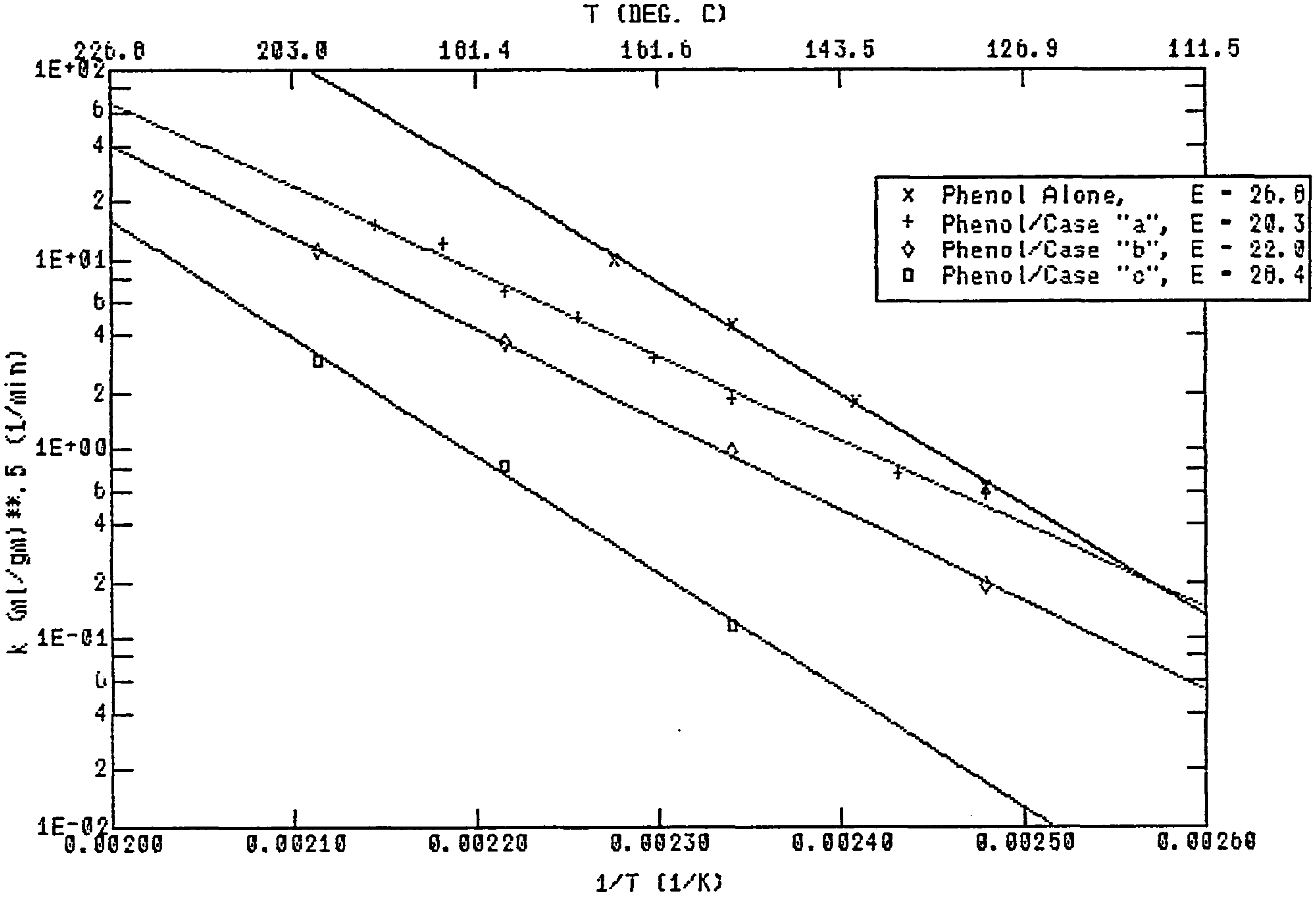


Figure 4.15 Rapid Reaction Arrhenius Plot for Phenol with Various Amounts of m-Xylene

value, but in this instance the confidence limits are too large for meaningful comparisons).

Figure 4.16 shows the degree of reduction in the phenol reaction rate by plotting the enhancement number <u>versus</u> 1/T. The case "a" reaction rates are slower than the unsynergized results by factors ranging from about one to five. The case "b" results are factors of three to ten slower, and the case "c" results are decreased by factors of 30 to 40.

An Arrhenius plot for the induction period is shown in Figure 4.17. It is apparent that as phenol concentration is reduced, induction times are very slightly increased. The initiation activation energies were calculated as 22.5 +/- 1.8, 21.7 +/- 8.9, and 34.4 +/- 27.5 kcal/mole for cases "a", "b", and "c", respectively. These are not significantly different from the unsynergized value given previously as 22.5 +/- 7.5 kcal/mole. The group of constants, $R\bullet_{crit}/A_0[RH]_0$, are 1.89×10^{-13}, 7.11×10^{-13}, and 4.42×10^{-19} (min gm/ml), respectively. Since the presence of m-xylene had such a small effect on phenol induction, a second Arrhenius plot was constructed correlating all of the synergized and unsynergized values as shown in Figure 4.18. The resulting values for initiation activation energy and $R\bullet_{crit}/A_0[RH]_0$ are 22.1 +/- 3.0 kcal/mole and 3.21×10^{-13} (min gm/ml), respectively.

It has now been established that combining m-xylene and phenol in one reaction vessel increases the m-xylene reaction rate and decreases the phenol reaction rate, resulting in enhancement numbers other than unity. To determine what type of interaction is occurring it is necessary to calculate the synergism numbers, Sy. Using the Arrhenius equation to

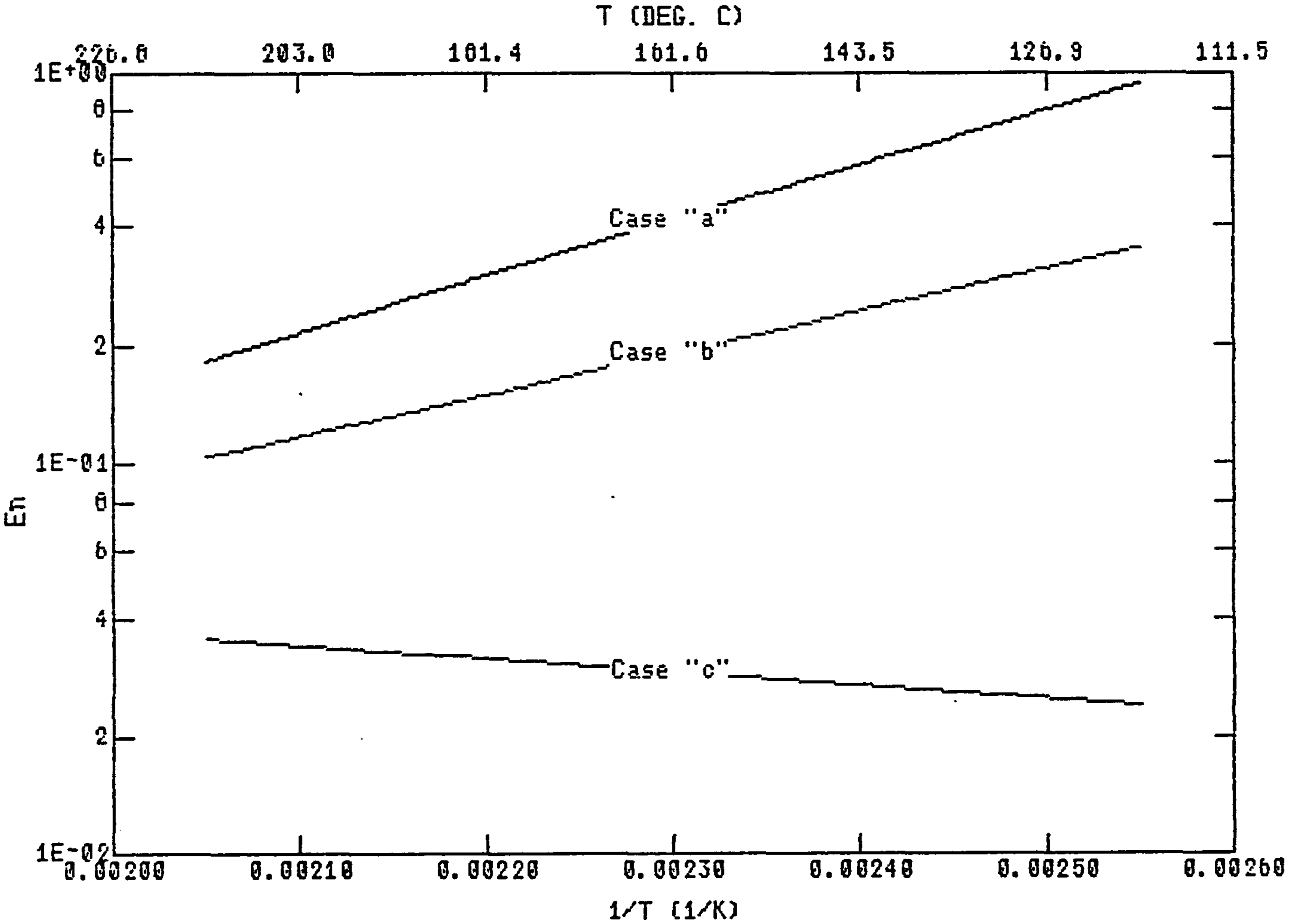


Figure 4.16 Enhancement Number Versus Temperature for Phenol

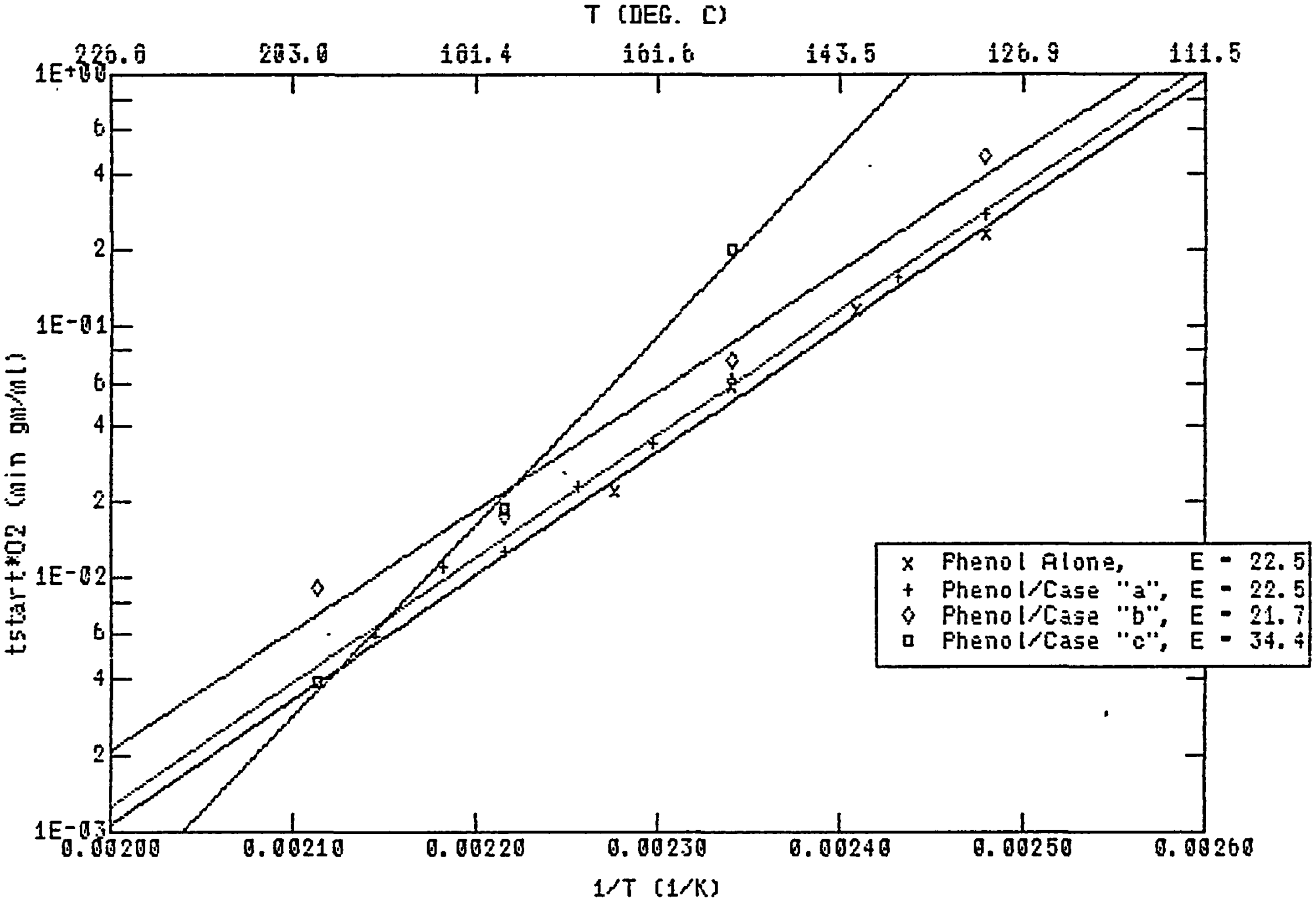


Figure 4.17 Induction Arrhenius Plot for Phenol Alone and with Various Amounts of m-Xylene

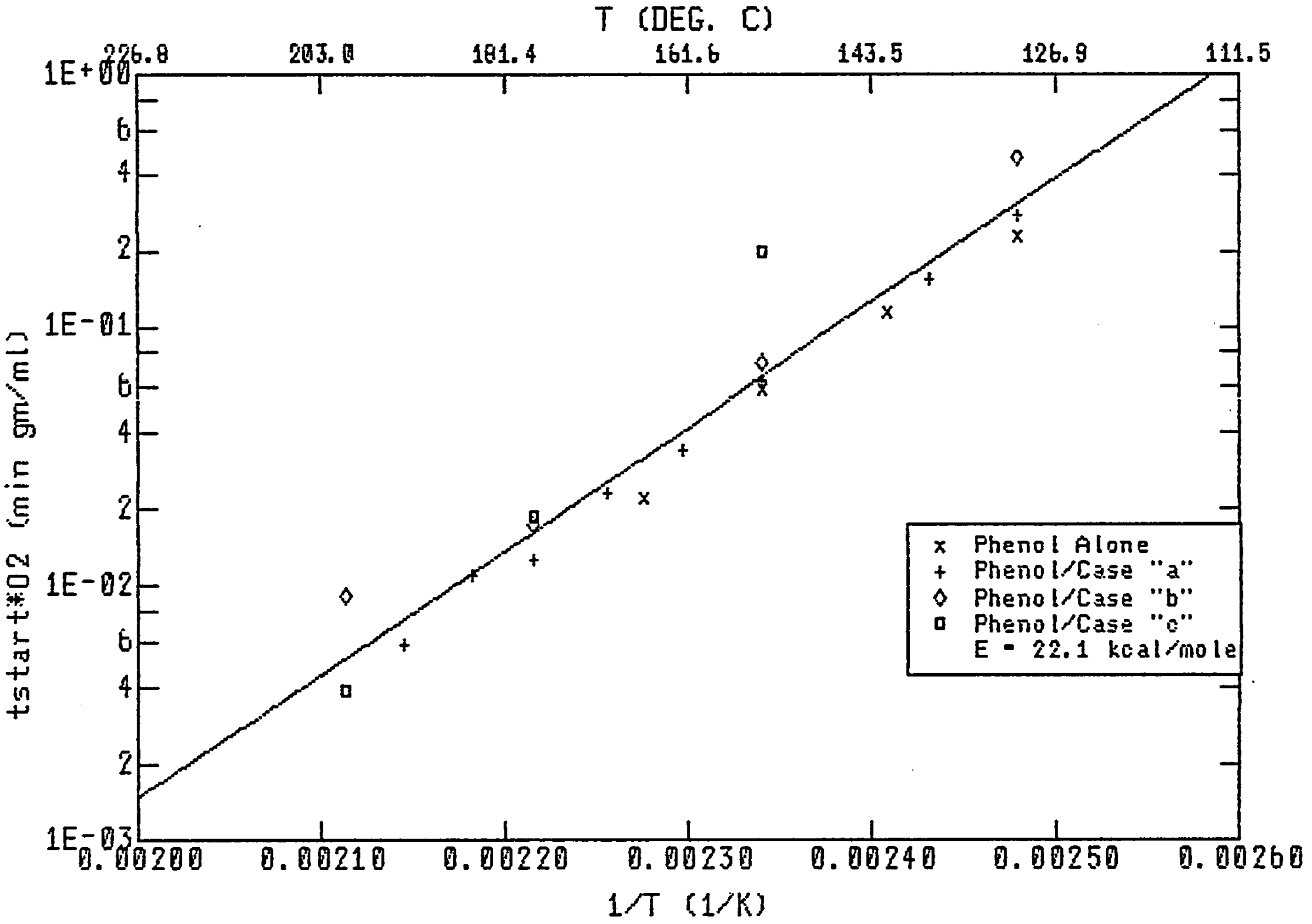


Figure 4.18 Induction Arrhenius Plot for Phenol Alone and with Various Amounts of m-Xylene--One Arrhenius Line

obtain values for k_i and k_i^s, Sy was calculated at temperatures of 125, 150, 175, and 200 °C, and plotted versus X_{xylene} as shown in Figure 4.19. At higher fractional concentrations of m-xylene all interactions exhibit negative synergism (Sy less than one). For the equimolar concentrations, however, the results are mixed. The 175 and 200 °C also display negative synergism, but the 150 °C result is essentially rate neutral, and the 125 °C result shows positive synergism. Sy appears to be a strong function of both temperature and fractional concentration. The mechanistic interpretation for each of these types of interaction was given above.

Finally, from the point of view of the design engineer concerned with destroying aqueous phase m-xylene waste, every synergistic experiment performed was a major improvement over the unenhanced runs. In each case both the induction and reaction time for m-xylene were significantly reduced. A potential problem with adding enhancers to the reactor is that the enhancers, themselves, may become the limiting component by taking longer to react than the original contaminant. This did not occur in any of the experiments conducted here, but would be a problem if much higher fractional concentrations of phenol were added. Thus, as a means of of reducing reactor residence times, the results obtained are very encouraging. Synergism is recommended as a very effective means of reaction rate enhancement.

Summary

A definite interaction has been observed between the oxidation of m-xylene and phenol. Depending on reaction conditions all three types of interactions--positive synergism, rate neutral, and negative

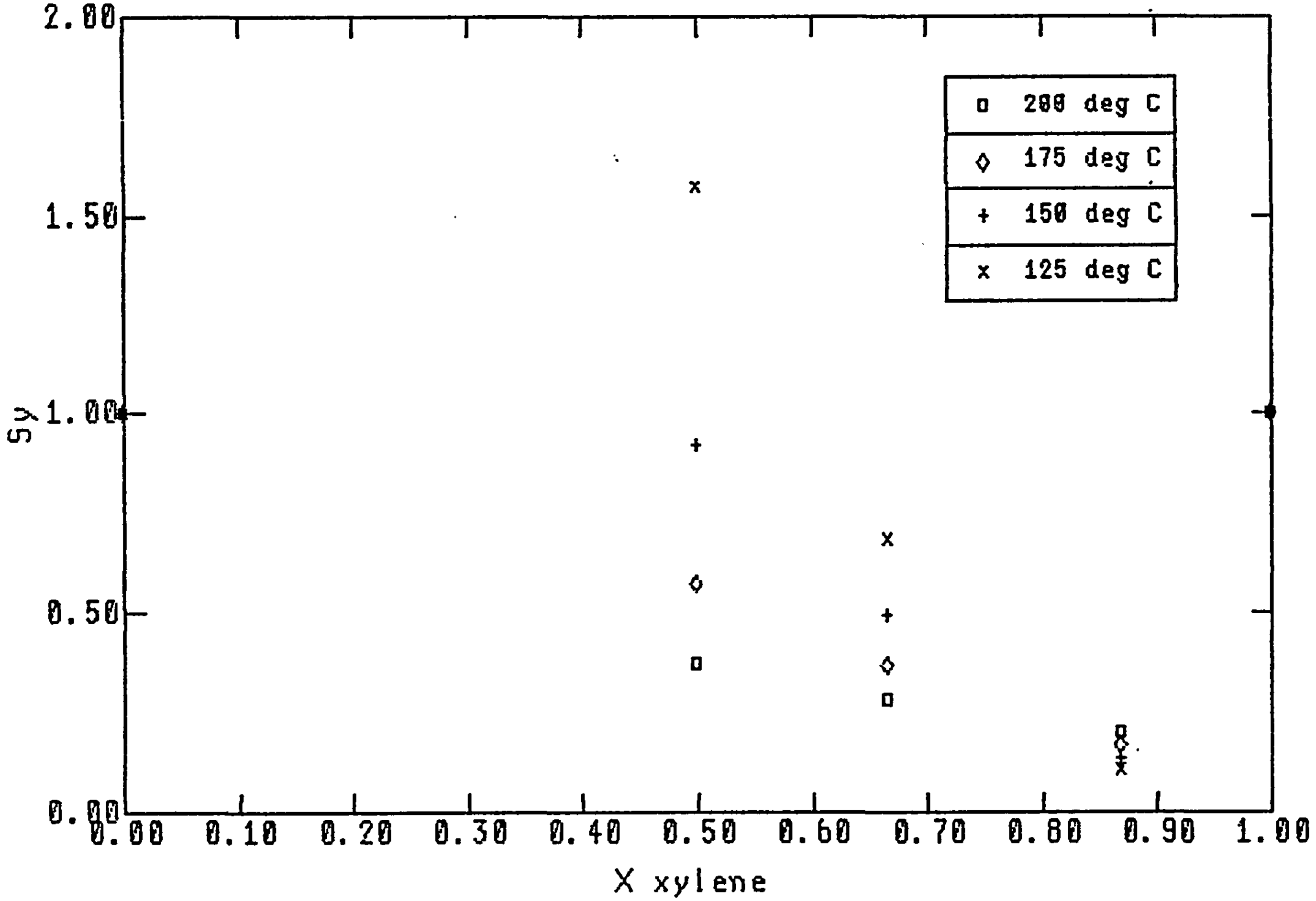


Figure 4.19 Synergism Number versus Fractional m-Xylene Concentration for the m-Xylene/Phenol System

synergism--were observed. In each experiment performed the m-xylene reaction rate was increased, and the phenol reaction rate decreased. For equimolar quantities, the m-xylene reaction rate was increased by factors of 10-60 while the phenol rate decreased by factors of 1-5.

Phenol induction times were very slightly increased, while m-xylene induction times were dramatically reduced to times approximately equal to those for phenol. These results establish synergism as a very effective means of improving the economics of an aqueous phase oxidation waste treatment facility.

These effects are attributed to cross-initiation. The interaction caused only minor variations in both initiation and active reaction activation energies. These values are summarized below.

Induction Phase

Both compounds

Order in organic unknown
First order in oxygen assumed

m-Xylene

Case "a"

$$t_{start} = (1.75 \times 10^{-13}/[O_2]) \exp(22400/RT) \quad \text{(min)}$$

Case "b"

$$t_{start} = (8.82 \times 10^{-13}/[O_2]) \exp(21400/RT) \quad \text{(min)}$$

Case "c"

$$t_{start} = (3.14 \times 10^{-16}/[O_2]) \exp(28900/RT) \quad \text{(min)}$$

Phenol

Case "a"

$$t_{start} = (1.89 \times 10^{-13}/[O_2]) \exp(22500/RT) \quad (min)$$

Case "b"

$$t_{start} = (7.11 \times 10^{-13}/[O_2]) \exp(21700/RT) \quad (min)$$

Case "c"

$$t_{start} = (4.42 \times 10^{-19}/[O_2]) \exp(34.40/RT) \quad (min)$$

Active Phase

Both Compounds

$$d[RH]/dt = k\ [O_2]^{0.5}[RH]^1$$

First order in organic shown
Half order in oxygen assumed

m-Xylene

Case "a"

$$k = 6.01 \times 10^9\ \exp(-18700/RT) \quad (1/min)(ml/gm)^{0.5}$$

Case "b"

$$k = 1.96 \times 10^{11}\ \exp(-22500/RT) \quad (1/min)(ml/gm)^{0.5}$$

Case "c"

$$k = 1.68 \times 10^{14}\ \exp(-30000/RT) \quad (1/min)(ml/gm)^{0.5}$$

Phenol

Case "a"

$$k = 5.09 \times 10^{10}\ \exp(-20300/RT) \quad (1/min)(ml/gm)^{0.5}$$

Case "b"

$$k = 1.61 \times 10^{11}\ \exp(-22000/RT) \quad (1/min)(ml/gm)^{0.5}$$

Case "c"

$$k = 3.99 \times 10^{13}\ \exp(-28400/RT) \quad (1/min)(ml/gm)^{0.5}$$

APPLICATIONS

Initiation

At least two practical applications are suggested by the initiation findings. The first is the use of an initiator such as H_2O_2 during reactor start-up. Especially for batch reactors, small additions of an initiator could translate into tremendous reductions in cycle times. A second potential application would occur during process upsets. When encountering an unusual "slug" of material, additions of H_2O_2 would increase the concentration of free radicals above the equilibrium level and facilitate quick disposal.

Synergism

The synergism findings are of interest particularly for their application to hazardous waste clean-up. It may be discovered that certain waste streams possess a hidden value due to their ability to favorably interact with other, more refractory, waste streams. If, for instance, aqueous phase oxidation were being used to clean-up a m-xylene contaminated stream, it would be advantageous to further "contaminate" the stream with phenol. This would result in shorter reactor residence times or greater fractional conversions. If a phenolic waste stream were not available, it may be possible to arrange for other manufacturers to donate or pay for their phenol "waste" to be used for this purpose.

CHAPTER 5

EFFECTS OF SOIL ON AQUEOUS PHASE OXIDATION

INTRODUCTION

As discussed in chapter one, waste disposal methods such as landfilling which were once considered safe are now becoming threats not only to the environment, but in certain cases to human life as well. One problem in particular is soils which have become contaminated with hazardous materials. Sites which need remediation range in size from a few cubic yards to many cubic miles. The most commonly used method for decontaminating such sites is incineration. Hitchcock (1979) gives a good description of the various types of incinerators currently being used. The cost of such an operation is typically 250-500 $/ton (Edwards _et_ _al._ (1983)).

Aqueous phase oxidation has been proposed as an alternative and potentially more economical method for detoxifying hazardous waste sites. Incineration requires large quantities of energy to raise temperatures high enough to support gas phase oxidation. When solids are wet, much of this cost is associated with vaporizing the large quantities of water. Aqueous phase oxidation requires much lower temperatures and does not necessitate the vaporization of water. Reaction products are essentially the same for both processes except that aqueous phase oxidation may result in some low molecular weight acids rather than all carbon dioxide and water. Though reaction rates would be slower than for incineration, reduced energy requirements could make aqueous phase oxidation the method of choice in certain hazardous waste clean-up applications.

Regeneration of activated carbon is the only process to date which has used aqueous phase oxidation to extract and destroy organics from solids. Results of such efforts are reported in Charest and Chornet (1976), Gitchel et al. (1975), and Knopp et al. (1978).

As an initial step in testing the feasibility of this idea for soil detoxification, experiments were conducted to determine the effects of soil on the disappearance kinetics of m-xylene, tetrachloroethylene, and malathion.

EXPERIMENTAL METHODS

Experiments were conducted according to the same procedures as described in chapter two except for the following adjustments. Five grams of soil were placed in the reactor with the initial charge of water before the reactor was heated. During the time between samples the soil was entrained in the water by the action of the impeller. The reactor was allowed to sit unstirred for two minutes rather than the usual 30 seconds before a sample was drawn. During this extra time suspended soil particles settled to the bottom and, thus, were not drawn into the sampling line. This worked surprisingly well in preventing clogging of valves and filters. Finally, extra cleaning was required after each of these runs to remove all residual soil from the reactor.

The soil used was obtained near Commerce, Louisiana in East Carroll Parish at a depth of 24-33 inches. An analysis by Dr. B. J. Miller of the Louisiana State University Agronomy Department indicated that the soil was composed of 19.4% sand, 63.2% silt, and 17.4% clay (mostly montmorillonite). Sieve analysis results showed that by weight 1/3 of the particles were less than 43 microns; 1/3 were greater than 43 microns, but less than 420 microns; and 1/3 were greater than 420 microns.

The three organics used in this study have been described in chapter three. As usual, 780 grams of distilled water were used as the solvent in each experiment.

CHARACTERIZATION OF REACTIONS

All experimental results for the organic/soil experiments are listed in tabular form in Appendix D. The characteristics of the results for each compound will be discussed in the following paragraphs.

m-Xylene

Five experiments were performed with soil and about 0.11 grams of m-xylene. Experimental conditions ranging from 250-275 °C and 1500-2500 psi air are listed in Table 5.1. All non-soil experiments had been conducted at or below 225 °C, but higher temperatures were required for appreciable reaction rates to occur. Figure 5.1 shows the concentration *versus* time data for these runs. It is important to notice that no induction period can be detected, but that an exponential decay starts from time zero. Induction periods may actually be occurring, but extrapolation of non-soil results indicates that they would only have durations of 2-10 minutes. It is impossible to distinguish such small times given the overall time scales considered in these experiments.

Table 5.1 Experimental Conditions and Model Results m-Xylene Tetrachloroethylene, and Malathion with Soil

T (°C)	P (psi)	m_2^0 (gm)	t_{start} (min)	k' (1/min)	O_2 (gm/ml)	k $(1/min)(ml/gm)^{0.5}$
			m-Xylene			
250	2000	0.0984	0.0	.000192	.001255	0.00542
260	2500	0.1107	0.0	.000394	.001789	0.00932
260	2500	0.1236	0.0	.000445	.001789	0.0105
275	1500	0.1176	0.0	.000654	.000744	0.0240
275	2500	0.1277	0.0	.00122	.001915	0.0279
			Tetrachloroethylene			
275	1500	0.1306	0.0	.000960	.000744	0.0352
275	2000	0.1216	0.0	.00155	.001330	0.0425
290	1500	0.1554	0.0	.00130	.000580	0.0540
290	2000	0.1375	0.0	.00154	.001273	0.0432
			Malathion			
130	1500	0.1850	0.0	-	.000544	-
130	2000	0.1841	0.0	-	.000730	-
160	1500	0.1858	0.0	-	.000606	-
160	2000	0.1845	0.0	-	.000821	-

Very easy to distinguish, however, are the dramatic reductions in the active reaction rates. Extrapolation using the chapter four Arrhenius results for initiated and uninitiated m-xylene indicates that reaction half-lives of 0.6-2 minutes would be expected if no soil were present. Instead, reaction half-lives of 700-3000 minutes are observed. Explanations for this behavior will be given in the results and discussion section below.

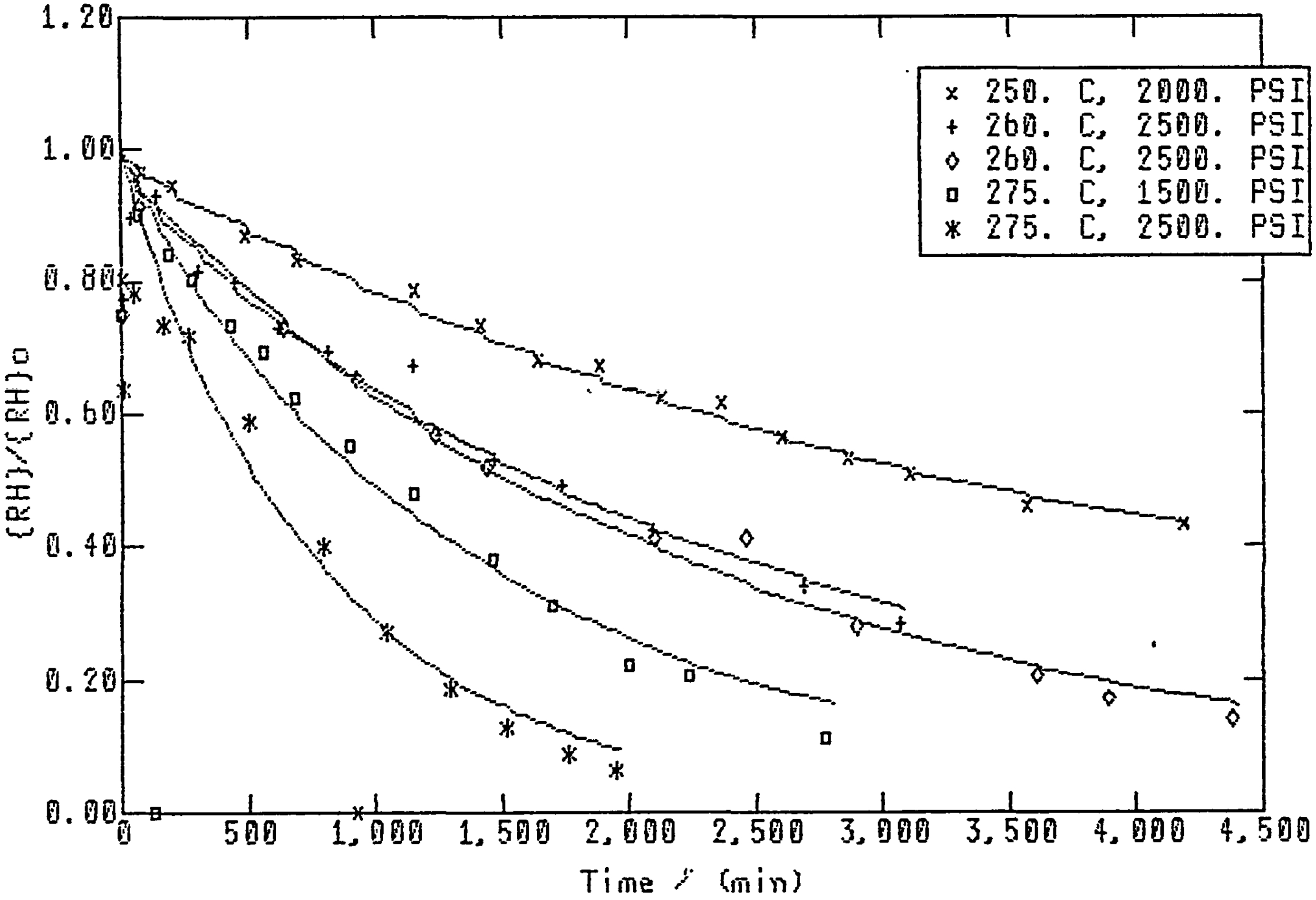


Figure 5.1 Experimental Data and Model Curves for m-Xylene/Soil Runs

Tetrachloroethylene

Four experiments were conducted with about 0.13 grams of tetrachloroethylene in the presence of soil. Two temperatures, 275 and 290 °C, and two pressures, 1500 and 2000 psi air, were used as shown in Table 5.1. The concentration histories for these runs are shown in Figure 5.2 and display behavior quite similar to the non-soil tetrachloroethylene experiments. Extrapolating chapter three non-soil results, reaction half-lives of 300-700 minutes would be expected at these conditions and, in fact, the soil results fall essentially within this range. In neither case were induction periods detectable. It is interesting to observe that at comparable reaction conditions, tetrachloroethylene now reacts faster than m-xylene.

Malathion

Four runs using about 0.18 grams of malathion with soil were performed at conditions ranging from 130-160 °C and 1500-2000 psi air. No malathion could be detected in any of the samples drawn from the reactor, indicating that all malathion had reacted in less than five minutes (the time of the first sample). This is identical to the non-soil findings of chapter three. As discussed there, this behavior is attributed to the belief that malathion quickly hydrolyzes rather than oxidizes. Only reaction product peaks which increased and subsequently either decreased or attained a steady state concentration were recorded on the GC chromatograms. No attempt was made to identify these peaks other than to determine that they were significantly different from the malathion retention time obtained during calibration.

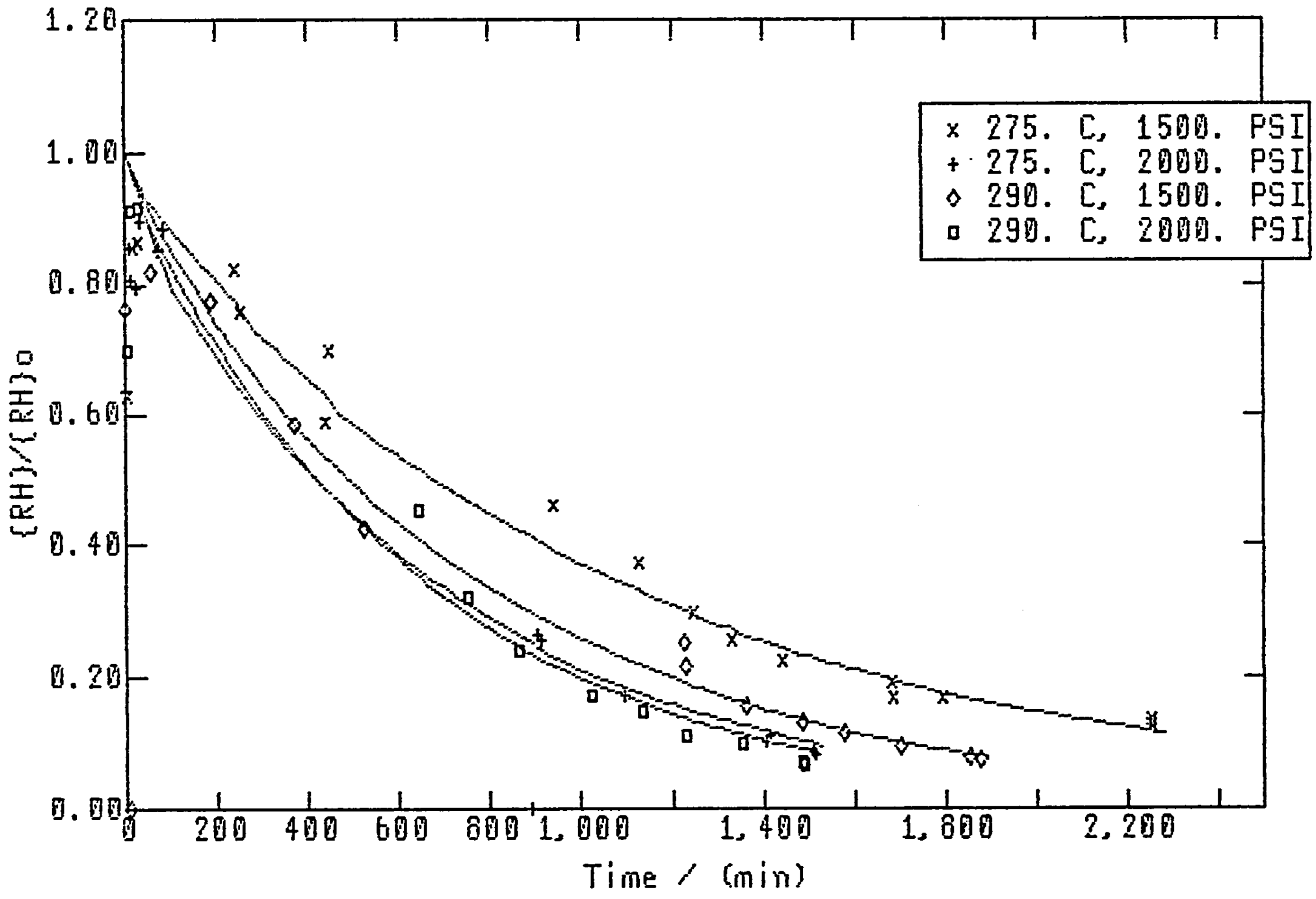


Figure 5.2 Experimental Data and Model Curves for Tetrachloroethylene/Soil Runs

RESULTS AND DISCUSSION

The chapter two mathematical model has been applied to the m-xylene and tetrachloroethylene data. It should be noted that the model was developed for two phase systems (liquid and vapor), but now an additional phase, soil, has been introduced. The model does not account for organic which may be adsorbed on soil surfaces. Based on the elevated temperatures and relatively low surface areas of soils (compared to solids such as activated carbon), it was not believed that significant amounts of adsorption were occurring. Extraction tests performed on the soil after each experiment provided evidence to support this belief. After each experiment the soil was recovered and refluxed for two hours in hexane. GC analysis indicated that only trace quantities of m-xylene and no tetrachloroethylene remained on the soil surfaces.

The value of t_{start} for both compounds was assumed to be zero, and the model regression was used to obtain values of k' and m_2^0. These values along with the oxygen concentration and k are listed in Table 5.1. It was assumed that reaction rates were 1/2 order in oxygen to calculate k. As previously shown in chapter three and confirmed below for these data, this assumption collapsed all rate constants collected at various pressures onto one Arrhenius line. The assumption of first order kinetics with respect to organic concentration was confirmed by observing the agreement between the experimental data and model lines in Figures 5.1 and 5.2. The m-xylene and tetrachloroethylene findings will now be discussed individually.

m-Xylene

The m-xylene rate constants could be correlated quite well with an Arrhenius plot as shown in the lower left corner of Figure 5.3. For comparison purposes non-soil m-xylene results from chapters three and four are included on this plot (both unenhanced and hydrogen peroxide enhanced data are shown since hydrogen peroxide did not affect reaction rates). Using the least squares line through the m-xylene/soil data, an activation energy of 37.4 +/- 8.7 kcal/mole was determined (confidence limits are at the 95% level). The preexponential is 2.79×10^{13} $(1/min)(ml/gm)^{0.5}$. The activation energy is significantly higher than the non-soil value of 24.2 +/- 2.0 kcal/mole reported in chapter four.

As noted earlier, the most important feature of these data is the dramatic reduction in reaction rates. The enhancement number, $k_{soil}/k_{non-soil}$, indicates that over three orders of magnitude of rate reduction has occurred. Possible explanations for this behavior are based on the reaction mechanism presented in chapter three. In addition to the one chain termination step shown there, the radical + soil interaction (similar to a radical + wall interaction) is now believed to be contributing to the chain termination. Soil is present in sufficient concentrations and this new reaction presumably has an appreciable rate constant. Thus, the radical + soil termination reaction is expected to proceed at a significant rate, producing the observed result of a drastic reduction in the rate of organic disappearance.

Tetrachloroethylene

Figure 5.4 shows an Arrhenius plot of both the soil and non-soil tetrachloroethylene results. In sharp contrast to the m-xylene

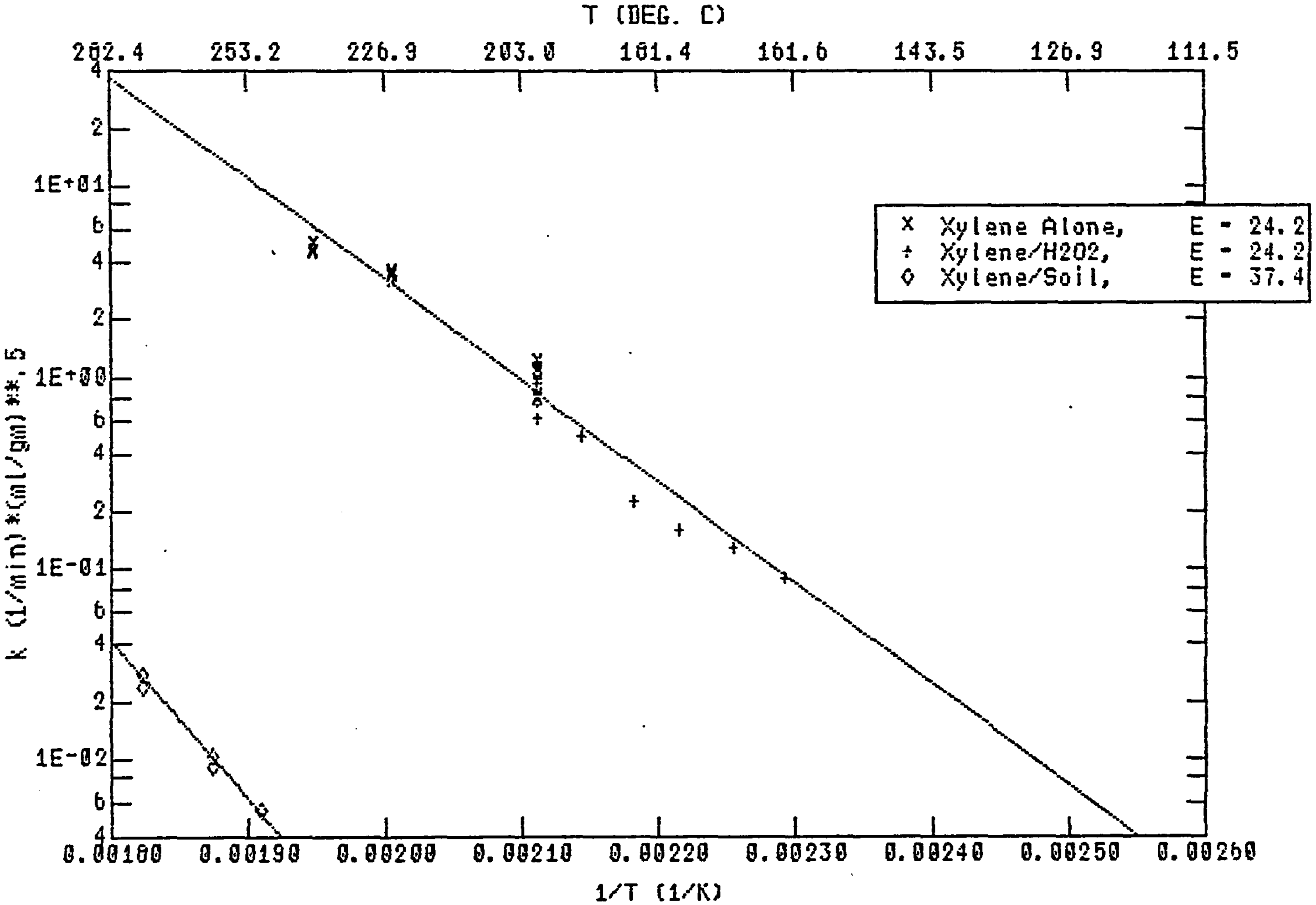


Figure 5.3 Rapid Reaction Arrhenius Plot for m-Xylene Alone, with H2O2, and with Soil

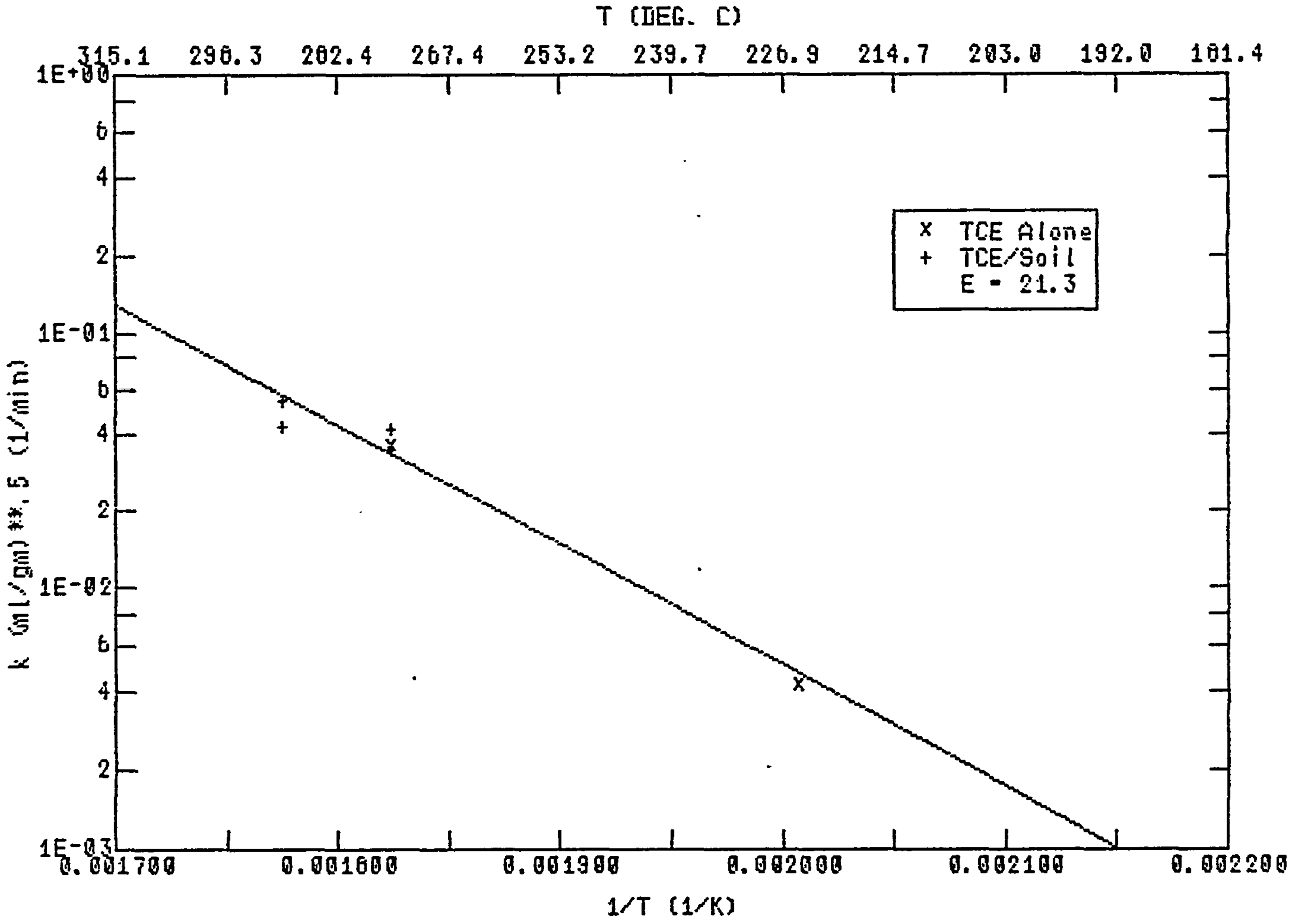


Figure 5.4 Rapid Reaction Arrhenius Plot for Tetrachloroethylene Alone and with Soil

findings, it is observed that the presence of soil has negligible influence on the tetrachloroethylene reaction rates. The activation energy based on these combined data is 21.3 +/- 5.5 kcal/mole. Undoubtedly this is a more reliable value than the one presented in chapter three based on just two data points. The preexponential is 1.09 x 10^7 $(1/min)(ml/gm)^{0.5}$.

The fact that tetrachloroethylene is not affected by the presence of soil is not altogether surprising. It was concluded in chapter three that though tetrachloroethylene may react according to a free radical mechanism, it was somewhat different from the scheme presented there. These tetrachloroethylene/soil results serve as a confirmation of this conclusion.

APPLICATION

With or without soil, the treatment of tetrachloroethylene by aqueous phase oxidation appears to be infeasible due to its slow reaction rates. On first inspection, the even slower reaction rates occurring in the m-xylene/soil system seem to indicate that aqueous phase oxidation is also an unreasonable technique for treating m-xylene contaminated soils. However, a quite feasible design might be to use a two stage process. The first stage would accomplish an extraction of the organic from the soil into the aqueous phase. This aqueous phase would then be routed to a reactor where the organic destruction would occur at the much more favorable non-soil reaction rates (assuming that soluble components of the soil are not effective inhibitors). A semi-batch process is envisioned with water being continuously circulated between a heated and agitated reactor (either impeller agitated or bubble column) and a soil-filled extraction column. More than one extraction column could be used with each column cycling through soil loading, extraction, and dumping. In this way the reactor could be operated continuously since at least one extractor would always be in its extraction phase. Minimal energy would be required to maintain the reactor at setpoint temperature except immediately after a new extractor was put on-line. The heats of reaction of the contaminants would help to minimize energy requirements.

SUMMARY

Experimental results have been shown for the aqueous phase oxidation of m-xylene, tetrachloroethylene, and malathion in the presence of soil. For m-xylene the addition of soil causes about three orders of magnitude of rate reduction, possibly because of enhanced free radical chain termination attributable to the soil. Tetrachloroethylene, on the other hand, was not affected by the presence of soil presumably because it follows a reaction mechanism somewhat different from that followed by m-xylene. Believed to hydrolyze rather than oxidize, malathion disappeared before the first sample could be taken.

Neither m-xylene nor tetrachloroethylene showed an induction period. Both displayed global disappearance kinetics which were 1/2 order in oxygen and first order in organic. The kinetics are summarized as follows.

m-Xylene

Induction Phase

None

Active Phase

$$d[RH]/dt = k\ [O_2]^{0.5}[RH]^1$$

$$k = 2.79 \times 10^{13}\exp(-37400/RT)$$

First order in organic shown
Half order in oxygen shown

Tetrachloroethylene

Induction Phase

None

Active Phase

$$d[RH]/dt = k\ [O_2]^{0.5}[RH]^1$$

$$k = 1.09 \times 10^{7}\ \exp(-21300/RT)$$

First order in organic shown
Half order in oxygen shown

Malathion

Induction Phase

None

Active Phase

Hydrolyzes completely in less than five minutes

CHAPTER 6

CONCLUSIONS AND PROJECTIONS

> "Graduate students traditionally hide their most radical statements in footnotes and appendices, where they can be disavowed if necessary."
>
> -- R. P. Crease and C. C. Mann
> "How the Universe Works"

INTRODUCTION

This chapter has been written in the spirit of Crease and Mann's "footnotes and appendices". The composition of each preceding chapter has been constrained by a sense of scientific responsibility which only allows statements of fact to appear on paper. To the best of the author's knowledge, all conclusions, claims, and assumptions to this point are valid. A restatement of such information (which is summarized at the end of each preceding chapter) seems tiresome to both reader and writer. The concluding paragraphs of this document are intended, rather, to project what might be true and to propose directions for future investigations. To provide at least some sense of structure, selected major chapter divisions will serve to categorize the following remarks.

EXPERIMENTAL APPARATUS AND MATHEMATICAL MODEL

Experimental Apparatus

The sampled batch reactor has served aqueous phase oxidation researchers rather well to this point. Though it will certainly continue its utility, the stopped flow reactor shows great promise as an experimental apparatus. To date, only Devlin and Harris (1984) have used this technique for collecting aqueous phase oxidation data. The ease by which concentration histories of numerous compounds can be monitored with such a simple apparatus indicates that it will be the method of choice in many future investigations.

Mathematical Model

The model used in this investigation is reasonable considering the current state of the art and may be more than adequate for many application purposes. Mass transfer will have to be included in the model for cases where it is important. The most drastic improvements will be made, however, when mechanistic steps and rate constants are identified. As was shown in Figure 3.16, the mechanism simulation displays concentration behavior which represents real data more accurately. Also, if the oxidation of reaction intermediates can be included in such a model, even the "tailing" at the end of some m-xylene experiments may become apparent in the model as well as the data.

INTRINSIC RATE DATA FOR SELECTED ORGANICS

Relevant Literature

At the beginning of his graduate research, this author began reading articles such as one published in Environmental Science and Technology in 1975 entitled, "Wet Air Oxidation Comes of Age". From titles such as this, it appeared that wet air oxidation must be a well developed technology which had reached its full industrial potential. As study of the literature continued, however, it became apparent that little more than scientific tinkering had been applied toward understanding the process. Components of "catalysts" were appearing as major reaction products, pressures were assumed constant though falling drastically, and one publication by the "experts" appeared practically unaltered in numerous journals and proceedings. Certainly there are a few well conducted investigations of aqueous phase oxidation, but not a sufficient number to consider it to have "come of age". It is hoped that future research will exercise greater care in both the experimental and data analysis phases.

Pure Component Results

A variety of questions remain unanswered concerning the simplest aqueous phase oxidation reaction system--water, air, and one organic. The most basic of these is, of course, the rate of disappearance of the parent organic. The studies listed in Table 3.2 and this work have begun this effort, but the database of information must be expanded before broader generalities and predictive theories can be promulgated.

Key to development of these theories will be studies of reaction products. Sadana and Katzer (1974), Baillod and Faith (1983), and especially Devlin and Harris (1984) as well as the large body of information on liquid phase oxidation (non-aqueous) provide a foundation for studies of this type. The aromatic ring opening, in particular, is a reaction pathway step that is interesting, potentially rate limiting, and not well understood. Studies of this type would confirm or deny suspicions that reaction products more toxic than the parent compounds are generated.

On an even more basic level, the underlying, mostly free radical mechanistic steps need elucidation. Though prevalent for liquid phase oxidations, investigations of this type are essentially nonexistent with aqueous solvent. Undoubtedly these mechanisms will be heavily dependant on hydroperoxides as intermediates as argued in chapter three. Exceptions to the general mechanism given in chapter three have already been identified as in the tetrachloroethylene case. Mechanistic steps must be postulated and verified, and values determined for their rate constants.

Regardless of how incomplete they may be, Benson and others have already developed frameworks for predicting gas phase reaction rate constants. It seems that aqueous phase mechanisms should be much less complicated than those occurring for gas phase reactions where higher temperatures make the existence of myriads of radicals possible. Nonetheless, the development of predictive techniques for aqueous phase rate constants has not moved past the germination stage.

A series of experiments which would contribute to this understanding would be to use one base compound (benzene, hexane, etc.) with various functional groups attached to the parent organic. The effects of these different substitutions could lead to "group contribution" relationships. This would at least indicate general trends of reactivities which untested compounds would be expected to exhibit.

Other questions of interest relate to the reaction behavior in the near supercritical region. Do rates increase or decrease when moving from sub- to supercritical conditions? It is not expected that the Arrhenius equation would hold in this region, but whatever the functional relationship between k and T, is it all points differentiable or discontinuous?

REACTION RATE ENHANCEMENT

Catalysis

The degree of rate enhancement reported in catalytic studies is disappointing, since rates were only increased by factors of two to three. Homogeneous catalysis holds little promise of practical utility since, not only were the rates only marginally increased, but the catalyst will also have to be separated from the waste after oxidation. Heterogeneous catalysis is the more likely of the two to actually find practical utility.

Initiation

The greatest utility of the initiation findings are as process stabilization aids, as alluded to in chapter four. Therein, it was proposed that this technique could be used to quickly destroy unusual "slugs" of material. This usage would be an overlap of two of the hazardous waste destruction techniques outlined in chapter one--chemical oxidation and aqueous phase oxidation. Chemicals which act as initiators would be the proper ones to use in this regard since they would result in more than stoichiometric oxidation. In other words, for each radical that is added (assuming it is not consumed by a termination reaction), one propagation chain will be initiated. If the chain length is 10, then 10 organic molecules will be consumed as a result of adding one radical.

It is unclear how such addition would affect product distributions. If hydrogen peroxide were used as an initiator, product distributions would not be expected to be much different than uninitiated results since HO• radicals are likely to be present in either case. If cumene hydroperoxide were added, though, cumene dimers almost certainly would occur, at least initially. Because of this and its relatively low cost, hydrogen peroxide is recommended as the most reasonable initiator.

No work has been done with initiators in conjunction with such compounds as tetrachloroethylene. It was observed that soil did not inhibit tetrachloroethylene oxidation; it would be interesting to determine if an initiator enhances it.

The "critical" amount of initiator which just eliminates the induction period as discussed in chapter four may provide useful information for mechanism research.

Lastly, it should be noted that the topic of initiation can be considered a special, yet extreme case of synergism.

Synergism

This topic is one of the most intriguing ones dealt with in this research. Very substantial m-xylene rate enhancement was attainable by "synergizing" it with a common waste component, phenol.

Equation 4.3 defines the residence time required to reduce the concentration of component i from its initial value to some target or final value. If pseudo first order kinetics are followed, this integration would be straightforward except for En_i. En_i is certainly a function of $[RH_j]$, and without this functional relationship, integration cannot be performed. As a crude first approximation, it can be assumed that En_i is constant at its initial conditions. In this case integration gives

$$t_{rt,i} = (1/En_i k'_i) \ln([RH_i]_f/[RH_i]_0) \ . \tag{6.1}$$

Now, consider a simple aqueous waste containing only one organic which is to be destroyed by aqueous phase oxidation. This organic will be referred to as component 2. A faster reacting component 3 is to be added to the system to enhance the reaction rate of component 2, and thus, reduce the reactor residence time. If too much component 3 is added, then this added component will, itself, become the problem waste compound and determine the required residence time. The minimum reactor residence time would occur when both compounds leave the reactor at their specified final concentration (<u>e.g.</u> the concentration set by EPA regulations). This would occur when

$$t_{rt,2} = t_{rt,3} \ . \tag{6.2}$$

Equation 6.1 can be substituted into 6.2 and solved for $[RH_3]_0$ to give

$$[RH_3]_0 = [RH_3]_f \left[\frac{[RH_2]_0}{[RH_2]_f} \right]^{(En_{3,0}k'_3/En_{2,0}k'_2)} \ . \tag{6.3}$$

A trial and error process must now be applied. First $[RH_3]_0$ is guessed so that values for $En_{2,0}$ and $En_{3,0}$ can be determined. Using these values in equation 6.3, a new value of $[RH_3]_0$ is calculated. If this agrees with the guessed value, the calculations are concluded. If they do not match, others values must be guessed and the calculations repeated until convergence.

The problem with this simplified analysis is, of course, that En_i has been held constant at $En_{i,0}$ which is not necessarily true over the range of integration. A better approach is to determine the actual relationship between En_i and $[RH_j]$. As a first step consider the limits of En_i at the two concentration extremes. It is immediately obvious that

$$\lim_{X_i \to 1} En_i = 1 . \tag{6.4}$$

For a binary mixture at least an educated guess can be made for the other extreme of fractional concentration equal to zero. In this case only a few molecules of component 2 are present with large quantities of component 3. Component 3 will react just as though no component 2 is present. Furthermore (and more importantly), cross-initiation will cause component 2 to be "swept along" at a reaction rate equal to that of component 3. Thus,

$$\lim_{X_2 \to 0} k_2^s = k_3 \qquad \text{(binary only)} \tag{6.5}$$

and

$$\lim_{X_2 \to 0} En_2 = k_3/k_2 . \qquad \text{(binary only)} \tag{6.6}$$

To test this postulation a semi-log plot of En_i for both m-xylene and phenol versus fractional concentration of m-xylene was constructed, and is shown in Figure 6.1. The Arrhenius parameters found in chapter four were used to obtain the necessary values of k. Points at the extreme concentrations were calculated according to the above defined limits. Points in between were determined from the usual definition of $En_i = k_i^s/k_i$. Though not conclusive, the points at the extremes do, in fact, appear to be the actual limits of the experimentally obtained values in the middle of the plot.

Now, as a first approximation to the relationship between fractional concentration and En_i, a straight line can be drawn between the two limits. (This could be considered analogous to drawing a straight line between zero and the saturation vapor pressure on a partial pressure versus liquid mole fraction plot, i.e. Raoult's Law). When experimental data actually fall on this straight line, the binary system is considered "ideal". The extreme practical utility of this approach is that only pure component data need be available for its use. Naturally, the danger exists that this ideal treatment may be far from reality. For the m-xylene/phenol binary shown in Figure 6.1, the experimental data for both compounds fall above what would be considered ideal, but not too badly. Thus, the equation for this straight line could be determined and substituted into equation 4.3. Then, using equation 6.2, the optimal initial concentration of rate enhancer could be determined. The completely accurate solution could only be found by determining the

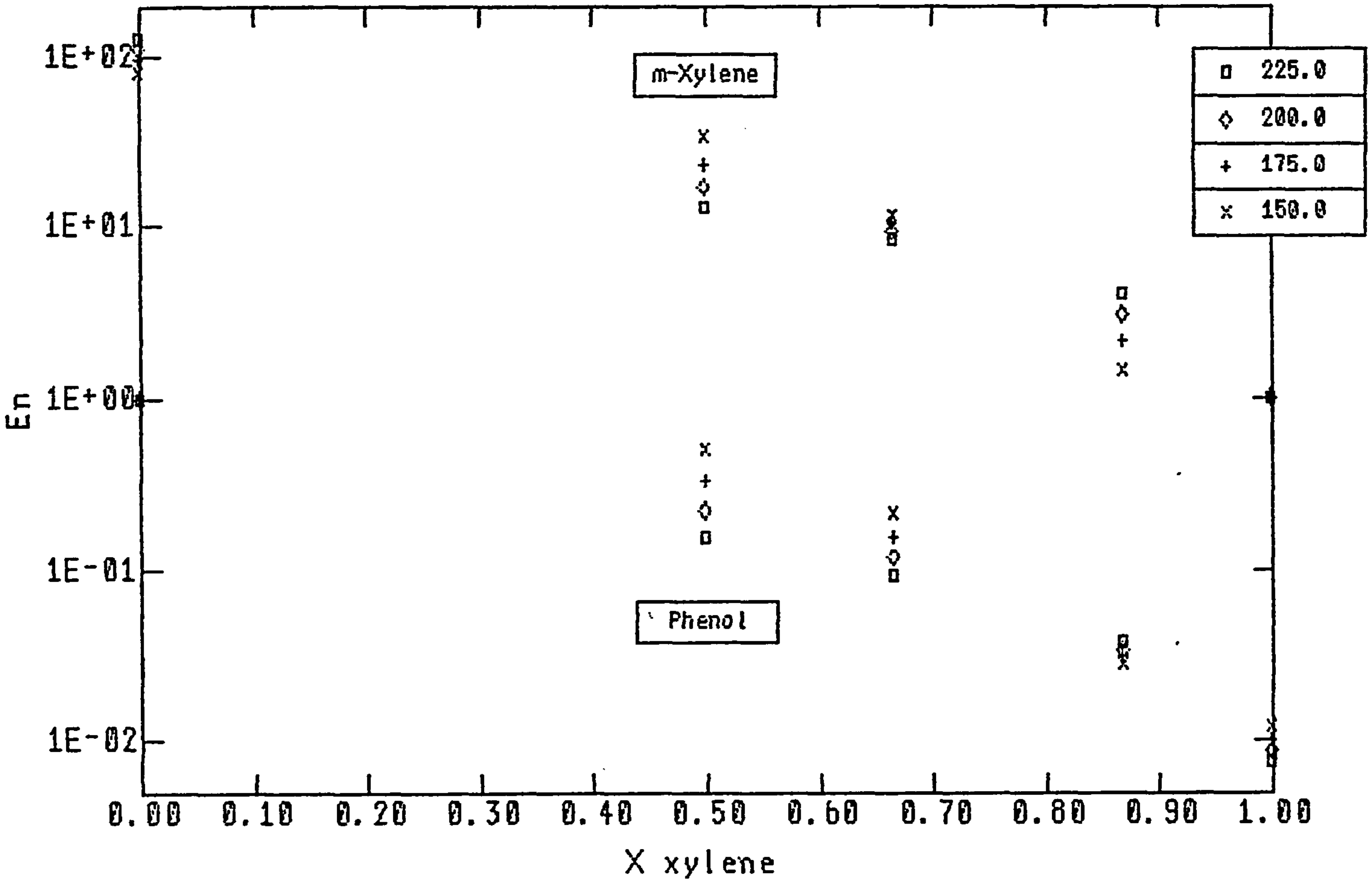


Figure 6.1 Enhancement Number for m-Xylene and Phenol versus m-Xylene Fractional Concentration

true functional relationship between En_i and fractional concentration, and substituting this into equation 4.3.

This topic is intriguing not only from this very practical application point of view, but also from a desire to understand the fundamentals of this interaction. If the mechanism steps of the individual components are known, it is only necessary to discover the important cross-initiation reactions to accurately model the synergism results. This would account for negative and positive synergism as identified in plots such as Figure 4.19.

Research on these, and related synergism topics are needed. How various types of compounds interact with one another will ultimately facilitate the prediction of the behavior of "chemical soups". It is believed that the full industrial potential of aqueous phase oxidation will never be realized without research of this nature.

EFFECTS OF SOIL

There are cases where literally cubic miles of contaminated soil must be cleaned-up. For cases such as this, even an increase in decontamination costs of a few cents per ton can cause budgetary nightmares. Since aqueous phase oxidation may be more economical than incineration (the current industrial standard), more research on this topic is needed.

This investigation has already established soil as a reaction inhibitor. It is unclear, however, which component of the soil is causing the inhibition--sand, silt, or clay. Further work using one component at a time is necessary to answer this question.

A two stage process of extraction followed by reaction was proposed in chapter five. This is expected to be a reasonable approach assuming that it is not a soluble portion of the soil which is causing the inhibition. Experimentation to verify this is needed.

SUMMARY

Aqueous phase oxidation has great industrial potential, but has met with only limited actual usefulness. At least part of this is attributed to the lack of a fundamental understanding of the physical and chemical nature of this technology. It is hoped that this and future research will provide the information necessary to accurately evaluate its utility.

NOMENCLATURE

English Symbols

A	Preexponential for the Arrhenius equation
a	Area of interface (length^2)
E	Activation energy (energy)
En	Enhancement number, defined in equation 4.1
H	Henry's law constant (pressure^{-1})
k	Intrinsic rate constant (time^{-1} $[O_2]^{-m}$)
k'	Pseudo first order rate constant (time^{-1})
m	Mass
MW	Molecular weight (mass mole^{-1})
P	Pressure
Pr	Reference pressure (vapor pressure of water)
p	Partial pressure
q	Flowrate (volume time^{-1})
r	Reaction rate (mass or mole volume^{-1} time^{-1})
R	Universal gas constant (energy mole^{-1} temperature^{-1})
RH	Organic
ROOH	Hydroperoxide
S	Stoichiometric ratio, <u>e.g.</u> moles O_2 reacting per mole of RH
Sy	Synergism number, defined in equation 4.2
t	Time

T	Temperature
V	Volume
X	Liquid phase fractional concentration, solvent free basis. In general, $X_i = [RH_i]/\Sigma[RH_j]$, $i \neq 1$, $j \neq 1$ For a binary, $X_2 = [RH_2]/([RH_2] + [RH_3])$
x	Liquid phase mole fraction
y	Gas phase mole fraction
[ ]	Concentration of the enclosed compound (mass or mole volume^{-1})
•	A radical

Greek Symbols

γ	ρ_0^L/ρ^L
μ	Micro
Π	[ROOH]/[RH]
ρ	Density (mass volume^{-1})
τ	A dimensionless time coordinate
ϕ	Defined in equation 2.13

Subscripts

0	At initial or previous conditions
1	Solvent (water) or reaction 1
2	Solute (organic) or reaction 2
3	Solute (organic) or reaction 3
crit	Critical
e	At exit conditions
f	Final
i	General component index

j	General component index
L	Liquid phase
out	Cumulative volume removed from the system
rt	Residence time
start	Beginning of active reaction period

Superscripts

0	At initial conditions
L	Liquid phase
m	Reaction order with respect to oxygen
max	Maximum
n	Reaction order with respect to organic
S	Sample
s	Synergism
T	Total, liquid and vapor phase
V	Vapor phase
*	At equilibrium or saturation conditions

Indices

i	Summation index
k	Total number of data points
m	Last datum point before the active reaction period
n	2k - m

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APPENDICES

APPENDIX A

Experimental Conditions and Data--Pure Components

This appendix contains experimental conditions and Concentration *versus* time data for m-xylene, phenol, tetrachloroethylene, and malathion. These experiments were summarized in Table 3.5, and are presented here in identical order.

```
                     Experiment: XYL-840920-1

 14 Total data points were collected
    13 Points were useful for processing
     1 Points were undefined

Run Characteristics:

    Set point temperature                   200. C
    Set point pressure                     2000. psi
    Initial liquid volume                   780. ml
    Mass of organic initially injected   0.1111 Grams
    Integrator start time               14.3657 hh.mmss
    Plot scale factor                      1.00
    Regression begin time                190.00 Minutes
    Regression end time                  250.00 Minutes


Data Summary:

Time of Day  Area     Temp  Vout  Elapsed Time      [RH]
  hh.mmss   /1.E+6     /F   /ml      /min       /(1.E-4 gm/ml)
----------- -------  ----  ----  ------------  --------------
  15.1259   4.43330  388.  10.0      36.03          0.5877
  15.4959   4.64020  392.  14.0      73.03          0.6132
  16.2959   4.46270  394.  21.0     113.03          0.5889
  17.4212   3.42050  393.  26.0     185.25          0.4517
  17.4912   2.83300  394.  32.0     192.25          0.3738
  18.0706   1.93300  394.  38.0     210.15          0.2551
  18.1331   1.48810  394.  46.0     216.57          0.1963
  18.2855   1.11600  394.  56.0     231.97          0.1472
  18.4407   0.81223  394.  65.0     247.17          0.1072
  19.0127   0.00000  394.  74.0     264.50          0.0000
  19.0556   0.58217  395.  79.0     268.98          0.0768
  20.4412   0.33797  391.  84.0     367.25          0.0447
  20.4907   0.29733  391.  89.0     372.17          0.0393
  20.5807   0.24015  391.  94.0     381.17          0.0318
```

```
                 Experiment: XYL-840921-1

 18 Total data points were collected
    16 Points were useful for processing
     2 Points were undefined

Run Characteristics:

    Set point temperature                200. C
    Set point pressure                  2000. psi
    Initial liquid volume                780. ml
    Mass of organic initially injected 0.1192 Grams
    Integrator start time             14.4303 hh.mmss
    Plot scale factor                    1.00
    Regression begin time              340.00 Minutes
    Regression end time                450.00 Minutes


Data Summary:

Time of Day  Area     Temp  Vout  Elapsed Time      [RH]
 hh.mmss    /1.E+6    /F    /ml      /min       /(1.E-4 gm/ml)
----------- -------  ----  ----  ------------  --------------
  15.0003   3.65070  393.   5.0      17.00         0.4821
  15.1004   4.37180  392.  10.0      27.02         0.5778
  15.3504   0.00000  391.  15.0      52.02         0.0000
  15.4004   4.63440  392.  20.0      57.02         0.6125
  16.0605   4.61370  393.  25.0      83.03         0.6093
  16.3807   4.48410  394.  30.0     115.07         0.5917
  17.0208   4.74850  393.  35.0     139.08         0.6270
  17.2309   4.55150  391.  40.0     160.10         0.6020
  18.1214   4.46150  390.  45.0     209.18         0.5906
  18.4910   4.44860  392.  50.0     246.12         0.5879
  19.2212   4.33010  392.  55.0     279.15         0.5723
  20.0505   0.00000  391.  60.0     322.03         0.0000
  20.2505   3.71170  392.  65.0     342.03         0.4905
  20.4650   2.76510  393.  70.0     363.78         0.3651
  21.1639   1.87570  393.  75.0     393.60         0.2477
  21.4939   1.19230  392.  80.0     426.60         0.1576
  23.4923   0.56634  391.  85.0     546.33         0.0749
  23.5323   0.54593  391.  90.0     550.33         0.0722
```

```
                    Experiment: XYL-840924-1

 10 Total data points were collected
    10 Points were useful for processing
     0 Points were undefined

Run Characteristics:

    Set point temperature                200.  C
    Set point pressure                  2000.  psi
    Initial liquid volume                780.  ml
    Mass of organic initially injected  0.1123 Grams
    Integrator start time              11.5948 hh.mmss
    Plot scale factor                    1.00
    Regression begin time              300.00 Minutes
    Regression end time                450.00 Minutes


Data Summary:

Time of Day  Area     Temp  Vout  Elapsed Time      [RH]
  hh.mmss   /1.E+6    /F   /ml       /min      /(1.E-4 gm/ml)
----------- -------  ----  ----  ------------  --------------
  12.3448   4.06120  390.  10.0      35.00          0.5376
  13.3503   4.63980  392.  15.0      95.25          0.6132
  14.3729   4.60300  393.  20.0     157.68          0.6078
  15.2330   4.65140  392.  25.0     203.70          0.6147
  16.2005   4.53310  391.  30.0     260.28          0.5996
  16.5305   4.45250  392.  35.0     293.28          0.5884
  17.2525   3.94190  393.  40.0     325.62          0.5205
  17.5113   2.63680  393.  45.0     351.42          0.3482
  18.4619   1.18070  392.  50.0     406.52          0.1560
  22.2828   0.49168  392.  55.0     628.67          0.0650
```

```
                    Experiment: XYL-850319-1

 21 Total data points were collected
    21 Points were useful for processing
     0 Points were undefined

Run Characteristics:

    Set point temperature                   200. C
    Set point pressure                     2000. psi
    Initial liquid volume                   780. ml
    Mass of organic initially injected    0.1105 Grams
    Integrator start time                21.0846 hh.mmss
    Plot scale factor                       2.00
    Regression begin time                 180.00 Minutes
    Regression end time                   265.00 Minutes


Data Summary:

Time of Day  Area    Temp  Vout  Elapsed Time      [RH]
  hh.mmss   /1.E+6    /F   /ml      /min       /(1.E-4 gm/ml)
----------- ------- ----  ----  ------------  --------------
  21.1147   6.26640 383.   5.0          3.02          0.6342
  21.2947   7.23430 391.  10.0         21.02          0.7277
  21.4546   7.11320 391.  15.0         37.00          0.7155
  22.0146   6.94730 392.  20.0         53.00          0.6982
  22.2047   6.99860 392.  25.0         72.02          0.7034
  22.4647   7.14040 390.  30.0         98.02          0.7188
  23.1748   6.72290 391.  35.0        129.04          0.6762
  23.4148   6.20130 392.  40.0        153.03          0.6233
  23.5248   5.21240 392.  45.0        164.03          0.5239
  24.0348   4.83870 392.  50.0        175.04          0.4863
  24.0948   3.86040 393.  55.0        181.03          0.3877
  24.1849   3.35400 393.  60.0        190.05          0.3368
  24.2349   2.93280 394.  65.0        195.05          0.2943
  24.2849   2.49800 394.  70.0        200.05          0.2507
  24.3349   2.37290 394.  75.0        205.05          0.2381
  24.3949   1.99420 394.  80.0        211.05          0.2001
  24.4649   1.82940 394.  85.0        218.05          0.1836
  24.5450   1.50410 394.  90.0        226.07          0.1509
  25.0550   1.27150 393.  95.0        237.07          0.1277
  25.1650   1.07830 393. 100.0        248.07          0.1083
  25.3051   0.91701 393. 105.0        262.08          0.0921
```

```
                     Experiment: XYL-840421-1

 39 Total data points were collected
    37 Points were useful for processing
     2 Points were undefined

Run Characteristics:

    Set point temperature                 225. C
    Set point pressure                   1000. psi
    Initial liquid volume                 744. ml
    Mass of organic initially injected  0.1116 Grams
    Integrator start time              10.2849 hh.mmss
    Plot scale factor                     1.00
    Regression begin time               185.00 Minutes
    Regression end time                 220.00 Minutes


Data Summary:

Time of Day  Area     Temp  Vout  Elapsed Time      [RH]
  hh.mmss   /1.E+6    /F   /ml      /min       /(1.E-4 gm/ml)
----------- -------  ----  ----  ------------  --------------
  10.3259   5.74490  436.   5.0       4.17         0.7314
  10.3759   6.83000  435.   9.5       9.17         0.8703
  10.4259   6.85450  436.  14.9      14.17         0.8726
  10.4959   6.79040  436.  20.1      21.17         0.8645
  10.5459   6.73530  436.  25.9      26.17         0.8575
  11.0000   6.68910  436.  31.4      31.18         0.8516
  11.0459   6.54490  437.  36.6      36.17         0.8325
  11.1000   6.47430  438.  41.8      41.18         0.8227
  11.1500   6.43210  438.  46.8      46.85         0.8174
  11.2000   6.32020  438.  51.1      51.85         0.8031
  11.2500   6.20310  439.  56.4      56.18         0.7875
  11.3100   6.23260  439.  61.6      62.18         0.7913
  11.3700   6.13230  440.  66.6      68.85         0.7778
  11.4200   6.02920  439.  71.7      73.18         0.7655
  11.4901   5.94950  439.  77.1      80.20         0.7553
  11.5501   5.92430  440.  82.3      86.20         0.7515
  12.0101   5.73740  439.  87.6      92.20         0.7284
  12.0901   5.74820  439.  92.7     100.20         0.7298
  12.2001   5.55380  440.  98.3     111.20         0.7045
  12.2801   5.42100  442. 103.5     119.20         0.6863
  12.4001   5.47690  441. 108.7     131.20         0.6941
  12.5001   5.29530  441. 113.1     141.20         0.6711
  13.0002   0.00000  441. 118.3     151.22         0.0000
  13.1002   5.15850  441. 123.4     161.22         0.6537
  13.2502   4.81030  441. 128.8     176.22         0.6096
  13.3503   4.20720  442. 134.1     186.23         0.5327
  13.4503   3.12000  443. 139.2     196.23         0.3946
  13.4903   2.59180  443. 144.1     200.23         0.3278
  13.5303   2.20820  442. 149.1     204.23         0.2796
```

13.5703	0.00000	442.	154.2	208.23	0.0000
14.0103	1.57490	443.	159.2	212.23	0.1992
14.0506	1.34870	444.	165.1	216.28	0.1704
14.0903	1.13600	444.	170.1	220.23	0.1436
14.1303	0.92020	444.	175.2	224.23	0.1163
14.1703	0.84682	444.	180.3	228.23	0.1070
14.2203	0.74315	444.	185.4	233.23	0.0939
14.2603	0.66381	445.	190.4	237.23	0.0838
14.3003	0.59258	444.	195.5	241.23	0.0749
14.3403	0.53832	445.	200.8	245.23	0.0680

```
                    Experiment: XYL-840422-1

 28 Total data points were collected
    27 Points were useful for processing
     1 Points were undefined

Run Characteristics:

    Set point temperature                       225. C
    Set point pressure                         1000. psi
    Initial liquid volume                       780. ml
    Mass of organic initially injected       0.1104 Grams
    Integrator start time                   10.3746 hh.mmss
    Plot scale factor                          1.00
    Regression begin time                    160.00 Minutes
    Regression end time                      200.00 Minutes


Data Summary:

Time of Day  Area     Temp  Vout  Elapsed Time       [RH]
  hh.mmss   /1.E+6    /F   /ml      /min        /(1.E-4 gm/ml)
----------- -------  ----  ----  ------------  --------------
  10.4107   6.55460  427.   6.0         3.35          0.8412
  10.4557   7.43550  429.  10.0         8.18          0.9526
  10.5057   7.42900  431.  15.0        13.18          0.9501
  11.0557   7.46710  434.  20.0        28.18          0.9524
  11.2057   7.29950  434.  26.0        43.18          0.9310
  11.3558   7.20450  435.  31.0        58.20          0.9180
  11.5058   7.07140  435.  37.0        73.20          0.9011
  12.0558   6.99480  436.  42.0        88.20          0.8905
  12.2058   6.83740  436.  48.0       103.20          0.8705
  12.3558   6.50280  437.  53.0       118.20          0.8271
  12.5058   6.71170  437.  59.0       133.20          0.8537
  13.0559   6.09560  438.  65.0       148.22          0.7746
  13.1059   5.73650  438.  70.0       153.22          0.7290
  13.1559   5.18400  438.  75.0       158.22          0.6588
  13.2059   4.56380  438.  81.0       163.22          0.5799
  13.2559   3.71980  438.  86.0       168.22          0.4727
  13.3059   2.87870  439.  91.0       173.22          0.3655
  13.3559   2.25230  438.  97.0       178.22          0.2862
  13.4059   1.73370  439. 102.0       183.22          0.2201
  13.4559   1.34730  441. 107.0       188.22          0.1707
  13.5059   0.00000  441. 113.0       193.22          0.0000
  13.5559   0.88829  441. 118.0       198.22          0.1126
  14.0059   0.70127  441. 123.0       203.22          0.0889
  14.0559   0.59924  442. 128.0       208.22          0.0759
  14.1059   0.51131  441. 133.0       213.22          0.0648
  14.1559   0.48630  442. 138.0       218.22          0.0616
  14.2059   0.38030  442. 143.0       223.22          0.0481
  14.2559   0.34045  442. 148.0       228.22          0.0431
```

```
                    Experiment: XYL-840411-1

 21 Total data points were collected
    20 Points were useful for processing
     1 Points were undefined

Run Characteristics:

    Set point temperature                   225. C
    Set point pressure                     1500. psi
    Initial liquid volume                   780. ml
    Mass of organic initially injected   0.1111 Grams
    Integrator start time               14.1833 hh.mmss
    Plot scale factor                      1.00
    Regression begin time                 60.00 Minutes
    Regression end time                   86.00 Minutes


Data Summary:

Time of Day  Area    Temp  Vout  Elapsed Time      [RH]
  hh.mmss   /1.E+6    /F   /ml       /min      /(1.E-4 gm/ml)
----------- ------- ---- ---- ------------ --------------
  14.2233   6.82700 431.  11.0      4.00         0.8731
  14.3033   0.00000 434.  21.0     12.00         0.0000
  14.3834   6.82700 435.  25.0     20.02         0.8699
  14.5033   6.68000 436.  30.0     32.00         0.8504
  14.5948   6.17330 437.  34.8     41.25         0.7852
  15.0434   6.16400 436.  39.6     46.02         0.7847
  15.0933   5.98700 437.  44.4     51.00         0.7615
  15.1333   5.61260 438.  49.3     55.00         0.7132
  15.1933   4.66400 439.  54.0     61.00         0.5921
  15.2433   3.47300 438.  59.2     66.00         0.4413
  15.2833   2.50180 439.  64.4     70.00         0.3176
  15.3233   1.89260 438.  69.4     74.00         0.2405
  15.3634   1.48000 439.  74.7     78.02         0.1879
  15.4034   1.16580 440.  79.9     82.02         0.1479
  15.4434   0.88466 439.  85.2     86.02         0.1123
  15.4834   0.70617 439.  90.4     90.02         0.0896
  15.5234   0.60532 438.  95.6     94.02         0.0769
  15.5634   0.50379 438. 100.6     98.02         0.0640
  16.0034   0.42895 438. 105.8    102.02         0.0545
  16.0434   0.36148 438. 110.8    106.02         0.0459
  16.1034   0.33415 439. 115.0    112.02         0.0424
```

```
                    Experiment: XYL-840412-1

 19 Total data points were collected
    19 Points were useful for processing
     0 Points were undefined

Run Characteristics:

    Set point temperature                     225. C
    Set point pressure                       1500. psi
    Initial liquid volume                     780. ml
    Mass of organic initially injected      0.1067 Grams
    Integrator start time                  10.1307 hh.mmss
    Plot scale factor                         1.00
    Regression begin time                    62.00 Minutes
    Regression end time                      84.00 Minutes


Data Summary:

Time of Day  Area    Temp  Vout  Elapsed Time       [RH]
  hh.mmss   /1.E+6    /F   /ml      /min        /(1.E-4 gm/ml)
----------- -------- ----  ----  ------------   --------------
  10.1717   4.66370  429.   4.6        4.17          0.5975
  10.3408   5.76440  437.   9.4       21.02          0.7332
  10.4108   5.86100  434.  14.4       28.02          0.7475
  10.4710   5.76790  435.  19.3       34.05          0.7350
  10.5308   5.63960  436.  24.3       40.02          0.7180
  10.5808   5.53440  436.  29.3       45.02          0.7046
  11.0508   5.31590  437.  34.4       52.02          0.6761
  11.1008   4.96480  437.  39.5       57.02          0.6315
  11.1408   4.36110  437.  44.6       61.02          0.5547
  11.1908   3.39400  438.  49.6       66.02          0.4313
  11.2408   2.56450  439.  54.6       71.02          0.3256
  11.2908   1.73960  439.  59.6       76.02          0.2209
  11.3609   1.10640  439.  64.6       83.03          0.1405
  11.4009   0.86449  440.  69.7       87.03          0.1097
  11.4309   0.76315  440.  74.3       90.03          0.0968
  11.4709   0.67355  439.  78.7       94.03          0.0855
  11.5115   0.55144  439.  83.5       98.13          0.0700
  11.5515   0.43029  438.  88.5      102.13          0.0547
  11.5915   0.38764  438.  93.5      106.13          0.0493
```

```
                    Experiment: XYL-840409-1

 37 Total data points were collected
    36 Points were useful for processing
     1 Points were undefined

Run Characteristics:

    Set point temperature                   225. C
    Set point pressure                     2000. psi
    Initial liquid volume                   780. ml
    Mass of organic initially injected    0.1160 Grams
    Integrator start time                15.2048 hh.mmss
    Plot scale factor                       1.00
    Regression begin time                 155.00 Minutes
    Regression end time                   190.00 Minutes


Data Summary:

Time of Day  Area    Temp  Vout  Elapsed Time       [RH]
  hh.mmss   /1.E+6    /F   /ml       /min      /(1.E-4 gm/ml)
----------- ------- ---- ----  ------------  --------------
  15.2348   0.00000 430.   5.0        3.00        0.0000
  15.2848   6.36240 432.  10.5        8.00        0.8129
  15.3348   6.54620 433.  18.0       13.00        0.8357
  15.3848   6.32540 434.  23.0       18.00        0.8067
  15.4449   6.24580 435.  28.0       24.02        0.7959
  15.5049   6.08050 436.  33.0       30.02        0.7741
  15.5648   6.02890 437.  38.0       36.00        0.7668
  16.0149   5.97240 438.  43.0       41.02        0.7589
  16.0749   6.18260 439.  48.0       47.02        0.7849
  16.1249   6.33900 439.  53.0       52.02        0.8048
  16.1749   5.79770 439.  56.0       57.02        0.7361
  16.2249   5.68920 440.  60.0       62.02        0.7216
  16.2749   5.60850 438.  65.0       67.02        0.7127
  16.3250   5.53640 438.  69.0       72.03        0.7035
  16.3750   5.44060 437.  73.0       77.03        0.6920
  16.4250   5.22820 437.  78.0       82.03        0.6650
  16.4750   5.24410 435.  82.0       87.03        0.6682
  16.5250   5.09930 437.  87.0       92.03        0.6486
  16.5850   5.06130 437.  91.0       98.03        0.6438
  17.0450   5.11690 437.  94.0      104.03        0.6508
  17.1050   4.94230 438. 101.0      110.03        0.6281
  17.1850   4.77570 437. 107.0      118.03        0.6074
  17.2451   4.61890 437. 112.0      124.05        0.5875
  17.3151   4.57250 437. 117.0      131.05        0.5816
  17.4151   4.42690 437. 121.0      141.05        0.5631
  17.5351   3.79840 438. 125.0      153.05        0.4827
  17.5952   3.07320 437. 130.0      159.07        0.3909
  18.0347   2.78190 438. 136.0      162.98        0.3535
  18.0752   1.94490 439. 140.0      167.07        0.2469
```

18.1152	1.57080	438.	145.0	171.07	0.1996
18.1452	1.32410	438.	149.0	174.07	0.1683
18.1852	1.14110	439.	155.0	178.07	0.1449
18.2252	0.90310	438.	160.0	182.07	0.1148
18.2653	0.78460	439.	165.0	186.08	0.0996
18.2955	0.69240	439.	169.0	189.12	0.0879
18.3353	0.63590	439.	175.0	193.08	0.0807
18.4153	0.51510	436.	179.0	201.08	0.0656

```
                    Experiment: XYL-840410-1

  18 Total data points were collected
     18 Points were useful for processing
      0 Points were undefined

 Run Characteristics:

     Set point temperature                    225. C
     Set point pressure                      2000. psi
     Initial liquid volume                    780. ml
     Mass of organic initially injected     0.1078 Grams
     Integrator start time                 14.1816 hh.mmss
     Plot scale factor                        1.00
     Regression begin time                   60.00 Minutes
     Regression end time                     76.00 Minutes


 Data Summary:

 Time of Day  Area    Temp  Vout  Elapsed Time      [RH]
   hh.mmss   /1.E+6    /F   /ml      /min       /(1.E-4 gm/ml)
 ----------- -------  ----  ----  ------------  --------------
   14.2215   4.87630  430.   5.0        3.98        0.6242
   14.2816   5.82320  431.  10.0       10.00        0.7447
   14.3616   5.87040  437.  15.5       18.00        0.7467
   14.4416   5.85390  436.  20.6       26.00        0.7452
   14.5016   5.68320  435.  25.6       32.00        0.7242
   14.5616   5.53550  436.  30.7       38.00        0.7047
   15.0316   5.38810  438.  35.7       45.00        0.6847
   15.0816   5.06680  438.  40.8       50.00        0.6439
   15.1316   4.52320  438.  45.8       55.00        0.5748
   15.1816   3.33160  437.  50.8       60.00        0.4237
   15.2216   2.41210  436.  55.8       64.00        0.3071
   15.2616   1.76720  437.  60.2       68.00        0.2248
   15.3016   1.50880  439.  64.5       72.00        0.1916
   15.3416   1.06820  439.  70.8       76.00        0.1356
   15.3816   0.76431  439.  76.9       80.00        0.0970
   15.4216   0.56387  439.  81.8       84.00        0.0716
   15.4618   0.47006  438.  85.8       88.03        0.0597
   15.5746   0.42256  435.  92.0       99.50        0.0538
```

```
                    Experiment: XYL-840419-1

 19 Total data points were collected
    17 Points were useful for processing
     2 Points were undefined

Run Characteristics:

    Set point temperature                   240. C
    Set point pressure                     1000. psi
    Initial liquid volume                   740. ml
    Mass of organic initially injected    0.1053 Grams
    Integrator start time                18.5728 hh.mmss
    Plot scale factor                       1.00
    Regression begin time                  45.00 Minutes
    Regression end time                    63.00 Minutes


Data Summary:

Time of Day  Area    Temp  Vout  Elapsed Time      [RH]
  hh.mmss   /1.E+6    /F   /ml      /min       /(1.E-4 gm/ml)
----------- -------  ----  ----  ------------  --------------
  19.0049   5.45620  460.   7.0         3.35        0.6790
  19.0649   5.77960  460.  13.2         9.35        0.7193
  19.1149   6.38350  464.  19.2        14.35        0.7913
  19.1649   5.97990  465.  25.1        19.35        0.7405
  19.2149   5.82280  465.  30.7        24.35        0.7211
  19.2649   5.59590  465.  36.6        29.35        0.6930
  19.2949   5.79460  464.  42.6        32.35        0.7183
  19.3349   5.21770  464.  49.0        36.35        0.6468
  19.3654   0.00000  464.  54.5        39.43        0.0000
  19.4049   3.80380  464.  60.1        43.35        0.4715
  19.4449   2.49340  465.  65.4        47.35        0.3088
  19.4849   1.86810  465.  70.9        51.35        0.2313
  19.5150   0.00000  466.  76.5        54.37        0.0000
  19.5455   1.22270  467.  82.0        57.45        0.1511
  19.5950   0.89955  465.  87.2        62.37        0.1114
  20.0250   0.76604  467.  92.6        65.37        0.0947
  20.0650   0.59008  467.  98.0        69.37        0.0729
  20.1050   0.51990  468. 103.1        73.37        0.0642
  20.1550   0.40250  466. 108.3        78.37        0.0498
```

```
                    Experiment: XYL-840422-2

   23 Total data points were collected
      22 Points were useful for processing
       1 Points were undefined

 Run Characteristics:

     Set point temperature                    240. C
     Set point pressure                      1000. psi
     Initial liquid volume                    780. ml
     Mass of organic initially injected     0.1082 Grams
     Integrator start time                 22.3152 hh.mmss
     Plot scale factor                        1.00
     Regression begin time                   70.00 Minutes
     Regression end time                     94.00 Minutes


 Data Summary:

 Time of Day  Area    Temp  Vout  Elapsed Time       [RH]
   hh.mmss   /1.E+6    /F   /ml       /min       /(1.E-4 gm/ml)
 ----------- ------- ----  ----  ------------   --------------
   22.3502   5.68700  459.   6.0        3.17          0.7084
   22.4502   6.40490  460.  11.0       13.17          0.7971
   22.5502   6.43080  463.  16.0       23.17          0.7979
   23.0502   6.33740  463.  21.0       33.17          0.7864
   23.0902   6.29250  462.  26.0       37.17          0.7815
   23.1303   6.18500  463.  31.0       41.18          0.7674
   23.1703   6.00820  463.  36.0       45.18          0.7455
   23.2103   5.92810  463.  42.0       49.18          0.7356
   23.2503   5.65220  463.  47.0       53.18          0.7013
   23.2903   5.41420  463.  52.0       57.18          0.6718
   23.3303   5.09970  463.  58.0       61.18          0.6328
   23.3703   0.00000  464.  63.0       65.18          0.0000
   23.4103   3.85230  464.  68.0       69.18          0.4775
   23.4503   3.14510  464.  73.0       73.18          0.3899
   23.4903   2.31060  464.  78.0       77.18          0.2864
   23.5304   1.76400  464.  84.0       81.20          0.2187
   23.5703   1.37650  463.  89.0       85.18          0.1708
   24.0104   1.08290  464.  94.0       89.20          0.1342
   24.0504   0.83483  464.  99.0       93.20          0.1035
   24.0904   0.69052  463. 104.0       97.20          0.0857
   24.1304   0.56870  464. 109.0      101.20          0.0705
   24.1704   0.54827  464. 113.0      105.20          0.0680
   24.2104   0.45019  463. 118.0      109.20          0.0559
```

```
                  Experiment: XYL-840413-1

 16 Total data points were collected
    16 Points were useful for processing
     0 Points were undefined

Run Characteristics:

    Set point temperature                   240. C
    Set point pressure                     1500. psi
    Initial liquid volume                   774. ml
    Mass of organic initially injected    0.1151 Grams
    Integrator start time                21.1235 hh.mmss
    Plot scale factor                       1.00
    Regression begin time                  25.00 Minutes
    Regression end time                    43.00 Minutes


Data Summary:

Time of Day  Area     Temp  Vout  Elapsed Time       [RH]
  hh.mmss   /1.E+6     /F   /ml       /min       /(1.E-4 gm/ml)
----------- -------  ----  ----  ------------  --------------
  21.1536   5.67640  464.   7.0       3.02          0.7036
  21.1935   6.32680  464.  11.0       7.00          0.7843
  21.2535   6.29290  464.  16.0      13.00          0.7800
  21.3035   6.09260  466.  21.0      18.00          0.7537
  21.3436   5.70860  466.  26.0      22.02          0.7062
  21.3835   4.33070  466.  31.0      26.00          0.5357
  21.4236   2.90300  466.  36.1      30.02          0.3591
  21.4636   1.89140  466.  41.1      34.01          0.2340
  21.5036   1.31450  466.  46.1      38.02          0.1626
  21.5436   0.98695  465.  51.1      42.01          0.1222
  21.5836   0.73065  464.  56.4      46.02          0.0906
  22.0236   0.54539  464.  62.3      50.02          0.0676
  22.0636   0.41090  464.  67.3      54.02          0.0509
  22.1036   0.30385  465.  72.1      58.02          0.0376
  22.1436   0.27219  464.  77.2      62.02          0.0337
  22.1937   0.25051  465.  82.2      67.03          0.0310
```

```
                    Experiment: XYL-840418-1

 14 Total data points were collected
    14 Points were useful for processing
     0 Points were undefined

Run Characteristics:

    Set point temperature                  240. C
    Set point pressure                    1500. psi
    Initial liquid volume                  744. ml
    Mass of organic initially injected   0.1102 Grams
    Integrator start time                8.3954 hh.mmss
    Plot scale factor                      1.00
    Regression begin time                 20.00 Minutes
    Regression end time                   43.00 Minutes


Data Summary:

Time of Day  Area     Temp  Vout  Elapsed Time      [RH]
  hh.mmss   /1.E+6     /F   /ml       /min      /(1.E-4 gm/ml)
----------- -------   ----  ----  ------------  --------------
   8.4205   7.11490   463.   8.4        2.18        0.8828
   8.4705   7.11490   465.  15.0        7.18        0.8811
   8.5205   6.95700   465.  21.5       12.18        0.8615
   8.5704   6.79360   465.  27.9       17.17        0.8413
   9.0205   5.58560   467.  33.0       22.18        0.6903
   9.0605   4.02870   467.  37.4       26.18        0.4979
   9.1105   2.41050   468.  42.4       31.18        0.2976
   9.1410   1.62430   468.  46.7       34.27        0.2005
   9.1805   1.36930   468.  51.0       38.18        0.1691
   9.2205   0.99888   469.  55.5       42.18        0.1232
   9.2605   0.78210   469.  60.0       46.18        0.0965
   9.3005   0.55520   468.  64.5       50.18        0.0685
   9.3405   0.48275   470.  68.9       54.18        0.0595
   9.4318   0.40532   470.  73.2       63.40        0.0499
```

```
                    Experiment: PHE-850303-2

 20 Total data points were collected
    20 Points were useful for processing
     0 Points were undefined

Run Characteristics:

    Set point temperature                   130. C
    Set point pressure                     2000. psi
    Initial liquid volume                   780. ml
    Mass of organic initially injected   0.0994 Grams
    Integrator start time               21.4905 hh.mmss
    Plot scale factor                      2.00
    Regression begin time                330.00 Minutes
    Regression end time                  450.00 Minutes


Data Summary:

Time of Day  Area     Temp  Vout  Elapsed Time        [RH]
  hh.mmss   /1.E+6    /F    /ml       /min       /(1.E-4 gm/ml)
----------- -------   ----  ----  ------------  --------------
  21.5205   3.44200   276.   5.0        3.00          1.4104
  22.2228   3.18100   266.  10.0       33.38          1.3101
  22.3328   3.21420   266.  15.0       44.38          1.3237
  23.0505   3.26440   267.  20.0       76.00          1.3438
  23.5920   3.31750   264.  25.0      130.25          1.3677
  24.3626   3.23610   265.  30.0      167.35          1.3334
  25.0544   3.17370   266.  35.0      196.65          1.3071
  25.3911   3.19320   266.  40.0      230.10          1.3151
  26.0640   3.07950   266.  45.0      257.58          1.2683
  26.2845   2.92340   266.  50.0      279.67          1.2040
  26.4330   2.84390   266.  55.0      294.42          1.1712
  27.0423   2.43960   266.  60.0      315.30          1.0047
  27.1724   2.16030   266.  65.0      328.32          0.8897
  27.3324   1.86460   266.  70.0      344.32          0.7679
  27.4837   1.53530   266.  75.0      359.53          0.6323
  28.0404   1.22460   266.  80.0      374.99          0.5043
  28.2036   0.91091   266.  85.0      391.52          0.3752
  28.3436   0.67556   266.  90.0      405.52          0.2782
  28.5036   0.45180   266.  95.0      421.52          0.1861
  29.0336   0.27641   266. 100.0      434.52          0.1138
```

```
                    Experiment: PHE-850305-2

  26 Total data points were collected
     24 Points were useful for processing
      2 Points were undefined

Run Characteristics:

    Set point temperature                      142. C
    Set point pressure                        2000. psi
    Initial liquid volume                      780. ml
    Mass of organic initially injected      0.0993 Grams
    Integrator start time                  19.3340 hh.mmss
    Plot scale factor                         2.00
    Regression begin time                   155.00 Minutes
    Regression end time                     215.00 Minutes


Data Summary:

Time of Day  Area    Temp  Vout  Elapsed Time       [RH]
  hh.mmss   /1.E+6    /F   /ml      /min       /(1.E-4 gm/ml)
----------- ------- ----  ---- ------------  --------------
  19.3640  3.47650  287.   5.0       3.00          1.4162
  19.5840  3.32530  287.  10.0      25.00          1.3546
  20.4746  3.45670  286.  15.0      74.10          1.4089
  21.1847  3.56450  287.  20.0     105.12          1.4521
  21.2947  3.56940  288.  25.0     116.12          1.4533
  21.3748  3.37060  289.  30.0     124.13          1.3716
  21.4230  3.27150  289.  35.0     128.83          1.3313
  21.4848  3.15140  289.  40.0     135.13          1.2824
  21.5248  3.01630  290.  45.0     139.13          1.2268
  21.5659  2.84490  289.  50.0     143.32          1.1577
  22.0231  2.56350  289.  55.0     148.85          1.0432
  22.0731  2.28610  289.  60.0     153.85          0.9303
  22.1235  1.98110  289.  65.0     158.92          0.8062
  22.1736  1.68070  289.  70.0     163.93          0.6839
  22.2135  1.43490  289.  75.0     167.92          0.5839
  22.2536  1.22750  290.  80.0     171.93          0.4992
  22.3036  0.91551  289.  85.0     176.93          0.3726
  22.3536  0.70585  288.  90.0     181.93          0.2874
  22.4036  0.51773  288.  95.0     186.93          0.2108
  22.4536  0.36220  288. 100.0     191.93          0.1475
  22.5036  0.23861  287. 105.0     196.93          0.0972
  22.5536  0.14325  287. 110.0     201.93          0.0584
  23.0036  0.07393  288. 115.0     206.93          0.0301
  23.0536  0.03405  288. 120.0     211.93          0.0139
  23.1036  0.00000  288. 125.0     216.93          0.0000
  23.1536  0.00000  289. 130.0     221.93          0.0000
```

```
                    Experiment: PHE-850303-1

  20 Total data points were collected
     18 Points were useful for processing
      2 Points were undefined

Run Characteristics:

    Set point temperature                    154. C
    Set point pressure                      2000. psi
    Initial liquid volume                    780. ml
    Mass of organic initially injected    0.0983 Grams
    Integrator start time                12.1511 hh.mmss
    Plot scale factor                       1.00
    Regression begin time                  80.00 Minutes
    Regression end time                   106.00 Minutes


Data Summary:

Time of Day  Area     Temp  Vout  Elapsed Time      [RH]
  hh.mmss   /1.E+6    /F    /ml      /min       /(1.E-4 gm/ml)
----------- -------  ----  ----  ------------   --------------
  12.1810   3.59180  303.   5.0        2.98         1.4502
  12.2210   3.50380  306.  10.0        6.98         1.4122
  12.2610   3.39600  309.  15.0       10.98         1.3663
  12.3010   3.51630  310.  20.0       14.98         1.4139
  12.3410   3.50710  311.  25.0       18.98         1.4094
  12.3810   3.41650  310.  30.0       22.98         1.3738
  12.4311   3.47150  309.  35.0       28.00         1.3967
  12.4810   3.44590  309.  40.0       32.98         1.3864
  12.5611   3.39420  309.  45.0       41.00         1.3656
  13.0611   3.29840  309.  50.0       51.00         1.3271
  13.1511   3.16190  309.  55.0       60.00         1.2721
  13.2911   2.04330  309.  60.0       74.00         0.8221
  13.3511   1.32290  309.  65.0       80.00         0.5322
  13.3834   0.94774  310.  70.0       83.38         0.3811
  13.4205   0.62279  310.  75.0       86.90         0.2504
  13.4533   0.37551  310.  80.0       90.37         0.1510
  13.4916   0.19082  311.  85.0       94.08         0.0767
  13.5248   0.08781  311.  90.0       97.62         0.0353
  13.5628   0.00000  311.  95.0      101.28         0.0000
  14.0024   0.00000  311. 100.0      105.22         0.0000
```

```
                    Experiment: PHE-850305-1

  9 Total data points were collected
     7 Points were useful for processing
     2 Points were undefined

Run Characteristics:

    Set point temperature                  166. C
    Set point pressure                    2000. psi
    Initial liquid volume                  780. ml
    Mass of organic initially injected   0.1008 Grams
    Integrator start time               15.4742 hh.mmss
    Plot scale factor                      1.00
    Regression begin time                 26.00 Minutes
    Regression end time                   40.00 Minutes


Data Summary:

Time of Day  Area     Temp  Vout  Elapsed Time      [RH]
  hh.mmss   /1.E+6     /F   /ml       /min      /(1.E-4 gm/ml)
----------- -------  ----  ----  ------------  --------------
  15.5042   3.57060  325.   5.0        3.00          1.4227
  16.0842   3.05470  327.  10.0       21.00          1.2156
  16.1242   2.84180  329.  15.0       25.00          1.1294
  16.1553   1.82820  330.  20.0       28.18          0.7261
  16.1911   0.78607  331.  25.0       31.48          0.3120
  16.2219   0.24374  332.  30.0       34.62          0.0967
  16.2535   0.03468  332.  35.0       37.88          0.0138
  16.2943   0.00000  332.  40.0       42.02          0.0000
  16.3443   0.00000  333.  45.0       47.02          0.0000
```

```
                    Experiment: PHE-850302-1

  6 Total data points were collected
     4 Points were useful for processing
     2 Points were undefined

Run Characteristics:

    Set point temperature                    178. C
    Set point pressure                      2000. psi
    Initial liquid volume                    780. ml
    Mass of organic initially injected    0.0996 Grams
    Integrator start time                20.5631 hh.mmss
    Plot scale factor                       1.00
    Regression begin time                   0.00 Minutes
    Regression end time                     0.00 Minutes


Data Summary:

Time of Day  Area    Temp  Vout  Elapsed Time      [RH]
  hh.mmss   /1.E+6    /F   /ml       /min      /(1.E-4 gm/ml)
----------- -------  ----  ----  ------------  --------------
  20.5930   3.60000  346.   5.0      2.98          1.4149
  21.0431   3.40650  349.  10.0      8.00          1.3361
  21.0931   3.02930  350.  15.0     13.00          1.1874
  21.1431   0.58868  352.  20.0     18.00          0.2304
  21.2054   0.00000  352.  25.0     24.38          0.0000
  21.2653   0.00000  353.  30.0     30.37          0.0000
```

```
                   Experiment: PHE-850218-1

  4 Total data points were collected
     1 Points were useful for processing
     3 Points were undefined

Run Characteristics:

    Set point temperature                 200. C
    Set point pressure                   2000. psi
    Initial liquid volume                 780. ml
    Mass of organic initially injected  0.0968 Grams
    Integrator start time              18.1918 hh.mmss
    Plot scale factor                     1.00
    Regression begin time                 0.00 Minutes
    Regression end time                   0.00 Minutes


Data Summary:

Time of Day  Area    Temp  Vout  Elapsed Time       [RH]
  hh.mmss   /1.E+6    /F   /ml      /min       /(1.E-4 gm/ml)
----------- ------- ---- ---- ------------ --------------
  18.2218   3.11820 384.   6.0       3.00           1.1924
  18.2718   0.00000 390.  11.0       8.00           0.0000
  18.3219   0.00000 392.  16.0      13.02           0.0000
  18.3818   0.00000 392.  21.0      19.00           0.0000
```

```
                    Experiment: TCE-840531-1

 15 Total data points were collected
    15 Points were useful for processing
     0 Points were undefined

Run Characteristics:

    Set point temperature                    225. C
    Set point pressure                      2500. psi
    Initial liquid volume                    780. ml
    Mass of organic initially injected    0.1281 Grams
    Integrator start time                13.1347 hh.mmss
    Plot scale factor                       4.00
    Regression begin time                   0.00 Minutes
    Regression end time                  1700.00 Minutes


Data Summary:

Time of Day  Area     Temp  Vout  Elapsed Time       [RH]
  hh.mmss   /1.E+6    /F    /ml       /min      /(1.E-4 gm/ml)
----------- -------   ----  ----  ------------  --------------
  13.1648   0.89233   430.   5.0        3.02         0.7018
  13.2648   1.03640   440.  10.0       13.02         0.8078
  13.3848   0.90869   437.  17.0       25.02         0.7102
  13.5748   0.96269   436.  21.0       44.02         0.7531
  14.2149   0.99613   435.  26.0       68.03         0.7800
  15.0250   0.87189   434.  31.0      109.05         0.6833
  16.0251   0.91334   438.  37.0      169.07         0.7132
  17.1046   0.81313   438.  41.0      236.98         0.6349
  18.2032   0.85632   439.  47.0      306.75         0.6680
  21.2637   0.85342   437.  52.0      492.83         0.6670
  23.0927   0.83148   438.  56.0      595.67         0.6493
  33.1359   0.82821   438.  60.0     1200.20         0.6467
  35.3031   0.72886   436.  65.0     1336.73         0.5702
  38.2149   0.73408   437.  70.0     1508.03         0.5737
  40.0826   0.71795   439.  75.0     1614.65         0.5601
```

```
                        Experiment: TCE-840604-1

 14 Total data points were collected
    14 Points were useful for processing
     0 Points were undefined

Run Characteristics:

    Set point temperature                 275. C
    Set point pressure                   2000. psi
    Initial liquid volume                 780. ml
    Mass of organic initially injected  0.1289 Grams
    Integrator start time              14.2346 hh.mmss
    Plot scale factor                     4.00
    Regression begin time               150.00 Minutes
    Regression end time                1600.00 Minutes


Data Summary:

Time of Day  Area    Temp  Vout  Elapsed Time      [RH]
  hh.mmss   /1.E+6    /F   /ml       /min      /(1.E-4 gm/ml)
----------- ------- ---- ----  ------------  --------------
  14.2647   1.26980 520.   5.0        3.02          0.9101
  14.3347   1.56800 527.  10.0       10.02          1.1144
  14.4547   1.58030 530.  15.0       22.02          1.1191
  15.0847   1.44890 528.  20.0       45.02          1.0285
  16.0550   1.15910 527.  25.0      102.07          0.8238
  17.0812   1.16260 528.  30.0      164.43          0.8253
  18.4151   1.02030 527.  35.0      258.08          0.7251
  21.2043   0.81078 524.  40.0      416.95          0.5783
  23.2758   0.66074 527.  46.0      544.20          0.4696
  25.3337   0.56805 527.  50.0      669.85          0.4037
  28.1935   0.49927 527.  55.0      835.82          0.3548
  31.3605   0.38043 526.  60.0     1032.32          0.2707
  36.1410   0.28195 527.  64.0     1310.40          0.2004
  40.3602   0.14201 526.  69.0     1572.27          0.1011
```

```
                        Experiment: MAL-831221-1

  3 Total data points were collected

Run Characteristics:

    Set point temperature                   160. C
    Set point pressure                     2000. psi
    Initial liquid volume                   780. ml
    Mass of organic initially injected    0.1270 Grams
    Integrator start time                11.2253 hh.mmss


Data Summary:

                       Chromatograph Retention Times/(min)
            --------------------------------------------------------------------------
            0.09     0.29     0.39     0.46     0.58     1.96     2.55     TOTAL
            --------------------------------------------------------------------------

Time/(min)                    Chromatogram Area/(mvolt sec)

    231.        0.  1553600. 24540992.    0.       0.       0.       0. 26094992.
    242.        0.  1581200. 20922000.    0.       0.       0.       0. 22504000.
    252.        0.  1628600. 19278000.    0.       0.       0.       0. 20906000.
```

```
                              Experiment: MAL-840104-1

  5 Total data points were collected

Run Characteristics:

    Set point temperature                 160. C
    Set point pressure                   2000. psi
    Initial liquid volume                 780. ml
    Mass of organic initially injected  0.0682 Grams
    Integrator start time              16.0347 hh.mmss

Data Summary:

                            Chromatograph Retention Times/(min)
            --------------------------------------------------------------------------------
            0.09      0.29      0.39      0.46      0.58      1.96      2.55      TOTAL
            --------------------------------------------------------------------------------

Time/(min)                    Chromatogram Area/(mvolt sec)

        3.        0.    19124. 15608000.        0.        0.        0.        0. 15702000.
       13.     2342.     5235.  2037300.        0.        0.        0.        0.  2075600.
       24.     4549.     7714.  1598000.        0.        0.        0.        0.  1612400.
       34.     2585.     7632.  1660800.        0.        0.        0.        0.  1671000.
       45.     2647.     7487.  1391200.        0.        0.        0.        0.  1401200.
```

```
                              Experiment: MAL-840109-1

 19 Total data points were collected

Run Characteristics:

    Set point temperature                 130. C
    Set point pressure                   2000. psi
    Initial liquid volume                 780. ml
    Mass of organic initially injected  0.1847 Grams
    Integrator start time              14.3928 hh.mmss

Data Summary:

                              Chromatograph Retention Times/(min)
            --------------------------------------------------------------------------------
            0.09      0.29      0.39      0.46      0.58      1.96      2.55      TOTAL
            --------------------------------------------------------------------------------

Time/(min)                      Chromatogram Area/(mvolt sec)

       2.         0.        0. 21190000.  1514430.        0.   207420.    68496. 23000992.
      13.         0.   478250.  2389500.  2152900.  5877100.    86072.     2267. 11780000.
      23.         0.   670810.  1635100.  1792500.  5715400.   167280.    13038.  9994100.
      33.         0.   759160.  1861200.   922930.  5046600.   115720.     5615.  8711200.
      43.         0.   981790.  2990600.        0.  6410600.    66690.        0. 10450000.
      51.         0.  1094800.  2264600.        0.  6382800.        0.        0.  9742200.
      59.         0.   645040.   614430.        0.  1998200.    42370.        0.  3300100.
      67.         0.   755410.   531140.        0.  2064800.        0.        0.  3351400.
      75.         0.   781340.   466230.        0.  2062700.        0.        0.  3310300.
      83.         0.  1372500.  1349900.        0.  5890000.        0.        0.  8612400.
      91.         0.   956330.   457450.        0.  2090500.        0.        0.  3504300.
      99.         0.  6720400.   403920.        0.  2498700.        0.        0.  9623000.
     110.         0.  6812300.   664430.        0.  2399400.        0.        0.  9876100.
     118.         0.  9180200.   393660.        0.  2344700.        0.        0. 11926000.
     126.         0.  6782700.   386030.        0.  2432500.        0.        0.  9601300.
     140.         0.  9205600.   718000.        0.  2287200.        0.        0. 12211000.
     148.         0.  9097700.   386920.        0.  2426700.        0.        0. 11911000.
     162.         0.  9445100.   701000.        0.  2175600.        0.        0. 12322000.
     171.         0.  8540000.   442970.        0.  2306200.        0.        0. 11289000.
```

```
                         Experiment: MAL-840110-1

 17 Total data points were collected

Run Characteristics:

    Set point temperature                     130. C
    Set point pressure                       2000.. psi
    Initial liquid volume                     780. ml
    Mass of organic initially injected     0.1847 Grams
    Integrator start time                 17.1216 hh.mmss

Data Summary:

                         Chromatograph Retention Times/(min)
          ------------------------------------------------------------------------------
          0.09      0.29      0.39      0.46      0.58      1.96      2.55      TOTAL
          ------------------------------------------------------------------------------

Time/(min)                   Chromatogram Area/(mvolt sec)

      2.          0.   108960.   593780.      0.        0.          0.        0.   702740.
     12.          0.   480670.   921750.      0.  3699000.          0.    49012.  5150400.
     23.          0.   634180.  1206400.      0.  1315600.          0.    12677.  3168900.
     33.          0.  1123700.  1456200.      0.  2981800.          0.        0.  5561700.
     42.          0.   920540.   515030.      0.  1278800.          0.        0.  2714400.
     52.          0.  6144700.   519110.      0.  1279700.          0.        0.  7943500.
     60.          0.  5338100.   397700.      0.  1320700.          0.        0.  7056500.
     70.          0.  5541300.   459140.      0.  1256100.          0.        0.  7256500.
     80.          0.  5547600.   432040.      0.  1165700.          0.        0.  7145400.
     93.          0.  6194100.   540970.      0.  1118700.          0.        0.  7853800.
    109.          0.  6587300.   604650.      0.  1129200.          0.        0.  8321100.
    114.          0.  5857100.   202120.      0.  1225400.          0.        0.  7284600.
    121.          0.  5812800.   279930.      0.  1172500.          0.        0.  7265300.
    126.          0.  5775000.   207680.      0.  1179400.          0.        0.  7162100.
    130.          0.  6224400.   147560.      0.  1130300.          0.        0.  7502200.
    134.          0.  6189100.   152890.      0.  1287500.          0.        0.  7629500.
    138.          0.  5449900.   137260.      0.  1156900.          0.        0.  6744000.
```

APPENDIX B

Experimental Conditions and Data--Initiation

This appendix contains experimental conditions and Concentration *versus* time data for m-xylene initiated with hydrogen peroxide. These experiments were summarized in Table 4.1, and are presented here in identical order.

```
                    Experiment: XYL-841016-1-H

 23 Total data points were collected
    23 Points were useful for processing
     0 Points were undefined

Run Characteristics:

    Set point temperature                      200. C
    Set point pressure                        2000. psi
    Initial liquid volume                      780. ml
    Mass of organic initially injected       0.1112 Grams
    Concentration of hydrogen peroxide        0.025 % Stoic.
    Integrator start time                   15.1737 hh.mmss
    Plot scale factor                          4.00
    Regression begin time                      0.00 Minutes
    Regression end time                        0.00 Minutes


Data Summary:

Time of Day  Area     Temp  Vout  Elapsed Time      [RH]
  hh.mmss   /1.E+6    /F    /ml      /min       /(1.E-4 gm/ml)
----------- -------  ----  ----  ------------  --------------
  15.2437   5.31060  386.  16.0       7.00         0.7051
  15.2937   4.42100  391.  21.0      12.00         0.5847
  15.3437   4.57450  392.  26.0      17.00         0.6046
  15.4037   4.63370  392.  31.0      23.00         0.6124
  15.4737   4.74740  393.  36.0      30.00         0.6269
  15.5937   4.72230  394.  40.0      42.00         0.6231
  16.1637   4.72670  393.  45.0      59.00         0.6242
  16.4337   4.96360  391.  50.0      86.00         0.6565
  17.2137   4.80940  391.  55.0     124.00         0.6361
  18.1933   4.79140  391.  60.0     181.93         0.6337
  23.3326   4.65230  393.  66.0     495.82         0.6144
  23.3703   4.50540  393.  71.0     499.43         0.5950
  23.4849   5.06840  393.  81.0     511.20         0.6693
  23.5720   1.79360  390.  89.0     519.72         0.2374
  24.0120   1.89520  390.  94.0     523.72         0.2509
  24.0521   1.90400  390.  99.0     527.73         0.2520
  24.1156   1.85270  392. 104.0     534.32         0.2448
  24.2707   1.60040  393. 109.0     549.50         0.2113
  24.4607   1.38240  393. 117.0     568.50         0.1826
  25.2324   1.11220  394. 122.0     605.78         0.1467
  34.2030   0.62446  390. 130.0    1142.88         0.0827
  34.2430   0.50982  392. 135.0    1146.88         0.0674
  34.2830   0.44132  392. 140.0    1150.88         0.0583
```

```
                    Experiment: XYL-841020-1-H

 19 Total data points were collected
    19 Points were useful for processing
     0 Points were undefined

Run Characteristics:

    Set point temperature                 200. C
    Set point pressure                   2000. psi
    Initial liquid volume                 780. ml
    Mass of organic initially injected  0.1118 Grams
    Concentration of hydrogen peroxide   0.025 % Stoic.
    Integrator start time               2.0329 hh.mmss
    Plot scale factor                     4.00
    Regression begin time                 0.00 Minutes
    Regression end time                   0.00 Minutes


Data Summary:

Time of Day  Area    Temp  Vout  Elapsed Time      [RH]
  hh.mmss   /1.E+6    /F   /ml       /min      /(1.E-4 gm/ml)
----------- ------- ---- ---- ------------ --------------
    2.0928  4.29320  386.  15.0       5.98        0.5701
    2.1329  4.18050  391.  20.0      10.00        0.5529
    2.1744  4.32020  392.  25.0      14.25        0.5709
    2.2329  4.44130  391.  30.0      20.00        0.5874
    2.3029  4.63800  392.  35.0      27.00        0.6130
    2.4129  4.58500  392.  40.0      38.00        0.6059
    2.5629  4.51670  392.  45.0      53.00        0.5969
    3.1730  4.57890  392.  50.0      74.02        0.6051
    4.0430  4.66910  392.  55.0     121.02        0.6171
    4.4831  4.77470  392.  60.0     165.03        0.6310
    5.3432  4.60320  392.  65.0     211.05        0.6083
    6.2506  4.62410  393.  70.0     261.62        0.6106
    7.4334  4.65180  392.  75.0     340.08        0.6148
   18.0835  1.86810  394.  80.0     965.10        0.2465
   18.5829  0.93419  335.  90.0    1015.00        0.1286
   19.0230  0.76248  331.  95.0    1019.02        0.1053
   19.0530  0.66440  330. 100.0    1022.02        0.0918
   19.0855  0.62232  332. 105.0    1025.43        0.0859
   19.1436  0.58609  337. 110.0    1031.12        0.0806
```

```
                    Experiment: XYL-840927-1-H

 18 Total data points were collected
    17 Points were useful for processing
     1 Points were undefined

Run Characteristics:

    Set point temperature                    200. C
    Set point pressure                      2000. psi
    Initial liquid volume                    780. ml
    Mass of organic initially injected     0.1116 Grams
    Concentration of hydrogen peroxide      0.250 % Stoic.
    Integrator start time                 16.4002 hh.mmss
    Plot scale factor                        1.00
    Regression begin time                   50.00 Minutes
    Regression end time                    130.00 Minutes


Data Summary:

Time of Day  Area    Temp  Vout  Elapsed Time       [RH]
  hh.mmss   /1.E+6    /F   /ml       /min       /(1.E-4 gm/ml)
----------- ------- ----  ----  ------------   --------------
  16.4602  3.53590  386.  10.0       6.00          0.4695
  16.5402  3.97910  391.  15.0      14.00          0.5263
  17.0502  3.96530  389.  20.0      25.00          0.5253
  17.1603  3.84930  391.  25.0      36.01          0.5091
  17.2603  3.53330  392.  30.0      46.02          0.4669
  17.3603  3.04950  393.  35.0      56.02          0.4027
  17.4603  2.50570  394.  40.0      66.01          0.3306
  17.5604  2.09460  394.  45.0      76.03          0.2764
  18.0804  1.56360  392.  50.0      88.03          0.2066
  18.2105  1.31280  392.  55.0     101.05          0.1735
  18.3205  1.08040  393.  60.0     112.05          0.1427
  18.4705  0.83225  393.  65.0     127.05          0.1099
  19.0206  0.69224  394.  70.0     142.07          0.0913
  19.1806  0.00000  392.  75.0     158.07          0.0000
  19.2306  0.53355  392.  80.0     163.07          0.0705
  20.2537  0.39171  391.  85.0     225.58          0.0518
  20.3900  0.36110  391.  90.0     239.63          0.0478
  21.0942  0.28128  391.  95.0     269.66          0.0372
```

```
                    Experiment: XYL-841020-2-H

 18 Total data points were collected
    18 Points were useful for processing
     0 Points were undefined

Run Characteristics:

    Set point temperature                    200. C
    Set point pressure                      2000. psi
    Initial liquid volume                    780. ml
    Mass of organic initially injected    0.1115 Grams
    Concentration of hydrogen peroxide     0.250 % Stoic.
    Integrator start time                22.4623 hh.mmss
    Plot scale factor                       1.00
    Regression begin time                  80.00 Minutes
    Regression end time                   140.00 Minutes


Data Summary:

Time of Day  Area    Temp  Vout  Elapsed Time       [RH]
  hh.mmss   /1.E+6    /F   /ml      /min       /(1.E-4 gm/ml)
----------- ------- ---- ---- ------------ --------------
  22.5223   3.89470  382.  10.0      6.00         0.5187
  22.5623   3.99260  389.  15.0     10.00         0.5289
  23.0023   4.12360  393.  20.0     14.00         0.5445
  23.0523   4.28820  393.  25.0     19.00         0.5663
  23.1123   4.29650  393.  30.0     25.00         0.5674
  23.2123   4.26330  393.  35.0     35.00         0.5630
  23.3523   4.17080  393.  40.0     49.00         0.5508
  23.5123   3.57270  394.  45.0     65.00         0.4714
  24.1323   2.78590  393.  50.0     87.00         0.3679
  24.1723   2.42770  392.  55.0     91.00         0.3208
  24.2123   2.18720  392.  60.0     95.00         0.2891
  24.2623   1.96520  392.  65.0    100.00         0.2597
  24.3323   1.72510  392.  70.0    107.00         0.2280
  24.4224   1.53610  393.  75.0    116.02         0.2028
  24.5724   1.27980  392.  80.0    131.02         0.1691
  25.1424   1.04530  392.  85.0    148.02         0.1381
  25.3424   0.90608  392.  90.0    168.02         0.1198
  25.5324   0.70869  392.  95.0    187.02         0.0937
```

```
                    Experiment: XYL-841021-1-H

  19 Total data points were collected
     19 Points were useful for processing
      0 Points were undefined

Run Characteristics:

    Set point temperature                       200. C
    Set point pressure                         2000. psi
    Initial liquid volume                       780. ml
    Mass of organic initially injected        0.1111 Grams
    Concentration of hydrogen peroxide         0.250 % Stoic.
    Integrator start time                    23.1438 hh.mmss
    Plot scale factor                           1.00
    Regression begin time                      50.00 Minutes
    Regression end time                       130.00 Minutes


Data Summary:

Time of Day  Area     Temp  Vout  Elapsed Time      [RH]
  hh.mmss   /1.E+6     /F   /ml       /min      /(1.E-4 gm/ml)
----------- -------   ----  ----  ------------  --------------
  23.2038   5.46710   384.  15.0       6.00          0.7270
  23.2438   4.36990   388.  22.0      10.00          0.5793
  23.2840   4.44030   392.  27.0      14.03          0.5868
  23.3238   4.65860   393.  33.0      18.00          0.6152
  23.3838   4.63570   392.  38.0      24.00          0.6126
  23.5339   4.68070   392.  42.0      39.02          0.6186
  24.1039   4.28260   392.  47.0      56.02          0.5660
  24.1539   3.95480   392.  51.0      61.02          0.5227
  24.2039   3.76870   392.  56.0      66.02          0.4981
  24.2539   3.44070   392.  61.0      71.02          0.4547
  24.3039   3.12140   392.  66.0      76.02          0.4125
  24.4039   2.81060   394.  70.0      86.02          0.3709
  24.5239   2.38280   394.  75.0      98.02          0.3144
  25.0240   1.96010   392.  79.0     108.03          0.2590
  25.1640   1.65440   392.  84.0     122.03          0.2186
  25.3140   1.28920   392.  89.0     137.03          0.1704
  25.4941   1.06590   392.  94.0     155.05          0.1409
  26.0941   0.87321   393.  99.0     175.05          0.1153
  26.3341   0.76584   393. 104.0     199.05          0.1011
```

```
                    Experiment: XYL-841023-1-H

16 Total data points were collected
   16 Points were useful for processing
    0 Points were undefined

Run Characteristics:

    Set point temperature                      200. C
    Set point pressure                        2000. psi
    Initial liquid volume                      780. ml
    Mass of organic initially injected       0.1106 Grams
    Concentration of hydrogen peroxide        0.500 % Stoic.
    Integrator start time                   21.1615 hh.mmss
    Plot scale factor                          1.00
    Regression begin time                     20.00 Minutes
    Regression end time                      100.00 Minutes


Data Summary:

Time of Day  Area     Temp  Vout  Elapsed Time      [RH]
  hh.mmss   /1.E+6     /F   /ml       /min      /(1.E-4 gm/ml)
----------- -------  ----  ----  ------------  --------------
  21.2115   3.30310  385.  10.0        5.00          0.4389
  21.2515   4.57880  390.  20.0        9.00          0.6061
  21.3116   3.83570  393.  24.0       15.02          0.5065
  21.3515   3.62230  393.  30.0       19.00          0.4783
  21.3915   3.53330  392.  35.0       23.00          0.4669
  21.4315   3.38940  392.  40.0       27.00          0.4479
  21.5016   3.05730  393.  45.0       34.02          0.4037
  21.5916   2.78730  393.  50.0       43.02          0.3681
  22.0916   2.42340  393.  55.0       53.02          0.3200
  22.2216   2.05400  392.  60.0       66.02          0.2714
  22.3716   1.68110  392.  65.0       81.02          0.2222
  23.1416   1.13530  392.  70.0      118.02          0.1500
  23.3916   0.85352  393.  76.0      143.02          0.1127
  24.0017   0.67870  393.  81.0      164.03          0.0896
  24.2017   0.56571  391.  86.0      184.03          0.0748
  24.3917   0.46929  392.  91.0      203.03          0.0620
```

```
                    Experiment: XYL-840926-1-H

 10 Total data points were collected
    10 Points were useful for processing
     0 Points were undefined

Run Characteristics:

    Set point temperature                  200. C
    Set point pressure                    2000. psi
    Initial liquid volume                  780. ml
    Mass of organic initially injected  0.1107 Grams
    Concentration of hydrogen peroxide   2.500 % Stoic.
    Integrator start time              14.3044 hh.mmss
    Plot scale factor                     1.00
    Regression begin time                10.00 Minutes
    Regression end time                  80.00 Minutes


Data Summary:

Time of Day  Area     Temp  Vout  Elapsed Time       [RH]
  hh.mmss   /1.E+6    /F   /ml       /min       /(1.E-4 gm/ml)
----------- -------  ----  ----  ------------  --------------
  14.3644   2.08600  382.  10.0      6.00          0.2778
  14.4244   2.22770  389.  20.0     12.00          0.2951
  14.5444   1.70960  399.  25.0     24.00          0.2247
  15.1045   1.11560  391.  30.0     40.02          0.1475
  15.2945   0.77580  392.  35.0     59.02          0.1025
  15.4345   0.61370  393.  40.0     73.02          0.0810
  15.5445   0.51759  393.  45.0     84.02          0.0684
  16.1045   0.39983  392.  50.0    100.02          0.0528
  16.3246   0.32490  390.  55.0    122.03          0.0430
  17.0346   0.28313  390.  60.0    153.03          0.0375
```

```
                    Experiment: XYL-841018-1-H

 14 Total data points were collected
    14 Points were useful for processing
     0 Points were undefined

Run Characteristics:

    Set point temperature                  200. C
    Set point pressure                    2000. psi
    Initial liquid volume                  780. ml
    Mass of organic initially injected   0.1100 Grams
    Concentration of hydrogen peroxide    2.500 % Stoic.
    Integrator start time               13.3911 hh.mmss
    Plot scale factor                      1.00
    Regression begin time                 20.00 Minutes
    Regression end time                   60.00 Minutes


Data Summary:

Time of Day  Area     Temp  Vout  Elapsed Time       [RH]
  hh.mmss   /1.E+6    /F    /ml       /min       /(1.E-4 gm/ml)
----------- -------  ----  ----  ------------  --------------
  13.5447   2.53860  398.  14.0      15.60         0.3339
  14.0012   1.78460  395.  19.0      21.02         0.2353
  14.0512   1.65240  392.  24.0      26.02         0.2184
  14.0912   1.52390  392.  27.0      30.02         0.2014
  14.1412   1.41740  393.  32.0      35.02         0.1872
  14.1912   1.25870  393.  37.0      40.02         0.1662
  14.2512   1.13100  394.  42.0      46.02         0.1492
  14.3213   0.96691  394.  47.0      53.03         0.1276
  14.3913   0.86350  393.  52.0      60.03         0.1140
  14.5013   0.71065  393.  57.0      71.03         0.0938
  15.0313   0.63682  392.  62.0      84.03         0.0842
  15.3519   0.48356  392.  68.0     116.13         0.0639
  16.1703   0.38402  392.  73.0     157.87         0.0507
  16.2303   0.33815  393.  78.0     163.87         0.0446
```

```
                    Experiment: XYL-840925-1-H

 12 Total data points were collected
    12 Points were useful for processing
     0 Points were undefined

Run Characteristics:

    Set point temperature                  200. C
    Set point pressure                    2000. psi
    Initial liquid volume                  780. ml
    Mass of organic initially injected  0.1101 Grams
    Concentration of hydrogen peroxide  25.000 % Stoic.
    Integrator start time              12.4429 hh.mmss
    Plot scale factor                     1.00
    Regression begin time                10.00 Minutes
    Regression end time                  50.00 Minutes


Data Summary:

Time of Day  Area     Temp  Vout  Elapsed Time       [RH]
  hh.mmss   /1.E+6    /F   /ml      /min       /(1.E-4 gm/ml)
----------- -------  ----  ----  ------------  --------------
  12.5129   1.43860  386.  17.0       7.00         0.1910
  12.5630   1.50150  390.  22.0      12.02         0.1988
  13.0032   1.44480  393.  28.0      16.05         0.1908
  13.0530   1.34520  392.  33.0      21.02         0.1778
  13.1530   1.08420  392.  38.0      31.02         0.1433
  13.2330   0.96854  392.  43.0      39.02         0.1280
  13.2930   0.85163  392.  48.0      45.02         0.1126
  13.4525   0.68230  392.  53.0      60.93         0.0902
  14.0831   0.50831  392.  58.0      84.03         0.0672
  14.2631   0.43091  391.  63.0     102.03         0.0570
  14.4032   0.37373  391.  68.0     116.05         0.0494
  14.5432   0.34235  392.  72.0     130.05         0.0452
```

```
                    Experiment: XYL-841029-1-H

 19 Total data points were collected
    19 Points were useful for processing
     0 Points were undefined

Run Characteristics:

    Set point temperature                   175. C
    Set point pressure                     2000. psi
    Initial liquid volume                   780. ml
    Mass of organic initially injected   0.1112 Grams
    Concentration of hydrogen peroxide    0.500 % Stoic.
    Integrator start time               17.1146 hh.mmss
    Plot scale factor                      2.00
    Regression begin time                500.00 Minutes
    Regression end time                  500.00 Minutes


Data Summary:

Time of Day  Area     Temp  Vout  Elapsed Time       [RH]
  hh.mmss   /1.E+6    /F    /ml       /min      /(1.E-4 gm/ml)
----------- -------  ----  ----  ------------  --------------
  17.1646   3.47170  344.  10.0       5.00          0.4752
  17.2146   3.65250  349.  15.0      10.00          0.4982
  17.2646   3.77580  349.  20.0      15.00          0.5150
  17.3146   3.88340  349.  26.0      20.00          0.5297
  17.3547   3.80040  348.  31.0      24.02          0.5188
  17.4947   3.96000  348.  36.0      38.02          0.5405
  19.0248   3.95800  344.  41.0     111.03          0.5417
  19.0948   3.90930  344.  47.0     118.03          0.5350
  19.3748   3.90460  349.  53.0     146.03          0.5326
  19.4248   3.82310  349.  63.0     151.04          0.5215
  19.5713   1.69240  346.  72.0     165.45          0.2313
  20.0213   1.77650  346.  77.0     170.45          0.2428
  20.0713   1.81400  346.  84.0     175.45          0.2479
  24.1751   1.35750  345.  90.0     426.08          0.1857
  24.2251   1.34700  345.  95.0     431.08          0.1842
  24.2751   1.13830  345. 100.0     436.08          0.1557
  24.3251   1.09030  346. 105.0     441.09          0.1490
  25.2604   1.05650  348. 112.0     494.30          0.1442
  25.3103   1.01440  349. 117.0     499.28          0.1384
```

```
                    Experiment: XYL-850826-1-H

 21 Total data points were collected
    19 Points were useful for processing
     2 Points were undefined

Run Characteristics:

    Set point temperature                   163. C
    Set point pressure                     2000. psi
    Initial liquid volume                   780. ml
    Mass of organic initially injected    0.1112 Grams
    Concentration of hydrogen peroxide     2.500 % Stoic.
    Integrator start time                 9.0850 hh.mmss
    Plot scale factor                       4.00
    Regression begin time                  60.00 Minutes
    Regression end time                  1200.00 Minutes


Data Summary:

Time of Day  Area    Temp  Vout  Elapsed Time       [RH]
  hh.mmss   /1.E+6   /F    /ml      /min       /(1.E-4 gm/ml)
----------- -------  ----  ----  ------------  --------------
    9.1539  2.67310  328.   5.0         6.82        0.3456
    9.4140  3.14181  329.  10.0        32.83        0.4059
   10.0641  2.97780  324.  15.0        57.85        0.3859
   10.5233  2.51340  325.  20.0       103.72        0.3255
   11.2958  2.35990  324.  25.0       141.13        0.3058
   12.4039  2.16240  324.  30.0       211.82        0.2802
   14.0313  1.85610  325.  35.0       294.38        0.2404
   15.4108  1.63150  325.  40.0       392.30        0.2113
   17.1555  1.43460  325.  45.0       487.08        0.1858
   18.4829  1.23730  325.  50.0       579.65        0.1603
   20.3913  1.11220  325.  55.0       690.38        0.1441
   22.0338  0.98128  325.  60.0       774.80        0.1271
   24.1852  0.83991  325.  67.0       910.03        0.1088
   26.5449  0.72844  326.  72.0      1065.98        0.0943
   32.1058  0.62480  325.  77.0      1382.13        0.0809
   34.1319 999.89990 325.  82.0      1504.48        0.0000
   34.1933  0.51326  326.  87.0      1510.72        0.0664
   36.0818  0.47554  325.  92.0      1619.47        0.0616
   38.1825  0.44768  325.  97.0      1749.58        0.0580
   40.1053 999.00000 325. 102.0      1862.05        0.0000
   40.1740  0.39407  325. 107.0      1868.83        0.0510
```

```
                 Experiment: XYL-850822-1-H

 22 Total data points were collected
    22 Points were useful for processing
     0 Points were undefined

Run Characteristics:

    Set point temperature                  170. C
    Set point pressure                    2000. psi
    Initial liquid volume                  780. ml
    Mass of organic initially injected   0.0956 Grams
    Concentration of hydrogen peroxide    2.500 % Stoic.
    Integrator start time                8.5513 hh.mmss
    Plot scale factor                      4.00
    Regression begin time                 70.00 Minutes
    Regression end time                  950.00 Minutes


Data Summary:

Time of Day  Area     Temp  Vout  Elapsed Time       [RH]
  hh.mmss   /1.E+6    /F    /ml      /min        /(1.E-4 gm/ml)
----------- -------  ----  ----  ------------   --------------
    9.0348  2.70140  336.   5.0         8.58          0.3474
    9.2134  3.03500  339.  10.0        26.35          0.3896
    9.4134  3.18880  337.  15.0        46.35          0.4098
   10.0310  2.87540  338.  20.0        67.95          0.3693
   10.2455  2.72020  338.  25.0        89.70          0.3494
   10.4456  2.50300  338.  30.0       109.72          0.3215
   11.0635  2.39590  338.  35.0       131.37          0.3077
   11.3145  2.02760  338.  40.0       156.53          0.2604
   12.0225  1.93690  336.  45.0       187.20          0.2491
   12.3426  1.81400  340.  50.0       219.22          0.2327
   13.3141  1.64250  338.  55.0       276.47          0.2110
   14.5955  1.43690  337.  60.0       364.70          0.1847
   16.0211  1.20730  338.  65.0       426.97          0.1551
   17.1017  1.06450  338.  70.0       495.07          0.1367
   18.2643  0.92782  337.  75.0       571.50          0.1192
   19.3753  0.86432  338.  80.0       642.67          0.1110
   20.4054  0.75829  338.  85.0       705.68          0.0974
   21.3555  0.71710  337.  90.0       760.70          0.0922
   22.4933  0.64723  337.  95.0       834.33          0.0832
   23.5917  0.59990  338. 100.0       904.07          0.0770
   25.0010  0.54202  339. 105.0       964.95          0.0696
   26.0447  0.52341  338. 110.0      1029.57          0.0672
```

```
                    Experiment: XYL-841103-1-H

 17 Total data points were collected
    17 Points were useful for processing
     0 Points were undefined

Run Characteristics:

    Set point temperature                  178. C
    Set point pressure                    2000. psi
    Initial liquid volume                  780. ml
    Mass of organic initially injected   0.1109 Grams
    Concentration of hydrogen peroxide    2.500 % Stoic.
    Integrator start time               16.0552 hh.mmss
    Plot scale factor                      1.00
    Regression begin time                 50.00 Minutes
    Regression end time                  500.00 Minutes


Data Summary:

Time of Day  Area     Temp  Vout  Elapsed Time       [RH]
  hh.mmss   /1.E+6    /F    /ml       /min       /(1.E-4 gm/ml)
----------- -------  ----  ----  ------------  --------------
  16.1052   2.39000  348.  15.0         5.00         0.3262
  16.1452   2.50980  351.  20.0         9.00         0.3419
  16.1753   2.56920  351.  24.0        12.01         0.3500
  16.2353   2.64310  349.  29.0        18.02         0.3605
  16.3953   2.61190  349.  34.0        34.01         0.3563
  16.5953   2.56580  352.  39.0        54.02         0.3493
  17.3955   2.29490  352.  44.0        94.05         0.3124
  18.1956   2.10070  351.  49.0       134.07         0.2861
  18.5657   1.85240  351.  54.0       171.08         0.2523
  20.0452   1.59630  351.  59.0       239.00         0.2174
  21.1040   1.35570  352.  64.0       304.80         0.1845
  22.0930   1.12770  352.  69.0       363.63         0.1535
  23.2338   0.96359  352.  74.0       437.76         0.1312
  24.2034   0.82649  352.  79.0       494.70         0.1125
  25.4551   0.71023  351.  84.0       579.98         0.0968
  25.4851   0.63685  351.  89.0       582.98         0.0867
  25.5404   0.61417  350.  94.0       588.20         0.0837
```

```
                     Experiment: XYL-841030-1-H

 16 Total data points were collected
    16 Points were useful for processing
     0 Points were undefined

Run Characteristics:

    Set point temperature                   185. C
    Set point pressure                     2000. psi
    Initial liquid volume                   780. ml
    Mass of organic initially injected    0.1112 Grams
    Concentration of hydrogen peroxide     2.500 % Stoic.
    Integrator start time                17.5551 hh.mmss
    Plot scale factor                       1.00
    Regression begin time                  50.00 Minutes
    Regression end time                   350.00 Minutes


Data Summary:

Time of Day  Area    Temp  Vout  Elapsed Time       [RH]
  hh.mmss   /1.E+6    /F   /ml       /min      /(1.E-4 gm/ml)
----------- -------  ----  ----  ------------  --------------
  18.0051   2.18340  357.  10.0       5.00          0.2962
  18.0452   2.38370  363.  15.0       9.02          0.3220
  18.0952   2.47060  364.  20.0      14.02          0.3335
  18.1752   2.43070  363.  25.0      22.02          0.3283
  18.2252   2.38520  364.  30.0      27.02          0.3220
  18.3252   2.29700  364.  35.0      37.02          0.3101
  18.5453   2.14390  364.  40.0      59.03          0.2894
  19.2653   1.95890  364.  45.0      91.03          0.2644
  21.3937   1.25660  364.  50.0     223.77          0.1696
  21.4437   1.09340  364.  55.0     228.77          0.1476
  22.2137   0.94847  366.  60.0     265.77          0.1278
  23.2044   0.77387  367.  66.0     324.88          0.1042
  24.3709   0.59893  366.  71.0     401.30          0.0807
  24.5540   0.54920  367.  76.0     419.82          0.0740
  25.2641   0.49558  367.  81.0     450.83          0.0667
  25.2941   0.43059  367.  86.0     453.83          0.0580
```

```
                    Experiment: XYL-841102-1-H

 17 Total data points were collected
    17 Points were useful for processing
     0 Points were undefined

Run Characteristics:

    Set point temperature                      193. C
    Set point pressure                        2000. psi
    Initial liquid volume                      780. ml
    Mass of organic initially injected      0.1115 Grams
    Concentration of hydrogen peroxide       2.500 % Stoic.
    Integrator start time                  21.1716 hh.mmss
    Plot scale factor                         1.00
    Regression begin time                    20.00 Minutes
    Regression end time                     140.00 Minutes


Data Summary:

Time of Day  Area     Temp  Vout  Elapsed Time      [RH]
  hh.mmss   /1.E+6    /F    /ml      /min       /(1.E-4 gm/ml)
----------- -------  ----  ----  ------------  --------------
  21.2316   2.41540  377.  15.0       6.00         0.3229
  21.2716   2.47020  381.  20.0      10.00         0.3292
  21.3016   2.40680  382.  25.0      13.00         0.3206
  21.3416   2.31070  380.  31.0      17.00         0.3082
  21.4416   2.15140  377.  36.0      27.00         0.2876
  21.5516   1.92020  379.  42.0      38.00         0.2563
  22.0516   1.72150  379.  47.0      48.00         0.2298
  22.1716   1.55870  380.  52.0      60.00         0.2079
  22.2716   1.39090  379.  57.0      70.00         0.1857
  22.4117   1.24670  379.  62.0      84.02         0.1664
  22.5717   1.06600  379.  67.0     100.02         0.1423
  23.1717   0.91762  379.  73.0     120.02         0.1225
  23.3918   0.75846  379.  78.0     142.03         0.1012
  24.0218   0.65392  389.  83.0     165.03         0.0866
  24.2518   0.57309  379.  88.0     188.03         0.0765
  24.4719   0.49307  379.  93.0     210.05         0.0658
  25.0916   0.45850  379.  98.0     232.00         0.0612
```

```
                    Experiment: XYL-841106-1-H

  19 Total data points were collected
     19 Points were useful for processing
      0 Points were undefined

Run Characteristics:

    Set point temperature                  200. C
    Set point pressure                    1500. psi
    Initial liquid volume                  780. ml
    Mass of organic initially injected   0.1111 Grams
    Concentration of hydrogen peroxide    2.500 % Stoic.
    Integrator start time               15.1921 hh.mmss
    Plot scale factor                      1.00
    Regression begin time                 20.00 Minutes
    Regression end time                   70.00 Minutes


Data Summary:

Time of Day  Area     Temp  Vout  Elapsed Time       [RH]
  hh.mmss   /1.E+6    /F    /ml      /min       /(1.E-4 gm/ml)
----------- -------   ----  ----  ------------  --------------
  15.2521   3.72560   394.  29.0      6.00          0.4916
  15.2921   3.07430   398.  39.0     10.00          0.4043
  15.3321   3.05320   394.  49.0     14.00          0.4029
  15.3721   2.60290   393.  59.0     18.00          0.3437
  15.4121   1.84920   392.  64.0     22.00          0.2444
  15.4522   1.72650   393.  69.0     26.02          0.2280
  15.4822   1.60510   393.  74.0     29.02          0.2120
  15.5222   1.54930   394.  79.0     33.02          0.2044
  15.5622   1.41530   393.  84.0     37.02          0.1869
  16.0122   1.32470   393.  89.0     42.02          0.1749
  16.0622   1.20030   393.  94.0     47.02          0.1585
  16.1122   1.14420   393.  99.0     52.02          0.1511
  16.1823   1.04950   393. 104.0     59.03          0.1386
  16.2623   0.91877   393. 109.0     67.03          0.1213
  16.3423   0.82572   393. 114.0     75.03          0.1090
  16.4524   0.74207   392. 119.0     86.05          0.0981
  17.0024   0.64444   393. 124.0    101.05          0.0851
  17.1325   0.56827   393. 129.0    114.07          0.0750
  17.2325   0.53222   393. 134.0    124.07          0.0703
```

APPENDIX C

Experimental Conditions and Data--Synergism

This appendix contains experimental conditions and Concentration *versus* time data for m-xylene/phenol synergism runs. Both m-xylene and phenol concentration results are listed after the "Run Characteristics" section which is common to both. These experiments were summarized in Table 4.2 and 4.3, and are presented here in identical order.

```
                    Experiment: XPH-850226-1

  7 Total data points were collected
     7 Points were useful for processing
     0 Points were undefined

Run Characteristics:

    Set point temperature                      114. C
    Set point pressure                        2000. psi
    Initial liquid volume                      780. ml
    Mass of m-xylene initially injected     0.1097 Grams
    Mass of phenol initially injected       0.0985 Grams
    Integrator start time                  16.0303 hh.mmss
    Plot scale factor                         3.00
    Regression begin time for m-xylene        0.00 Minutes
    Regression end time for m-xylene          0.00 Minutes
    Regression begin time for phenol          0.00 Minutes
    Regression end time for phenol            0.00 Minutes


Data Summary for m-Xylene:

Time of Day  Area     Temp  Vout  Elapsed Time       [RH]
  hh.mmss   /1.E+6    /F    /ml      /min       /(1.E-4 gm/ml)
----------- -------  ----  ----  ------------  --------------
  16.0603   4.53510  242.   5.0         3.00        0.4996
  17.1850   4.62030  239.  10.0        75.78        0.5097
  18.0726   4.12540  238.  15.0       124.38        0.4553
  21.2358   4.43240  222.  20.0       320.92        0.4925
  22.3210   3.60150  238.  25.0       389.12        0.3975
  25.0643   4.28710  233.  30.0       543.67        0.4742
  25.1143   3.55150  233.  35.0       548.67        0.3928
```

Data Summary for Phenol:

Time of Day hh.mmss	Area /1.E+6	Temp /F	Vout /ml	Elapsed Time /min	[RH] /(1.E-4 gm/ml)
16.0603	4.43460	242.	5.0	3.00	1.8472
17.1850	4.14900	239.	10.0	75.78	1.7306
18.0726	3.36240	238.	15.0	124.38	1.4031
21.2358	4.50390	222.	20.0	320.92	1.8922
22.3210	3.37010	238.	25.0	389.12	1.4063
25.0643	4.28660	233.	30.0	543.67	1.7926
25.1143	3.37230	233.	35.0	548.67	1.4103

```
                    Experiment: XPH-850225-1

  18 Total data points were collected
     18 Points were useful for processing
      0 Points were undefined

 Run Characteristics:

     Set point temperature                    130. C
     Set point pressure                      2000. psi
     Initial liquid volume                    780. ml
     Mass of m-xylene initially injected    0.1107 Grams
     Mass of phenol initially injected      0.0973 Grams
     Integrator start time                 15.0903 hh.mmss
     Plot scale factor                        2.00
     Regression begin time for m-xylene     400.00 Minutes
     Regression end time for m-xylene       600.00 Minutes
     Regression begin time for phenol       425.00 Minutes
     Regression end time for phenol         600.00 Minutes


 Data Summary for m-Xylene:

 Time of Day  Area     Temp  Vout  Elapsed Time       [RH]
   hh.mmss   /1.E+6     /F   /ml       /min      /(1.E-4 gm/ml)
 ----------- -------  ----  ----  ------------  --------------
   15.1203   4.56260  266.   5.0       3.00          0.4970
   16.4946   5.34580  266.  10.0     100.72          0.5823
   18.1618   5.90610  267.  15.0     187.25          0.6430
   20.3648   4.60420  266.  20.0     327.75          0.5015
   20.4237   3.97850  266.  25.0     333.57          0.4334
   20.4637   4.87440  266.  30.0     337.57          0.5309
   22.1349   3.32810  267.  35.0     424.77          0.3623
   22.1849   2.99050  267.  40.0     429.77          0.3256
   22.2252   2.81440  268.  45.0     433.82          0.3062
   22.2653   2.77316  268.  50.0     437.83          0.3018
   22.4450   2.51043  268.  55.0     455.78          0.2732
   23.0920   2.20035  266.  60.0     480.28          0.2397
   23.3420   1.91142  265.  65.0     505.28          0.2083
   23.5120   1.74881  266.  70.0     522.28          0.1905
   24.0420   1.62778  267.  75.0     535.28          0.1772
   24.2202   1.47526  267.  80.0     552.98          0.1606
   24.3747   1.37723  267.  85.0     568.73          0.1499
   24.5931   1.19311  267.  90.0     590.47          0.1299
```

Data Summary for Phenol:

Time of Day hh.mmss	Area /1.E+6	Temp /F	Vout /ml	Elapsed Time /min	[RH] /(1.E-4 gm/ml)
15.1203	3.32200	266.	5.0	3.00	1.3681
16.4946	3.19370	266.	10.0	100.72	1.3153
18.1618	4.05710	267.	15.0	187.25	1.6701
20.3648	2.63000	266.	20.0	327.75	1.0831
20.4237	2.52370	266.	25.0	333.57	1.0394
20.4637	2.35080	266.	30.0	337.57	0.9682
22.1349	1.63040	267.	35.0	424.77	0.6711
22.1849	1.29440	267.	40.0	429.77	0.5328
22.2252	1.22940	268.	45.0	433.82	0.5058
22.2653	1.17610	268.	50.0	437.83	0.4839
22.4450	0.91906	268.	55.0	455.78	0.3781
23.0920	0.61532	266.	60.0	480.28	0.2534
23.3420	0.41501	265.	65.0	505.28	0.1710
23.5120	0.30308	266.	70.0	522.28	0.1248
24.0420	0.21901	267.	75.0	535.28	0.0901
24.2202	0.17204	267.	80.0	552.98	0.0708
24.3747	0.11278	267.	85.0	568.73	0.0464
24.5931	0.09611	267.	90.0	590.47	0.0396

```
                    Experiment: XPH-850224-1

 20 Total data points were collected
    20 Points were useful for processing
     0 Points were undefined

Run Characteristics:

    Set point temperature                     138. C
    Set point pressure                       2000. psi
    Initial liquid volume                     780. ml
    Mass of m-xylene initially injected     0.1100 Grams
    Mass of phenol initially injected       0.0964 Grams
    Integrator start time                  16.3001 hh.mmss
    Plot scale factor                         2.00
    Regression begin time for m-xylene      228.00 Minutes
    Regression end time for m-xylene        310.00 Minutes
    Regression begin time for phenol        225.00 Minutes
    Regression end time for phenol          310.00 Minutes


Data Summary for m-Xylene:

Time of Day  Area     Temp  Vout  Elapsed Time      [RH]
  hh.mmss   /1.E+6     /F   /ml      /min      /(1.E-4 gm/ml)
----------- -------  ----  ----  ------------  --------------
  16.3300   4.58810  374.    5.0        2.98        0.4675
  17.1001   5.19280  279.   10.0       40.00        0.5619
  17.5702   4.80840  274.   15.0       87.02        0.5216
  19.2950   4.68400  281.   20.0      179.82        0.5063
  20.1428   4.67770  283.   25.0      224.45        0.5051
  20.1829   3.13970  283.   30.0      228.47        0.3390
  20.2329   3.01630  283.   35.0      233.47        0.3257
  20.2829   2.84600  284.   40.0      238.47        0.3071
  20.3329   2.66710  284.   45.0      243.47        0.2878
  20.4229   2.42015  283.   50.0      252.47        0.2613
  20.4829   2.34991  282.   55.0      258.47        0.2539
  21.0229   2.01154  282.   60.0      272.47        0.2173
  21.1129   1.81757  282.   65.0      281.47        0.1963
  21.2145   1.65398  281.   70.0      291.73        0.1788
  21.3305   1.45177  281.   75.0      303.07        0.1569
  21.4434   1.32889  281.   80.0      314.55        0.1436
  22.0506   1.12974  281.   85.0      335.08        0.1221
  22.3419   0.93463  280.   90.0      364.30        0.1011
  22.5950   0.84159  280.   95.0      389.82        0.0910
  23.3242   0.73035  280.  100.0      422.68        0.0790
```

Data Summary for Phenol:

Time of Day hh.mmss	Area /1.E+6	Temp /F	Vout /ml	Elapsed Time /min	[RH] /(1.E-4 gm/ml)
16.3300	3.23130	374.	5.0	2.98	1.2450
17.1001	2.91690	279.	10.0	40.00	1.1933
17.5702	3.05070	274.	15.0	87.02	1.2513
19.2950	2.92350	281.	20.0	179.82	1.1948
20.1428	2.12060	283.	25.0	224.45	0.8657
20.1829	1.81610	283.	30.0	228.47	0.7414
20.2329	1.55630	283.	35.0	233.47	0.6354
20.2829	1.45760	284.	40.0	238.47	0.5947
20.3329	1.44340	284.	45.0	243.47	0.5890
20.4229	1.21370	283.	50.0	252.47	0.4955
20.4829	1.04130	282.	55.0	258.47	0.4253
21.0229	0.75500	282.	60.0	272.47	0.3084
21.1129	0.58950	282.	65.0	281.47	0.2408
21.2145	0.44122	281.	70.0	291.73	0.1803
21.3305	0.33186	281.	75.0	303.07	0.1356
21.4434	0.22233	281.	80.0	314.55	0.0909
22.0506	0.12467	281.	85.0	335.08	0.0509
22.3419	0.00000	280.	90.0	364.30	0.0000
22.5950	0.06341	280.	95.0	389.82	0.0259
23.3242	0.14371	280.	100.0	422.68	0.0588

```
                    Experiment: XPH-850222-1

   21 Total data points were collected
      21 Points were useful for processing
       0 Points were undefined

 Run Characteristics:

     Set point temperature                  154. C
     Set point pressure                    2000. psi
     Initial liquid volume                  780. ml
     Mass of m-xylene initially injected  0.1106 Grams
     Mass of phenol initially injected    0.0974 Grams
     Integrator start time               14.4101 hh.mmss
     Plot scale factor                      1.00
     Regression begin time for m-xylene    85.00 Minutes
     Regression end time for m-xylene     115.00 Minutes
     Regression begin time for phenol      90.00 Minutes
     Regression end time for phenol       130.00 Minutes


 Data Summary for m-Xylene:

 Time of Day  Area    Temp  Vout  Elapsed Time       [RH]
   hh.mmss   /1.E+6    /F   /ml       /min      /(1.E-4 gm/ml)
 ----------- -------  ----  ----  ------------  --------------
   14.4401   4.93580  305.   5.0          3.00        0.5264
   14.4901   6.09960  306.  10.0          8.00        0.6502
   14.5601   5.72620  306.  15.0         15.00        0.6104
   15.0501   5.47690  303.  20.0         24.00        0.5848
   15.1601   4.59890  304.  25.0         35.00        0.4908
   15.2202   5.27800  306.  30.0         41.02        0.5626
   15.4202   5.22170  309.  35.0         61.02        0.5556
   15.5802   4.62410  308.  40.0         77.02        0.4923
   16.0303   4.32350  308.  45.0         82.03        0.4603
   16.0703   3.07830  308.  50.0         86.03        0.3278
   16.1103   2.90380  308.  55.0         90.03        0.3092
   16.1503   2.62765  309.  60.0         94.03        0.2796
   16.1903   2.53995  309.  65.0         98.03        0.2703
   16.2304   2.31904  310.  70.0        102.05        0.2466
   16.2703   2.10367  310.  75.0        106.03        0.2237
   16.3103   1.85324  311.  80.0        110.03        0.1970
   16.3503   1.69924  311.  85.0        114.03        0.1806
   16.3903   1.59666  311.  90.0        118.03        0.1697
   16.4604   1.37170  311.  95.0        125.05        0.1458
   16.5604   1.17352  310. 100.0        135.05        0.1248
   17.1504   0.92968  310. 105.0        154.05        0.0989
```

Data Summary for Phenol:

Time of Day hh.mmss	Area /1.E+6	Temp /F	Vout /ml	Elapsed Time /min	[RH] /(1.E-4 gm/ml)
14.4401	3.78820	305.	5.0	3.00	1.5277
14.4901	3.47220	306.	10.0	8.00	1.3994
14.5601	3.51120	306.	15.0	15.00	1.4152
15.0501	3.49190	303.	20.0	24.00	1.4098
15.1601	3.02020	304.	25.0	35.00	1.2187
15.2202	3.56530	306.	30.0	41.02	1.4370
15.4202	3.51910	309.	35.0	61.02	1.4158
15.5802	2.84220	308.	40.0	77.02	1.1442
16.0303	2.50470	308.	45.0	82.03	1.0083
16.0703	2.07490	308.	50.0	86.03	0.8353
16.1103	1.79650	308.	55.0	90.03	0.7232
16.1503	1.63870	309.	60.0	94.03	0.6593
16.1903	1.35390	309.	65.0	98.03	0.5447
16.2304	1.08300	310.	70.0	102.05	0.4355
16.2703	0.85374	310.	75.0	106.03	0.3433
16.3103	0.64897	311.	80.0	110.03	0.2608
16.3503	0.48464	311.	85.0	114.03	0.1948
16.3903	0.36776	311.	90.0	118.03	0.1478
16.4604	0.22545	311.	95.0	125.05	0.0906
16.5604	0.09703	310.	100.0	135.05	0.0390
17.1504	0.13372	310.	105.0	154.05	0.0538

```
                    Experiment: XPH-850221-2

 21 Total data points were collected
    21 Points were useful for processing
     0 Points were undefined

Run Characteristics:

    Set point temperature                     162. C
    Set point pressure                       2000. psi
    Initial liquid volume                     780. ml
    Mass of m-xylene initially injected     0.1104 Grams
    Mass of phenol initially injected       0.0953 Grams
    Integrator start time                  18.0450 hh.mmss
    Plot scale factor                         1.00
    Regression begin time for m-xylene       46.00 Minutes
    Regression end time for m-xylene         70.00 Minutes
    Regression begin time for phenol         40.00 Minutes
    Regression end time for phenol           65.00 Minutes


Data Summary for m-Xylene:

Time of Day  Area     Temp  Vout  Elapsed Time      [RH]
  hh.mmss   /1.E+6     /F   /ml      /min       /(1.E-4 gm/ml)
----------- -------   ----  ----  ------------  --------------
  18.0750   5.09610   321.    5.0      3.00          0.5383
  18.1206   4.36060   323.   10.0      7.27          0.4601
  18.1608   4.07530   324.   15.0     11.30          0.4297
  18.2008   4.02920   324.   20.0     15.30          0.4248
  18.2408   4.14390   323.   25.0     19.30          0.4372
  18.2808   4.05040   323.   30.0     23.30          0.4273
  18.3208   3.94980   323.   35.0     27.30          0.4167
  18.3708   4.79420   324.   40.0     32.30          0.5055
  18.4408   4.17240   324.   45.0     39.30          0.4399
  18.5008   3.84400   325.   50.0     45.30          0.4051
  18.5409   2.62949   325.   55.0     49.32          0.2771
  18.5809   2.29776   325.   60.0     53.32          0.2421
  19.0209   1.96222   325.   65.0     57.32          0.2068
  19.0609   1.69051   325.   70.0     61.32          0.1781
  19.1009   1.46038   325.   75.0     65.32          0.1539
  19.1409   1.28818   325.   80.0     69.32          0.1357
  19.1810   1.17118   325.   85.0     73.33          0.1234
  19.2210   1.04615   325.   90.0     77.33          0.1102
  19.3010   0.96072   325.   95.0     85.33          0.1012
  19.4310   0.84250   324.  100.0     98.33          0.0888
  19.5511   0.76264   324.  105.0    110.35          0.0804
```

Data Summary for Phenol:

Time of Day hh.mmss	Area /1.E+6	Temp /F	Vout /ml	Elapsed Time /min	[RH] /(1.E-4 gm/ml)
18.0750	3.90090	321.	5.0	3.00	1.5581
18.1206	3.14960	323.	10.0	7.27	1.2565
18.1608	3.12050	324.	15.0	11.30	1.2441
18.2008	3.15700	324.	20.0	15.30	1.2586
18.2408	3.07750	323.	25.0	19.30	1.2277
18.2808	3.12500	323.	30.0	23.30	1.2467
18.3208	3.16090	323.	35.0	27.30	1.2610
18.3708	3.53630	324.	40.0	32.30	1.4099
18.4408	2.93210	324.	45.0	39.30	1.1690
18.5008	2.08790	325.	50.0	45.30	0.8319
18.5409	1.54760	325.	55.0	49.32	0.6166
18.5809	1.07010	325.	60.0	53.32	0.4264
19.0209	0.70703	325.	65.0	57.32	0.2817
19.0609	0.44803	325.	70.0	61.32	0.1785
19.1009	0.28058	325.	75.0	65.32	0.1118
19.1409	0.18769	325.	80.0	69.32	0.0748
19.1810	0.12605	325.	85.0	73.33	0.0502
19.2210	0.09665	325.	90.0	77.33	0.0385
19.3010	0.07965	325.	95.0	85.33	0.0317
19.4310	0.06850	324.	100.0	98.33	0.0273
19.5511	0.06200	324.	105.0	110.35	0.0247

```
                    Experiment: XPH-850221-1

 17 Total data points were collected
    17 Points were useful for processing
     0 Points were undefined

Run Characteristics:

    Set point temperature                     170. C
    Set point pressure                       2000. psi
    Initial liquid volume                     780. ml
    Mass of m-xylene initially injected    0.1097 Grams
    Mass of phenol initially injected      0.0962 Grams
    Integrator start time                 13.2704 hh.mmss
    Plot scale factor                        1.00
    Regression begin time for m-xylene      30.00 Minutes
    Regression end time for m-xylene        50.00 Minutes
    Regression begin time for phenol        30.00 Minutes
    Regression end time for phenol          60.00 Minutes


Data Summary for m-Xylene:

Time of Day  Area    Temp  Vout  Elapsed Time      [RH]
  hh.mmss   /1.E+6    /F   /ml      /min      /(1.E-4 gm/ml)
----------- ------- ----  ----  ------------  --------------
  13.3004   5.21380 336.   5.0       3.00         0.5456
  13.3415   5.25880 338.  10.0       7.18         0.5495
  13.3816   5.11320 338.  15.0      11.20         0.5343
  13.4219   5.26100 337.  20.0      15.25         0.5501
  13.4632   4.40320 336.  25.0      19.47         0.4607
  13.5042   4.91300 337.  30.0      23.63         0.5138
  13.5444   3.61670 337.  35.0      27.67         0.3782
  13.5842   3.67500 338.  40.0      31.63         0.3840
  14.0242   2.47501 339.  45.0      35.63         0.2585
  14.0644   1.88534 339.  50.0      39.67         0.1969
  14.1042   1.50331 339.  55.0      43.63         0.1570
  14.1442   1.30638 339.  60.0      47.63         0.1364
  14.1842   1.11047 339.  65.0      51.63         0.1160
  14.2243   1.02390 339.  70.0      55.65         0.1069
  14.2643   0.93072 340.  75.0      59.65         0.0971
  14.3643   0.83983 340.  80.0      69.65         0.0877
  14.4943   0.70501 338.  85.0      82.65         0.0737
```

Data Summary for Phenol:

Time of Day hh.mmss	Area /1.E+6	Temp /F	Vout /ml	Elapsed Time /min	[RH] /(1.E-4 gm/ml)
13.3004	3.77270	336.	5.0	3.00	1.4927
13.3415	3.44990	338.	10.0	7.18	1.3631
13.3816	3.46000	338.	15.0	11.20	1.3671
13.4219	3.40790	337.	20.0	15.25	1.3474
13.4632	2.95840	336.	25.0	19.47	1.1705
13.5042	2.96790	337.	30.0	23.63	1.1735
13.5444	2.44150	337.	35.0	27.67	0.9653
13.5842	1.70580	338.	40.0	31.63	0.6740
14.0242	1.01010	339.	45.0	35.63	0.3989
14.0644	0.53374	339.	50.0	39.67	0.2108
14.1042	0.26150	339.	55.0	43.63	0.1033
14.1442	0.14597	339.	60.0	47.63	0.0576
14.1842	0.08826	339.	65.0	51.63	0.0349
14.2243	0.06459	339.	70.0	55.65	0.0255
14.2643	0.03599	340.	75.0	59.65	0.0142
14.3643	0.05441	340.	80.0	69.65	0.0215
14.4943	0.00000	338.	85.0	82.65	0.0000

```
                     Experiment: XPH-850220-2

 13 Total data points were collected
    13 Points were useful for processing
     0 Points were undefined

Run Characteristics:

    Set point temperature                   178. C
    Set point pressure                     2000. psi
    Initial liquid volume                   780. ml
    Mass of m-xylene initially injected   0.1093 Grams
    Mass of phenol initially injected     0.0965 Grams
    Integrator start time                20.3743 hh.mmss
    Plot scale factor                       1.00
    Regression begin time for m-xylene     12.00 Minutes
    Regression end time for m-xylene       30.00 Minutes
    Regression begin time for phenol       15.00 Minutes
    Regression end time for phenol         36.00 Minutes


Data Summary for m-Xylene:

Time of Day  Area    Temp  Vout  Elapsed Time       [RH]
  hh.mmss   /1.E+6    /F   /ml      /min       /(1.E-4 gm/ml)
----------- -------  ----  ----  ------------  --------------
  20.4043   7.35840  350.   5.0        3.00        0.7628
  20.4447   5.05950  352.  10.0        7.07        0.5238
  20.4844   4.79320  352.  15.0       11.02        0.4962
  20.5244   4.02070  352.  20.0       15.02        0.4162
  20.5645   2.72088  353.  25.0       19.03        0.2815
  21.0044   1.74328  354.  30.0       23.02        0.1802
  21.0446   1.21882  354.  35.0       27.05        0.1260
  21.0845   1.01496  355.  40.0       31.03        0.1048
  21.1244   0.92513  355.  45.0       35.02        0.0956
  21.1644   0.87615  355.  50.0       39.02        0.0905
  21.2044   0.81753  354.  55.0       43.02        0.0845
  21.3244   0.73579  352.  60.0       55.02        0.0762
  21.5145   0.62726  352.  65.0       74.03        0.0649
```

Data Summary for Phenol:

Time of Day hh.mmss	Area /1.E+6	Temp /F	Vout /ml	Elapsed Time /min	[RH] /(1.E-4 gm/ml)
20.4043	3.60810	350.	5.0	3.00	1.4142
20.4447	3.20840	352.	10.0	7.07	1.2558
20.4844	3.10200	352.	15.0	11.02	1.2142
20.5244	2.66230	352.	20.0	15.02	1.0421
20.5645	1.31620	353.	25.0	19.03	0.5148
21.0044	0.44626	354.	30.0	23.02	0.1744
21.0446	0.13720	354.	35.0	27.05	0.0536
21.0845	0.05213	355.	40.0	31.03	0.0204
21.1244	0.00000	355.	45.0	35.02	0.0000
21.1644	0.00000	355.	50.0	39.02	0.0000
21.2044	0.00000	354.	55.0	43.02	0.0000
21.3244	0.00000	352.	60.0	55.02	0.0000
21.5145	0.00000	352.	65.0	74.03	0.0000

```
                    Experiment: XPH-850220-1

 11 Total data points were collected
    11 Points were useful for processing
     0 Points were undefined

Run Characteristics:

    Set point temperature                  185. C
    Set point pressure                    2000. psi
    Initial liquid volume                  780. ml
    Mass of m-xylene initially injected 0.1083 Grams
    Mass of phenol initially injected   0.0957 Grams
    Integrator start time              14.2731 hh.mmss
    Plot scale factor                     1.00
    Regression begin time for m-xylene   10.00 Minutes
    Regression end time for m-xylene     30.00 Minutes
    Regression begin time for phenol     12.00 Minutes
    Regression end time for phenol       23.00 Minutes


Data Summary for m-Xylene:

Time of Day  Area     Temp  Vout  Elapsed Time      [RH]
  hh.mmss   /1.E+6    /F    /ml      /min       /(1.E-4 gm/ml)
----------- -------  ----  ----  ------------  --------------
  14.3030   7.98070  360.   5.0       2.98          0.8216
  14.3431   5.27020  363.  10.0       7.00          0.5414
  14.3831   5.31070  363.  15.0      11.00          0.5455
  14.4231   2.88860  362.  20.0      15.00          0.2969
  14.4631   1.75668  364.  25.0      19.00          0.1803
  14.5031   1.17565  366.  30.0      23.00          0.1205
  14.5433   0.93596  366.  35.0      27.03          0.0959
  14.5931   0.85022  365.  40.0      32.00          0.0872
  15.0531   0.72844  365.  45.0      38.00          0.0747
  15.1431   0.63113  365.  50.0      47.00          0.0647
  15.3131   0.52938  365.  55.0      64.00          0.0543
```

Data Summary for Phenol:

Time of Day hh.mmss	Area /1.E+6	Temp /F	Vout /ml	Elapsed Time /min	[RH] /(1.E-4 gm/ml)
14.3030	3.26460	360.	5.0	2.98	1.2707
14.3431	3.06040	363.	10.0	7.00	1.1887
14.3831	2.60370	363.	15.0	11.00	1.0113
14.4231	1.08010	362.	20.0	15.00	0.4198
14.4631	0.27216	364.	25.0	19.00	0.1056
14.5031	0.00000	366.	30.0	23.00	0.0000
14.5433	0.00000	366.	35.0	27.03	0.0000
14.5931	0.00000	365.	40.0	32.00	0.0000
15.0531	0.00000	365.	45.0	38.00	0.0000
15.1431	0.00000	365.	50.0	47.00	0.0000
15.3131	0.00000	365.	55.0	64.00	0.0000

```
                    Experiment: XPH-850219-2

 13 Total data points were collected
    13 Points were useful for processing
     0 Points were undefined

Run Characteristics:

    Set point temperature                  193. C
    Set point pressure                    2000. psi
    Initial liquid volume                  780. ml
    Mass of m-xylene initially injected  0.1096 Grams
    Mass of phenol initially injected    0.0980 Grams
    Integrator start time               19.5525 hh.mmss
    Plot scale factor                      1.00
    Regression begin time for m-xylene     5.00 Minutes
    Regression end time for m-xylene      19.00 Minutes
    Regression begin time for phenol       5.00 Minutes
    Regression end time for phenol        18.00 Minutes


Data Summary for m-Xylene:

Time of Day  Area    Temp  Vout  Elapsed Time      [RH]
  hh.mmss   /1.E+6    /F   /ml      /min       /(1.E-4 gm/ml)
----------- ------- ----  ----  ------------   --------------
  19.5825   6.11050 377.   5.0       3.00          0.6213
  20.0226   4.71680 377.  10.0       7.02          0.4796
  20.0725   1.77034 377.  15.0      12.00          0.1800
  20.1125   0.95065 378.  20.0      16.00          0.0966
  20.1525   0.79764 379.  25.0      20.00          0.0810
  20.1925   0.71215 379.  30.0      24.00          0.0723
  20.2326   0.64210 379.  35.0      28.02          0.0652
  20.2726   0.56789 380.  40.0      32.02          0.0576
  20.3126   0.52765 380.  45.0      36.02          0.0535
  20.3726   0.46938 381.  50.0      42.02          0.0476
  20.4426   0.41546 382.  55.0      49.02          0.0421
  20.5427   0.35953 380.  60.0      59.03          0.0365
  21.0928   0.32315 380.  65.0      74.05          0.0328
```

Data Summary for Phenol:

Time of Day hh.mmss	Area /1.E+6	Temp /F	Vout /ml	Elapsed Time /min	[RH] /(1.E-4 gm/ml)
19.5825	3.60990	377.	5.0	3.00	1.3878
20.0226	2.38000	377.	10.0	7.02	0.9150
20.0725	0.23356	377.	15.0	12.00	0.0898
20.1125	0.00000	378.	20.0	16.00	0.0000
20.1525	0.00000	379.	25.0	20.00	0.0000
20.1925	0.00000	379.	30.0	24.00	0.0000
20.2326	0.00000	379.	35.0	28.02	0.0000
20.2726	0.00000	380.	40.0	32.02	0.0000
20.3126	0.00000	380.	45.0	36.02	0.0000
20.3726	0.00000	381.	50.0	42.02	0.0000
20.4426	0.00000	382.	55.0	49.02	0.0000
20.5427	0.00000	380.	60.0	59.03	0.0000
21.0928	0.00000	380.	65.0	74.05	0.0000

```
                      Experiment: XPH-850219-1

 13 Total data points were collected
    13 Points were useful for processing
     0 Points were undefined

Run Characteristics:

    Set point temperature                        200. C
    Set point pressure                          2000. psi
    Initial liquid volume                        780. ml
    Mass of m-xylene initially injected        0.1110 Grams
    Mass of phenol initially injected          0.0967 Grams
    Integrator start time                     11.4652 hh.mmss
    Plot scale factor                            1.00
    Regression begin time for m-xylene           0.00 Minutes
    Regression end time for m-xylene             0.00 Minutes
    Regression begin time for phenol             0.00 Minutes
    Regression end time for phenol               0.00 Minutes


Data Summary for m-Xylene:

Time of Day  Area    Temp  Vout  Elapsed Time      [RH]
  hh.mmss   /1.E+6    /F   /ml      /min       /(1.E-4 gm/ml)
----------- ------- ----  ----  ------------  --------------
  11.4952   5.66780  384.   4.0       3.00        0.5732
  11.5457   2.53122  391.   8.0       8.08        0.2546
  11.5955   0.99437  396.  14.0      13.05        0.0996
  12.0353   0.77775  395.  20.0      17.02        0.0780
  12.0753   0.60655  393.  25.0      21.02        0.0609
  12.1153   0.54414  390.  30.0      25.02        0.0548
  12.1554   0.44672  390.  35.0      29.03        0.0450
  12.1953   0.39349  392.  40.0      33.02        0.0395
  12.2353   0.34843  392.  45.0      37.02        0.0350
  12.2754   0.32631  392.  50.0      41.03        0.0328
  12.3153   0.29841  392.  55.0      45.02        0.0300
  12.3553   0.26675  392.  60.0      49.02        0.0268
  12.3953   0.24848  393.  65.0      53.02        0.0250
```

Data Summary for Phenol:

Time of Day hh.mmss	Area /1.E+6	Temp /F	Vout /ml	Elapsed Time /min	[RH] /(1.E-4 gm/ml)
11.4952	2.97310	384.	4.0	3.00	1.1369
11.5457	0.57979	391.	8.0	8.08	0.2205
11.5955	0.00000	396.	14.0	13.05	0.0000
12.0353	0.00000	395.	20.0	17.02	0.0000
12.0753	0.00000	393.	25.0	21.02	0.0000
12.1153	0.00000	390.	30.0	25.02	0.0000
12.1554	0.00000	390.	35.0	29.03	0.0000
12.1953	0.00000	392.	40.0	33.02	0.0000
12.2353	0.00000	392.	45.0	37.02	0.0000
12.2754	0.00000	392.	50.0	41.03	0.0000
12.3153	0.00000	392.	55.0	45.02	0.0000
12.3553	0.00000	392.	60.0	49.02	0.0000
12.3953	0.00000	393.	65.0	53.02	0.0000

```
                    Experiment: XPH-850308-1

 19 Total data points were collected
    19 Points were useful for processing
     0 Points were undefined

Run Characteristics:

    Set point temperature                  130. C
    Set point pressure                    2000. psi
    Initial liquid volume                  780. ml
    Mass of m-xylene initially injected  0.1106 Grams
    Mass of phenol initially injected    0.0511 Grams
    Integrator start time               14.2819 hh.mmss
    Plot scale factor                      0.00
    Regression begin time for m-xylene   748.00 Minutes
    Regression end time for m-xylene    1900.00 Minutes
    Regression begin time for phenol     700.00 Minutes
    Regression end time for phenol      1200.00 Minutes


Data Summary for m-Xylene:

Time of Day  Area     Temp  Vout  Elapsed Time       [RH]
  hh.mmss   /1.E+6    /F    /ml      /min       /(1.E-4 gm/ml)
----------- -------  ----  ----  ------------  --------------
  14.3119   5.50200  264.   5.0        3.00        0.5999
  16.2125   6.56560  266.  10.0      113.10        0.7151
  18.2713   6.16060  266.  15.0      238.90        0.6710
  19.5141   6.21580  266.  20.0      323.37        0.6770
  21.0043   6.31460  266.  25.0      392.40        0.6878
  21.5041   6.44180  267.  30.0      442.37        0.7013
  22.5821   6.15620  266.  35.0      510.03        0.6705
  24.0959   5.06060  265.  40.0      581.67        0.5515
  24.2435   5.46340  266.  45.0      596.27        0.5951
  25.3958   5.41450  267.  50.0      671.65        0.5895
  26.2709   5.88890  267.  55.0      718.83        0.6411
  26.5629   5.06150  267.  60.0      748.17        0.5510
  28.1137   4.17180  266.  65.0      823.30        0.4544
  32.4536   3.04120  266.  70.0     1097.28        0.3313
  37.0130   2.07920  266.  75.0     1353.18        0.2265
  41.2454   1.80620  266.  80.0     1616.58        0.1967
  46.5922   1.58170  267.  85.0     1951.05        0.1722
  62.3154   1.31050  266.  90.0     2883.58        0.1427
  62.3554   1.26370  266.  95.0     2887.58        0.1377
```

Data Summary for Phenol:

Time of Day hh.mmss	Area /1.E+6	Temp /F	Vout /ml	Elapsed Time /min.	[RH] /(1.E-4 gm/ml)
14.3119	2.18280	264.	5.0	3.00	0.8999
16.2125	2.11730	266.	10.0	113.10	0.8720
18.2713	2.05870	266.	15.0	238.90	0.8479
19.5141	1.94350	266.	20.0	323.37	0.8004
21.0043	1.93190	266.	25.0	392.40	0.7956
21.5041	1.87540	267.	30.0	442.37	0.7720
22.5821	1.87560	266.	35.0	510.03	0.7725
24.0959	1.79540	265.	40.0	581.67	0.7398
24.2435	1.66090	266.	45.0	596.27	0.6840
25.3958	1.59430	267.	50.0	671.65	0.6563
26.2709	1.27670	267.	55.0	718.83	0.5255
26.5629	1.13700	267.	60.0	748.17	0.4680
28.1137	0.70613	266.	65.0	823.30	0.2908
32.4536	0.21070	266.	70.0	1097.28	0.0868
37.0130	0.00000	266.	75.0	1353.18	0.0000
41.2454	0.00000	266.	80.0	1616.58	0.0000
46.5922	0.00000	267.	85.0	1951.05	0.0000
62.3154	0.00000	266.	90.0	2883.58	0.0000
62.3554	0.00000	266.	95.0	2887.58	0.0000

```
                    Experiment: XPH-850301-1

 17 Total data points were collected
    17 Points were useful for processing
     0 Points were undefined

Run Characteristics:

    Set point temperature                    154. C
    Set point pressure                      2000. psi
    Initial liquid volume                    780. ml
    Mass of m-xylene initially injected    0.1121 Grams
    Mass of phenol initially injected      0.0520 Grams
    Integrator start time                 10.3636 hh.mmss
    Plot scale factor                        3.00
    Regression begin time for m-xylene     100.00 Minutes
    Regression end time for m-xylene       300.00 Minutes
    Regression begin time for phenol       120.00 Minutes
    Regression end time for phenol         250.00 Minutes


Data Summary for m-Xylene:

Time of Day  Area     Temp  Vout  Elapsed Time        [RH]
  hh.mmss   /1.E+6    /F    /ml      /min         /(1.E-4 gm/ml)
----------- -------   ----  ----  ------------    --------------
  10.3936   5.82620   306.   5.0      3.00            0.6210
  11.0336   5.40380   306.  10.0     27.00            0.5760
  11.3337   5.31580   308.  15.0     57.02            0.5660
  12.3009   4.23450   308.  20.0    113.55            0.4509
  12.4150   3.19820   309.  25.0    125.23            0.3403
  12.5314   2.72654   309.  30.0    136.63            0.2901
  13.0627   2.39518   310.  35.0    149.85            0.2547
  13.1727   2.14143   310.  40.0    160.85            0.2277
  13.3127   1.89481   310.  45.0    174.85            0.2015
  13.4627   1.69961   310.  50.0    189.85            0.1807
  14.0328   1.53233   310.  55.0    206.87            0.1629
  14.4242   1.32200   308.  60.0    246.10            0.1407
  15.1207   1.20706   308.  65.0    275.52            0.1285
  16.2941   0.99944   310.  70.0    353.08            0.1063
  19.2648   0.87407   309.  75.0    530.20            0.0930
  22.5516   0.74583   310.  80.0    738.67            0.0793
  23.0026   0.70799   311.  85.0    743.83            0.0753
```

Data Summary for Phenol:

Time of Day hh.mmss	Area /1.E+6	Temp /F	Vout /ml	Elapsed Time /min	[RH] /(1.E-4 gm/ml)
10.3936	1.91930	306.	5.0	3.00	0.7736
11.0336	1.44880	306.	10.0	27.00	0.5839
11.3337	1.65730	308.	15.0	57.02	0.6672
12.3009	1.05210	308.	20.0	113.55	0.4235
12.4150	0.65170	309.	25.0	125.23	0.2622
12.5314	0.47282	309.	30.0	136.63	0.1902
13.0627	0.31248	310.	35.0	149.85	0.1256
13.1727	0.21320	310.	40.0	160.85	0.0857
13.3127	0.18194	310.	45.0	174.85	0.0732
13.4627	0.14578	310.	50.0	189.85	0.0586
14.0328	0.06838	310.	55.0	206.87	0.0275
14.4242	0.00000	308.	60.0	246.10	0.0000
15.1207	0.00000	308.	65.0	275.52	0.0000
16.2941	0.00000	310.	70.0	353.08	0.0000
19.2648	0.00000	309.	75.0	530.20	0.0000
22.5516	0.00000	310.	80.0	738.67	0.0000
23.0026	0.00000	311.	85.0	743.83	0.0000

```
                    Experiment: XPH-850307-2

 22 Total data points were collected
    22 Points were useful for processing
     0 Points were undefined

Run Characteristics:

    Set point temperature                  178. C
    Set point pressure                    2000. psi
    Initial liquid volume                  780. ml
    Mass of m-xylene initially injected  0.1110 Grams
    Mass of phenol initially injected    0.0507 Grams
    Integrator start time               21.2042 hh.mmss
    Plot scale factor                      1.00
    Regression begin time for m-xylene    22.00 Minutes
    Regression end time for m-xylene      50.00 Minutes
    Regression begin time for phenol      22.00 Minutes
    Regression end time for phenol        45.00 Minutes


Data Summary for m-Xylene:

Time of Day  Area    Temp  Vout  Elapsed Time      [RH]
  hh.mmss   /1.E+6    /F   /ml      /min       /(1.E-4 gm/ml)
----------- ------- ---- ---- ------------ --------------
  21.2342  6.10830 347.   5.0      3.00          0.6345
  21.2842  5.99410 351.  10.0      8.00          0.6209
  21.3342  5.34470 352.  15.0     13.00          0.5533
  21.3742  5.48910 352.  20.0     17.00          0.5682
  21.4142  5.09050 352.  25.0     21.00          0.5270
  21.4442  4.06620 352.  30.0     24.00          0.4209
  21.4942  3.76320 352.  35.0     29.00          0.3896
  21.5242  2.76737 352.  40.0     32.00          0.2865
  21.5642  2.32064 353.  45.0     36.00          0.2401
  22.0042  2.06824 353.  50.0     40.00          0.2140
  22.0442  1.84143 353.  55.0     44.00          0.1905
  22.0942  1.67796 353.  60.0     49.00          0.1736
  22.1342  1.55700 353.  65.0     53.00          0.1611
  22.1742  1.42750 353.  70.0     57.00          0.1477
  22.2142  1.37390 353.  75.0     61.00          0.1421
  22.2542  1.28950 353.  80.0     65.00          0.1334
  22.3342  1.20600 352.  85.0     73.00          0.1248
  22.4543  1.04270 351.  90.0     85.02          0.1080
  22.5942  0.94883 351.  95.0     99.00          0.0983
  23.1742  0.87624 352. 100.0    117.00          0.0907
  23.3543  0.78207 352. 105.0    135.02          0.0810
  24.0043  0.71221 351. 110.0    160.02          0.0738
```

Data Summary for Phenol:

Time of Day hh.mmss	Area /1.E+6	Temp /F	Vout /ml	Elapsed Time /min	[RH] /(1.E-4 gm/ml)
21.2342	2.07910	347.	5.0	3.00	0.8166
21.2842	1.95860	351.	10.0	8.00	0.7672
21.3342	1.63050	352.	15.0	13.00	0.6382
21.3742	1.70190	352.	20.0	17.00	0.6662
21.4142	1.36270	352.	25.0	21.00	0.5334
21.4442	1.09770	352.	30.0	24.00	0.4297
21.4942	0.66876	352.	35.0	29.00	0.2618
21.5242	0.46429	352.	40.0	32.00	0.1817
21.5642	0.27564	353.	45.0	36.00	0.1078
22.0042	0.18123	353.	50.0	40.00	0.0709
22.0442	0.11978	353.	55.0	44.00	0.0468
22.0942	0.07550	353.	60.0	49.00	0.0295
22.1342	0.07036	353.	65.0	53.00	0.0275
22.1742	0.06466	353.	70.0	57.00	0.0253
22.2142	0.04178	353.	75.0	61.00	0.0163
22.2542	0.04254	353.	80.0	65.00	0.0166
22.3342	0.00000	352.	85.0	73.00	0.0000
22.4543	0.00000	351.	90.0	85.02	0.0000
22.5942	0.00000	351.	95.0	99.00	0.0000
23.1742	0.00000	352.	100.0	117.00	0.0000
23.3543	0.00000	352.	105.0	135.02	0.0000
24.0043	0.00000	351.	110.0	160.02	0.0000

```
                    Experiment: XPH-850307-1

 13 Total data points were collected
    13 Points were useful for processing
     0 Points were undefined

Run Characteristics:

    Set point temperature                   200. C
    Set point pressure                     2000. psi
    Initial liquid volume                   780. ml
    Mass of m-xylene initially injected   0.1103 Grams
    Mass of phenol initially injected     0.0500 Grams
    Integrator start time                15.2036 hh.mmss
    Plot scale factor                       1.00
    Regression begin time for m-xylene     10.00 Minutes
    Regression end time for m-xylene       25.00 Minutes
    Regression begin time for phenol       10.00 Minutes
    Regression end time for phenol         20.00 Minutes


Data Summary for m-Xylene:

Time of Day  Area     Temp  Vout  Elapsed Time       [RH]
  hh.mmss   /1.E+6     /F   /ml       /min       /(1.E-4 gm/ml)
----------- ------- ---- ---- ------------ --------------
  15.2335   6.12310 381.   5.0        2.98          0.6207
  15.2736   5.80340 386.  10.0        7.00          0.5860
  15.3135   4.77040 392.  15.0       10.98          0.4794
  15.3536   2.29948 397.  20.0       15.00          0.2302
  15.3936   1.40072 398.  25.0       19.00          0.1401
  15.4336   1.14025 396.  30.0       23.00          0.1142
  15.4736   0.92583 392.  35.0       27.00          0.0931
  15.5136   0.79539 392.  40.0       31.00          0.0799
  15.5536   0.69636 393.  45.0       35.00          0.0699
  16.0036   0.65715 394.  50.0       40.00          0.0659
  16.0536   0.54774 393.  55.0       45.00          0.0550
  16.1436   0.38938 392.  60.0       54.00          0.0391
  16.2236   0.37568 392.  65.0       62.00          0.0378
```

Data Summary for Phenol:

Time of Day hh.mmss	Area /1.E+6	Temp /F	Vout /ml	Elapsed Time /min	[RH] /(1.E-4 gm/ml)
15.2335	1.84360	381.	5.0	2.98	0.7066
15.2736	1.43020	386.	10.0	7.00	0.5461
15.3135	0.84797	392.	15.0	10.98	0.3222
15.3536	0.19982	397.	20.0	15.00	0.0756
15.3936	0.05941	398.	25.0	19.00	0.0225
15.4336	0.00000	396.	30.0	23.00	0.0000
15.4736	0.00000	392.	35.0	27.00	0.0000
15.5136	0.00000	392.	40.0	31.00	0.0000
15.5536	0.00000	393.	45.0	35.00	0.0000
16.0036	0.00000	394.	50.0	40.00	0.0000
16.0536	0.00000	393.	55.0	45.00	0.0000
16.1436	0.00000	392.	60.0	54.00	0.0000
16.2236	0.00000	392.	65.0	62.00	0.0000

```
                    Experiment: XPH-850311-1

 11 Total data points were collected
    11 Points were useful for processing
     0 Points were undefined

Run Characteristics:

    Set point temperature                   154. C
    Set point pressure                     2000. psi
    Initial liquid volume                   780. ml
    Mass of m-xylene initially injected   0.1114 Grams
    Mass of phenol initially injected     0.0139 Grams
    Integrator start time                22.3638 hh.mmss
    Plot scale factor                       0.00
    Regression begin time for m-xylene    400.00 Minutes
    Regression end time for m-xylene     1500.00 Minutes
    Regression begin time for phenol      300.00 Minutes
    Regression end time for phenol       1400.00 Minutes


Data Summary for m-Xylene:

Time of Day  Area    Temp  Vout  Elapsed Time      [RH]
  hh.mmss   /1.E+6    /F   /ml      /min      /(1.E-4 gm/ml)
----------- ------- ---- ---- ------------ --------------
  22.3938   5.00000 305.   5.0       3.00        0.5333
  24.0219   5.97360 305.  10.0      85.68        0.6371
  24.4940   5.33690 307.  15.0     133.03        0.5685
  25.1034   5.25210 309.  20.0     153.93        0.5589
  25.4100   5.54050 310.  25.0     184.37        0.5892
  26.1843   5.42670 311.  30.0     222.08        0.5767
  27.1153   5.14490 310.  35.0     275.25        0.5471
  29.0158   4.95110 309.  40.0     385.33        0.5268
  32.3218   3.84680 308.  45.0     595.67        0.4096
  44.1424   1.92480 310.  50.0    1297.77        0.2047
  47.1124   1.62520 309.  55.0    1474.77        0.1729
```

```
Data Summary for Phenol:

Time of Day  Area     Temp  Vout  Elapsed Time      [RH]
  hh.mmss   /1.E+6    /F    /ml      /min       /(1.E-4 gm/ml)
----------- -------  ----  ----  ------------  --------------
  22.3938   0.37837  305.   5.0          3.00       0.1526
  24.0219   0.37016  305.  10.0         85.68       0.1493
  24.4940   0.34975  307.  15.0        133.03       0.1409
  25.1034   0.32813  309.  20.0        153.93       0.1320
  25.4100   0.38799  310.  25.0        184.37       0.1560
  26.1843   0.36668  311.  30.0        222.08       0.1474
  27.1153   0.33986  310.  35.0        275.25       0.1367
  29.0158   0.25194  309.  40.0        385.33       0.1014
  32.3218   0.13239  308.  45.0        595.67       0.0533
  44.1424   0.00000  310.  50.0       1297.77       0.0000
  47.1124   0.00000  309.  55.0       1474.77       0.0000
```

```
                    Experiment: XPH-850228-1

  23 Total data points were collected
     23 Points were useful for processing
      0 Points were undefined

Run Characteristics:

    Set point temperature                   178. C
    Set point pressure                     2000. psi
    Initial liquid volume                   780. ml
    Mass of m-xylene initially injected   0.1106 Grams
    Mass of phenol initially injected     0.0152 Grams
    Integrator start time                14.5350 hh.mmss
    Plot scale factor                       2.00
    Regression begin time for m-xylene     38.00 Minutes
    Regression end time for m-xylene      250.00 Minutes
    Regression begin time for phenol       25.00 Minutes
    Regression end time for phenol         75.00 Minutes


Data Summary for m-Xylene:

Time of Day  Area     Temp  Vout  Elapsed Time      [RH]
  hh.mmss   /1.E+6     /F   /ml      /min       /(1.E-4 gm/ml)
----------- -------   ----  ----  ------------  -------------
  14.5657   4.29630   346.   5.0       3.12         0.4466
  15.0157   5.10000   350.  10.0       8.12         0.5287
  15.0730   5.44840   349.  15.0      13.67         0.5652
  15.1131   5.28800   350.  20.0      17.68         0.5482
  15.1530   4.85230   350.  25.0      21.67         0.5030
  15.1930   4.83230   350.  30.0      25.67         0.5009
  15.2526   4.97910   351.  35.0      31.60         0.5158
  15.2927   4.35730   352.  40.0      35.62         0.4511
  15.3326   4.15110   352.  45.0      39.60         0.4297
  15.3726   3.94260   352.  50.0      43.60         0.4081
  15.4126   3.74710   353.  55.0      47.60         0.3876
  15.4526   3.59890   353.  60.0      51.60         0.3723
  15.5126   3.30190   353.  65.0      57.60         0.3416
  15.5827   3.03710   352.  70.0      64.62         0.3144
  16.0826   2.67697   352.  75.0      74.60         0.2771
  16.1855   2.44598   351.  80.0      85.08         0.2534
  16.3113   2.20379   351.  85.0      97.38         0.2283
  16.5144   1.88436   352.  90.0     117.90         0.1951
  17.1311   1.64869   352.  95.0     139.35         0.1707
  17.5505   1.33344   351. 100.0     181.25         0.1381
  19.0722   1.02915   352. 105.0     253.53         0.1065
  19.5439   0.90129   353. 110.0     300.82         0.0932
  21.0325   0.76628   352. 115.0     369.58         0.0793
```

Data Summary for Phenol:

Time of Day hh.mmss	Area /1.E+6	Temp /F	Vout /ml	Elapsed Time /min	[RH] /(1.E-4 gm/ml)
14.5657	0.57681	346.	5.0	3.12	0.2267
15.0157	0.42792	350.	10.0	8.12	0.1677
15.0730	0.38368	349.	15.0	13.67	0.1505
15.1131	0.36782	350.	20.0	17.68	0.1442
15.1530	0.39648	350.	25.0	21.67	0.1554
15.1930	0.37520	350.	30.0	25.67	0.1471
15.2526	0.34082	351.	35.0	31.60	0.1335
15.2927	0.31805	352.	40.0	35.62	0.1245
15.3326	0.29079	352.	45.0	39.60	0.1138
15.3726	0.26329	352.	50.0	43.60	0.1031
15.4126	0.23072	353.	55.0	47.60	0.0903
15.4526	0.19755	353.	60.0	51.60	0.0773
15.5126	0.17705	353.	65.0	57.60	0.0692
15.5827	0.13837	352.	70.0	64.62	0.0542
16.0826	0.11003	352.	75.0	74.60	0.0431
16.1855	0.00000	351.	80.0	85.08	0.0000
16.3113	0.05627	351.	85.0	97.38	0.0220
16.5144	0.10296	352.	90.0	117.90	0.0403
17.1311	0.00000	352.	95.0	139.35	0.0000
17.5505	0.00000	351.	100.0	181.25	0.0000
19.0722	0.00000	352.	105.0	253.53	0.0000
19.5439	0.00000	353.	110.0	300.82	0.0000
21.0325	0.00000	352.	115.0	369.58	0.0000

```
                    Experiment: XPH-850227-1

 20 Total data points were collected
    20 Points were useful for processing
     0 Points were undefined

Run Characteristics:

    Set point temperature                  200. C
    Set point pressure                    2000. psi
    Initial liquid volume                  780. ml
    Mass of m-xylene initially injected  0.1103 Grams
    Mass of phenol initially injected    0.0143 Grams
    Integrator start time               16.3506 hh.mmss
    Plot scale factor                      1.00
    Regression begin time for m-xylene    20.00 Minutes
    Regression end time for m-xylene      46.00 Minutes
    Regression begin time for phenol       5.00 Minutes
    Regression end time for phenol        30.00 Minutes


Data Summary for m-Xylene:

Time of Day  Area    Temp  Vout  Elapsed Time      [RH]
  hh.mmss   /1.E+6   /F    /ml      /min       /(1.E-4 gm/ml)
----------- ------- ----  ----  ------------  --------------
  16.3806  5.46850  389.   5.0       3.00         0.5509
  16.4206  5.78440  389.  10.0       7.00         0.5827
  16.4706  5.66530  388.  15.0      12.00         0.5712
  16.5124  4.76580  390.  20.0      16.30         0.4797
  16.5534  3.64590  392.  25.0      20.47         0.3664
  16.5948  2.91560  392.  30.0      24.70         0.2930
  17.0400  2.40145  392.  35.0      29.57         0.2414
  17.0837  1.96049  392.  40.0      33.52         0.1970
  17.1237  1.66554  392.  45.0      37.52         0.1674
  17.1637  1.43627  393.  50.0      41.52         0.1442
  17.2037  1.22603  393.  55.0      45.52         0.1231
  17.2437  1.09527  393.  60.0      49.52         0.1100
  17.2837  0.95169  393.  65.0      53.52         0.0956
  17.3237  0.84925  393.  70.0      57.52         0.0853
  17.3637  0.76409  393.  75.0      61.52         0.0767
  17.4037  0.70098  393.  80.0      65.52         0.0704
  17.4538  0.62244  393.  85.0      70.53         0.0625
  17.5238  0.56816  392.  90.0      77.53         0.0571
  18.0338  0.48694  393.  95.0      88.53         0.0489
  18.1639  0.41142  393. 100.0     101.55         0.0413
```

Data Summary for Phenol:

Time of Day hh.mmss	Area /1.E+6	Temp /F	Vout /ml	Elapsed Time /min	[RH] /(1.E-4 gm/ml)
16.3806	0.54318	389.	5.0	3.00	0.2069
16.4206	0.31563	389.	10.0	7.00	0.1202
16.4706	0.22728	388.	15.0	12.00	0.0866
16.5124	0.15292	390.	20.0	16.30	0.0582
16.5534	0.09622	392.	25.0	20.47	0.0366
16.5948	0.05326	392.	30.0	24.70	0.0202
17.0400	0.00000	392.	35.0	29.57	0.0000
17.0837	0.00000	392.	40.0	33.52	0.0000
17.1237	0.00000	392.	45.0	37.52	0.0000
17.1637	0.00000	393.	50.0	41.52	0.0000
17.2037	0.00000	393.	55.0	45.52	0.0000
17.2437	0.00000	393.	60.0	49.52	0.0000
17.2837	0.00000	393.	65.0	53.52	0.0000
17.3237	0.00000	393.	70.0	57.52	0.0000
17.3637	0.00000	393.	75.0	61.52	0.0000
17.4037	0.00000	393.	80.0	65.52	0.0000
17.4538	0.00000	393.	85.0	70.53	0.0000
17.5238	0.00000	392.	90.0	77.53	0.0000
18.0338	0.00000	393.	95.0	88.53	0.0000
18.1639	0.00000	393.	100.0	101.55	0.0000

APPENDIX D

Experimental Conditions and Data--Soil

This appendix contains experimental conditions and Concentration *versus* time data for m-xylene, tetrachloroethylene, and malathion with soil present in the reactor. These experiments were summarized in Table 5.1, and are presented here in identical order.

```
                    Experiment: XYL-840501-1-S

 17 Total data points were collected
    16 Points were useful for processing
     1 Points were undefined

Run Characteristics:

    Set point temperature                       250. C
    Set point pressure                         2000. psi
    Initial liquid volume                       780. ml
    Mass of organic initially injected       0.1118 Grams
    Mass of soil present                         5.0 Grams
    Integrator start time                    12.3431 hh.mmss
    Plot scale factor                           1.00
    Regression begin time                      50.00 Minutes
    Regression end time                      4400.00 Minutes


Data Summary:

Time of Day  Area    Temp  Vout  Elapsed Time      [RH]
  hh.mmss   /1.E+6    /F   /ml      /min      /(1.E-4 gm/ml)
----------- -------  ----  ----  ------------  --------------
  12.4432  5.85700  477.   5.0        10.02        0.7165
  14.0133  7.07100  480.  10.0        87.03        0.8623
  16.0050  6.94800  483.  15.0       206.32        0.8446
  20.4711  6.37800  483.  20.0       492.67        0.7753
  24.1107  6.12100  483.  25.0       696.60        0.7441
  28.0903  0.00000  482.  30.0       934.53        0.0000
  31.5909  5.79000  482.  35.0      1164.63        0.7046
  36.1705  5.40300  481.  40.0      1422.57        0.6582
  40.0144  5.02500  482.  45.0      1647.22        0.6115
  44.0713  4.96000  483.  50.0      1892.70        0.6030
  48.0730  4.58600  482.  55.0      2132.98        0.5581
  52.0302  4.53200  482.  60.0      2368.52        0.5515
  56.0318  4.16400  481.  65.0      2608.78        0.5073
  60.2205  3.91300  481.  70.0      2867.57        0.4767
  64.2928  3.74600  482.  75.0      3114.95        0.4559
  72.0403  3.40600  483.  79.0      3569.53        0.4141
  82.2713  3.16300  480.  84.0      4192.70        0.3857
```

```
                    Experiment: XYL-840510-1-S

 13 Total data points were collected
    13 Points were useful for processing
     0 Points were undefined

Run Characteristics:

    Set point temperature                   260. C
    Set point pressure                     2500. psi
    Initial liquid volume                   780. ml
    Mass of organic initially injected   0.1121 Grams
    Mass of soil present                    5.0 Grams
    Integrator start time               13.3850 hh.mmss
    Plot scale factor                      1.00
    Regression begin time                200.00 Minutes
    Regression end time                 3200.00 Minutes


Data Summary:

Time of Day  Area    Temp  Vout  Elapsed Time       [RH]
  hh.mmss   /1.E+6   /F    /ml      /min       /(1.E-4 gm/ml)
----------- -------  ----  ----  ------------  --------------
  13.4850   6.64200  494.   7.0      10.00         0.7980
  14.1851   7.69300  499.  15.0      40.02         0.9191
  16.0016   8.00500  500.  21.0     141.43         0.9554
  18.5031   7.01000  499.  25.0     311.68         0.8375
  21.1034   6.88300  500.  30.0     451.73         0.8215
  24.0111   6.28900  500.  34.0     622.35         0.7506
  27.1633   5.98500  500.  39.0     817.72         0.7143
  32.5207   5.83700  502.  45.0    1153.28         0.6951
  38.1417   4.60500  498.  50.0    1475.45         0.5508
  42.3829   4.27000  501.  55.0    1739.65         0.5090
  48.3438   3.67400  501.  60.0    2095.80         0.4380
  58.3203   2.93900  499.  65.0    2693.22         0.3511
  64.5555   2.44300  500.  70.0    3077.08         0.2916
```

```
                    Experiment: XYL-840515-1-S

 12 Total data points were collected
    12 Points were useful for processing
     0 Points were undefined

Run Characteristics:

    Set point temperature                  260. C
    Set point pressure                    2500. psi
    Initial liquid volume                  780. ml
    Mass of organic initially injected  0.1117 Grams
    Mass of soil present                   5.0 Grams
    Integrator start time               0.1025 hh.mmss
    Plot scale factor                     1.00
    Regression begin time               500.00 Minutes
    Regression end time                4500.00 Minutes


Data Summary:

Time of Day  Area    Temp  Vout  Elapsed Time      [RH]
  hh.mmss   /1.E+6    /F   /ml      /min       /(1.E-4 gm/ml)
----------- ------- ----  ----  ------------  --------------
    0.2225  7.19600 495.   6.0      12.00         0.8636
    1.2855  8.78700 500.  12.0      78.50         1.0487
   10.5616  7.03700 500.  18.0     645.85         0.8398
   15.4156  6.30500 500.  24.0     931.52         0.7525
   20.5120  5.51500 502.  29.0    1240.92         0.6567
   24.1545  5.03900 500.  33.0    1445.33         0.6014
   35.1701  3.95800 497.  38.0    2106.60         0.4740
   41.1713  4.00300 501.  44.0    2466.80         0.4772
   48.3544  2.71400 500.  49.0    2905.32         0.3239
   60.2252  1.99400 499.  54.0    3612.45         0.2382
   65.0749  1.65000 501.  59.0    3897.40         0.1967
   73.1430  1.37400 502.  64.0    4384.08         0.1636
```

```
                    Experiment: XYL-840505-1-S

 15 Total data points were collected
    14 Points were useful for processing
     1 Points were undefined

Run Characteristics:

    Set point temperature                   275. C
    Set point pressure                     1500. psi
    Initial liquid volume                   780. ml
    Mass of organic initially injected    0.1122 Grams
    Mass of soil present                     5.0 Grams
    Integrator start time                12.5027 hh.mmss
    Plot scale factor                       1.00
    Regression begin time                  50.00 Minutes
    Regression end time                  2900.00 Minutes


Data Summary:

Time of Day  Area    Temp  Vout  Elapsed Time      [RH]
  hh.mmss   /1.E+6   /F    /ml      /min       /(1.E-4 gm/ml)
----------- ------- ----  ----  ------------  --------------
  12.5927   7.37500 520.   5.0        9.00        0.8602
  13.5954   8.89100 525.  11.0       69.45        1.0309
  15.0616   0.00000 526.  17.0      135.82        0.0000
  16.0636   8.30700 527.  22.0      196.15        0.9608
  17.3448   7.96100 527.  27.0      284.35        0.9208
  20.0519   7.30400 529.  32.0      434.87        0.8428
  22.1411   6.90700 529.  36.0      563.73        0.7969
  24.1731   6.24600 533.  41.0      687.07        0.7172
  27.5506   5.50900 530.  46.0      904.65        0.6349
  32.0606   4.77200 524.  50.0     1155.65        0.5540
  37.1718   3.77500 528.  55.0     1466.85        0.4361
  41.0957   3.09200 529.  60.0     1699.50        0.3568
  46.1624   2.23400 528.  65.0     2005.95        0.2581
  50.1609   2.06400 529.  70.0     2245.70        0.2382
  59.1329   1.11300 525.  75.0     2783.03        0.1290
```

```
                    Experiment: XYL-840519-1-S

 11 Total data points were collected
    11 Points were useful for processing
     0 Points were undefined

Run Characteristics:

    Set point temperature                 275. C
    Set point pressure                   2500. psi
    Initial liquid volume                 780. ml
    Mass of organic initially injected   0.1123 Grams
    Mass of soil present                    5.0 Grams
    Integrator start time               16.2355 hh.mmss
    Plot scale factor                      1.00
    Regression begin time                100.00 Minutes
    Regression end time                 2000.00 Minutes


Data Summary:

Time of Day  Area    Temp  Vout  Elapsed Time      [RH]
  hh.mmss   /1.E+6    /F   /ml       /min      /(1.E-4 gm/ml)
----------- -------  ----  ----  ------------  --------------
  16.3358   6.82700  522.   5.0      10.05         0.7944
  17.2056   8.44200  527.  10.0      57.02         0.9764
  19.1436   7.91700  527.  15.0     170.68         0.9157
  20.5317   7.71000  526.  20.0     269.36         0.8928
  24.5200   6.34300  527.  26.0     508.08         0.7337
  29.4206   4.29200  525.  30.0     798.18         0.4976
  33.5443   2.91900  526.  36.0    1050.80         0.3380
  38.0554   2.02900  527.  40.0    1301.98         0.2347
  41.4814   1.36900  528.  45.0    1524.32         0.1582
  45.5323   0.95100  528.  53.0    1769.47         0.1099
  48.5919   0.69200  526.  58.0    1955.40         0.0801
```

```
                    Experiment: TCE-840607-1-S

 17 Total data points were collected
    17 Points were useful for processing
     0 Points were undefined

Run Characteristics:

    Set point temperature                  275. C
    Set point pressure                    1500. psi
    Initial liquid volume                  780. ml
    Mass of organic initially injected  0.1249 Grams
    Mass of soil present                   5.0 Grams
    Integrator start time              17.2222 hh.mmss
    Plot scale factor                     4.00
    Regression begin time               200.00 Minutes
    Regression end time                2300.00 Minutes


Data Summary:

Time of Day  Area    Temp  Vout  Elapsed Time      [RH]
  hh.mmss   /1.E+6   /F   /ml       /min      /(1.E-4 gm/ml)
----------- ------- ---- ---- ------------ --------------
  17.2823   1.12330 523.   5.0       6.02         0.8022
  17.4223   1.53460 526.  10.0      20.02         1.0920
  17.5423   1.54280 525.  15.0      32.02         1.0991
  21.2524   1.46720 522.  20.0     243.03         1.0491
  21.3747   1.35700 524.  25.0     255.42         0.9679
  24.4608   1.06040 527.  30.0     443.77         0.7537
  24.5208   1.25170 527.  36.0     449.77         0.8896
  33.0237   0.83067 528.  41.0     940.25         0.5897
  36.1332   0.66617 525.  46.0    1131.17         0.4746
  38.1209   0.53335 528.  51.0    1249.78         0.3786
  39.3745   0.46137 527.  56.0    1335.38         0.3279
  41.2743   0.40620 529.  61.0    1445.35         0.2880
  45.2838   0.34656 526.  67.0    1686.27         0.2466
  45.3239   0.30092 526.  72.0    1690.28         0.2141
  47.1905   0.30305 529.  77.0    1796.72         0.2149
  54.5651   0.22799 527.  82.0    2254.48         0.1620
  54.5951   0.24417 527.  87.0    2257.48         0.1735
```

```
                    Experiment: TCE-840605-1-S

 15 Total data points were collected
    14 Points were useful for processing
     1 Points were undefined

Run Characteristics:

    Set point temperature                  275. C
    Set point pressure                    2000. psi
    Initial liquid volume                  780. ml
    Mass of organic initially injected  0.1277 Grams
    Mass of soil present                   5.0 Grams
    Integrator start time              23.4327 hh.mmss
    Plot scale factor                     4.00
    Regression begin time                80.00 Minutes
    Regression end time                1600.00 Minutes


Data Summary:

Time of Day  Area    Temp  Vout  Elapsed Time      [RH]
  hh.mmss   /1.E+6    /F   /ml      /min       /(1.E-4 gm/ml)
----------- ------- ----  ----  ------------  --------------
  23.4828   1.05450 520.   5.0       5.02          0.7558
  23.5427   1.41900 524.  10.0      11.00          1.0122
  24.0027   1.34480 528.  15.0      17.00          0.9546
  24.1028   1.32670 527.  20.0      27.02          0.9429
  24.1828   1.49040 527.  25.0      35.02          1.0593
  25.0028   1.41530 527.  30.0      77.02          1.0059
  25.0928   1.47080 527.  35.0      86.02          1.0453
  38.3742 999.00000 529.  39.0     894.25          0.0000
  38.4909   0.44487 529.  44.0     905.70          0.3154
  38.5553   0.42727 529.  49.0     912.43          0.3029
  42.0232   0.28742 528.  53.0    1099.08          0.2040
  47.1354   0.17573 527.  58.0    1410.45          0.1249
  47.1933   0.18986 527.  64.0    1416.10          0.1349
  48.5704   0.14814 529.  68.0    1513.62          0.1050
  49.0009   0.14225 529.  73.0    1516.70          0.1009
```

```
                    Experiment: TCE-840612-1-S

  14 Total data points were collected
     13 Points were useful for processing
      1 Points were undefined

 Run Characteristics:

     Set point temperature                 290. C
     Set point pressure                   1500. psi
     Initial liquid volume                 780. ml
     Mass of organic initially injected  0.1282 Grams
     Mass of soil present                   5.0 Grams
     Integrator start time              15.1955 hh.mmss
     Plot scale factor                     4.00
     Regression begin time               100.00 Minutes
     Regression end time                2000.00 Minutes


 Data Summary:

 Time of Day  Area    Temp  Vout  Elapsed Time      [RH]
   hh.mmss   /1.E+6   /F    /ml      /min       /(1.E-4 gm/ml)
 ----------- ------- ---- ---- ------------ --------------
   15.2455  1.69320 551.   6.0        5.00         1.1677
   15.3156  2.12870 554.  13.0       12.02         0.0000
   16.2108  1.83600 559.  17.0       61.22         1.2528
   18.2929  1.73250 556.  24.0      189.57         1.1869
   21.3400  1.31020 557.  29.0      374.75         0.8964
   24.0614  0.95052 553.  34.0      526.32         0.6538
   35.4924  0.56275 549.  40.0     1229.48         0.3891
   35.5224  0.47903 551.  45.0     1232.48         0.3303
   38.0717  0.34744 553.  49.0     1367.37         0.2390
   40.0809  0.29713 555.  54.0     1488.23         0.2038
   41.3949  0.25448 553.  59.0     1579.90         0.1750
   43.4609  0.21024 554.  64.0     1706.23         0.1444
   46.1743  0.17872 554.  68.0     1857.80         0.1228
   46.4057  0.16616 554.  74.0     1881.03         0.1141
```

```
                    Experiment: TCE-840610-1-S

 12 Total data points were collected
    12 Points were useful for processing
     0 Points were undefined

Run Characteristics:

    Set point temperature                  290. C
    Set point pressure                    2000. psi
    Initial liquid volume                  780. ml
    Mass of organic initially injected  0.1303 Grams
    Mass of soil present                   5.0 Grams
    Integrator start time              21.2805 hh.mmss
    Plot scale factor                     3.00
    Regression begin time                10.00 Minutes
    Regression end time                1600.00 Minutes


Data Summary:

Time of Day  Area    Temp  Vout  Elapsed Time      [RH]
  hh.mmss   /1.E+6    /F   /ml       /min      /(1.E-4 gm/ml)
----------- ------- ---- ---- ------------ --------------
  21.3405   1.37500  551.   5.0        6.00        0.9482
  21.4205   1.80540  553.  11.0       14.00        1.2418
  21.5805   1.82410  558.  18.0       30.00        1.2464
  32.1308   0.89353  550.  24.0      645.05        0.6170
  34.0158   0.63779  553.  29.0      753.88        0.4387
  35.5604   0.47790  555.  35.0      867.98        0.3278
  38.3531   0.34485  554.  40.0     1027.43        0.2369
  40.2405   0.29141  555.  44.0     1136.00        0.1999
  42.0235   0.22157  554.  49.0     1234.50        0.1522
  44.0354   0.19720  554.  54.0     1355.82        0.1355
  46.1722   0.14664  555.  58.0     1489.28        0.1006
  46.2154   0.13460  555.  63.0     1493.82        0.0923
```

```
                                   Experiment: MAL-840523-1-S

 10 Total data points were collected

Run Characteristics:

    Set point temperature                   160. C
    Set point pressure                     1500. psi
    Initial liquid volume                   780. ml
    Mass of organic initially injected    0.1858 Grams
    Integrator start time                21.1336 hh.mmss

Data Summary:

                                     Chromatograph Retention Times/(min)
            ----------------------------------------------------------------------------------------------------
            0.09      0.21      0.30      0.36      0.43      0.54      1.09      2.70      3.89      TOTAL
            ----------------------------------------------------------------------------------------------------

Time/(min)                             Chromatogram Area/(mvolt sec)

       5.     5459.        0.   610640.  9608900.        0.        0.        0.        0.        0. 10330000.
      15.     8534.        0. 12621000.  1615400.        0.        0.        0.    63545.    41323. 14278000.
      26.     8509.        0. 13104000.  1256400.        0.        0.        0.    33019.        0. 14397000.
      38.     7569.        0. 12531000.  1248300.        0.    56969.        0.    27729.        0. 13871000.
      48.    12563.        0. 11989000.   553200.        0.        0.        0.    26659.        0. 12554000.
      59.        0.     4479. 11511000.   531790.   767930.    66426.        0.        0.        0. 12904000.
      71.        0.     6852. 11528000.   585860.        0.        0.        0.    22538.        0. 12144000.
     103.     5626.        0. 12144000.   963240.        0.        0.    14357.    23207.        0. 13202000.
     113.     7203.        0. 10369000.   609480.   714060.        0.        0.    55422.    20044. 11719000.
     123.     5982.        0. 10766000.   513900.   727050.        0.        0.    19070.        0. 12013000.
```

```
                       Experiment: MAL-840524-1-S

  8 Total data points were collected

Run Characteristics:

    Set point temperature                 160. C
    Set point pressure                   2000. psi
    Initial liquid volume                 780. ml
    Mass of organic initially injected  0.1845 Grams
    Integrator start time              16.3229 hh.mmss

Data Summary:

                         Chromatograph Retention Times/(min)
           ----------------------------------------------------------------------------------------------------
           0.09     0.21     0.30     0.36     0.43     0.54     1.09     2.70     3.89     TOTAL
           ----------------------------------------------------------------------------------------------------

Time/(min)                  Chromatogram Area/(mvolt sec)

     5.      3008.       0.   705780.  1991000.       0.       0.       0.   33912.       0.  2733700.
    15.        0.        0.  9417900.   259080.   191090.      0.       0.       0.        0.  9868000.
    26.      5224.       0. 10123000.   264860.   498210.      0.       0.       0.        0. 10891000.
    36.     13759.       0.  9036200.   277420.   502740.      0.       0.       0.        0.  9830200.
    46.        0.        0.  9892600.   287980.   492080.      0.       0.       0.        0. 10673000.
    58.        0.        0.  9791700.   373210.   567700.      0.       0.   19857.       0. 10752000.
    67.        0.        0.  3605300.   348010.   565880.      0.       0.       0.        0.  4519200.
    78.        0.        0.  8680800.   446480.   743250.  160580.      0.       0.        0. 10031000.
```

```
                                Experiment: MAL-840525-1-S

  3 Total data points were collected

 Run Characteristics:

     Set point temperature                130. C
     Set point pressure                  2000. psi
     Initial liquid volume                780. ml
     Mass of organic initially injected  0.1841 Grams
     Integrator start time              12.2550 hh.mmss


 Data Summary:

                                     Chromatograph Retention Times/(min)
                 --------------------------------------------------------------------------------------------
                 0.09      0.21      0.30      0.36      0.43      0.54      1.09      2.70      3.89      TOTAL
                 --------------------------------------------------------------------------------------------

 Time/(min)                            Chromatogram Area/(mvolt sec)

      5.         0.        0.    331190.  2045800.  1892700.  1111600.        0.        0.        0.   5381400.
     17.      4036.        0.    533680.  1739900.  1829000.  1505700.        0.        0.    13125.   5625400.
     28.      3808.        0.    568890.  1524200.  1953400.  1427400.        0.    14411.    18782.   5511000.
```

Experiment: MAL-840525-2-S

12 Total data points were collected

Run Characteristics:

Set point temperature	130. C
Set point pressure	1500. psi
Initial liquid volume	780. ml
Mass of organic initially injected	0.1850 Grams
Integrator start time	23.1840 hh.mmss

Data Summary:

Chromatograph Retention Times/(min)

Chromatogram Area/(mvolt sec)

Time/(min)	0.09	0.21	0.30	0.36	0.43	0.54	1.09	2.70	3.89	TOTAL
5.	0.	0.	282240.	1777300.	2315500.	0.	0.	0.	0.	4993100.
16.	4063.	0.	494440.	1316900.	2025000.	1422500.	0.	10518.	27333.	5300800.
27.	4081.	0.	591760.	1352200.	1977700.	0.	0.	68611.	138930.	5674300.
38.	8569.	4947.	631460.	1246100.	6775400.	0.	0.	0.	0.	8666400.
47.	7646.	0.	670380.	1229800.	6930200.	0.	0.	0.	0.	8838000.
58.	6011.	0.	684530.	1357000.	6617500.	0.	0.	0.	0.	8665000.
69.	4136.	0.	796300.	1443500.	1920900.	1376400.	0.	0.	0.	5541100.
79.	0.	0.	779900.	1391800.	1793500.	1292200.	0.	0.	0.	5257400.
90.	0.	0.	795910.	1435800.	1684400.	1230000.	0.	0.	0.	5146100.
100.	0.	0.	793530.	1407100.	1644300.	1206800.	0.	0.	0.	5051700.
112.	0.	0.	849010.	1361400.	1609900.	1081300.	0.	0.	0.	4901600.
129.	2429.	0.	921830.	1416600.	3080000.	0.	0.	0.	0.	5420800.

APPENDIX E

Detailed Experimental Procedures

Experimental Procedure

Calibration - m-Xylene, Phenol and TCE

Calibrations were required to translate GC integrator area counts into concentrations. The following procedure was used for m-xylene, phenol, and tetrachloroethylene:

1) A sample of the pure organic was injected with a 250 µl syringe into a clean, 1 liter volumetric flask partially filled with distilled water. Weighing the syringe before and after injection established the weight to +/- 0.0001 gm.
2) The flask was filled to 1 liter with distilled water. A magnetic stirring bar was added and the flask was stoppered. The flask was stirred until all of the organic had dissolved (2 to 12 hours depending on the concentration).
3) A funnel was rinsed with about 5 ml of this standard solution and the remainder poured immediately into the reactor.
4) The reactor was closed and pressurized with N_2 to 1000 psi.
5) The reactor solution was then sampled using standard sampling procedures. At least six samples were collected to ensure accuracy.

Initially, this procedure was repeated a number of times with a range of solution concentrations so that a complete curve of concentration versus area counts could be constructed. It was discovered that over the range of concentrations considered, these curves were linear. Therefore, subsequent calibrations only established the GC peak area associated with one, relatively high, concentration.

It was suspected that small amounts of organic might adsorb on the metal walls of the reactor. Because of this the reactor was not cleaned between calibration solutions. One solution was removed as completely as possible and followed immediately by the next calibration solution. The first one or two samples of each calibration solution were not used in the area count average as these were affected by the previous solution in the sampling lines.

To determine the chromatogram area associated with a particular concentration, steps 1-5 were repeated five times. The first two solutions were not used for actual calibration, but were used to thoroughly clean the reactor and sampling lines. The calibration was established by averaging the GC results from the last three solutions.

Calibration - Malathion

Malathion could not be calibrated using the above procedure because it hydrolyzed too quickly, especially in the hot sampling line and valve. A rough calibration was done by injecting 1 µl samples of various concentrations of malathion in hexane.

Reactor Sampling

Rather extensive work was performed to develop a reliable method for drawing samples from the reactor and injecting them into the GC. In early work, samples were drawn from the reactor into vials and subsequently injected into the GC using 1 µl syringes. This produced very unreliable results due largely to varying amounts of organic vaporization before injection, temperature (and thus density) changes, and varying injection volumes. Greatly increased reproducibility was achieved by incorporating a Valco sampling valve into the system, so direct GC injection could be performed. A standardized sampling procedure was developed by systematically altering each sampling parameter while holding all others constant and choosing the one which gave the best (most reproducible) results. The resulting sampling procedure was:

1) Turn the stirrer off. Wait 30 seconds.
2) Draw a sample from the reactor through the Valco valve at a rate of 30 ml/min for 10 seconds. Wait 30 seconds.
3) Actuate the Valco valve to the inject position for 5 seconds then return to the load position.

Superior results occurred when the last 20 inches of the line leading from the reactor to the valve was heated to the same temperature as the valve.

The only deviation from this procedure was on runs with solids present, in which case it was necessary to leave the stirrer off for 2 minutes rather than 30 seconds to allow the solids to settle.

Reactor clean out

1) For clean out after soil runs copious amounts of tap water were flushed through the reactor with the stirrer on. The water was withdrawn via a vacuum pump. This was repeated until no solids were observed in the effluent water (8-12 times).
2) After all runs, the reactor was flushed with distilled water.
3) The reactor was then filled about 3/4 full with distilled water, the reactor was closed and pressurized to 1000 psi, and 15-20 ml of water was flushed through the sampling line.

4) The reactor was stirred while depressurizing it and removing the water.
5) The reactor was flushed twice with distilled water.

Kinetic Runs

The following procedure was used for all kinetic runs.

1) Each run began with a clean reactor (see reactor clean out procedure). Five grams of soil were added if this was to be a soil run.
2) 700 ml of distilled water were placed in the reactor, all ports were closed, and the reactor was pressurized with air to 200-500 psi.
3) The reactor was heated to the desired reaction temperature.
4) While the reactor was heating, a 100 ml sample bomb was flushed three times with distilled water, then filled with 80 ml of distilled water.
5) The bomb was mounted in the experimental system by its top connection. When the reactor was at or near its set point, the bomb was heated to about 160 °C.
6) The carrier gas flow rate and temperatures of the sample valve, sample line, GC column, and manifold were checked. The flame ionization detector was also checked to ensure stability and the integrator parameters were checked.
7) When both reactor and bomb temperatures were stable, the prescribed amount of organic was measured into a 250 μl syringe which was then weighed.

8) The organic was injected into the line between the bomb and the reactor. This tube was then quickly attached to the bottom of the bomb.
9) The syringe was again weighed and compared to the previous weight to establish the mass injected.
10) The reactor was checked to ensure that its pressure was at least 500 psi below the target operating pressure.
11) Both bomb valves were opened, and the bomb was pressurized to the operating pressure.
12) The stirrer was turned on.
13) The valve between the sample bomb and reactor was opened, allowing the 80 ml of distilled water to flush the organic into the reactor. This established "time zero".
14) The reactor temperature and pressure were adjusted as necessary while beginning to take reactor samples according to the standard reactor sampling procedure at the appointed times.

Soil Extraction

To determine how much organic remained adsorbed to the soil after a run, the reactor contents were filtered to recover most of the solid. This was quickly washed with water, scrapped off the filter paper, and weighed wet. This was refluxed with 50 ml of hexane for at least 2 hours. Afterwards 1 µl samples of the extract were injected into the GC to determine organic concentration.

Quality Assurance/Quality Control

Various activities served to insure that scientifically defensible data were collected. Formally, weekly meetings were held for all project personnel to report and evaluate current progress and to plan forthcoming efforts. Furthermore, all project personnel have offices and labs in close proximity so that informal discussions were held with even greater frequency. Data were collected by an experienced graduate student, or under the close supervision of a graduate student. All concentration data, in raw form as signals from the chromatograph, were processed by a Hewlett Packard recording integrator which produced a chromatogram, and the area and retention time for each peak. The recorder tape also contained the time and date. These tapes were the raw data and are on file. To facilitate analysis and as insurance against such things as loss due to fire, these data were also transferred to magnetic tape and stored in a separate building.

Having only completely reliable data as the objective, and initially not being sure of the data quality, a project was initiated to study every aspect of reactor sampling and analysis procedures. Factors studied included: 1) time the stirrer remained off before drawing a sample, 2) volume drawn through the sampling valve, 3) time a sample spent in the sampling valve, 4) time the sampling valve spent in the inject position before returning it to the normal load position, 5) GC column temperature, 6) whether or not, and how much of, the sample line leading to the sampling valve should be heated, 7) rate at which a sample was drawn through the sampling valve, and 8) GC carrier gas flow rate. In each case, all other parameters were held constant while the one in question was varied as a standard m-xylene and water solution was analyzed. It was observed that certain parameter settings gave highly erratic results, while others produced very reliable responses. Choosing all settings in the reliable regions engendered a procedure which reproduced previous results with less than 1.5% variation.

While experimental error is a ubiquitous problem of which one must always be wary, a diligent effort to strictly follow thoroughly developed procedures and to constantly monitor the possible development of any abnormalities gives the researchers a high degree of confidence in the data collected during this project.

APPENDIX F

Computer Programs

Computer Programs

All computer programs are written in FORTRAN 77. System requirements to run these programs include IBM's Presentation Graphics Feature, LSODE (Lawerence Livermore's ordinary differential equation solver), and PCD (an optimization routine which used Powell's method of conjugate directions) as well as a FORTRAN 77 compiler. Also used is a routine named RTC (available in IBM's CMS utilities) to translate real variables to character. All programs are intended to be run interactively.

The following is a list of the programs included in this appendix. Each name is accompanied by a brief description. Each description is prefaced by either an M or an S, signifying that the program is either a main routine or a subprogram, respectively.

Program Name	Description
APOACT	M, Activation energy
APOCAL	S, Calibration program
APOCMP	S, Compound determination routine
APOCON	S, Physical constants
APODEN	S, Density determination
APOELP	S, Elapsed time determination
APOEP	S, End plot
APOHD	S, Reads and formats a figure title
APOHEN	S, Henry's law constant evaluation
APOIN	M, Chromatograph data input
APOLIN	S, Plot line
APOMEC1	M, APO mechanism simulation
APOMEC2	M, Match mechanism to idealized data
APOMEC3	M, Generate Objective Fcn Data for 3D plotting
APOMOD	M, Aqueous phase oxidation model
APOOXY	S, Calculates the oxygen concentration
APOPHI	S, Phi calcuation
APOPLT	M, Plotting program
APOPLTN	M, Plotting program (nice)
APORD	S, Data read routine
APOREG1	M, Regression program 1
APOREG2	M, Regression program 2

Program Name	Description
APOSAT	S, Saturation vapor pressure
APOSP1	S, Start plot 1
APOSP2	S, Start plot 2
APOSP3	S, Start plot 3
APOVL	S, Volume of liquid
CORDEN1	M, Correlate density 1
CORDEN2	M, Correlate density 2
CORHEN1	M, Correlate Henry's law constant 1
CORHEN2	M, Correlate Henry's law constant 2
CORVP1	M, Correlate vapor pressure 1
CORVP2	M, Correlate vapor pressure 2
PHEARRH	M, Phenol results
PHEEN	M, Phenol results--enhancement number
TCEARRH	M, Tetrachloroethylene results
XPHEN	M, Plots En versus X for both m-xylene and phenol
XPHSY1	M, Sy versus X (m-xylene/phenol system)
XPHSY2	M, ln(Sy) versus 1/T (m-xylene/phenol system)
XYLARRH	M, m-Xylene results
XYLEN	M, m-Xylene results--enhancement number
XYLORDER	M, m-Xylene reaction order analysis
XYLSEN	M, m-Xylene/Soil results--enhancement number

Program Name: APOACT

```
C----------------------------------------------------------------------
C   Program Description: Activation energy
C
C   Programmer: David Wetzel and Scott Willms
C
C   Usage: This program is used to calculate the activation energy
C      with 95% confidence limits and the preexponential for a group
C      of k versus temperature data.  The data which is read from
C      unit 1 must be in the following form.
C
C         Record 1:   Title
C         Record 2:   N(the number of T,k pairs)
C         Record 3-N: T(temperature in C), k(the rate constant)
C----------------------------------------------------------------------
      IMPLICIT REAL*8 (A-H,O-Z)
      CHARACTER*70 TITLE
      REAL*8 M
      DIMENSION X(100), Y(100), V(100), W(100), YCALC(100), TC(302)
      DATA TC/0.,0.,12.7,4.3,3.18,2.78,2.57,2.45,2.37,2.31,2.26,2.23,
     1 2.2,2.18,2.16,2.15,2.13,2.12,2.11,2.1,2.09,2.09,2.08,2.07,2.05,
     2 3*2.06,3*2.05,5*2.04,5*2.03,10*2.02,10*2.01,15*2.0,25*1.99,
     3 100*1.98,101*1.97/
      SUMX = 0.0
      SUMY = 0.0
      SUMXSQ = 0.0
      SUMXY = 0.0
      SYYCSQ = 0.0
      SXXBSQ = 0.0
C  Read the title
      READ (1,1009) TITLE
      WRITE (6,1010) (TITLE,I=1,5)
C  Read the number of T,k pairs
      READ (1,*) N
C  Determine Student's t
      NN = N - 2
      IF (N.GT.302) T = 1.96
      IF (N.LE.302) T = TC(N)
      WRITE (6,1001) N, NN, T
      WRITE (6,1002)
C  Read the T,k pairs
      DO 10 I = 1, N
      READ (1,*) V(I), W(I)
C  If the coordinates of the plot you wish to make are not x and y,
C  enter the new functions here.  If they are, set y = w and x = v
C  by removing the comment symbols in front of statements 1 and 2.
C  Use functions 3 and 4 for an Arrhenius plot.
C   1 Y(I) = W(I)
C   2 X(I) = V(I)
    3 Y(I) = DLOG(W(I))
```

```
    4 X(I) = 1/(V(I)+273.15)
C  Write out the input data and the functions of the data
      WRITE (6,1008) V(I), X(I), W(I), Y(I)
C  Find the best line through the data
      SUMX = SUMX + X(I)
      SUMY = SUMY + Y(I)
      SUMXSQ = SUMXSQ + X(I)**2
  10  SUMXY = SUMXY + X(I)*Y(I)
      YBAR = SUMY/N
      XBAR = SUMX/N
      WRITE (6,1003) XBAR
      SXSQ = SUMX**2
      M = (SUMXY - SUMX*SUMY/N) / (SUMXSQ - SXSQ/N)
      B = (SUMY - M*SUMX) / N
      WRITE (6,1004) M, B
C  Calculate the statistics
      SUMXY  = 0.
      SUMXXB = 0.
      SUMYYB = 0.
      DO 20 I=1,N
      SUMXY  = SUMXY  + (XBAR-X(I))*(YBAR-Y(I))
      SUMXXB = SUMXXB + (XBAR-X(I))**2
   20 SUMYYB = SUMYYB + (YBAR-Y(I))**2
      WRITE (6,1011) SUMXY,SUMXXB,SUMYYB
      S2Y    = DABS((SUMYYB - M*SUMXY)/(N-2.))
      S2M    = S2Y/SUMXXB
      S2YB   = S2Y/N
      S2B    = S2Y*(1./N + (XBAR-0.)**2/SUMXXB)
      WRITE (6,1005) S2Y,S2M,S2YB,S2B
      CONFM  = T*DSQRT(S2M)
      CONFYB = T*DSQRT(S2YB)
      CONFB  = T*DSQRT(S2B)
      WRITE (6,1006) XBAR, B, CONFB, YBAR, CONFYB, M, CONFM
      E = -0.001987 * M
      ECONF = 0.001987 * CONFM
      WRITE (6,1007) E,ECONF
      STOP
C----------Formats----------------------------------------
 1001 FORMAT (' There are ', I3, ' points and ', I3, ' degrees of',
     1 ' freedom',/,' Student''s T is', F8.4,//)
 1002 FORMAT ( 8X, ' X ', 10X, ' F(X) ', 10X, ' Y ', 10X, ' F(Y) ')
 1003 FORMAT (/, 5X, ' f(x)bar = ', G13.5 /)
 1004 FORMAT (1X, ' The equation is '/, 1X, ' Y = ', G13.5, ' X + ',
     1  G13.5 /)
 1005 FORMAT (/,
     1 ' The residual variance, s**2(y), is:        ', G13.5,/,
     2 ' The variance of the slope, s**2(m), is:    ', G13.5,/,
     3 ' The variance of the mean, s**2(ybar), is: ', G13.5,/,
     4 ' The variance at x=0, s**2(y0), is:        ', G13.5)
 1006 FORMAT ( 1X,//,
     1  '  xbar  = ', G13.5,/,
     2  '  b     = ', G13.5, ' +/- ', G13.5,/,
```

```
    3  '  ybar  = ', G13.5, ' +/- ', G13.5,/,
    4  '  slope = ', G13.5, ' +/- ', G13.5)
1007 FORMAT (//,' The activation energy is',F13.5,' +/-',F13.6,
    1 ' kcal/gmole')
1008 FORMAT (4G15.5)
1009 FORMAT (A70)
1010 FORMAT (//,20X,' ACTIVATION ENERGY PROGRAM',//,
    1 ' This program finds the best Arrhenius equation line through ',
    2 'a set of data',//,' This run is for:',/,
    4 '+',17X,A70,/,
    5 '+',17X,A70,/,
    6 '+',17X,A70,/,
    7 '+',17X,A70,/,
    8 '+',17X,A70,//)
1011 FORMAT (/,
    1 ' Sum(xbar - x)(ybar - y) = ',G13.5,/,
    2 ' Sum(xbar - x)**2        = ',G13.5,/,
    3 ' Sum(ybar - y)**2        = ',G13.5)
     END
```

Program Name: APOCAL

```
C------------------------------------------------------------------
C   Program Description: Calibration program
C
C   Programmer: Scott Willms
C
C   Usage: Given the GC integrator area and temperature in degrees F,
C          this program will return the concentration.  The calibration
C          data is read from unit 3 in the form:
C
C              area1 conc1
C              area2 conc2
C                .     .
C              arean concn
C
C          The concentration returned by this program is the linear
C          interpolation between the two calibration points bounding
C          the area in question.  If the area in question is outside
C          the calibrated range, the concentration is set to zero and
C          a message is printed.
C
C          Of course, if the calibration curve is linear only two
C          calibration points need be supplied.  For nonlinear curves
C          a sufficient number of points must be supplied so that linear
C          interpolation provided sufficient accuracy.
C
C          Areas are usually divided by 1.E+6, and concentration are
C          divided by 1.E-4 before being entered in the calibration
C          table (and supplied to this program).
C
C          To save time the calibration data is only read the first
C          time this routine is called.  A message is printed after
C          this read has occurred.
C
C          The desity of water is required to account for its effect
C          on concentration.  This will be called from function
C          subpgm APODEN.
C
C------------------------------------------------------------------
      FUNCTION APOCAL (AREA,T)
      DATA IFLAG/0/
C-------------------------------------------------
C   FILE 3 - CALIBRATION DATA
C-------------------------------------------------
      DIMENSION X(100),Y(100),A(10)
C-------------------------------------------------
C    ONLY EXECUTE THIS CODE THE FIRST TIME THROUGH
C-------------------------------------------------
      IF (IFLAG.EQ.1) GO TO 50
      IFLAG=1
```

```
      IDIM=100
      IFILE1=3
      WRITE (6,100) IFILE1
  100 FORMAT (/,' READING CALIBRATION DATA FROM FILE ',I2)
      DO 1 I=1,IDIM
      READ (IFILE1,*,END=99) X(I),Y(I)
      N=I
    1 CONTINUE
      WRITE (6,101) IDIM
  101 FORMAT (/,' *** ERROR IN READING DATA',/,
     1 ' *** THERE ARE OVER ',I3,' POINTS IN THE CALIBRATION DATA',/,
     2 ' *** YOU MUST INCREASE THE DIMENSIONS IN THE LOOK UP PGM.')
      STOP
   99 WRITE (6,*) N,' CALIBRAION POINTS WERE READ'
      WRITE (6,112) X(1),X(N)
  112 FORMAT (/,' CALIBRATION DATA IS FOR VALUES OF X FROM ',G8.2,
     1 ' TO',G8.2)
C-------------------------------------------------------
C      EXECUTE HERE EVERY TIME THROUGH
C-------------------------------------------------------
   50 CONTINUE
C-------------------------------------------------------------------
C      THIS DO LOOP DETERMINES WHICH POINTS TO INTERPOLATE BETWEEN
C-------------------------------------------------------------------
      NM1=N-1
      DO 3 I=1,NM1
      IF (AREA.GE.X(I).AND.AREA.LT.X(I+1)) THEN
         APOCAL= Y(I) + (Y(I+1)-Y(I))/(X(I+1)-X(I))*(AREA-X(I))
         APOCAL= (APODEN(T,0,1)/APODEN(77.,0,1))*APOCAL
         RETURN
         END IF
    3 CONTINUE
C---------------------------------------------------------------------
C      IF THE AREA IS NOT IN ANY OF THE ABOVE RANGES, CHECK TO SEE
C      IF IT IS EQUAL TO THE END POINT.  IF IT IS NOT PRINT AN ERROR
C      MESSAGE AND SET CONC = 0
C---------------------------------------------------------------------
      IF (AREA.NE.X(N)) THEN
         WRITE (6,105) AREA
         APOCAL=0.
         RETURN
      ELSE
         APOCAL=Y(N)
         APOCAL= (APODEN(T,0,1)/APODEN(77.,0,1))*APOCAL
         RETURN
      END IF
  105 FORMAT (1X,G10.4,' IS OUTSIDE THE CALIBRATION RANGE,',
     1         ' CONC IS SET TO 0.')
      END
```

Program Name: APOCMP

```
C-----------------------------------------------------------------------
C   Program Description: Compound determination routine
C
C   Programmer: Scott Willms
C
C   Usage: This routine first asks the user which compound is to be
C          considered.  The user responds by answering with a number
C          which is stored in ICOMP.  Based on this number a character
C          variable, COMP, is set to the compound name and the variable,
C          YRNG is set for plotting routines.  The user can optionally
C          override the default YRNG setting.
C
C   Updating: To add new compounds the following step should occur.
C
C          1) Add a WRITE statement under the current list of compounds
C             with the new compound's number.
C          2) Add the compound number to the computed GO TO statement.
C          3) Add the following statements immediately before the END
C             statement:
C
C            1...v.7..v....v....v....v....v....v....v   columns
C           cmpd # COMP = 'Compound Data'            : must be 13 space
C                  YRNG = Y-axis plotting maximum value
C                  GO TO 90
C
C             Use the existing statements as further examples.
C          4) Save this edited version.
C          5) Compile the new code with:  FORTVS APOCMP (OPT(2))
C          6) Erase the old version from the text library with:
C             TXTLIB DEL APOLIB APOCMP
C          7) Add the new compiled version to the text library with:
C             TXTLIB ADD APOLIB APOCMP
C          8) Erase the text and listing files with: ERASE APOCMP TEXT
C             and ERASE APOCMP LISTING
C          9) Update subroutines APOCON, APODEN and APOHEN to include
C             the new compound.
C-----------------------------------------------------------------------
      SUBROUTINE APOCMP (ICOMP,COMP,YRNG)
      CHARACTER*13 COMP
      CHARACTER*1  ANS
   91 CONTINUE
      WRITE (5,*) 'Which compound is being considered on this run?'
      WRITE (5,*) '     1 - m-Xylene'
      WRITE (5,*) '     2 - Phenol  '
      WRITE (5,*) '     3 - TCE     '
      READ (5,*) ICOMP
      GO TO (1,2,3),ICOMP
      WRITE (5,*) 'Invalid number entered'
      GO TO 91
```

```
  1 COMP = 'm-Xylene Data'
    YRNG = 1.2
    GO TO 90
  2 COMP = ' Phenol Data '
    YRNG = 2.0
    GO TO 90
  3 COMP = '   TCE Data  '
    YRNG = 1.6
    GO TO 90
 90 WRITE (5,101) YRNG
    READ (5,100) ANS
    IF (ANS.EQ.'N'.OR.ANS.EQ.'n') RETURN
    WRITE (5,*) 'Enter new value for YRNG'
    READ (5,*) YRNG
    RETURN
100 FORMAT (A1)
101 FORMAT (' Current YRNG setting is:',F8.2,/,
   1 ' Do you want to reset (y/n)?')
    END
```

Program Name: APOCON

```
C----------------------------------------------------------------------
C   Program Description: Physical constants
C
C   Programmer: Scott Willms
C
C   Usage: This routine sets a number of physical constants, and sets
C          the molecular weight of organic, MW2, based on the compound
C          number specifed with ICOMP in the arguement list.  The values
C          are returned to the calling routine through a common
C          blocks.
C
C   Updating: To include new compounds in this routine perform the
C             following steps.
C
C          1) Add the compound number (set in subroutine APOCMP) to
C             the computed GO TO statement.
C          2) Add the following statements immediately before the END
C             statement:
C
C              1...v.7..v....v....v....v....v....v....v  columns
C             cmpd # CONTINUE
C                    MW2 = Molecular weight of new compound
C                    RETURN
C
C          3) Save this updated version.
C          4) Follow steps 5-8 outlined in APOCMP for adding this
C             updated version to the text library.  Simply substitute
C             "APOCON" for "APOCMP".
C
C----------------------------------------------------------------------
      SUBROUTINE APOCON (ICOMP)
      REAL*4 MW1,MW2
      COMMON/APO4/MW1,MW2,VT,R,TAMB
      MW1=18.
      VT=1022.
      R=82.04
      TAMB=77.
      GO TO (1,2,3),ICOMP
      WRITE (6,*) 'Unspecified component in subroutine APOCON'
      STOP
C  m-Xylene
    1 CONTINUE
      MW2=106.
      RETURN
C  Phenol
    2 CONTINUE
      MW2=94.
      RETURN
C  Tetrachloroethylene
```

```
    3 CONTINUE
      MW2=165.8
      RETURN
      END
```

Program Name: APODEN

```
C-----------------------------------------------------------------------
C   Program Description: Density determination
C
C   Programmer: Scott Willms
C
C   Usage: This routine returns the density at temperature, TEMP, of
C          component, ICOMP, with the temperature in units, IUNIT.
C          The density is in gm/ml.  The temperature may be supplied
C          in degrees F or degrees C as specified by arguement IUNIT.
C          The following key applies:
C
C        TEMP Supplied in Degrees        IUNIT Must Be
C        ------------------------        -------------
C                  F                           1
C                  C                           2
C
C          The following compounds are currently included.
C
C      Component   ICOMP      TEMP Range       Accuracy
C      ---------   -----      ----------       --------
C        Water       0       32  TF  600     +/- .007 gm/ml
C        m-Xylene    1       20  TC  285          ?
C        Phenol      2       Number reserved but no correlation supplied
C        TCE         3       Number reserved but no correlation supplied
C
C   Updating: To add new compounds to this routine perform the following
C             steps.
C
C      1) Add the component number (defined in APOCMD) to the computed
C         GO TO statement (immediately after statement number 300).
C      2) Add one of the following sets of statements immediately before
C         the FORMAT statements:
C
C           ....v.7..v....v....v....v....v....v....v   columns
C         If Henry's law constant is finite:
C          cmpd # APODEN = fcn(TC or TF)
C                 IF (cond) WRITE (6,100) ICOMP,TC,TF
C                 RETURN
C
C         If Henry's law constant is zero
C          cmpd # APODEN = 1.
C                 IF (IFLAG.EQ.0) WRITE (6,101) ICOMP
C                 IFLAG = 1
C                 RETURN
C
C         Use the existing statements as actual examples.
C
C         The density of each component is only used for the pressure
C         correction in APOHEN.  Thus, if Henry's law constant is set
```

```
C          to a finite value, its density must also be defined.  If
C          Henry's law constant is always set to zero for a particular
C          compound, the density does not need to be correlated and can
C          simply be set to zero.
C          The IFLAG condition is included for the undefined density
C          case so that the message will only print once per run.
C       3) Add the new compound to the table shown above.
C       4) Save the updated version.
C       5) Follow steps 5-8 outlined in APOCMP for adding this
C          updated version to the text library.  Simply substitute
C          "APODEN" for "APOCMP".
C
C-----------------------------------------------------------------------
      FUNCTION APODEN (TEMP,ICOMP,IUNIT)
      DATA IFLAG/0/
      IF (IUNIT.EQ.1) THEN
         TF = TEMP
         TC =(TEMP-32.)/1.8
         GO TO 200
      END IF
      IF (IUNIT.EQ.2) THEN
         TF = TEMP*1.8 + 32.
         TC = TEMP
         GO TO 200
      END IF
      WRITE (6,*) 'Invalid value supplied for IUNIT in APODEN'
      STOP
  200 CONTINUE
      IF (ICOMP.NE.0) GO TO 300
      APODEN = 1.0 - 0.86127E-6*(TF-32.)**2 - 0.63692E-4*(TF-32.)
      IF (TF.LT.32..OR.TF.GT.600) WRITE (6,100) ICOMP,TC,TF
      RETURN
  300 CONTINUE
      GO TO (1,2,3),ICOMP
      WRITE (6,*) 'Invalid value for ICOMP in APODEN'
      STOP
    1 APODEN = -.363197E-06*TC**2 -.763859E-03*TC + 0.891398
      IF (TC.LT.20..OR.TC.GT.285.) WRITE (6,100) ICOMP,TC,TF
      RETURN
    2 APODEN = 1.
      IF (IFLAG.EQ.0) WRITE (6,101) ICOMP
      IFLAG = 1
      RETURN
    3 APODEN = 1.
      IF (IFLAG.EQ.0) WRITE (6,101) ICOMP
      IFLAG = 1
      RETURN
C---Formats-------------------------------------------------------------
  100 FORMAT (' Density was extrapolated outside correlated range in',
     1 ' APODEN for component',I3,/,
     2 ' Requested temperature was',F7.2,' C or',F7.2,' F')
  101 FORMAT (' No density correlation has been supplied for component'
```

```
1 ,I3,/,' The density was set to one')
 END
```

Program Name: APOELP

```
C-----------------------------------------------------------------------
C   Program Description: Elapsed time determination
C
C   Programmer: Scott Willms
C
C   Usage: Given TINT, the current integrator time, and TINTO, the
C          beginning integrator time, this routine will return the
C          elapsed time in minutes between TINT and TINTO.
C          The integrator time must be expressed as hh.mmss
C-----------------------------------------------------------------------
      FUNCTION APOELP (TINT,TINTO)
      TOHR=IFIX(TINTO)
      TOMIN=IFIX((TINTO-TOHR)*100.)
      TOSEC=(TINTO-TOHR-TOMIN/100.)*10000.
      TO=TOHR*60.+TOMIN+TOSEC/60.
      THR=IFIX(TINT)
      TMIN=IFIX((TINT-THR)*100.)
      TSEC=(TINT-THR-TMIN/100.)*10000.
      T=THR*60.+TMIN+TSEC/60.
      APOELP=T-TO
      RETURN
      END
```

Program Name: APOEP

```
C-----------------------------------------------------------------------
C   Program Description: End plot
C
C   Programmer: Scott Willms
C
C   Usage: This routine handled plot display and printing functions.
C          If IOPT = 1 the plot will first be displayed on the terminal.
C          Then the user will be asked if the plot should be printed,
C          and the appropriate action is envoked based on the response
C          (y or n) stored in variable ANS.  This response is also
C          returned to the calling routine, so ANS must be declared
C          as CHARACTER*1 in the calling routine.
C          If IOPT = 2 the terminal display set is skipped.  This is
C          usually used when the calling routine is performing
C          interactive graphics, and this routine would only be called
C          once after numerous terminal displays had occurred.
C-----------------------------------------------------------------------
      SUBROUTINE APOEP (IOPT,ANS)
      CHARACTER*1 ANS
      GO TO (1,2),IOPT
      WRITE (6,*) 'Invalid value assigned to IOPT in APOEP'
      WRITE (6,*) 'IOPT = 1 assumed'
    1 CALL ASREAD (I1,I2,I3)
    2 WRITE (6,*) 'Do you want this plot printed (Y/N)?'
      READ (5,100) ANS
      IF (ANS.NE.'Y'.AND.ANS.NE.'y') RETURN
      WRITE (5,*) 'Plot sent to printer'
      CALL GSCOPY (52,88)
      CALL FSCLS (1)
      CALL CHTERM
      RETURN
  100 FORMAT (A1)
      END
```

Program Name: APOHD

```
C----------------------------------------------------------------------
C   Program Description: Reads and formats a figure title
C
C   Programmer: Scott Willms
C
C   Usage: A figure title is read from two input records on unit 5 into
C      variables HEAD1 and HEAD2.  These two variables will then be
C      combined in the single variable HEAD.  Blanks will be added
C      before the first line so that it is centered under an axis which
C      is 60 spaces long and preceeded by a 10 space margin.  The same
C      number of spaces will be added before the second line.
C
C   Example:  The two input records (Figure starts in column 1):
C
C      Figure 3.2 Experimental and Model Data for m-Xylene at;
C                 200 deg. C and 2000 psi air;
C
C      Would produce:
C
C       +----+----+----+----+----+----+----+----+----+----+----+----+
C       0         1         2         3         4         5         6
C          Figure 3.2 Experimental and Model Data for m-Xylene at
C                     200 deg. C and 2000 psi air
C
C      This routine should be followed by: CALL CHHEAD (132,HEAD)
C      Note that HEAD must be declared CHARACTER*132 in the calling
C      routine.
C----------------------------------------------------------------------
      SUBROUTINE APOHD (HEAD)
      CHARACTER*80 HEAD1
      CHARACTER*52 HEAD2
      CHARACTER*132 HEAD
      DO 30 I=1,132
   30 HEAD(I:I)= ' '
      DO 31 I=1,80
   31 HEAD1(I:I)= ' '
      DO 32 I=1,52
   32 HEAD2(I:I)= ' '
C  Read in a title on two lines
      WRITE (6,*) 'Enter the Figure Title'
      WRITE (6,*) 'Use two lines and end each line with '';'''
      READ (5,120) HEAD1
      READ (5,121) HEAD2
  120 FORMAT (A80)
  121 FORMAT (A52)
C  Determine the length of the first line
      LL = 0
      DO 10 I=1,80
      LL = LL + 1
```

```
      IF (HEAD1(I:I).EQ.';') GO TO 11
   10 CONTINUE
   11 LL = LL - 1
C  Calculate the indention so the title will be centered
      INDENT = (60 - LL)/2 + 10
C  Combine the two lines into one with the proper indentation
      INDEX=0
      DO 4 I=1,INDENT
      INDEX=INDEX+1
    4 HEAD(INDEX:INDEX) = ' '
C
      DO 1 I=1,80
      INDEX=INDEX+1
      I1=I+1
      IF (HEAD1(I:I).EQ.';'.AND.HEAD1(I1:I1).EQ.' ') GO TO 2
    1 HEAD(INDEX:INDEX)=HEAD1(I:I)
    2 HEAD(INDEX:INDEX)=';'
C
      DO 3 I=1,INDENT
      INDEX=INDEX+1
    3 HEAD(INDEX:INDEX) = ' '
C
      DO 5 I=1,80
      INDEX=INDEX+1
      I1=I+1
      IF (HEAD2(I:I).EQ.';'.AND.HEAD2(I1:I1).EQ.' ') GO TO 6
    5 HEAD(INDEX:INDEX)=HEAD2(I:I)
    6 HEAD(INDEX:INDEX)=';'
      RETURN
      END
```

Program Name: APOHEN

```
C-----------------------------------------------------------------------
C   Program Description: Henry's law constant evaluation
C
C   Programmer: Scott Willms
C
C   Usage: This routine calcuates and returns the Henry's law constant
C      at temperature, T, and pressure, P, for component, ICOMP.  T
C      can be expressed in degrees F (IUNIT = 1) or degrees C
C      (IUNIT = 2).  P must be in psi.
C
C      The correlation of H must be performed using the vapor pressure
C      of water as the reference pressure.  Deviations from this
C      pressure are accounted for by Heidman et al. (1985) as
C
C              p       pr   !¯MW (p - pr)¯!
C             H    =  H  exp! ----------- !
C                           !   rho R T   !
C                           -             -
C      The current list of compounds is
C
C       Compound      ICOMP   Temperature Range
C      ----------     -----   -----------------
C       m-Xylene        1         20 - 320 C
C       Phenol          2         H = 0 at all T
C       TCE             3         H = 0 at all T
C
C      If H is nonzero for a compound, its density must be available
C      from routine APODEN.
C
C   Updating: New compounds can be added to this routine by performing
C      the following steps.
C
C      1) Add the new compound number (defined in APOCMP) to the
C         computed GO TO statement.
C      2) Add the following statements immediately before the pressure
C         correction statements.
C
C      ....v.7..v....v....v....v....v....v....v....v   columns
C     cmpd # CONTINUE
C            IF ((TC.LT.______.OR.TC.GT.______).AND.IFLAG.EQ.0) THEN
C               IFLAG = 1
C               WRITE (6,100)
C            END IF
C            APOHEN = fcn(TC or TF)
C            GO TO 90
C
C         Use the existing statements as an example.  The blanks are
C         left in the IF statement for the lower and upper temperature
C         limits on the correlation.
```

```
C
C          If Henry's law constant is assumed to be zero at all
C          temperatures, the IF through END IF statements can be deleted.
C
C       3) Save the updated version.
C       4) Add the new compound to the table shown above
C       5) Follow steps 5-8 outlined in APOCMP for adding this
C          updated version to the text library.  Simply substitute
C          "APOHEN" for "APOCMP".
C
C---------------------------------------------------------------------
      FUNCTION APOHEN (T,P,ICOMP,IUNIT)
      DATA IFLAG/0/
      IF (IUNIT.EQ.1) THEN
         TF = T
         TC =(T-32.)/1.8
         GO TO 200
      END IF
      IF (IUNIT.EQ.2) THEN
         TF = T*1.8 + 32.
         TC = T
         GO TO 200
      END IF
      WRITE (6,101)
  200 CONTINUE
      GO TO (1,2,3),ICOMP
      WRITE (6,102)
      STOP
C
C    m-Xylene
C
    1 CONTINUE
      IF ((TC.LT.20..OR.TC.GT.320.).AND.IFLAG.EQ.0) THEN
         IFLAG = 1
         WRITE (6,100)
      END IF
      APOHEN=70177.3*SIN(.0152504*TC)-.0256662*TC**3+13.1530*TC**2
     1 - 1336.95*TC+3580.24
      GO TO 90
C
C    Phenol
C
    2 CONTINUE
      APOHEN = 0.
      GO TO 90
C
C    Tetrachloroethylene
C
    3 CONTINUE
      APOHEN = 0.
      GO TO 90
C
```

```
C   Apply the pressure correction
C
   90 TK=TC+273.15
      PREF = APOSAT(TC,0,2)
      APOHEN=APOHEN*EXP(106.*(P-PREF)/APODEN(TC,ICOMP,2)/82.04/14.7/TK)
      RETURN
C--- Formats -----------------------------------------------------------
  100 FORMAT (' Henry''s law function evaluation occurred outside the',
     1 ' correlated range',/,' Check subroutine APOHEN')
  101 FORMAT (' Invalid value specified for IUNIT in subroutine APOHEN')
  102 FORMAT (' Henry''s law constant correlation has not be specified',
     1 'for the requested compound',/,' Check your value for ICOMP',
     2 'and/or add the new compound to subroutine APOHEN')
      END
```

Program Name: APOIN

```
C----------------------------------------------------------------------
C   Program Description: Chromatograph data input
C
C   Programmer: Scott Willms
C
C   Usage: This program is used to processed raw chromatograph data.
C      The user is prompted for the necessary input as follows:
C
C        Line    Variables
C        ----   -------------------------------------
C         1     Name of the Run.
C               This can be up to 16 alphanumeric characters which
C               usually take the form:
C
C                   XXX-yymmdd-n-Y
C
C               where XXX is a three letter identifier indicating the
C               compound under study (eg. XYL for xylene), yy is the
C               year, mm is the month, dd is the day, n is number of
C               the run on any one day, and Y is an optional
C               post-identifier for additives (eg. H for hydrogen
C               peroxide or S for soil).  Thus, PHE-850221-2 would
C               be used for the second phenol run on Feb. 21, 1985.
C               XYL-851001-1-H would be used for the first hydrogen
C               peroxide initiated xylene run on Oct. 1, 1985.
C
C         2     Set point temperature (C), set point pressure (psi),
C               initial volume of liquid measured at ambient
C               conditions charged into the reactor (including flush
C               liquid) (ml), initial mass of organic injected into the
C               inlet tube (gm), mass of soil (gm), integrator time
C               at the beginning of an experiment (hh.mmss), a plotting
C               scale factor (0-4, see APOPLT), the beginning time
C               for rate constant regression (min), and the ending
C               time for rate constant regression (min).
C
C        3-N    The integrator time (hh.mmss), the integrator peak
C               area (divided by 1.E+6), the temperature (F), and
C               the cumulative volume removed from the reactor measured
C               at ambient conditions (ml).
C               One such record is entered for each of the N
C               chromatograms.
C               A null line is entered to signify that the last
C               chromatogram has been entered.
C
C      The following files must be defined before running this pgm:
C
C         File 2 - Formatted output from this program (subsequently
C                  read by APORD)
```

```
C         File 3 - Calabration data (for APOCMP)
C         File 5 - Input to this program
C         File 6 - Terminal output from this program
C
C      The data entered will be written in a standard format to unit 2.
C      In addition to the information defined above for records 3-N,
C      this program will calculated elapsed time (min.) and
C      concentration (divided by 1.E-4).  All six numbers will be
C      written to unit 2.
C
C      This program can also accomodate the following two scenarios.
C
C      Scenario 1: APOIN has been run once and the data is successfully
C         stored in file 8501011 XYL.  A new calibation curve is
C         developed and the concentrations must be recalculated.  The
C         data does not have to be reentered.  The recalculation can
C         be easily accomplished with the following commands:
C
C            RENAME 8501011 XYL A $$BACK$$ XYL A
C            FILEDEF FT02F001 DISK 8501011 XYL A
C            FILEDEF FT03F001 DISK NEW CALI A      : new calibartion file
C            FILEDEF FT05F001 DISK $$BACK$$ XYL A
C            FILEDEF FT05F002 TERMINAL
C            FILEDEF FT05F003 TERMINAL
C            FILEDEF FT06F001 TERMINAL
C            LOAD XYLIN (START
C
C         In this scenario the only terminal input is to answer "y" to
C         the question, "Is that all the entries for this file (Y/N)?"
C
C      Scenario 2: APOIN has been run once and the data is successfully
C         stored in file 8501011 XYL.  Addition data needs to be added
C         to the end of the file.  Only this additional data must be
C         entered by using the same commands as in scenario 1, except
C         that the old calibration data file name is used instead of
C         a new one.  In this case, however, the question is answered
C         "n", and the new chromatograms are entered.  The end of input
C         is signified by a null line, as usual.
C
C-----------------------------------------------------------------
      CHARACTER*16 NAME
      CHARACTER*1  ANS
      REAL*4 M20,MSOIL
      WRITE (6,*) 'Enter the name of this run'
      READ (5,100) NAME
  100 FORMAT (A16)
      WRITE (2,100) NAME
      WRITE (6,*) 'Enter TSET, PSET, VOL, M20, MSOIL, TINTO, SCALE, ',
     1 'TBGN & TEND'
      READ (5,*) TSET, PSET, VOL, M20, MSOIL, TINTO, SCALE, TBGN, TEND
      WRITE (2,101) TSET,PSET,VOL,M20,MSOIL,TINTO,SCALE,TBGN,TEND
  101 FORMAT (F6.1,F7.0,F7.0,F8.4,F6.1,F8.4,F6.2,F8.2,F8.2)
```

```
      WRITE (6,*)'Enter the Integrator Time (hh.mmss), Peak Area/1.E6,',
     1  ' Temp (F), & Volume out (ml)'
      WRITE (6,*) 'Enter a null line to end'
      N=1
    1 CONTINUE
      WRITE (6,102) N
  102 FORMAT (' Chromatogram',I4)
      READ (5,*,END=99) TINT,AREA,TEMP,VOUT
      TELP=APOELP(TINT,TINTO)
      CONC=APOCAL(AREA,TEMP)
      WRITE (2,103) TINT,AREA,TEMP,VOUT,TELP,CONC
  103 FORMAT (F10.4,F10.5,F10.0,F10.1,F10.2,F10.5)
      N=N+1
      GO TO 1
   99 WRITE (6,107)
      READ (5,106) ANS
      IF (ANS.EQ.'N'.OR.ANS.EQ.'n') GO TO 1
      N=N-1
      WRITE (6,104) NAME,N
  104 FORMAT (//,' The appropriate file has now been completed for run '
     1 ,A16,/,I5,' chromatogram entries were written',/)
  106 FORMAT (A1)
  107 FORMAT (' Is that all the entries for this file (Y/N)?')
      STOP
      END
```

Program Name: APOLIN

```
C-----------------------------------------------------------------------
C   Program Description: Plot line
C
C   Programmer: Scott Willms
C
C   Usage: This routine is used to plot a line without markers.  It is
C      used primarily for plotting lines on Arrhenius plots.
C-----------------------------------------------------------------------
      SUBROUTINE APOLIN (X1,Y1,X2,Y2)
      DIMENSION X(2),Y(2)
      X(1)=X1
      X(2)=X2
      Y(1)=Y1
      Y(2)=Y2
      CALL CHSET ('LINE')
      CALL CHSET ('NOMARK')
      CALL CHPLOT (1,2,X,Y)
      CALL CHSET ('NOLINE')
      CALL CHSET ('MARK')
      RETURN
      END
```

Program Name: APOMEC1

```
C----------------------------------------------------------------------
C   Program Description: APO mechanism simulation
C
C   Programmer: Scott Willms
C
C   Usage: This program allows the user to enter the rate constants
C      in the mechanism described for aqueous phase oxidation in
C      the dissertation by Willms (1985).  These values will be used
C      to simulate the radical, hydroperoxide, and parent organic
C      concentrations.  All data is read from the terminal.  All output
C      is in plotted form.
C----------------------------------------------------------------------
      IMPLICIT REAL*8 (A-H,K,O-Z)
      INTEGER ARRAY(3)
      INTEGER ATYPE,ATMOD,FLDCT,PL(10)
      INTEGER WKLEN
      CHARACTER*6 KEY1(2),KEY2(2)
      CHARACTER*111 NOTE
      CHARACTER*80  HEAD1
      CHARACTER*52  HEAD2
      CHARACTER*132 HEAD
      CHARACTER*12 STRING(7),NTEXT
      CHARACTER*1 ANS,PANS
      CHARACTER*8 NL(3)
      CHARACTER*8 NOTE1
      INTEGER NATT1(6),NATT2(6)
      REAL*4 NUM(7),T(5000),Y1(5000),Y2(5000),Y3(5000),Y4(5000),W,H
      REAL*4 YRNG1,YRNG2
      REAL*4 XE(100),YE(100)
      DIMENSION Y(4),WK(25000),IWK(300),YSTART(4),K(9)
      DATA IK/8/
      DATA ARRAY/0,0,0/,YRNG1/2.0E-3/,YRNG2/1.E-08/
      DATA PL/4,5,0,1,66,5,11,0,0,0/
      DATA NATT1/0,0,0,100,100,0/,NATT2/0,0,0,70,100,0/
      COMMON/UCOM1/O2,K
      COMMON/UCOM2/YSTART
      EXTERNAL RATES,JACRAT
      ANS='N'
      PANS='Y'
      NL(1)='WILLMS'
      KEY1(1)='RH    '
      KEY1(2)='ROO.  '
      KEY2(1)='R.    '
      KEY2(2)='ROOH  '
      XSTOP=30000.
C   Generate idealized experimental data
         CONCI = 1.2D-3
         DO 42 I=1,50
         XE(I) = I*5
```

```
         IF ((I*5).LE.120) THEN
            YE(I)= CONCI
         ELSE
            YE(I)= CONCI*EXP(-0.04*((I*5)-120))
         END IF
   42    CONTINUE
      WRITE (6,*) '           APO MECHANISM SIMULATION'
      WRITE (6,*) '           --- --------- ----------'
C---------------------------------------------------
C From Denisova and Denisov
      K(1)=1.D-06
C From transition state theory
      K(2)=3.D+07
C Assume E=7 and log(A2) = 2 + 0.5 E2
      K(3)=2.D+02
C For cumyl radical k(4) = 2.7E12 exp(-30400/RT)
      K(4)=0.02
C Dilute and plenty of O2, so zero
      K(5)=0.
      K(6)=0.
C k(7) = 1.7E9 exp(-1500/RT) from p. 98. E is 1-2, so assume 1.5.
C Get A6 from k=1.9E7 at 70 deg C for ethylbenzene.
      K(7)=1.D+07
C Set oxygen concentration
      O2=0.031
C---------------------------------------------------
C  Initialize the plotting package using a standard format
      CALL FSINIT
      CALL GSCLR
      CALL CHRNIT
    6 CONTINUE
C  Read in a title on two lines
      CALL APOHD (HEAD)
      WRITE (6,*) 'Which marking method should be used (0,1,2)?'
      READ (5,*) NPM
      IF (NPM.EQ.1) NPLOT = 1
      IF (NPM.EQ.2) NPLOT = 3
      WRITE (6,*) 'Which of the rate constants is to be varied (1-7)?'
      READ (5,*) IVAR
      WRITE (6,*) 'Enter beginning value for ki, the number of orders'
      WRITE (6,*) 'of magnitude variation, and the number of orders of'
      WRITE (6,*) 'magnitude for each variation'
      READ (5,*) KIS,KIMAG,KITIME
      K(IVAR)=KIS
      KIE=KIS*10**(KIMAG*KITIME)
      WRITE (6,114) IVAR,KIS,KIE
  114 FORMAT (' k(',I2,') will vary from ',G12.5,' to ',G12.5)
    7 WRITE (6,*) ' '
      WRITE (6,110) (K(I),I=1,7),O2
      READ (5,*) IK,XK
      K(IK)=XK
      IF (IK.EQ.8) O2=XK
```

```
      IF (IK.NE.9) GO TO 7
  110 FORMAT (' Enter subscript and new value for one value of k',/,
     1       ' The current values are:',/,5G15.5,/,2G15.5,/,
     2       ' The oxygen concentration (subscript 8) is:',G15.5,//,
     2       ' Enter ''9 9'' for no change')
    5 CONTINUE
      IF (PANS.EQ.'Y'.OR.PANS.EQ.'y') THEN
         CALL DSOPEN (11,2,'*        ',7,PL,1,NL)
         CALL DSUSE (2,11)
         PANS='N'
      END IF
      IF (ANS.EQ.'R'.OR.ANS.EQ.'r') THEN
         CALL GSCLR
         CALL CHRNIT
      ELSE
         CALL CHSTRT
      END IF
C----------------------------------------------------
C   Initialize values for call to LSODES
C----------------------------------------------------
      N=4
      Y(1)=0.
      Y(2)=0.
      Y(3)=1.2D-03
      Y(4)=0.
      TOL=0.0001
      ISTATE=1
      MF=22
      IWKLEN=300
      IOPT=0
      ITOL=1
      ATOL=1.D-25
      ITASK=1
      WKLEN=25000
C   Call to O.D.E. solver
      X=0.0D+00
      XPRT=60.
      XEND=X+XPRT
      ICNT=1
      T(ICNT)=X
      Y1(ICNT)=Y(1)
      Y2(ICNT)=Y(2)
      Y3(ICNT)=Y(3)
      Y4(ICNT)=Y(4)
    1 CONTINUE
      CALL LSODE (RATES,N,Y,X,XEND,ITOL,TOL,ATOL,ITASK,ISTATE,IOPT,
     1WK,WKLEN,IWK,IWKLEN,JACRAT,MF)
      ICNT=ICNT+1
      T(ICNT)=X/60.
      Y1(ICNT)=Y(1)
      Y2(ICNT)=Y(2)
      Y3(ICNT)=Y(3)
```

```
      Y4(ICNT)=Y(4)
  100 FORMAT (5G15.7)
      XEND = XEND + XPRT
      IF (XEND.LE.XSTOP+XSTOP*0.00001) GO TO 1
      IF (ICNT.GT.5000) WRITE (6,*) 'You have a problem'
C   Determine half height point
      YHALF = (NPLOT*.075+0.5)*(Y3(1) - Y3(ICNT)) + Y3(ICNT)
      IF (NPM.EQ.1) NPLOT = NPLOT * (-1)
      IF (NPM.EQ.2) NPLOT = NPLOT - 1
      DO 40 I=1,ICNT
      IPOS = I
      IF (Y3(I).LT.YHALF) GO TO 41
   40 CONTINUE
   41 CONTINUE
C-----------------------------------------------------
    8 CALL GSQPS(W,H)
      CALL CHHATT (3,ARRAY)
      CALL CHSET ('BKEY')
      CALL CHSET ('KBOX')
      CALL CHYRNG (0.,YRNG1)
C  Specify bottom and top margins
      CALL CHHMAR (7,2)
C  Plot the heading
      CALL CHHATT (3,ARRAY)
      CALL CHSET ('HBOTTOM')
      CALL CHSET ('HLEFT')
      CALL CHHEAD (132,HEAD)
C  Specify the tick mark directions
      CALL CHXSET ('PTICK')
      CALL CHYSET ('PTICK')
C  Axis titles
      CALL CHXTTL (12,'Time / (min)')
      CALL CHYTTL (19,'²RH³ / (Mole/Liter)')
C  Specify the secondary axis
      CALL CHXSEL (2)
      CALL CHYSEL (2)
      CALL CHSET  ('XDUP')
      CALL CHSET  ('YDUP')
      CALL CHXSET ('NTIC')
      CALL CHYSET ('NTIC')
      CALL CHXSET ('NOLA')
      CALL CHYSET ('NOLA')
      CALL CHXSEL (1)
      CALL CHYSEL (1)
C  Chart notes
      NUM(1) = K(1)
      NUM(2) = K(2)
      NUM(3) = K(3)
      NUM(4) = K(4)
      NUM(5) = K(5)
      NUM(6) = K(6)
      NUM(7) = K(7)
```

```
      CALL RTC (NUM,7,12,5,STRING)
      NINDEX=0
      IF (K(IVAR).GE.(KIE-KIE*0.000001)) THEN
         WRITE (6,*) 'Do you need to overwrite one of the notes?'
         READ (5,101) ANS
         IF (ANS.EQ.'Y'.OR.ANS.EQ.'y') THEN
            WRITE (6,*) 'Enter the note index and text (I1,1X,A12)'
            READ (5,113) NINDEX,NTEXT
  113       FORMAT (I1,1X,A12)
            STRING(NINDEX)=NTEXT
         END IF
      END IF
      NOTE =  'kOb=' // STRING(1) // ';k1 =' // STRING(2) //
     1       ';k2 =' // STRING(3) // ';k3 =' // STRING(4) //
     2       ';k4c=' // STRING(7) // ';'
      CALL CHSET ('BNOTE')
      CALL CHSET ('NBOX')
      CALL CHNATT (4,NATT1)
      CALL CHNOFF (56.,22.)
C  Plot the conc. vs. t
      CALL CHSET ('LINE')
      CALL CHSET ('NOMARK')
      CALL CHPLOT (1,ICNT,T,Y3)
C  Plot idealized experimental data
      CALL CHSET ('NOLINE')
      CALL CHSET ('MARK')
      CALL CHPLOT (1,50,XE,YE)
      CALL CHNOTE ('C7',84,NOTE)
      CALL CHNATT (4,NATT2)
      CALL RTC (K(IVAR),1,8,4,NOTE1)
      CALL CHSET ('NONBOX')
      CALL CHNOFF (T(IPOS),Y3(IPOS))
      IF (NPM.NE.0) CALL CHNOTE ('Z5',8,NOTE1)
      CALL ASREAD (ATYPE,ATMOD,FLDCT)
C-----------------------------------------------
      IF (K(IVAR).GE.(KIE-KIE*0.000001)) THEN
         WRITE (6,*) 'Do you want this plot printed (Y/N)?'
         READ (5,101) PANS
         IF (PANS.EQ.'Y'.OR.PANS.EQ.'y') THEN
           IF (NINDEX.EQ.0) THEN
              WRITE (6,*) 'DON''T YOU NEED TO CHANGE THE NOTE?'
              READ (5,101) ANS
              IF (ANS.EQ.'Y'.OR.ANS.EQ.'y') GO TO 5
           END IF
           WRITE (6,*) 'PLOT SENT TO PLOTTER'
           CALL GSCOPY (52,88)
           CALL FSCLS (1)
         END IF
C-----------------------------------------------
         WRITE (6,111) YRNG1,YRNG2
  111    FORMAT (' The current plot ranges are:',2G14.6)
         WRITE (6,*) 'Do you wish to change them (Y/N)?'
```

```
         READ (5,101) ANS
         IF (ANS.EQ.'Y'.OR.ANS.EQ.'y') THEN
            WRITE (6,*) 'Enter the new ranges'
            READ (5,*) YRNG1,YRNG2
            CALL CHSTRT
            GO TO 8
         END IF
         WRITE (6,*) 'Another go round (Y=Yes, N=No, R=Reinitialize)?'
         READ (5,101) ANS
         IF(ANS.EQ.'Y'.OR.ANS.EQ.'y'.OR.ANS.EQ.'R'.OR.ANS.EQ.'r')GO TO 6
      ELSE
         ANS='Y'
         K(IVAR)=K(IVAR)*(10.**KITIME)
         GO TO 5
      END IF
      CALL CHTERM
      STOP
  101 FORMAT (A1)
      END
      SUBROUTINE RATES(N,X,Y,F)
      IMPLICIT REAL*8 (A-H,K,O-Z)
      DIMENSION Y(4),F(4),K(8)
      COMMON/UCOM1/O2,K
C
C   1 - R.
C   2 - ROO.
C   3 - RH
C   4 - ROOH
C
      F(1)=K(1)*Y(3)*O2-K(2)*Y(1)*O2+K(3)*Y(2)*Y(3)+2*K(4)*Y(4)-
     1     2*K(5)*Y(1)**2-K(6)*Y(1)*Y(2)
      F(2)=K(2)*Y(1)*O2-K(3)*Y(2)*Y(3)-K(6)*Y(1)*Y(2)-2*K(7)*Y(2)**2
      F(3)=-K(1)*Y(3)*O2-K(3)*Y(2)*Y(3)
      F(4)=K(3)*Y(2)*Y(3)-K(4)*Y(4)
      RETURN
      END
      SUBROUTINE JACRAT(N,X,Y,ID1,ID2,PD,NPD)
      REAL*8  Y(4),PD(4,4),X
      RETURN
      END
```

Program Name: APOMEC2

```
C-------------------------------------------------------------------
C   Program Description: Match mechanism to idealized data
C
C   Programmer: Scott Willms
C
C   Usage: This program is used to determine the values of mechanism
C      rate constants which minimize the sum of the squares of the
C      differences between the mechanism and idealized data.  Currently
C      the idealized data has an induction period of 120 min and a
C      pseuo first order rate constant of 0.04 1/min.  This is typical
C      of m-xylene at 200 C and 2000 psi air.  Powell's method of
C      conjugate directions is used for the minimization.
C
C      The user must provide the guesses for the independent variables
C      (XO(1), XO(2), etc.) shown below in the first few lines of code.
C      Further down in the code these XO's are associated with a
C      corresponding values of K's, the mechism rate constants.  These
C      lines of code must be altered for each unique problem
C      encountered.  Also N must be set equal to the number of
C      independent variables.
C-------------------------------------------------------------------
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION XO(3),WX1(3),WX2(3),S(3),A(3,3)
      EXTERNAL F
C  Guess values for independent variables (see below for rate constant
C  corresponding to each independent variable
      XO(1) =  .00037
      XO(2) =  1.05
      XO(3) =  1000000
      N=3
      LTYPE=2
      MAXI=500
      EPSLS=1.E-15
      CRIT =1.E-20
      CALL PCD (XO,WX1,WX2,S,A,F,N,EPSLS,CRIT,LTYPE,MAXI)
      STOP
      END
      FUNCTION F (XO)
      IMPLICIT REAL*8 (A-H,K,O-Z)
      INTEGER WKLEN
      REAL*4 NUM(7),T(5000),Y1(5000),Y2(5000),Y3(5000),Y4(5000),W,H
      DIMENSION Y(4),WK(25000),IWK(300),YSTART(4),K(8),XO(1),YE(5000)
      DATA IK/8/,IFIRST/0/
      COMMON/UCOM1/O2,K
      COMMON/UCOM2/YSTART
      EXTERNAL RATES,JACRAT
      IF (IFIRST.EQ.0) THEN
         IFIRST = 1
```

```
          ICNT = 0
C   Generate the idealized data
          CONCI = 1.2D-3
          DO 8 I=5,200,5
          IF (I.LE.120) THEN
             YE(I)= CONCI
          ELSE
             YE(I)= CONCI*EXP(-0.04*(I-120))
          END IF
          ICNT = ICNT + 1
    8     CONTINUE
       END IF
       DO 6 I=1,3
       IF (XO(I).LT.0.) THEN
          F=1.D+30
          RETURN
       END IF
     6 CONTINUE
       XSTOP=13000.
C-----------------------------------------------------------
C DO NOT CHANGE THIS SECTION OF CODE
C From Denisova and Denisov
       K(1)=1.D-06
C From transition state theory
       K(2)=3.D+07
C Assume E=7 and log(A2) = 2 + 0.5 E2
       K(3)=2.D+02
C For cumyl radical k(4) = 2.7E12 exp(-30400/RT)
       K(4)=0.02
C Dilute and plenty of O2, so zero
       K(5)=0.
       K(6)=0.
C k(7) = 1.7E9 exp(-1500/RT) from p. 98. E is 1-2, so assume 1.5.
C Get A6 from k=1.9E7 at 70 deg C for ethylbenzene.
       K(7)=1.D+07
C-----------------------------------------------------------
C  CHANGE THIS SECTION OF CODE FOR EACH UNIQUE PROBLEM
C  Associate rate constants with optimization variables
       K(1)=XO(1)
       K(3)=XO(2)
       K(4)=0.000
       K(7)=XO(3)
C-----------------------------------------------------------
C  Initialize values for call to LSODES
       N=4
       Y(1)=0.
       Y(2)=0.
       Y(3)=1.2D-03
       CONCI = Y(3)
       Y(4)=0.
       O2=3.1D-02
       TOL=0.0001
```

```
      ISTATE=1
      MF=22
      IWKLEN=300
      IOPT=0
      ITOL=1
      ATOL=1.D-25
      ITASK=1
      WKLEN=25000
C   Call to O.D.E. solver
      X=0.0D+00
      XPRT=60.
      XEND=X+XPRT
      ICNT=1
      T(ICNT)=X
      Y1(ICNT)=Y(1)
      Y2(ICNT)=Y(2)
      Y3(ICNT)=Y(3)
      Y4(ICNT)=Y(4)
    1 CONTINUE
      CALL LSODE (RATES,N,Y,X,XEND,ITOL,TOL,ATOL,ITASK,ISTATE,IOPT,
     1WK,WKLEN,IWK,IWKLEN,JACRAT,MF)
      ICNT=ICNT+1
      T(ICNT)=X/60.
      Y1(ICNT)=Y(1)
      Y2(ICNT)=Y(2)
      Y3(ICNT)=Y(3)
      Y4(ICNT)=Y(4)
  100 FORMAT (5G15.7)
      XEND = XEND + XPRT
      IF (XEND.LE.XSTOP+XSTOP*0.00001) GO TO 1
      IF (ICNT.GT.5000) WRITE (6,*) 'You have a problem'
      F=0.
      DO 9 I=5,120,5
    9 F = F + (YE(I) - Y3(I))**2
      DO 7 I=5,200,5
    7 F = F + (YE(I) - Y3(I))**2
      RETURN
  102 FORMAT (7G12.5)
      END
      SUBROUTINE RATES(N,X,Y,F)
      IMPLICIT REAL*8 (A-H,K,O-Z)
      DIMENSION Y(4),F(4),K(8)
      COMMON/UCOM1/O2,K
      F(1)=K(1)*Y(3)*O2-K(2)*Y(1)*O2+K(3)*Y(2)*Y(3)+2*K(4)*Y(4)-
     1     2*K(5)*Y(1)**2-K(6)*Y(1)*Y(2)
      F(2)=K(2)*Y(1)*O2-K(3)*Y(2)*Y(3)-K(6)*Y(1)*Y(2)-2*K(7)*Y(2)**2
      F(3)=-K(1)*Y(3)*O2-K(3)*Y(2)*Y(3)
      F(4)=K(3)*Y(2)*Y(3)-K(4)*Y(4)
      RETURN
      END
      SUBROUTINE JACRAT(N,X,Y,ID1,ID2,PD,NPD)
      REAL*8  Y(4),PD(4,4),X
```

```
RETURN
END
```

Program Name: APOMEC3

```
C-----------------------------------------------------------------------
C   Program Description: Generate Objective Fcn Data for 3D plotting
C
C   Programmer: Scott Willms
C
C   Usage: This program is used to generate values for the sum of the
C      squares of the differences between idealized data and mechanism
C      simulation results.  This data is used for 3D plotting.  The
C      idealized data is described in APOMEC2.  The data is written
C      to unit 1.
C-----------------------------------------------------------------------
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION XO(2),WX1(2),WX2(2),S(2),A(2,2)
      EXTERNAL F
      XO(1) =  5.
      XO(2) =  10.
      DO 1 I=1,41
      DO 1 J=1,41
      XO(1)=(I-1)*2.*.126
      XO(2)=(J-1)*2.*0.0001
      OBJ=F(XO)
    1 WRITE (1,100) XO(1),XO(2),OBJ
      STOP
  100 FORMAT (3G15.6)
      END
      FUNCTION F (XO)
      IMPLICIT REAL*8 (A-H,K,O-Z)
      INTEGER WKLEN
      REAL*4 NUM(7),Y3(5000),W,H
      DIMENSION Y(4),WK(25000),IWK(300),YSTART(4),K(8),XO(1),YE(5000)
      DATA IK/8/,IFIRST/0/
      COMMON/UCOM1/O2,K
      COMMON/UCOM2/YSTART
      EXTERNAL RATES,JACRAT
      IF (IFIRST.EQ.0) THEN
         IFIRST = 1
         ICNT = 0
         CONCI = 1.2D-3
         DO 8 I=5,200,5
         ICNT = ICNT + 1
         IF (I.LE.120) THEN
            YE(ICNT)= CONCI
         ELSE
            YE(ICNT)= CONCI*EXP(-0.04*(I-120))
         END IF
    8    CONTINUE
      END IF
      DO 6 I=1,2
      IF (XO(I).LT.0.) THEN
```

```
           F=1.D+30
           RETURN
        END IF
      6 CONTINUE
        XSTOP=12000.
C------------------------------------------------------------
C DO NOT CHANGE THIS SECTION OF CODE
C From Denisova and Denisov
        K(1)=1.D-06
C From Transition state theory
        K(2)=3.D+07
C Assume E=7 and log(A2) = 2 + 0.5 E2
        K(3)=2.D+02
C For cumyl radical k(4) = 2.7E12 exp(-30400/RT)
        K(4)=0.02
C Dilute and plenty of O2, so zero
        K(5)=0.
        K(6)=0.
C k(7) = 1.7E9 exp(-1500/RT) from p. 98. E is 1-2, so assume 1.5.
C Get A6 from k=1.9E7 at 70 deg C for ethylbenzene.
        K(7)=1.D+07
C------------------------------------------------------------
C CHANGE THIS SECTION OF CODE FOR EACH UNIQUE PROBLEM
C Associate rate constants with independent variables
        K(1)=1.E-06
        K(3)=X0(1)
        K(4)=X0(2)
        K(7)=0.5
C------------------------------------------------------------
C  Initialize values for call to LSODES
        N=4
        Y(1)=0.
        Y(2)=0.
        Y(3)=1.2D-03
        Y(4)=0.
        O2=3.1D-02
        TOL=0.0001
        ISTATE=1
        MF=22
        IWKLEN=300
        IOPT=0
        ITOL=1
        ATOL=1.D-25
        ITASK=1
        WKLEN=25000
C  Call to O.D.E. solver
        X=0.0D+00
        XPRT=60.*5.
        XEND=X+XPRT
        ICNT=1
        Y3(ICNT)=Y(3)
      1 CONTINUE
```

```
      CALL LSODE (RATES,N,Y,X,XEND,ITOL,TOL,ATOL,ITASK,ISTATE,IOPT,
     1WK,WKLEN,IWK,IWKLEN,JACRAT,MF)
      ICNT=ICNT+1
      Y3(ICNT)=Y(3)
  100 FORMAT (5G15.7)
      XEND = XEND + XPRT
      IF (XEND.LE.XSTOP+XSTOP*0.00001) GO TO 1
      IF (ICNT.GT.5000) WRITE (6,*) 'You have a problem'
      F=0.
      IEND = 200/5
      DO 7 I=1,IEND
    7 F = F + (YE(I) - Y3(I))**2
      RETURN
  102 FORMAT (7G12.5)
      END
      SUBROUTINE RATES(N,X,Y,F)
      IMPLICIT REAL*8 (A-H,K,O-Z)
      DIMENSION Y(4),F(4),K(8)
      COMMON/UCOM1/O2,K
      F(1)=K(1)*Y(3)*O2-K(2)*Y(1)*O2+K(3)*Y(2)*Y(3)+2*K(4)*Y(4)-
     1     2*K(5)*Y(1)**2-K(6)*Y(1)*Y(2)
      F(2)=K(2)*Y(1)*O2-K(3)*Y(2)*Y(3)-K(6)*Y(1)*Y(2)-2*K(7)*Y(2)**2
      F(3)=-K(1)*Y(3)*O2-K(3)*Y(2)*Y(3)
      F(4)=K(3)*Y(2)*Y(3)-K(4)*Y(4)
      RETURN
      END
      SUBROUTINE JACRAT(N,X,Y,ID1,ID2,PD,NPD)
      REAL*8  Y(4),PD(4,4),X
      RETURN
      END
```

Program Name: APOMOD

```
C----------------------------------------------------------------------
C   Program Description: Aqueous phase oxidation model
C
C   Programmer: Scott Willms
C
C   Usage: This program uses the model presented in Willms et al. (1985)
C      to generate plots of experimental data and corresponding model
C      curves.  The following units must be defined:
C
C         Unit       Description
C         ----    ----------------------------------------------
C       FT01F001   Input experimental data file 1 (formatted by APOIN)
C       FT01F002   Input experimental data file 2 (formatted by APOIN)
C         . . .
C       FT01F001   Input experimental data file 3 (formatted by APOIN)
C           5      Terminal
C           6      Terminal
C
C      The user has a choice of two options for the type of plots
C      that he wants.
C
C      Option 1 is an analysis mode.  By choosing this option
C      the same set of data can be plotted numerous times with
C      various various values for m20, the pseudo-first order rate
C      constant, and tstart.  Though numerous model curves may be
C      generated on one plot, only one set of experimental data may
C      be shown at any time.  This option requires minimal user input.
C
C      Option 2 is a display mode.  More than one set of experimental
C      data can be shown on one plot, but only one model curve can be
C      shown for each set of data.  The plotting format is more
C      appropriate for publication purposes than option 1.
C
C----------------------------------------------------------------------
      INTEGER HATT(3),MARK(8)
      CHARACTER*16 NAME
      CHARACTER*13 COMP
      CHARACTER*231 NOTE
      CHARACTER*132 HEAD
      CHARACTER*12 STR1(5)
      CHARACTER*5  STR2(5)
      CHARACTER*1  ANS,PANS,NANS
      REAL*4 NUM(5)
      REAL*4 M20,MSOIL,MW1,MW2,M2T,M1V,M1V0
      INTEGER COLOR(8),PC(2)
      REAL*4 XMARK(1),YMARK(20)
      COMMON/APO1/TINT(200),AREA(200),TEMP(200),VOUT(200),
     1            TELP(200),CONC(200),NG
      COMMON/APO2/TSET,PSET,VOL,M20,MSOIL,TINT0,SCALE,TBGN,TEND,NAME
```

```
      COMMON/APO3/TINTB(200),AREAB(200),TEMPB(200),VOUTB(200),
     1            TELPB(200),CONCB(200),NB
      COMMON/APO4/MW1,MW2,VT,R,TAMB
      INTEGER ATYPE,ATMOD,FLDCT
      INTEGER PL(10)
      CHARACTER*8 NL(3)
      DIMENSION CCALC(8000),TCALC(8000),SC(200),ST(200)
      DATA PC/1,2/
      DATA PL/4,5,0,1,66,10,11,0,0,0/
      DATA IFLAG/0/,IMARK/0/
      DATA HATT/0,0,0/,MARK/1,2,3,4,5,6,7,8/
      DATA COLOR/1,1,1,1,1,1,1,1/
      HEAD(60:60) = ' '
      PANS = 'Y'
      ANS = 'Y'
      NL(1)='WILLMS'
C    Read user input information
      WRITE (6,*) ' '
      WRITE (6,*) 'What type of plots are needed?  Enter'
      WRITE (6,*) ' '
      WRITE (6,*) '   1 for single run per plot with detailed ',
     1            'kinetic information'
      WRITE (6,*) '   2 for multiple runs per plot with only ',
     1            'temperature and pressure noted'
      READ (5,*) JOPT
      WRITE (6,*) 'Do you want the data normalized (Y/N)?'
      READ (5,100) NANS
      CALL APOCMP (ICOMP,COMP,YRNG)
      IF (NANS.EQ.'Y'.OR.NANS.EQ.'y') YRNG = 1.2
      WRITE (6,*) 'Enter DELT'
      READ (5,*) DELT
      IF (JOPT.NE.1) THEN
         WRITE (6,*) 'Enter XRNG'
         READ (5,*) XRNG
         CALL APOHD (HEAD)
      END IF
      CALL APOCON (ICOMP)
C   Initialize the plotting package
      CALL FSINIT
C   Read APO run data
   20 CALL APORD (1)
      IF (PANS.EQ.'Y'.OR.PANS.EQ.'y') THEN
         CALL DSOPEN (11,2,'*       ',7,PL,1,NL)
         CALL DSUSE (2,11)
         CALL GSCLR
         CALL CHRNIT
      END IF
      AM2T=0.
    5 CONTINUE
      IF (ANS.EQ.'R'.OR.ANS.EQ.'r') THEN
         CALL GSCLR
         CALL CHRNIT
```

```
         IMARK=1
      ELSE
         CALL CHSTRT
         IMARK=IMARK+1
      END IF
      WRITE (6,110) AM2T
  110 FORMAT (' Enter m2T. Last entry was:',F7.4)
      READ (5,*) AM2T
      M2T   = AM2T
      WRITE (6,*) 'Enter the rate constant and tstart'
      READ (5,*) RATE,TSTART
      VOUTO = 0.
      TC    = (TEMPB(1)-32.)/1.8
C---------------------------------------------------------------------
C   CALCULATE THE INITIAL CONCENTRATION
C---------------------------------------------------------------------
      C2L      = M2T/APOPHI(TC,APOVL(VOUTO,M1V,TC),ICOMP)
      CCALC(1) = C2L * 1.E+4
      TCALC(1) = 0.
      TIME     = DELT
      ICNT     = 2
C---------------------------------------------------------------------
C   CALCULATE CONCENTRATION VS. TIME
C---------------------------------------------------------------------
      DO 15 I=1,NB
   10 TC = (TEMPB(I)-32.)/1.8
      IF (TIME.GE.TSTART) THEN
         VL    = APOVL(VOUTO,M1V,TC)
         C2L   = C2L*EXP(-RATE*VL/APOPHI(TC,VL,ICOMP)*DELT)
      END IF
      IF (TIME.GE.TELPB(I)) THEN
         PHIO  = APOPHI(TC,APOVL(VOUTO,   M1V,TC),ICOMP)
         PHI   = APOPHI(TC,APOVL(VOUTB(I),M1V,TC),ICOMP)
         VS    = APODEN(TAMB,0,1)/APODEN(TC,0,2)*(VOUTB(I)-VOUTO)
         C2L   = C2L * (PHIO - VS)/PHI
         VOUTO = VOUTB(I)
         CCALC(ICNT) = C2L * 1.E+4
         IF (NANS.EQ.'Y'.OR.NANS.EQ.'y')CCALC(ICNT)=CCALC(ICNT)/CCALC(1)
         TCALC(ICNT) = TIME
         TIME        = TIME + DELT
         ICNT        = ICNT + 1
      ELSE
         CCALC(ICNT) = C2L * 1.E+4
         IF (NANS.EQ.'Y'.OR.NANS.EQ.'y')CCALC(ICNT)=CCALC(ICNT)/CCALC(1)
         TCALC(ICNT) = TIME
         TIME        = TIME+DELT
         ICNT        = ICNT+1
         GO TO 10
      END IF
   15 CONTINUE
      ICNT=ICNT-1
      IREG = 0
```

```
      DO 2 I=1,NB
      IF (TELPB(I).GE.TBGN.AND.TELPB(I).LE.TEND.AND.CONCB(I).NE.0.)THEN
         IREG     = IREG + 1
         SC(IREG) = CONCB(I)
         ST(IREG) = TELPB(I)
      END IF
    2 CONTINUE
C   Normalize data if requested
      IF (NANS.EQ.'Y'.OR.NANS.EQ.'y') THEN
         DO 21 I=1,NB
   21    CONCB(I) = CONCB(I)/CCALC(1)
      CCALC(1) = 1.0
      END IF
C  Begin plotting calls
C  Colors
      CALL CHCOL (2,PC)
C  Specify plotting ranges
      YMIN= 0.
      YMAX= YRNG
      CALL CHYRNG (YMIN,YMAX)
      IF (JOPT.NE.1) CALL CHXRNG (0.,XRNG)
C  Axis titles
      CALL CHXTTL (12,'Time / (min)')
      CALL CHYTTL (21,'²RH³ / (gm/ml 1.0E-4)')
      CALL CHHMAR (7,2)
C  Plot the heading
      CALL CHHATT (3,HATT)
      CALL CHSET ('HBOTTOM')
      IF (JOPT.EQ.1) THEN
         HEAD='EXPERIMENTAL DATA & MODEL CURVE;' // COMP // ';' // NAME
         IF (HEAD(60:60) .NE. ' ') THEN
            CALL CHHEAD (60,HEAD)
         ELSE
            CALL CHHEAD (58,HEAD)
         END IF
      ELSE
         CALL CHSET ('HLEFT')
         CALL CHHEAD (132,HEAD)
      END IF
C  Specify the tick mark directions
      CALL CHXSET ('PTICK')
      CALL CHYSET ('PTICK')
C  Specify the secondary axis
      CALL CHXSEL (2)
      CALL CHYSEL (2)
      CALL CHSET  ('XDUP')
      CALL CHSET  ('YDUP')
      CALL CHXSET ('NTIC')
      CALL CHYSET ('NTIC')
      CALL CHXSET ('NOLA')
      CALL CHYSET ('NOLA')
      CALL CHXSEL (1)
```

```
      CALL CHYSEL (1)
C  Chart notes
      NUM(1) = TSET
      NUM(2) = PSET
      NUM(3) = RATE
      NUM(4) = TSTART
      NUM(5) = M2T
      IF (JOPT.EQ.1) THEN
         CALL RTC (NUM,5,12,6,STR1)
         NOTE =  'T    =' // STR1(1) // ';P    =' // STR1(2) //
     1          ';K''   =' // STR1(3) // ';TSTRT=' // STR1(4) //
     2          ';M20  =' // STR1(5)
         JNOTE = 95
         IMARK = 1
      ELSE
         CALL RTC (NUM,2,5,0,STR2)
         INOTE=(IMARK-1)*21 + 1
         JNOTE=INOTE+21
         NOTE(INOTE:JNOTE) = '  ' // STR2(1) // ' C, ' // STR2(2) //
     1                       ' PSI;'
      END IF
      CALL CHSET ('BNOTE')
      CALL CHSET ('NBOX')
C     NOTE = '    0.025% H2O2;    0.25%  H2O2;    0.5%   H2O2;' //
C    1       '    2.5%   H2O2;   25.%    H2O2'
      CALL CHNOFF (52.,23.)
C  Plot conc. vs. temp.
      CALL CHSET ('NOLINE')
      CALL CHSET ('MARK')
      CALL CHSET ('NDRAW')
      IF (JOPT.EQ.1) THEN
         CALL CHPLOT (1,NB,TELPB,CONCB)
         CALL CHPLOT (1,IREG,ST,SC)
      ELSE
         CALL CHMARK (1,MARK(IMARK))
         CALL CHPLOT (1,NB,TELPB,CONCB)
      END IF
      CALL CHSET ('LINE')
      CALL CHSET ('NOMARK')
      CALL CHPLOT (1,ICNT,TCALC,CCALC)
      JNOTE=JNOTE-1
      CALL CHDRAX
      CALL CHNOTE ('C7',JNOTE,NOTE)
C     CALL CHNOTE ('C7',79,NOTE)
C  Plot symbols with the notes
      IF (JOPT.NE.1) THEN
         XFRAC= 0.73
         XMARK(1)=XRNG * XFRAC
         FRAC1 = 0.73
         FRAC2 = 0.044
         DO 40 I=1,IMARK
         FRAC = (IMARK-I)*FRAC2 + FRAC1
```

```
 40    YMARK(I) = FRAC*(YMAX-YMIN) + YMIN
       CALL CHSTRT
       CALL CHMARK (8,MARK)
       CALL CHCOL  (8,COLOR)
       CALL CHPLOT (IMARK,1,XMARK,YMARK)
    END IF
    CALL ASREAD (ATYPE,ATMOD,FLDCT)
    IF (JOPT.EQ.1) THEN
       WRITE (6,111) CCALC(1)
111    FORMAT (' C2LO IS:',F10.4)
       WRITE (6,*) 'Another value of m2T (Y,N OR R)?'
       WRITE (6,*) 'Y=Yes, N=No, R=Reinitialize'
       READ (5,100) ANS
       IF(ANS.EQ.'Y'.OR.ANS.EQ.'y'.OR.ANS.EQ.'R'.OR.ANS.EQ.'r')GO TO 5
       CALL APOEP (2,ANS)
       WRITE (6,*) 'Process another set of data (Y/N)?'
       READ (5,100) ANS
       IF (ANS.EQ.'Y'.OR.ANS.EQ.'y') GO TO 20
    ELSE
       CALL APOEP (2,PANS)
       WRITE (6,*) 'Process another set of data (Y, N, OR R)?'
       WRITE (6,*) 'Y=Yes, N=No, R=Reinitialize'
       READ (5,100) ANS
       IF(ANS.EQ.'Y'.OR.ANS.EQ.'y'.OR.ANS.EQ.'R'.OR.ANS.EQ.'r')GOTO 20
    END IF
    CALL CHTERM
    STOP
100 FORMAT (A1)
    END
```

Program Name: APOOXY

```
C----------------------------------------------------------------------
C   Program Description: Calculates the oxygen concentration
C
C   Programmer: Scott Willms
C
C   Usage: The calling routine must provide the temperature in deg. C
C      and the pressure in psi.  This routine will then return the
C      oxygen concentration in gm/ml.
C      The correlation is only valid for 60  T  300 deg C.
C      An error message is printed when this is called with a
C      temperature outside the valid range.
C----------------------------------------------------------------------
      FUNCTION APOOXY (T,P)
      DATA IFLAG/0/
      IF ((T.LT.60..OR.T.GT.300.).AND.IFLAG.EQ.0) THEN
         IFLAG = 1
         WRITE (6,100)
      END IF
      H = 49134.3*SIN(.0286863*T) + .203670*T**3 - 124.429*T**2
     1    + 18921.9*T + 163228.
      APOOXY = 32./18. * APODEN(T,0,2) * 0.21*(P - APOSAT(T,0,2))/ H
      RETURN
  100 FORMAT (' Henry''s law for O2 extrapolated outside the',
     1 ' correlated range.',/,' Check APOOXY for limits.')
      END
```

Program Name: APOPHI

```
C-----------------------------------------------------------------------
C   Program Description: Phi calcuation
C
C   Programmer: Scott Willms
C
C   Usage: This routine is used to caculate phi (defined in Willms
C      et al. (1985)) given the temperature in degrees C, TC, the
C      liquid volume in ml (VL), and the component number, ICOMP.
C      See APOCMP for a list of valid compounds.  Two common block,
C      APO2 and APO4 provided additional necessary information.
C-----------------------------------------------------------------------
      FUNCTION APOPHI (TC,VL,ICOMP)
      IMPLICIT REAL*4 (M)
      COMMON/APO2/TSET,PSET,VOL,M20,MSOIL,TINTO,SCALE,TBGN,TEND,NAME
      COMMON/APO4/MW1,MW2,VT,R,TAMB
      TK=TC+273.15
      APOPHI=VL+APOHEN(TC,PSET,ICOMP,2)*MW1/R/TK/APODEN(TC,0,2)/14.7*
     1       (VT-VL)
      RETURN
      END
```

Program Name: APOPLT

```
C-------------------------------------------------------------------------
C   Program Description: Plotting program
C
C   Programmer: Scott Willms
C
C   Usage: This program is used to plot experimental data.  Data is
C      read from unit 1.
C-------------------------------------------------------------------------
      INTEGER ARRAY(3)
      CHARACTER*16 NAME
      CHARACTER*32 NOTE
      CHARACTER*50 HEAD
      CHARACTER*8 STRING(7)
      CHARACTER*1 ANS
      REAL*4 NUM(7)
      REAL*4 M20,MSOIL,MW1,MW2
      COMMON/APO1/TINT(200),AREA(200),TEMP(200),VOUT(200),
     1            TELP(200),CONC(200),NG
      COMMON/APO2/TSET,PSET,VOL,M20,MSOIL,TINTO,SCALE,TBGN,TEND,NAME
      COMMON/APO3/TINTB(200),AREAB(200),TEMPB(200),VOUTB(200),
     1            TELPB(200),CONCB(200),NB
      DATA ARRAY/0,0,0/
      DATA STRING/7*'        '/
C  Read run data
      CALL APORD (1)
C  Initialize the plotting package using a standard format
      CALL APOSP1 (1)
C  Plot a heading
      CALL CHHATT (3,ARRAY)
      HEAD = 'AQUEOUS PHASE OXIDATION DATA;' // NAME // ';'
      CALL CHHEAD (50,HEAD)
C  Axis titles
      CALL CHXTTL (12,'Time / (min)')
      CALL CHYTTL (21,'Conc / (gm/ml 1.0E-4)')
C  Set ranges
      CALL CHYRNG (0.,1.40)
      IF (SCALE.EQ.1.) CALL CHXRNG (0.,180.)
      IF (SCALE.EQ.2.) CALL CHXRNG (0.,600.)
      IF (SCALE.EQ.3.) CALL CHXRNG (0.,1000.)
      IF (SCALE.EQ.4.) CALL CHXRNG (0.,2400.)
C  Chart notes
      NUM(1) = TSET
      NUM(2) = PSET
      CALL RTC (NUM,2,7,1,STRING)
      NOTE = 'T  =' // STRING(1) // ' C ;P  = ' // STRING(2) // 'PSI'
      CALL CHSET ('BNOTE')
      CALL CHSET ('NBOX')
      CALL CHNOFF (55.,23.)
C  Plot conc. vs. temp.
```

```
      CALL CHPLOT (1,NB,TELPB,CONCB)
      CALL CHNOTE ('C7',32,NOTE)
C  Close the plot routine
      CALL APOEP (1,ANS)
      STOP
      END
```

Program Name: APOPLTN

```
C-----------------------------------------------------------------------
C   Program Description: Plotting program (nice)
C
C   Programmer: Scott Willms
C
C   Usage: This program accomplished the same purpose as APOPLT, but
C      uses a little "nicer" format.
C-----------------------------------------------------------------------
      INTEGER KATT(4)
      CHARACTER*16 NAME
      CHARACTER*23 NOTE
      CHARACTER*8 STRING(7)
      CHARACTER*1 ANS
      REAL*4 NUM(4)
      REAL*4 M20,MSOIL,MW1,MW2
      COMMON/APO1/TINT(200),AREA(200),TEMP(200),VOUT(200),
     1            TELP(200),CONC(200),NG
      COMMON/APO2/TSET,PSET,VOL,M20,MSOIL,TINTO,SCALE,TBGN,TEND,NAME
      COMMON/APO3/TINTB(200),AREAB(200),TEMPB(200),VOUTB(200),
     1            TELPB(200),CONCB(200),NB
      DATA KATT/0,0,0,80/
      STRING(1) = 'm-Xylene'
      STRING(2) = 'Phenol  '
      CALL APOCON (1)
C  Read run data
      CALL APORD (1)
C  Initialize the plotting package using a standard format
      CALL APOSP3
      CALL CHSET ('NOLINE')
C  Axis titles
      CALL CHXTTL (12,'Time / (min)')
      CALL CHYTTL (21,'Conc / (gm/ml 1.0E-4)')
C  Set ranges
      CALL CHYRNG (0.,2.00)
      IF (SCALE.EQ.1.) CALL CHXRNG (0.,120.)
      IF (SCALE.EQ.2.) CALL CHXRNG (0.,600.)
      IF (SCALE.EQ.3.) CALL CHXRNG (0.,1000.)
C  Key
      CALL CHSET ('BKEY')
      CALL CHSET ('KBOX')
      CALL CHKOFF (-15.,8.)
      CALL CHKATT (4,KATT)
      CALL CHKEY (2,8,STRING)
C  Plot conc. vs. temp.
      CALL CHPLOT (1,NB,TELPB,CONCB)
      CALL APORD (1)
      CALL CHPLOT (1,NB,TELPB,CONCB)
C  Close the plot routine
      CALL APOEP (1,ANS)
```

```
STOP
END
```

Program Name: APOPLTXP

```
C-----------------------------------------------------------------------
C   Program Description: Synergism plotting program
C
C   Programmer: Scott Willms
C
C   Usage: This program performs the same plotting as APOPLT and
C      APOPLTN, but plots two set of experimental data on one plot.
C      The first set must be assigned to FT01F001 and the second to
C      FT01F002.
C-----------------------------------------------------------------------
      INTEGER ARRAY(3)
      CHARACTER*16 NAME
      CHARACTER*23 NOTE
      CHARACTER*8 STRING(7)
      CHARACTER*1 ANS
      REAL*4 NUM(4)
      REAL*4 M20,MSOIL,MW1,MW2
      COMMON/AP01/TINT(200),AREA(200),TEMP(200),VOUT(200),
     1            TELP(200),CONC(200),NG
      COMMON/AP02/TSET,PSET,VOL,M20,MSOIL,TINTO,SCALE,TBGN,TEND,NAME
      COMMON/AP03/TINTB(200),AREAB(200),TEMPB(200),VOUTB(200),
     1            TELPB(200),CONCB(200),NB
      DATA ARRAY/0,0,0/
      CALL APOCON (1)
C  Read run data
      CALL APORD (1)
C  Initialize the plotting package using a standard format
      CALL APOSP1 (1)
      CALL GSLSS (2,'ADMUWGGP',65)
      CALL CHHATT (3,ARRAY)
      CALL CHHEAD (16,NAME)
C  Axis titles
      CALL CHXTTL (12,'Time / (min)')
      CALL CHYTTL (21,'Conc / (gm/ml 1.0E-4)')
C  Set ranges
      CALL CHYRNG (0.,2.00)
      IF (SCALE.EQ.1.) CALL CHXRNG (0.,180.)
      IF (SCALE.EQ.2.) CALL CHXRNG (0.,600.)
      IF (SCALE.EQ.3.) CALL CHXRNG (0.,1000.)
C  Chart notes
      NUM(1) = TSET
      NUM(2) = PSET
      CALL RTC (NUM,2,7,1,STRING)
      NOTE = 'T  =' // STRING(1) // ';P  = ' // STRING(2)
      CALL CHSET ('BNOTE')
      CALL CHSET ('NBOX')
      CALL CHNOFF (55.,23.)
C  Plot conc. vs. temp.
      CALL CHPLOT (1,NB,TELPB,CONCB)
```

```
      CALL CHNOTE ('C7',22,NOTE)
      CALL APORD (1)
      CALL CHPLOT (1,NB,TELPB,CONCB)
C  Close the plot routine
      CALL APOEP (1,ANS)
      STOP
      END
```

Program Name: APORD

```
C-----------------------------------------------------------------------
C   Program Description: Data read routine
C
C   Programmer: Scott Willms
C
C   Usage: This is the data read routine.  It assumes that the
C      experimental data were processed and formatted by APOIN.
C      This routine reads all the information in such a data file,
C      and makes them available to the calling routine through common
C      blocks APO1, APO2, and APO3.  The arrays in APO1 contain NG
C      (number good) values which do not include any chromatograms
C      with undefined concentrations.  The arrays in APO3 contain
C      NB (number bad) values with include both defined and undefined
C      (set to zero) concentration data.
C
C      Data is read from unit 1.
C
C      Summary reports are written to unit 6 if requested by IPRINT
C      which controls the level of output.  These levels are:
C
C        IPRINT        Output
C      --------      -----------------------------------------
C          0          All run conditions and data are printed
C          1          Only run conditions are printed
C          2          No output
C
C-----------------------------------------------------------------------
      SUBROUTINE APORD (IPRINT)
      CHARACTER*16 NAME
      REAL*4 M20,MSOIL
      COMMON/APO1/TINT(200),AREA(200),TEMP(200),VOUT(200),
     1            TELP(200),CONC(200),NG
      COMMON/APO2/TSET,PSET,VOL,M20,MSOIL,TINTO,SCALE,TBGN,TEND,NAME
      COMMON/APO3/TINTB(200),AREAB(200),TEMPB(200),VOUTB(200),
     1            TELPB(200),CONCB(200),NB
      IDIM = 200
C   Read input data
      READ (1,108) NAME
      READ (1,*) TSET,PSET,VOL,M20,MSOIL,TINTO,SCALE,TBGN,TEND
      NG=0
      DO 1 I=1,IDIM
      READ (1,*,END=99) TINTB(I),AREAB(I),TEMPB(I),VOUTB(I),
     1                  TELPB(I),CONCB(I)
      NB=I
      IF (CONCB(I).NE.0.) THEN
         NG=NG+1
         TINT(NG)=TINTB(I)
         AREA(NG)=AREAB(I)
         TEMP(NG)=TEMPB(I)
```

```
         VOUT(NG)=VOUTB(I)
         TELP(NG)=TELPB(I)
         CONC(NG)=CONCB(I)
         END IF
    1 CONTINUE
C   If reading occurs up to IDIM points, print error and stop
      WRITE (6,100) IDIM,TELP(IDIM),CONC(IDIM)
      STOP
C   Once all reading is complete, print desired level of output
   99 IF (IPRINT.EQ.2) RETURN
      WRITE (6,101) NAME
      WRITE (6,102) NB,NG,NB-NG
      WRITE (6,103) TSET,PSET,VOL,M20,MSOIL,TINTO,SCALE,TBGN,TEND
      IF (IPRINT.EQ.1) RETURN
      WRITE (6,104)
      WRITE (6,105)
      WRITE (6,106) (TINT(I),AREA(I),TEMP(I),VOUT(I),TELP(I),
     1                   CONC(I),I=1,NG)
      WRITE (6,107)
      WRITE (6,105)
      WRITE (6,106) (TINTB(I),AREAB(I),TEMPB(I),VOUTB(I),TELPB(I),
     1                   CONCB(I),I=1,NB)
      RETURN
C-------------------------------------------------------------------
C      FORMAT STATEMENTS
C-------------------------------------------------------------------
  100 FORMAT (/,' Error reading data - over',I5,' data points read',/,
     1 ' the last two data points were',2G15.4)
  101 FORMAT (/,' Processing data for run ',A16)
  102 FORMAT (/,I4,' Total data points were read',/,
     1          I7,' Points were useful for processing',/,
     2          I7,' Points were undefined')
  103 FORMAT (/,' Run Characteristics:',//,
     1 5X,'Set point temperature             ', F10.0, ' C      ',/,
     2 5X,'Set point pressure                ', F10.0, ' psi    ',/,
     2 5X,'Initial liquid volume             ', F10.0, ' ml     ',/,
     3 5X,'Mass of organic initially injected', F10.4, ' Grams  ',/,
     4 5X,'Mass of soil present              ', F10.1, ' Grams  ',/,
     5 5X,'Integrator start time             ', F10.4, ' Hours  ',/,
     6 5X,'Plot scale factor                 ', F10.2, '        ',/,
     7 5X,'Regression begin time             ', F10.2, ' Minutes',/,
     8 5X,'Regression end time               ', F10.2, ' Minutes')
  104 FORMAT (//,15X,'Summary of Useful Data',/)
  105 FORMAT (
     1 ' Time/(hrs)  Area/1.E+6  Temp/(F)  Vout/(ml)  Elapsed Time/',
     2 '(min)  C/(gm/ml 1.E-4)',/,
     3 ' ----------  ----------  --------  ---------  -------------',
     4 '-----  ---------------')
  106 FORMAT (F10.4,F12.5,F10.1,F11.1,F16.2,F19.4)
  107 FORMAT (//,15X,'Summary of Both Useful and Undefined Data',/)
  108 FORMAT (A16)
      END
```

Program Name: APOREG1

```
C-------------------------------------------------------------------
C   Program Description: Regression program 1
C
C   Programmer: Scott Willms
C
C   Usage: This is the regression program used for data with an
C      induction period.  The program assumes that m20 has been
C      determined previously.  Guesses are required for k' and tstart.
C      The program will use Powell's Conjugate Directions Method to
C      find the values of k' and tstart which minimize the sum of the
C      squares of the differences between the experimental data and
C      the mathematical model (given in Willms et al. (1985)).
C
C      The data is read from unit 1.
C
C-------------------------------------------------------------------
      IMPLICIT REAL*8 (A-H,O-Z)
      REAL*4 SFAC,YRNG
      REAL*4 TSET,PSET,VOL,M20,MSOIL,TINTO,SCALE,TBGN,TEND
      CHARACTER*16 NAME
      CHARACTER*13 COMP
      DIMENSION X0(2),WX1(2),WX2(2),S(2),A(2,2)
      COMMON/APO2/TSET,PSET,VOL,M20,MSOIL,TINTO,SCALE,TBGN,TEND,NAME
      COMMON/REG/SFAC,JFLAG,NREG,ICOMP
      EXTERNAL F
      CALL APOCMP (ICOMP,COMP,YRNG)
      WRITE (5,*) 'Enter a guess for k'' and tstart'
      READ (5,*) X0(1),X0(2)
      SFAC = X0(2) / X0(1)
      X0(1) = X0(1) * SFAC
      JFLAG = 0
      WRITE (6,101)
      N=2
      LTYPE=2
      MAXI=100
      EPSLS=1.E-15
      CRIT =1.E-20
      CALL PCD (X0,WX1,WX2,S,A,F,N,EPSLS,CRIT,LTYPE,MAXI)
      JFLAG = 1
      V=F(X0)
      SQRTO2 = DSQRT(APOOXY(TSET,PSET))
      WRITE (6,100) (X0(1)/SFAC),X0(2),(V/NREG),NREG,(X0(1)/SFAC/SQRTO2)
  100 FORMAT (//,' k''        =',F13.5,/,
     1          ' TSTART    =',F10.2,//,
     2          ' SUMSQD/N  =',E12.4,/,
     3          ' N         =',I12,/,
     4          ' k         =',F13.5)
  101 FORMAT (1H1,/,8X,'Regression on Rate Constant and Tstart',/,
     1          '+',7X,'__________ __ ____ ________ ___ ______'//)
```

```
      STOP
      END
      FUNCTION F (X)
      REAL*8    X(2)
      CHARACTER*16 NAME
      REAL*4 M20,MSOIL,MW1,MW2,M2T,M1V,M1V0
      COMMON/AP01/TINT(200),AREA(200),TEMP(200),VOUT(200),
     1            TELP(200),CONC(200),NG
      COMMON/AP02/TSET,PSET,VOL,M20,MSOIL,TINT0,SCALE,TBGN,TEND,NAME
      COMMON/AP03/TINTB(200),AREAB(200),TEMPB(200),VOUTB(200),
     1            TELPB(200),CONCB(200),NB
      COMMON/AP04/MW1,MW2,VT,R,TAMB
      COMMON/REG/SFAC,JFLAG,NREG,ICOMP
      DATA IFLAG/0/
      IF (JFLAG.EQ.1) WRITE (6,101)
C  Read experimental data and terminal input only on first call
      IF (IFLAG.EQ.0) THEN
         IFLAG = 1
         CALL APOCON (ICOMP)
         CALL APORD (1)
         IF (TBGN.EQ.TEND) THEN
            WRITE (6,*) 'Unable to perform regression'
            WRITE (6,*) 'tbegin is equal to tend'
            STOP
         END IF
         WRITE (5,*) 'Enter M20'
         READ (5,*) AM2T
         WRITE (6,102) AM2T
         WRITE (6,103) SFAC
      END IF
C   Initialize variables
      NREG   = 0
      F      = 0.
      M2T    = AM2T
      RATE   = X(1) / SFAC
      TSTART = X(2)
      VOUT0  = 0.
      TC     = (TEMPB(1)-32.)/1.8
C   Calculate the initial concentration
      C2L     = M2T/APOPHI(TC,APOVL(VOUT0,M1V,TC),ICOMP)
C-----------------------------------------------------------------
C   CALCULATE CONCENTRATION VS. TIME
C-----------------------------------------------------------------
      T0   = TSTART
      DO 15 I=1,NB
      IF (TELPB(I).GT.TEND) RETURN
      TC   = (TEMPB(I)-32.)/1.8
C   Reaction
      IF (TELPB(I).GE.TSTART) THEN
         VL    = APOVL(VOUT0,M1V,TC)
         C2L   = C2L*EXP(-RATE*VL/APOPHI(TC,VL,ICOMP)*(TELPB(I)-T0))
         T0    = TELPB(I)
```

```
      END IF
C   Square the difference
      IF (TELPB(I).GE.TBGN.AND.TELPB(I).LE.TEND.AND.CONCB(I).NE.0.)THEN
         F = F + (C2L*1.E+4 - CONCB(I))**2
         IF (JFLAG.EQ.1) WRITE (6,100) I,TELPB(I),CONCB(I),(C2L*1.E+4)
         NREG = NREG + 1
      END IF
C   Sampling
      PHIO  = APOPHI(TC,APOVL(VOUTO,   M1V,TC),ICOMP)
      PHI   = APOPHI(TC,APOVL(VOUTB(I),M1V,TC),ICOMP)
      VS    = APODEN(TAMB,0,1)/APODEN(TC,0,2)*(VOUTB(I)-VOUTO)
      C2L   = C2L * (PHIO - VS)/PHI
      VOUTO = VOUTB(I)
   15 CONTINUE
      RETURN
C-----Formats---------------------------------------------------------
  100 FORMAT (I5,F10.2,F10.4,F12.4)
  101 FORMAT(//,' Comparison of Calculated & Experimental Concentration'
     1        ,/,'+__________ __ __________ _ ____________ _____________'
     2 ,//,'              Time      Cexp       Ccalc',/,
     3      ' PNT#     min.   gm/ml*1E+4  gm/ml*1E+4',/,
     4      '+____    ____   __________  __________')
  102 FORMAT (/,5X,'Mass of organic actually in the reactor:',F10.4,/)
  103 FORMAT (5X,'Regression scale factor:               ',F12.2,/)
      END
```

Program Name: APOREG2

```
C----------------------------------------------------------------------
C   Program Description: Regression program 2
C
C   Programmer: Scott Willms
C
C   Usage: This is the regression program used for data without an
C      induction period.  The program assumes that tstart is zero.
C      Guesses are required for k' and m20.
C      The program will use Powell's Conjugate Directions Method to
C      find the values of k' and m20 which minimize the sum of the
C      squares of the differences between the experimental data and
C      the mathematical model (given in Willms et al. (1985)).
C
C      The data is read from unit 1.
C
C----------------------------------------------------------------------
      IMPLICIT REAL*8 (A-H,O-Z)
      REAL*4 SFAC,YRNG
      REAL*4 TSET,PSET,VOL,M20,MSOIL,TINTO,SCALE,TBGN,TEND
      CHARACTER*13 COMP
      CHARACTER*16 NAME
      DIMENSION XO(2),WX1(2),WX2(2),S(2),A(2,2)
      COMMON/APO2/TSET,PSET,VOL,M20,MSOIL,TINTO,SCALE,TBGN,TEND,NAME
      COMMON/REG/SFAC,JFLAG,NREG,ICOMP
      EXTERNAL F
      CALL APOCMP (ICOMP,COMP,YRNG)
      WRITE (5,*) 'Enter guesses for M20 and k'''
      READ (5,*) XO(2),XO(1)
      SFAC = XO(2) / XO(1)
      XO(1) = XO(1) * SFAC
      JFLAG = 0
      WRITE (6,101)
      N=2
      LTYPE=2
      MAXI=100
      EPSLS=1.E-20
      CRIT =1.E-20
      CALL PCD (XO,WX1,WX2,S,A,F,N,EPSLS,CRIT,LTYPE,MAXI)
      JFLAG = 1
      V=F(XO)
      TSTART = 0.
      SQRTO2 = DSQRT(APOOXY(TSET,PSET))
      WRITE (6,100) (XO(1)/SFAC),XO(2),(V/NREG),NREG,(XO(1)/SFAC/SQRTO2)
  100 FORMAT (//,' k''     =',F12.8,/,
     1          ' M20    =',F10.4,//,
     2          ' SUMSQD/N  =',E12.4,/,
     3          ' N         =',I12,/,
     4          ' k         =',F12.6)
  101 FORMAT (1H1,/,8X,'Regression on Rate Constant and  M20 ',/,
```

```
     1          '+',7X,'___________ _ ____ _______ ___ _____'//)
      STOP
      END
      FUNCTION F (X)
      REAL*8    X(1)
      CHARACTER*16 NAME
      REAL*4 M20,MSOIL,MW1,MW2,M2T,M1V,M1V0
      COMMON/AP01/TINT(200),AREA(200),TEMP(200),VOUT(200),
     1            TELP(200),CONC(200),NG
      COMMON/AP02/TSET,PSET,VOL,M20,MSOIL,TINT0,SCALE,TBGN,TEND,NAME
      COMMON/AP03/TINTB(200),AREAB(200),TEMPB(200),VOUTB(200),
     1            TELPB(200),CONCB(200),NB
      COMMON/AP04/MW1,MW2,VT,R,TAMB
      COMMON/REG/SFAC,JFLAG,NREG,ICOMP
      DATA IFLAG/0/
      IF (JFLAG.EQ.1) WRITE (6,101)
C   Read experimental data and terminal input on first call
      IF (IFLAG.EQ.0) THEN
         IFLAG = 1
         CALL APOCON (ICOMP)
         CALL APORD (1)
         IF (TBGN.EQ.TEND) THEN
            WRITE (6,*) 'Unable to perform regression'
            WRITE (6,*) 'tbegin is equal to tend'
            STOP
         END IF
         WRITE (6,103) SFAC
      END IF
C   Initialize variables
      NREG   = 0
      F      = 0.
      M2T    = X(2)
      RATE   = X(1) / SFAC
      TSTART = 0.
      VOUT0  = 0.
      TC     = (TEMPB(1)-32.)/1.8
C   Calculate the initial concentration
      C2L      = M2T/APOPHI(TC,APOVL(VOUT0,M1V,TC),ICOMP)
C---------------------------------------------------------------------
C   CALCULATE CONCENTRATION VS. TIME
C---------------------------------------------------------------------
      T0   = TSTART
      DO 15 I=1,NB
      IF (TELPB(I).GT.TEND) RETURN
      TC   = (TEMPB(I)-32.)/1.8
C   Reaction
      IF (TELPB(I).GE.TSTART) THEN
         VL    = APOVL(VOUT0,M1V,TC)
         C2L   = C2L*EXP(-RATE*VL/APOPHI(TC,VL,ICOMP)*(TELPB(I)-T0))
         T0    = TELPB(I)
      END IF
C   Square the difference
```

```
      IF (TELPB(I).GE.TBGN.AND.TELPB(I).LE.TEND.AND.CONCB(I).NE.0.)THEN
         F = F + (C2L*1.E+4 - CONCB(I))**2
         IF (JFLAG.EQ.1) WRITE (6,100) I,TELPB(I),CONCB(I),(C2L*1.E+4)
         NREG = NREG +1
      END IF
C   Sampling
      PHIO  = APOPHI(TC,APOVL(VOUTO,   M1V,TC),ICOMP)
      PHI   = APOPHI(TC,APOVL(VOUTB(I),M1V,TC),ICOMP)
      VS    = APODEN(TAMB,0,1)/APODEN(TC,0,2)*(VOUTB(I)-VOUTO)
      C2L   = C2L * (PHIO - VS)/PHI
      VOUTO = VOUTB(I)
      IF (C2L.LT.1.E-20) C2L=0.
   15 CONTINUE
      RETURN
C----Formats-------------------------------------------------------
  100 FORMAT (I5,F10.2,F10.4,F12.4)
  101 FORMAT(//,' Comparison of Calculated & Experimental Concentration'
     1       ,/,'+__________ __ __________ _ ___________ _____________'
     2 ,//,'          Time      Cexp       Ccalc',/,
     3      ' PNT#     min.   gm/ml*1E+4  gm/ml*1E+4',/,
     4      '+____    ____   __________  __________')
  102 FORMAT (/,5X,'Mass of Organic Actually in the Reactor:',F10.4,/)
  103 FORMAT (/,5X,'Regression Scale Factor:              ',F12.2,/)
      END
```

Program Name: APOSAT

```
C----------------------------------------------------------------------
C   Program Description: Saturation vapor pressure
C
C   Programmer: Scott Willms
C
C   Usage: This routine is used to calculate the saturation vapor
C      pressure in psi given the temperature.  The temperature can
C      be given in degrees F (IUNIT = 1) or degrees C (IUNIT = 2).
C      The vapor pressure correlations were accomplished using equation
C      6-39 in Smith and Van Ness.  The list of available compounds,
C      specified with ICOMP, are
C
C      ICOMP     Compound    Correlated Range
C      -----     ----------  ----------------
C        0       Water        32 - 600 F
C        1       m-Xylene     30 - 320 C
C
C   Notes: The data for water was obtained from Himmelblau (1974).  The
C      accuracy of the correlation can be estimated from the following
C      table.
C
C           T (F)         Psat Actual    Psat calc.
C          -----------    -----------    ----------
C              32             0.0886        0.06524
C             100             0.9487        0.93698
C             200            11.525        11.643
C             400           247.25        246.82
C             600          1543.2        1541.1
C
C      The data for m-xylene was obtained from Vargaftik (1983).
C
C----------------------------------------------------------------------
      FUNCTION APOSAT (T,ICOMP,IUNIT)
      DATA IFLAG/0/
      IF (IUNIT.EQ.1) THEN
         TF = T
         TC =(T-32.)/1.8
         GO TO 200
      END IF
      IF (IUNIT.EQ.2) THEN
         TF = T*1.8 + 32.
         TC = T
         GO TO 200
      END IF
      WRITE (6,*) 'Invalid value supplied for IUNIT in APOSAT'
      STOP
  200 CONTINUE
      IF (ICOMP.NE.0) GO TO 300
C   Water
```

```
      IF ((TF.LT.32..OR.TF.GT.600.).AND.IFLAG.EQ.0) THEN
         IFLAG = 1
         WRITE (6,100)
      END IF
      APOSAT=EXP(-6367.92/(TF+402.520)+9.85836+.0000344047 *TF+.596088*
     1 ALOG(TF))
      RETURN
  300 CONTINUE
      GO TO (1),ICOMP
      WRITE (6,*) 'Invalid compound requested in APOSAT'
      STOP
C   VAPOR PRESSURE OF XYLENE
    1 IF ((TC.LT.30..OR.TC.GT.320.).AND.IFLAG.EQ.0) THEN
         WRITE (6,100)
         IFLAG = 1
      END IF
      APOSAT=EXP((-2536.15/(TC+173.553))+11.7953+.00286488*TC-.282677*
     1 ALOG(TC))
      RETURN
C----Formats-----------------------------------------------------------
  100 FORMAT (' Vapor pressure is being extrapolated outside the',
     1 ' correlated range',/,
     2 ' See APOSAT for the correlated range.')
      END
```

Program Name: APOSP1

```
C-----------------------------------------------------------------------
C   Program Description: Start plot 1
C
C   Programmer: Scott Willms
C
C   Usage: This routine is used to initialize the plotting package.
C     It also initialized the plotter for hard copy output.  Some other
C     plotting specifications are made.  These can be overridden in
C     the calling routine.
C-----------------------------------------------------------------------
      SUBROUTINE APOSP1 (IOPT)
      INTEGER ARRAY(6),PL(10)
      CHARACTER*8 NL(3)
      DATA ARRAY /0,1,0,0,1,0/
      DATA PL/4,5,0,1,66,10,11,0,0,0/
      NL(1)='WILLMS'
      GO TO (1),IOPT
      WRITE (6,*) 'Invalid value for IOPT in APOSP.  Option 1 assumed'
C-----------------------------------------------------------------
C   Plot Option 1
C-----------------------------------------------------------------
C  Open the plot package
    1 CALL FSINIT
C  Set up for plotter output
      CALL DSOPEN (11,2,'*        ',7,PL,1,NL)
      CALL DSUSE (2,11)
C  Specify no line between markers
      CALL CHSET ('NOLINES')
C  Blank background and put box around ledgend
      CALL CHSET ('BKEY')
      CALL CHSET ('KBOX')
C  Grid
      CALL CHGATT (6,ARRAY)
      CALL CHXSET ('GRID')
      CALL CHYSET ('GRID')
C  Axis Titles
      IF (IOPT.EQ.1) THEN
         CALL CHXTTL (12,'Time / (min)')
         CALL CHYTTL (21,'²RH³ / (gm/ml 1.0E-4)')
      END IF
      RETURN
      END
```

Program Name: APOSP2

```
C-----------------------------------------------------------------------
C   Program Description: Start plot 2
C
C   Programmer: Scott Willms
C
C   Usage: This routine is used to initialize the plotting package.
C     It also initialized the plotter for hard copy output.  Some other
C     plotting specifications are made.  These can be overridden in
C     the calling routine.  This routine is usually used for Arrhenius
C     plots.  XINC is the increment in 1/T associated with the tick
C     marks on the x-axis.
C-----------------------------------------------------------------------
      SUBROUTINE APOSP2 (YTTL,XL,XH,YL,YH,XINC)
      INTEGER ATYPE,ATMOD,FLDCT,PL(10),ARRAY(6),MARK(2),CL(2)
      INTEGER TATT(5),AATT(6),NATT(5),HATT(4)
      INTEGER INUM(20)
      DIMENSION XLAB(20)
      CHARACTER*5 CLAB(20)
      CHARACTER*8 NL(3)
      CHARACTER*28 YTTL
      CHARACTER*132 HEAD
      DATA PL/4,5,0,1,66,10,11,0,0,0/
      DATA ARRAY/0,1,0,0,1,0/,MARK/03,03/,CL/0,0/
      DATA TATT/0,0,00, 80, 80/,AATT/0,0,1,0,0,1/
      DATA NATT/0,0,00,100,100/,HATT/0,0,0,100/
      DATA XINC1/0.0001/
      DO 1 I=1,132
    1 HEAD(I:I)=' '
      IF (XINC.GT.1.E-10) XINC1=XINC
      WRITE (6,*) 'The deg. C axis increment is:',XINC1
      NL(1)='WILLMS'
C--- Initialize the plotting package and set up a print file ---
      CALL FSINIT
      CALL DSOPEN (11,2,'*       ',7,PL,1,NL)
      CALL DSUSE (2,11)
      CALL APOHD (HEAD)
C--- Specify bottom and top margins ---
      CALL CHHMAR (7,2)
C--- Specify range of x and y axises
      CALL CHXRNG(XL,XH)
      CALL CHYRNG(YL,YH)
C--- Specify the axis and title attributes
      CALL CHAATT (6,AATT)
      CALL CHTATT (4,TATT)
C--- Specify the axis titles and type
      CALL CHYSET ('ATCENTER')
      CALL CHXTTL (09,'1/T (1/K)')
      CALL CHYTTL (28,YTTL)
```

```
      CALL CHYSET ('LOGARITHMIC')
C--- Print a Heading ---
      CALL CHHATT (4,HATT)
      CALL CHSET ('HBOTTOM')
      CALL CHSET ('HLEFT')
      CALL CHHEAD (132,HEAD)
C--- Print only markers (no line), blank the key area, & box it ---
      CALL CHSET ('MARK')
      CALL CHSET ('NOLINE')
C--- Plot the tick markers in the positive direction & specify interval
      CALL CHXSET ('PTICK')
      CALL CHYSET ('PTICK')
      CALL CHYTIC (2.,0.)
      CALL CHLATT (4,TATT)
C--- Specify chart note attributes and position ---
      CALL CHNATT (4,TATT)
      CALL CHNOFF (47.,22.)
C--- Specify the secondary axis ---
      CALL CHXSEL (2)
      CALL CHYSEL (2)
      CALL CHSET  ('XDUP')
      CALL CHSET  ('YDUP')
      CALL CHXSET ('NTIC')
      CALL CHYSET ('NTIC')
      CALL CHYSET ('NOLAB')
      NLAB = (XH-XL)/XINC1 + 1.9
      DO 2 I = 1,NLAB
    2 XLAB(I)= 1.0 / ((I-1)*XINC1 + XL) - 273.15
      CALL RTC (XLAB,NLAB,5,1,CLAB)
      CALL CHXLAB (NLAB,5,CLAB)
      CALL CHXTTL (10,'T (DEG. C)')
      CALL CHXSEL (1)
      CALL CHYSEL (1)
      RETURN
      END
```

Program Name: APOSP3

```
C----------------------------------------------------------------------
C   Program Description: Start plot 3
C
C   Programmer: Scott Willms
C
C   Usage: This routine is used to initialize the plotting package.
C     It also initialized the plotter for hard copy output.  Some other
C     plotting specifications are made.  These can be overridden in
C     the calling routine.  The plotting format generated with this
C     routine is sometimes refered to as the "nice" format.
C----------------------------------------------------------------------
      SUBROUTINE APOSP3
      CHARACTER*132 HEAD
      CHARACTER*231 NOTE
      CHARACTER*5 STRING(5)
      CHARACTER*1 ANS,PANS
      REAL*4 NUM(5)
      INTEGER PL(10)
      CHARACTER*8 NL(3)
      DATA PL/4,5,0,1,66,10,11,0,0,0/
    1 NL(1)='WILLMS  '
      CALL FSINIT
      CALL DSOPEN (11,2,'*       ',7,PL,1,NL)
      CALL DSUSE (2,11)
      CALL GSCLR
      CALL CHRNIT
    2 CALL APOHD (HEAD)
C  Specify bottom and top margins
    3 CALL CHHMAR (7,2)
C  Plot the heading
      CALL CHSET ('HBOTTOM')
      CALL CHSET ('HLEFT')
      CALL CHHEAD (132,HEAD)
C  Specify the tick mark directions
      CALL CHXSET ('PTICK')
      CALL CHYSET ('PTICK')
C  Specify the secondary axis
      CALL CHXSEL (2)
      CALL CHYSEL (2)
      CALL CHSET  ('XDUP')
      CALL CHSET  ('YDUP')
      CALL CHXSET ('NTIC')
      CALL CHYSET ('NTIC')
      CALL CHXSET ('NOLA')
      CALL CHYSET ('NOLA')
      CALL CHXSEL (1)
      CALL CHYSEL (1)
      RETURN
      END
```

Program Name: APOVL

```
C-----------------------------------------------------------------------
C   Program Description: Volume of liquid
C
C   Programmer: Scott Willms
C
C   Usage: This routine returns the liquid volume in ml given the
C      cummulative volume withdrawn from the reactor, VOUT, and
C      the temperature in degrees C, TC.  The routine also returns
C      the mass of water in the vapor, M1V.
C-----------------------------------------------------------------------
      FUNCTION APOVL (VOUT,M1V,TC)
      IMPLICIT REAL*4 (M)
      COMMON/AP02/TSET,PSET,VOL,M20,MSOIL,TINTO,SCALE,TBGN,TEND,NAME
      COMMON/AP04/MW1,MW2,VT,R,TAMB
      DATA M1V0/0./
      TF=TC*1.8+32.
      TK=TC+273.15
    1 APOVL=( (VOL - VOUT)*APODEN(TAMB,0,1) - M1V0 ) / APODEN(TF,0,1)
      M1V=APOSAT(TF,0,1)*MW1*(VT - APOVL) / (14.7*R*TK)
      IF (ABS(M1V-M1V0).GT.0.000001) THEN
         M1V0=M1V
         GO TO 1
      END IF
      RETURN
      END
```

Program Name: CORDEN1

```
C-----------------------------------------------------------------------
C   Program Description: Correlate density 1
C
C   Programmer: Scott Willms
C
C   Usage: This program is used to correlate density as a function of
C      temperature using nonlinear least squares regression.  The
C      mathematical function is defined in function subpgm DNS.
C      The temperature versus density data are read from unit 1.
C-----------------------------------------------------------------------
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION X0(5),WX1(5),WX2(5),S(5),A(5,5)
      DATA X0/-1.E-6,0.,0.,1.,1./
      COMMON/U1/TEMP(100),DENS(100),ICNT
      EXTERNAL F
      N=3
      LTYPE=2
      MAXI=100
      ICNT=1
    1 READ (1,*,END=99) TEMP(ICNT),DENS(ICNT)
      ICNT=ICNT+1
      GO TO 1
   99 ICNT=ICNT-1
      EPSLS=1.E-20
      CRIT =1.E-20
      CALL PCD (X0,WX1,WX2,S,A,F,N,EPSLS,CRIT,LTYPE,MAXI)
      V=F(X0)
      STD=DSQRT(V/ICNT)
      WRITE (6,*) 'Avg. Difference:',STD
      STOP
      END
      FUNCTION F (X)
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION X(1)
      COMMON/U1/TEMP(100),DENS(100),ICNT
      F=0.
      DO 1 I=1,ICNT
    1 F=F+(DNS(TEMP(I),X)-DENS(I))**2
      RETURN
      END
      FUNCTION DNS (TEMP,X)
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION X(1)
      T=TEMP
      DNS= X(1)*T**2    + X(2)*T   + X(3)
      RETURN
      END
```

Program Name: CORDEN2

```
C-----------------------------------------------------------------------
C   Program Description: Correlate density 2
C
C   Programmer: Scott Willms
C
C   Usage: This program is used to compare actual and correlated density
C      values in tabular and plotted form.  The density function must be
C      provided as a function subpgm as shown below.  The actual density
C      versus temperature data is read from unit 1.
C-----------------------------------------------------------------------
      DIMENSION TEMP(100),DEN(100),DCAL(100)
      N=1
      WRITE (6,*) 'Temperature(F)   Density(gm/ml)   Calc. Density'
      WRITE (6,*) '--------------   --------------   -------------'
    1 READ (1,*,END=99) TEMP(N),DEN(N)
      DCAL(N)=APODEN(TEMP(N),1,2)
      WRITE (6,100) TEMP(N),DEN(N),DCAL(N)
  100 FORMAT (F10.1,F18.5,F20.5)
      N=N+1
      GO TO 1
   99 N=N-1
C  Initialize the plotting package using a standard format
      CALL APOSP1 (1)
      CALL CHXTTL (21,'TEMPERATURE / (DEG C)')
      CALL CHYTTL (17,'DENSITY / (GM/ML)')
      CALL CHHEAD (36,'DENSITY VS. TEMP. CORRELATION;XYLENE')
      CALL CHYRNG (0.60,1.10)
      CALL CHPLOT (1,N,TEMP,DEN)
      CALL CHSET('LINE')
      CALL CHSET('NOMARK')
      CALL CHPLOT (1,N,TEMP,DCAL)
C  Close out the plot routine
      CALL APOEP (1)
      STOP
      END
```

Program Name: CORHEN1

```
C------------------------------------------------------------------------
C   Program Description: Correlate Henry's law constant 1
C
C   Programmer: Scott Willms
C
C   Usage: This program is used to correlate Henry's law constant as a
C      function of temperature using nonlinear least squares regression.
C      The mathematical function is defined in function subpgm HEN.
C      The temperature versus H data are read from unit 1.
C------------------------------------------------------------------------
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION X0(7),WX1(7),WX2(7),S(7),A(6,6)
      DATA X0/3234.49,-1284.05,12.7699,-.0250348,  0.0152356  ,68479.8 ,
     1       0./
      COMMON/U1/TEMP(100),HENRY(100),ICNT
      EXTERNAL F
      N=6
      LTYPE=2
      MAXI=1000
      ICNT=1
    1 READ (1,*,END=99) TEMP(ICNT),HENRY(ICNT)
      ICNT=ICNT+1
      GO TO 1
   99 ICNT=ICNT-1
      EPSLS=1.E-30
      CRIT =1.E-30
      CALL PCD (X0,WX1,WX2,S,A,F,N,EPSLS,CRIT,LTYPE,MAXI)
      V=F(X0)
      STD=DSQRT(V/ICNT)
      WRITE (6,*) 'Avg. Difference:',STD
      STOP
      END
      FUNCTION F (X)
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION X(1)
      COMMON/U1/TEMP(100),HENRY(100),ICNT
      F=0.
      DO 1 I=1,ICNT
    1 F=F+(HEN(TEMP(I),X)-HENRY(I))**2
      RETURN
      END
      FUNCTION HEN (TEMP,X)
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION X(1)
      T=TEMP
      HEN= X(6)  *DSIN(X(5) *T)  + X(4)*T**3 +
     1     X(3)*T**2 + X(2)*T + X(1)
      RETURN
      END
```

Program Name: CORHEN2

```
C---------------------------------------------------------------------
C   Program Description: Correlate Henry's law constant 2
C
C   Programmer: Scott Willms
C
C   Usage: This program will compare actual and calulated values of
C      Henry's law constant in tabluar and plotted form.
C      H will be determined at the vapor pressure of water and at 1000,
C      1500, 2000, and 2500 psi air.  The actual values of H versus
C      temperature will be read from unit 1.  The calculation of H must
C      available in a function subpgm as defined below.  The vapor
C      pressure of water is also required in a function subpgm.
C---------------------------------------------------------------------
      CHARACTER*8 PRES(5)
      CHARACTER*1 ANS
      INTEGER NATT(4)
      DIMENSION TEMP(200),HENRY(200),HCAL(200)
      DATA NATT/0,0,0,70/
      PRES(1)='  Psat  '
      PRES(2)='1000 psi'
      PRES(3)='1500 psi'
      PRES(4)='2000 psi'
      PRES(5)='2500 psi'
      N=1
      WRITE (6,*) 'TEMPERATURE(F)    HENRY (PSI)      CALC. HENRY     '
     1 ,'% ERROR'
      WRITE (6,*) '--------------   --------------   -------------    '
     1 ,'-------'
    1 READ (1,*,END=99) TEMP(N),HENRY(N)
      P = APOSAT(TEMP(N),0,2)
      ICOMP=1
      HCAL(N)=APOHEN(TEMP(N),P,ICOMP,2)
      WRITE (6,100) TEMP(N),HENRY(N),HCAL(N),((HENRY(N)-HCAL(N))/
     1  HENRY(N)*100.)
  100 FORMAT (F10.1,F18.5,F20.5,F10.2)
      N=N+1
      GO TO 1
   99 N=N-1
C  Initialize the plotting package using a standard format
      CALL APOSP1 (1)
C  Turn the grid off
      CALL CHXSET ('NOGRID')
      CALL CHYSET ('NOGRID')
C  Define the plotting scales
      CALL CHXRNG (0.,350.)
      CALL CHYRNG (0.,140000.)
C  Define the axis titles
      CALL CHXTTL (21,'Temperature / (deg C)')
```

```
      CALL CHYTTL (11,'Henry (PSI)')
C  Specify bottom and top margins
      CALL CHHMAR (6,2)
C  Define the heading
      CALL CHSET ('HBOTTOM')
      CALL CHHEAD(045,'Figure 3.1 Henry''s Law Constant for m-Xylene;')
C  Specify the tick mark directions
      CALL CHXSET ('PTICK')
      CALL CHYSET ('PTICK')
C  Specify the secondary axis
      CALL CHXSEL (2)
      CALL CHYSEL (2)
      CALL CHSET  ('XDUP')
      CALL CHSET  ('YDUP')
      CALL CHXSET ('NTIC')
      CALL CHYSET ('NTIC')
      CALL CHXSET ('NOLA')
      CALL CHYSET ('NOLA')
      CALL CHXSEL (1)
      CALL CHYSEL (1)
C  Plot data
      CALL CHPLOT (1,N,TEMP,HENRY)
      CALL CHSET('LINE')
      CALL CHSET('NOMARK')
      CALL CHNATT (4,NATT)
      DO 2 I=1,200
      TEMP(I)= (FLOAT(I)/200.)*250. + 50.
    2 HCAL(I) = APOHEN(TEMP(I),APOSAT(TEMP(I),0,2),ICOMP,2)
      CALL CHPLOT (1,200,TEMP,HCAL)
      CALL CHNOFF (TEMP(90),HCAL(90))
      CALL CHNOTE ('Z8',8,PRES(1))
      DO 6 I=1,200
      TEMP(I)= (FLOAT(I)/200.)*250. + 50.
    6 HCAL(I) = APOHEN(TEMP(I),1000.,ICOMP,2)
      CALL CHPLOT (1,200,TEMP,HCAL)
      CALL CHNOFF (TEMP(90),HCAL(90))
      CALL CHNOTE ('Z8',8,PRES(2))
      DO 3 I=1,200
      TEMP(I)= (FLOAT(I)/200.)*250. + 50.
    3 HCAL(I) = APOHEN(TEMP(I),1500.,ICOMP,2)
      CALL CHPLOT (1,200,TEMP,HCAL)
      CALL CHNOFF (TEMP(90),HCAL(90))
      CALL CHNOTE ('Z8',8,PRES(3))
      DO 4 I=1,200
      TEMP(I)= (FLOAT(I)/200.)*250. + 50.
    4 HCAL(I) = APOHEN(TEMP(I),2000.,ICOMP,2)
      CALL CHPLOT (1,200,TEMP,HCAL)
      CALL CHNOFF (TEMP(90),HCAL(90))
      CALL CHNOTE ('Z8',8,PRES(4))
      DO 5 I=1,200
      TEMP(I)= (FLOAT(I)/200.)*250. + 50.
    5 HCAL(I) = APOHEN(TEMP(I),2500.,ICOMP,2)
```

```
      CALL CHPLOT (1,200,TEMP,HCAL)
      CALL CHNOFF (TEMP(90),HCAL(90))
      CALL CHNOTE ('Z8',8,PRES(5))
C  Close out the plot routine
      CALL APOEP (1,ANS)
      STOP
      END
```

Program Name: CORVP1

```
C-----------------------------------------------------------------------
C   Program Description: Correlate vapor pressure 1
C
C   Programmer: Scott Willms
C
C   Usage: This program is used to correlate vapor pressure as a functio
C      of temperature using nonlinear least squares regression.  The
C      mathematical function is defined in function subpgm VP.
C      The temperature versus vapor pressure data are read from unit 1.
C-----------------------------------------------------------------------
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION X0(5),WX1(5),WX2(5),S(5),A(5,5)
      DATA X0/4545.79, 7.13644,323.229, .000890599 ,.718218/
      COMMON/U1/TEMP(100),PSAT(100),ICNT
      EXTERNAL F
      N=5
      LTYPE=2
      MAXI=500
      ICNT=1
    1 READ (1,*,END=99) TEMP(ICNT),PSAT(ICNT)
      ICNT=ICNT+1
      GO TO 1
   99 ICNT=ICNT-1
      EPSLS=1.E-35
      CRIT =1.E-35
      CALL PCD (X0,WX1,WX2,S,A,F,N,EPSLS,CRIT,LTYPE,MAXI)
      V=F(X0)
      STD=DSQRT(V/ICNT)
      WRITE (6,*) 'Avg. Difference:',STD
      STOP
      END
      FUNCTION F (X)
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION X(1)
      COMMON/U1/TEMP(100),PSAT(100),ICNT
      F=0.
      DO 1 I=1,ICNT
      PCAL=VP(TEMP(I),X)
      IF (PCAL.GT.1000000000) THEN
         F=1.E30
         RETURN
      ELSE
         F=F+((PCAL-PSAT(I))/DSQRT(PSAT(I)))**2
      END IF
    1 CONTINUE
      RETURN
      END
      FUNCTION VP (TEMP,X)
      IMPLICIT REAL*8 (A-H,O-Z)
```

```
DIMENSION X(1)
ARG= -X(1)/(TEMP+X(3))+X(2)+X(4)*TEMP+X(5)*DLOG(TEMP)
IF (ARG.GT.172.) THEN
   VP=10.
   RETURN
ELSE
   VP= DEXP(ARG)
   RETURN
END IF
END
```

Program Name: CORVP2

```
C-----------------------------------------------------------------------
C   Program Description: Correlate vapor pressure 2
C
C   Programmer: Scott Willms
C
C   Usage: This program is used to compare actual and correlated vapor
C      pressure values in tabular and plotted form.  The vapor pressure
C      function must be provided as a function subpgm as shown below.
C      The actual vapor pressure versus temperature data is read from
C      unit 1.
C-----------------------------------------------------------------------
      INTEGER ATYPE,ATMOD,FLDCT
      DIMENSION TEMP(100),PSAT(100),DCAL(100)
      N=1
      WRITE (6,*) 'TEMPERATURE(F)    PSAT (PSI)      CALC. PSAT   '
      WRITE (6,*) '--------------   --------------   -------------'
    1 READ (1,*,END=99) TEMP(N),PSAT(N)
      DCAL(N)=APOSAT(TEMP(N),1,2)
      WRITE (6,100) TEMP(N),PSAT(N),DCAL(N)
  100 FORMAT (F10.1,F18.5,F20.5)
      N=N+1
      GO TO 1
   99 N=N-1
C  Initialize the plotting package
      CALL APOSP1 (1)
C  Specify plot characteristics
      CALL CHXTTL (21,'TEMPERATURE / (DEG C)')
      CALL CHYTTL (10,'PSAT (PSI)')
      CALL CHHEAD(102,'PSAT VS. TEMP. CORRELATION;LN(PSAT) =-2536.15 /
     1(T+173.553) + 11.7953 + .00286488 T - .282677 LN(T)')
C  Plot the data
      CALL CHPLOT (1,N,TEMP,PSAT)
      CALL CHSET('LINE')
      CALL CHSET('NOMARK')
      CALL CHPLOT (1,N,TEMP,DCAL)
      CALL ASREAD (ATYPE,ATMOD,FLDCT)
C  Close the plotting package
      CALL APOEP (1)
      STOP
      END
```

Program Name: PHEARRH

```
C----------------------------------------------------------------------
C   Program Description: Phenol results
C
C   Programmer: Scott Willms
C
C   Usage: This program generates two types of plots.  For IPLOT = 1
C      an active reaction Arrhenius plot is produced, For IPLOT = 2
C      an induction period Arrhenius plot is produced.  The data read
C      from unit 1 includes:
C
C         Record 1:    A dummy identifier
C         Record 2:    The number of entries in this group, ID
C         Record 3-ID: Run name, T(C), P(psi), M20(gm), k'(1/min),
C                      tstart(min), variance(SUMSQ/N from APOREG1 or
C                      APOREG2), number of regression points
C
C      This pattern can be repeated in one data file for multiple
C      groups of data per plot.  The number of read sections and
C      calculation sections must match the number of groups.
C
C      Following the read and calculation section is the plotting
C      sections.  The array LT is used to store legend titles for
C      each group of data.  Since not all groups of data will always
C      be plotted on every plot, as "construct the proper note" section
C      is included.  The desired elements of the LT array are
C      concatenated with the "//" operator.  INOTE must be set equal
C      to the number of LT elements included in the note.  Subsequent
C      to this is the actual plotting.  CHPLOT is used to plot the
C      individual markers and APOLIN is used to draw a line through
C      the data.  Again, since all groups of data are not always
C      desired on any particular plot, the undesired CHPLOT/APOLIN
C      combinations should be commented out.  Finally, each plotting
C      section includes code entitled "plot symbols with the notes".
C      This requires no adaptation and should work as written.
C----------------------------------------------------------------------
      REAL*4 XMARK(1),YMARK(20)
      INTEGER MARK1(16),COLOR1(16),NATT(4)
      INTEGER MARK2( 8),COLOR2( 8)
      CHARACTER*23 LT(10),DUMB
      CHARACTER*182 NOTE
      CHARACTER*28 YTTL
      CHARACTER*1 ANS
      CHARACTER*14 NAME1(20),NAME2(20),NAME3(20),NAME4(20)
      REAL*4 T1(20),P1(20),TS1(20),KP1(20),K1(20),V1(20),N1(20),M1(20)
      REAL*4 T2(20),P2(20),TS2(20),KP2(20),K2(20),V2(20),N2(20),M2(20)
      REAL*4 T3(20),P3(20),TS3(20),KP3(20),K3(20),V3(20),N3(20),M3(20)
      REAL*4 T4(20),P4(20),TS4(20),KP4(20),K4(20),V4(20),N4(20),M4(20)
      DATA NATT/0,0,0,80/
      DATA MARK1 /1,2,3,4,5,6,7,8,1,2,3,4,5,6,7,8/
```

```
      DATA COLOR1/1,2,3,4,5,6,7,8,1,2,3,4,5,6,7,8/
      DATA MARK2 /1,2,3,4,5,6,7,8/
      DATA COLOR2/1,2,3,4,5,6,7,8/
C--- Read Section ---
      READ (1,100) DUMB
      READ (1,*) ID
      READ (1,101)(NAME1(I),T1(I),P1(I),M1(I),KP1(I),TS1(I),V1(I),N1(I),
     1     I=1,ID)
      READ (1,100) DUMB
      READ (1,*) ID
      READ (1,101)(NAME2(I),T2(I),P2(I),M2(I),KP2(I),TS2(I),V2(I),N2(I),
     1     I=1,ID)
      READ (1,100) DUMB
      READ (1,*) ID
      READ (1,101)(NAME3(I),T3(I),P3(I),M3(I),KP3(I),TS3(I),V3(I),N3(I),
     1     I=1,ID)
      READ (1,100) DUMB
      READ (1,*) ID
      READ (1,101)(NAME4(I),T4(I),P4(I),M4(I),KP4(I),TS4(I),V4(I),N4(I),
     1     I=1,ID)
  100 FORMAT (A20)
  101 FORMAT (A14,F5.0,F6.0,F6.0,F8.0,F7.0,F7.0,I3)
C--- Calculation Section ---
      DO 1 I=1,4
      O2   = APOOXY(T1(I),P1(I))
      K1(I)= KP1(I)/SQRT(O2)
      T    = T1(I)
      TS1(I)=TS1(I)*O2
      T1(I)= 1./(T1(I)+273.15)
    1 WRITE (6,102)NAME1(I),T,T1(I),P1(I),TS1(I),KP1(I),O2,K1(I)
  102 FORMAT (1X,A14,F6.1,F9.5,F7.0,F8.5,F10.6,F09.6,F09.3)
      WRITE (6,*) ' '
      DO 2 I=1,8
      O2   = APOOXY(T2(I),P2(I))
      K2(I)= KP2(I)/SQRT(O2)
      T    = T2(I)
      TS2(I)=TS2(I)*O2
      T2(I)= 1./(T2(I)+273.15)
    2 WRITE (6,102)NAME2(I),T,T2(I),P2(I),TS2(I),KP2(I),O2,K2(I)
      WRITE (6,*) ' '
      DO 3 I=1,4
      O2   = APOOXY(T3(I),P3(I))
      K3(I)= KP3(I)/SQRT(O2)
      T    = T3(I)
      TS3(I)=TS3(I)*O2
      T3(I)= 1./(T3(I)+273.15)
    3 WRITE (6,102)NAME3(I),T,T3(I),P3(I),TS3(I),KP3(I),O2,K3(I)
      WRITE (6,*) ' '
      DO 4 I=1,3
      O2   = APOOXY(T4(I),P4(I))
      K4(I)= KP4(I)/SQRT(O2)
      T    = T4(I)
```

```
      TS4(I)=TS4(I)*O2
      T4(I)= 1./(T4(I)+273.15)
    4 WRITE (6,102)NAME4(I),T,T4(I),P4(I),TS4(I),KP4(I),O2,K4(I)
C
C--- Choose the plotting format ---
C
      IPLOT = 2
      GO TO (10,20),IPLOT
C------------------------------------------
C   k VS. 1/T Section
C------------------------------------------
   10 CONTINUE
      YTTL='k (ml/gm)**.5 (1/min)'
      LT(1)='    Phenol Alone,    E = 26.8;'
C     LT(1)='    E = 26.8 kcal/mole       ;'
      LT(2)='    Phenol/Case "a", E = 20.3;'
      LT(3)='    Phenol/Case "b", E = 22.0;'
      LT(4)='    Phenol/Case "c", E = 28.4;'
C----------------
C  Construct the proper note
      NOTE = LT(1) // LT(2) // LT(3) //LT(4)
      INOTE = 4
      NOTELN = INOTE * 30 - 1
C----------------
      XMIN=0.0020
      XMAX=0.0026
      YMIN=0.01
      YMAX=100.
      CALL APOSP2 (YTTL,XMIN,XMAX,YMIN,YMAX)
      CALL CHMARK (16,MARK1)
      CALL CHCOL  (16,COLOR1)
      CALL CHSET ('BNOTE')
      CALL CHSET ('NBOX')
      CALL CHNOFF (52.,23.)
      CALL CHSET ('NDRAW')
C   Phenol alone
      CALL CHPLOT (1,4, T1, K1)
      CALL APOLIN (.002109,100.     ,.00260 ,.13311  )
C   100% Phenol with m-xylene
      CALL CHPLOT (1,08,T2, K2)
      CALL APOLIN (.002   ,67.830   ,.00260 ,.14752  )
C   50% Phenol with m-xylene
      CALL CHPLOT (1,4, T3, K3)
      CALL APOLIN (.002   ,40.205   ,.00260 ,.052919 )
C   15% Phenol with m-xylene
      CALL CHPLOT (1,03,T4, K4)
      CALL APOLIN (.002   ,16.087   ,.002517,.01    )
C
      CALL CHDRAX
      CALL CHNOTE ('C7',NOTELN,NOTE)
C  Plot symbols with the notes
      XFRAC= 0.73
```

```
      XMARK(1)= (XMAX-XMIN)*XFRAC + XMIN
      FRAC1 = 0.73
      FRAC2 = 0.034
      FRAC2 = 0.034
      DO 30 I=1,INOTE
      FRAC = (INOTE-I)*FRAC2 + FRAC1
   30 YMARK(I) = EXP(FRAC*(ALOG(YMAX/YMIN)) + ALOG(YMIN))
      CALL CHSTRT
      CALL CHMARK (8,MARK2)
      CALL CHCOL  (8,COLOR2)
      CALL CHPLOT (INOTE,1,XMARK,YMARK)
C   Close the plotting package
      CALL APOEP (1,ANS)
      STOP
C
C-----------------------------------------
C   Tstart * O2 VS. 1/T Section
C-----------------------------------------
   20 CONTINUE
      YTTL='tstart*O2 (min gm/ml)'
C     LT(1)='    Phenol Alone,    E = 22.5;'
C     LT(1)='    E = 22.5 kcal/mole       ;'
C     LT(2)='    Phenol/Case "a", E = 22.5;'
C     LT(3)='    Phenol/Case "b", E = 21.7;'
C     LT(4)='    Phenol/Case "c", E = 34.4;'
C     LT(5)='    Combined Phenol, E = 22.1;'
C
      LT(1)='    Phenol Alone      ;'
      LT(2)='    Phenol/Case "a"   ;'
      LT(3)='    Phenol/Case "b"   ;'
      LT(4)='    Phenol/Case "c"   ;'
      LT(5)='    E = 22.1 kcal/mole;'
C---------------
C  Construct the proper note
      NOTE = LT(1) // LT(2) // LT(3) // LT(4) // LT(5)
      INOTE = 5
      NOTELN = INOTE * 30 - 1
      NOTELN = INOTE * 23 - 1
C---------------
      XMIN=0.002
      XMAX=0.0026
      YMIN=0.001
      YMAX=1.
      CALL APOSP2 (YTTL,XMIN,XMAX,YMIN,YMAX)
      CALL CHMARK (16,MARK1)
      CALL CHCOL  (16,COLOR1)
      CALL CHNATT (4,NATT)
      CALL CHSET ('BNOTE')
      CALL CHSET ('NBOX')
      CALL CHNOFF (52.,12.)
```

```
      CALL CHSET ('NDRAW')
C--- Plot the data ---
C   Phenol alone
      CALL CHPLOT (1,4, T1,TS1)
C     CALL APOLIN (.002   ,.001068  ,.0026   , .95066 )
C   100% Phenol with m-xylene
      CALL CHPLOT (1,08,T2,TS2)
C     CALL APOLIN (.002   ,.001252  ,.002591,1.      )
C    50% Phenol with m-xylene
      CALL CHPLOT (1,4, T3,TS3)
C     CALL APOLIN (.002   ,.002104  ,.002565,1.      )
C    15% Phenol with m-xylene
      CALL CHPLOT (1,03,T4,TS4)
C     CALL APOLIN (.002039,.001     ,.002438,1.      )
C   All Phenol runs
      CALL APOLIN (.002   ,.001477  ,.002586,1.      )
C
      CALL CHDRAX
      CALL CHNOTE ('C7',NOTELN,NOTE)
C  Plot symbols with the notes
      XFRAC= 0.73
      XMARK(1)= (XMAX-XMIN)*XFRAC + XMIN
      FRAC1 = 0.25
      FRAC2 = 0.034
      DO 40 I=1,INOTE
      FRAC = (INOTE-I)*FRAC2 + FRAC1
   40 YMARK(I) = EXP(FRAC*(ALOG(YMAX/YMIN)) + ALOG(YMIN))
      INOTE = INOTE - 1
      CALL CHSTRT
      CALL CHMARK (8,MARK2)
      CALL CHCOL  (8,COLOR2)
      CALL CHPLOT (INOTE,1,XMARK,YMARK)
C  Close the plotting package
      CALL APOEP (1,ANS)
      STOP
      END
```

Program Name: PHEEN

```
C-----------------------------------------------------------------------
C   Program Description: Phenol results--enhancement number
C
C   Programmer: Scott Willms
C
C   Usage: This program is used to generate semi-log plots of En
C      versus 1/T
C-----------------------------------------------------------------------
      INTEGER MARK(20),COLOR(20),NATT(4)
      CHARACTER*20 LED(20)
      CHARACTER*28 YTTL
      CHARACTER*1 ANS
      CHARACTER*14 NAME1(20),NAME2(20),NAME3(20),NAME4(20)
      REAL*4 T(500),K1(500),K2(500),K3(500),K4(500)
      DATA NATT/0,0,0,80/
C
      LED(1)='Case "a"'
      LED(2)='Case "b"'
      LED(3)='Case "c"'
      DO 1 I=1,201
      T(I)=(I-1)/200.*0.0005 + 0.00205
      K1(I) =         EXP(-13476*T(I) + 33.021)
      K2(I) =         EXP(-10218*T(I) + 24.653) / K1(I)
      K3(I) =         EXP(-11055*T(I) + 25.804) / K1(I)
      K4(I) =         EXP(-14270*T(I) + 31.318) / K1(I)
    1 CONTINUE
C
      YTTL='           En          '
      CALL APOSP2 (YTTL,0.0020,0.0026,0.01,1.  )
      CALL CHSET ('LINE')
      CALL CHSET ('NOMARK')
      CALL CHPLOT (1,201,T,K2)
      CALL CHPLOT (1,201,T,K3)
      CALL CHPLOT (1,201,T,K4)
      CALL CHNATT (4,NATT)
      CALL CHSET ('NONBOX')
      CALL CHSET ('BNOTE')
      CALL CHNOFF (T(100),K2(100))
      CALL CHNOTE ('Z5',8,LED(1))
      CALL CHNOFF (T(100),K3(100))
      CALL CHNOTE ('Z5',8,LED(2))
      CALL CHNOFF (T(100),K4(100))
      CALL CHNOTE ('Z5',8,LED(3))
      CALL APOEP (1,ANS)
      STOP
      END
```

Program Name: TCEARRH

```
C---------------------------------------------------------------------
C   Program Description: Tetrachloroethylene results
C
C   Programmer: Scott Willms
C
C   Usage: This program generates two types of plots.  For IPLOT = 1
C      an active reaction Arrhenius plot is produced, For IPLOT = 2
C      an induction period Arrhenius plot is produced.  The data read
C      from unit 1 includes:
C
C         Record 1:    A dummy identifier
C         Record 2:    The number of entries in this group, ID
C         Record 3-ID: Run name, T(C), P(psi), M20(gm), k'(1/min),
C                      tstart(min), variance(SUMSQ/N from APOREG1 or
C                      APOREG2), number of regression points
C
C      This pattern can be repeated in one data file for multiple
C      groups of data per plot.  The number of read sections and
C      calculation sections must match the number of groups.
C
C      Following the read and calculation section is the plotting
C      sections.  The array LT is used to store legend titles for
C      each group of data.  Since not all groups of data will always
C      be plotted on every plot, as "construct the proper note" section
C      is included.  The desired elements of the LT array are
C      concatenated with the "//" operator.  INOTE must be set equal
C      to the number of LT elements included in the note.  Subsequent
C      to this is the actual plotting.  CHPLOT is used to plot the
C      individual markers and APOLIN is used to draw a line through
C      the data.  Again, since all groups of data are not always
C      desired on any particular plot, the undesired CHPLOT/APOLIN
C      combinations should be commented out.  Finally, each plotting
C      section includes code entitled "plot symbols with the notes".
C      This requires no adaptation and should work as written.
C---------------------------------------------------------------------
      REAL*4 XMARK(1),YMARK(20)
      INTEGER MARK1(16),COLOR1(16)
      INTEGER MARK2( 8),COLOR2( 8)
      CHARACTER*14 LT(10),DUMB
      CHARACTER*182 NOTE
      CHARACTER*28 YTTL
      CHARACTER*1 ANS
      CHARACTER*14 NAME1(20),NAME2(20)
      REAL*4 T1(20),P1(20),TS1(20),KP1(20),K1(20),V1(20),N1(20),M1(20)
      REAL*4 T2(20),P2(20),TS2(20),KP2(20),K2(20),V2(20),N2(20),M2(20)
      INTEGER ID(5)
      DATA MARK1 /1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8/
      DATA COLOR1/1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8/
      DATA MARK2 /1,2,3,4,5,6,7,8/
```

```
      DATA COLOR2/1,2,3,4,5,6,7,8/
C--- Read Data ---
      READ (1,100) DUMB
      READ (1,*) ID(1)
      READ (1,101)(NAME1(I),T1(I),P1(I),M1(I),KP1(I),TS1(I),V1(I),N1(I),
     1     I=1,ID(1))
      READ (1,100) DUMB
      READ (1,*) ID(2)
      READ (1,101)(NAME2(I),T2(I),P2(I),M2(I),KP2(I),TS2(I),V2(I),N2(I),
     1     I=1,ID(2))
  100 FORMAT (A20)
  101 FORMAT (A14,F5.0,F6.0,F6.0,F8.0,F7.0,F7.0,I3)
C--- Calculate K ---
      DO 1 I=1,ID(1)
      O2   = APOOXY(T1(I),P1(I))
      K1(I)= KP1(I)/SQRT(O2)
      T    = T1(I)
      T1(I)= 1./(T1(I)+273.15)
    1 WRITE (6,102)NAME1(I),T,T1(I),P1(I),TS1(I),KP1(I),O2,K1(I)
      WRITE (6,*) ' '
  102 FORMAT (1X,A14,F6.1,F9.5,F7.0,F8.5,F10.6,F09.6,F09.5)
      DO 2 I=1,ID(2)
      O2   = APOOXY(T2(I),P2(I))
      K2(I)= KP2(I)/SQRT(O2)
      T    = T2(I)
      T2(I)= 1./(T2(I)+273.15)
    2 WRITE (6,102)NAME2(I),T,T2(I),P2(I),TS2(I),KP2(I),O2,K2(I)
C
C   TCE only runs
C     LT(1)= '    E = 23.2 kcal/mole   ;'
      LT(1)= '    TCE Alone;'
C
C   All five TCE runs together
      LT(2)= '    TCE/Soil ;'
      LT(3)= '    E = 21.3 ;'
C
C----------------
C  Construct the proper note
      NOTE = LT(1) // LT(2) // LT(3)
      INOTE = 3
      NOTELN = INOTE * 14 - 1
C----------------
      XMIN=0.0017
      XMAX=0.0022
      YMIN=0.001
      YMAX=1.0
      YTTL='k (ml/gm)**.5 (1/min)'
      CALL APOSP2 (YTTL,XMIN,XMAX,YMIN,YMAX,0.00005)
C
      CALL CHSET ('BNOTE')
      CALL CHSET ('NBOX')
      CALL CHNOFF (52.,23.)
```

```
      CALL CHSET ('NDRAW')
C--- Plot the data ---
      CALL CHPLOT (1,ID(1), T1, K1)
      CALL CHPLOT (1,ID(2), T2, K2)
C
C   TCE only runs
C     CALL APOLIN (0.0017, .1558   ,.002135,0.001)
C   All six  TCE runs together (Soil and Non-Soil)
      CALL APOLIN (0.0017, .1268   ,.002151,.001)
C
      CALL CHDRAX
      CALL CHNOTE ('C7',NOTELN,NOTE)
C  Plot symvols with the notes
      XFRAC= 0.73
      XMARK(1)= (XMAX-XMIN)*XFRAC + XMIN
      FRAC1 = 0.73
      FRAC2 = 0.034
      DO 30 I=1,INOTE
      FRAC = (INOTE-I)*FRAC2 + FRAC1
   30 YMARK(I) = EXP(FRAC*(ALOG(YMAX/YMIN)) + ALOG(YMIN))
      CALL CHSTRT
      CALL CHMARK (8,MARK2)
      CALL CHCOL  (8,COLOR2)
      INOTE=INOTE-1
      CALL CHPLOT (INOTE,1,XMARK,YMARK)
C
      CALL APOEP (1,ANS)
      STOP
      END
```

Program Name: XPHEN

```
C----------------------------------------------------------------------
C   Program Description: Plots En versus X for both m-xylene and phenol.
C
C   Programmer: Scott Willms
C
C   Usage: The main concern is that the Arrhenius parameters for
C      calculating the rate constants are correct.  No data is
C      read.  Only plotted output is generated.  An error will
C      occur during execution because data is intensionally plotted
C      offscale at the end of the program so that the proper markers
C      will be associated with the key.
C----------------------------------------------------------------------
      INTEGER NATT(4)
      INTEGER MARK1(8),MARK2(8),COLOR(1)
      CHARACTER*7 NOTE(5)
      CHARACTER*10 LAB(2)
      CHARACTER*1 ANS
      REAL*4 C1(100),C2(100)
      REAL*4 EN1(100),EN2(100)
      DATA NATT/0,0,0,70/
      DATA COLOR /0/
      DATA MARK1/1,1,2,2,3,3,4,4/
      DATA MARK2/1,2,3,4,5,6,7,8/
      LAB(1) = ' m-Xylene '
      LAB(2) = '  Phenol  '
      NOTE(1) = ' 150 C '
      NOTE(2) = ' 175 C '
      NOTE(3) = ' 200 C '
      NOTE(4) = ' 225 C '
C
      CALL APOSP3
      CALL CHCOL (1,COLOR)
      CALL CHMARK (8,MARK1)
      CALL CHXRNG (0.0,1.)
      CALL CHYRNG (0.005,200.)
      CALL CHYTTL (21,'        En          ')
      CALL CHXTTL (21,'      X xylene      ')
      CALL CHYSET ('LOGARITHMIC')
      CALL CHSET ('NOLINE')
      CALL CHSET ('MARK')
      CALL CHNATT (4,NATT)
      CALL CHSET ('BNOTE')
      CALL CHSET ('NBOX')
C
      C1(1)= 1./(1.+1.)
      C1(2)= 1./(1.+.5)
      C1(3)= 1./(1.+.15)
      C1(4)= 1./(1.+0. )
C
```

```
      C2(1)= 0./(0.+1.)
      C2(2)= 1./(1.+1.)
      C2(3)= 1./(1.+.5)
      C2(4)= 1./(1.+.15)
      C2(5)= 1./(1.+0.)
C
      DO 1 I=1,4
      T = (I-1)*25 + 150
      CALL RTC (T,1,7,3,NOTE(I))
      TI = 1./(T+273.15)
      RXP   =         EXP(-12190.*TI + 25.559)
      RX15  =         EXP(-15074 *TI + 32.757)
      RX50  =         EXP(-11335.*TI + 26.001)
      RX100 =         EXP(-9399.8*TI + 22.516)
C
      RPP   =         EXP(-13476.*TI + 33.021)
      RP15  =         EXP(-14270.*TI + 31.318)
      RP50  =         EXP(-11055.*TI + 25.804)
      RP100 =         EXP(-10218.*TI + 24.653)
C
      EN1(1) = RPP   / RXP
      EN1(2) = RX100 / RXP
      EN1(3) = RX50  / RXP
      EN1(4) = RX15  / RXP
      EN1(5) = RXP   / RXP
C
      EN2(1) = RPP   / RPP
      EN2(2) = RP100 / RPP
      EN2(3) = RP50  / RPP
      EN2(4) = RP15  / RPP
      EN2(5) = RXP   / RPP
      NPNT = 5
C
      CALL CHPLOT (1,NPNT,C2,EN1)
      FRAC = 0.25
      XPOS = C1(1)  + (C1(2)-C1(1))*FRAC
      YPOS = EN1(1) + (EN1(2)-EN1(1))*FRAC
      CALL CHPLOT (1,NPNT,C2,EN2)
      FRAC = .4
      XPOS = C2(2)  + (C2(3) - C2(2))*FRAC
      YPOS = EN2(2) + (EN2(3)-EN2(2))*FRAC
    1 CONTINUE
      CALL CHNOFF (0.5,80.)
      CALL CHNOTE ('Z5',10,LAB(1))
      CALL CHNOFF (0.5,.05)
      CALL CHNOTE ('Z5',10,LAB(2))
C
      CALL CHSTRT
      CALL CHMARK (8,MARK2)
      CALL CHSET ('BKEY')
      CALL CHSET ('KBOX')
      CALL CHKATT (4,NATT)
```

```
      CALL CHKOFF (-05.,10.)
      CALL CHKEY (4,7,NOTE)
      CALL CHSET ('MARK')
      CALL CHSET ('NOLINE')
      DO 2 I=1,4
    2 CALL CHPLOT (1,1,9999999.,999999999.)
      CALL APOEP (1,ANS)
      STOP
      END
```

Program Name: XPHSY1

```
C-----------------------------------------------------------------------
C   Program Description: Sy versus X (m-xylene/phenol system)
C
C   Programmer: Scott Willms
C
C   Usage: This program plots the Synergism number versus fractional
C      concentration for the m-xylene/phenol system.
C-----------------------------------------------------------------------
      INTEGER NATT(4)
      CHARACTER*9 NOTE(5)
      CHARACTER*1 ANS
      REAL*4 C(100)
      REAL*4 SY(100)
      DATA NATT/0,0,0,80/
C
      NOTE(1)='125 deg C'
      NOTE(2)='150 deg C'
      NOTE(3)='175 deg C'
      NOTE(4)='200 deg C'
      CALL APOSP3
      CALL CHXRNG (0.0,1.)
      CALL CHYRNG (0.,2.)
      CALL CHYTTL (21,'         Sy          ')
      CALL CHXTTL (21,'      X xylene       ')
      CALL CHSET ('NOLINE')
      CALL CHSET ('MARK')
      CALL CHKATT (4,NATT)
      CALL CHSET ('BKEY')
      CALL CHSET ('KBOX')
      CALL CHKOFF (-15.,9.)
      CALL CHKEY (4,9,NOTE)
C
      C(1)= 0./(0.+1.)
      C(2)= 1./(1.+1.)
      C(3)= 1./(1.+.5)
      C(4)= 1./(1.+.15)
      C(5)= 1./(1.+0. )
C
      DO 1 I=1,4
      T = (I-1)*25 + 125
      TI = 1./(T+273.15)
      RXP   =         EXP(-12190.*TI + 25.559)
      RX15  =         EXP(-15074 *TI + 32.757)
      RX50  =         EXP(-11335.*TI + 26.001)
      RX100 =         EXP(-9399.8*TI + 22.516)
C
      RPP   =         EXP(-13476.*TI + 33.021)
      RP15  =         EXP(-14270.*TI + 31.318)
      RP50  =         EXP(-11055.*TI + 25.804)
```

```
      RP100 =          EXP(-10218.*TI + 24.653)
C
      SY(1)= (  RXP*1.0 +        0. ) / (RXP*1.0 +      0. )
      SY(2)= (RX100*1.0 + RP100*1.0 ) / (RXP*1.0 + RPP*1.0 )
      SY(3)= (RX50 *1.0 + RP50 *0.5 ) / (RXP*1.0 + RPP*0.5 )
      SY(4)= (RX15 *1.0 + RP15 *0.15) / (RXP*1.0 + RPP*0.15)
      SY(5)= (      0.0 + RPP  *1.0 ) / (    0.0 + RPP*1.0 )
      NPNT = 5
C
      CALL CHPLOT (1,NPNT,C,SY)
    1 CONTINUE
      CALL APOEP (1,ANS)
      STOP
      END
```

Program Name: XPHSY2

```
C---------------------------------------------------------------------
C   Program Description: ln(Sy) versus 1/T (m-xylene/phenol system)
C
C   Programmer: Scott Willms
C
C   Usage: This program plots the Synergism number versus 1/T
C      on a semi-log plot.
C---------------------------------------------------------------------
      INTEGER MARK(20),COLOR(20)
      CHARACTER*28 YTTL
      CHARACTER*1 ANS
      CHARACTER*14 NAME1(20),NAME2(20),NAME3(20),NAME4(20)
      REAL*4 T(500),KP1(500),KP2(500),KP3(500),KP4(500)
      REAL*4        KX1(500),KX2(500),KX3(500),KX4(500)
      REAL*4        KR1(500),KR2(500),KR3(500),KR4(500)
C
      DO 1 I=1,201
      T(I)=(I-1)/200.*0.0005  + 0.00205
C
      KX1(I) =         EXP(-12190.*T(I) + 25.559)
      KX2(I) =         EXP(-9399.8*T(I) + 22.516)
      KX3(I) =         EXP(-11335.*T(I) + 26.001)
      KX4(I) =         EXP(-15074 *T(I) + 32.757)
C
      KP1(I) =         EXP(-13476*T(I) + 33.021)
      KP2(I) =         EXP(-10218*T(I) + 24.653)
      KP3(I) =         EXP(-11055*T(I) + 25.804)
      KP4(I) =         EXP(-14270*T(I) + 31.318)
C
      KR2(I) = (KX2(I)*1.0 + KP2(I)*1.0 ) / (KX1(I)*1.0 + KP1(I)*1.0 )
      KR3(I) = (KX3(I)*1.0 + KP3(I)*0.5 ) / (KX1(I)*1.0 + KP1(I)*0.5 )
      KR4(I) = (KX4(I)*1.0 + KP4(I)*0.15) / (KX1(I)*1.0 + KP1(I)*0.15)
    1 CONTINUE
C
      YTTL='     Sy        '
      CALL APOSP2 (YTTL,0.0020,0.0026,0.05,5.)
      CALL CHSET ('LINE')
      CALL CHSET ('NOMARK')
      CALL CHPLOT (1,201,T,KR2)
      CALL CHPLOT (1,201,T,KR3)
      CALL CHPLOT (1,201,T,KR4)
      CALL APOEP (1,ANS)
      STOP
      END
```

Program Name: XYLARRH

```
C-----------------------------------------------------------------------
C   Program Description: m-Xylene results
C
C   Programmer: Scott Willms
C
C   Usage: This program generates two types of plots.  For IPLOT = 1
C      an active reaction Arrhenius plot is produced, For IPLOT = 2
C      an induction period Arrhenius plot is produced.  The data read
C      from unit 1 includes:
C
C         Record 1:    A dummy identifier
C         Record 2:    The number of entries in this group, ID
C         Record 3-ID: Run name, T(C), P(psi), M20(gm), k'(1/min),
C                      tstart(min), variance(SUMSQ/N from APOREG1 or
C                      APOREG2), number of regression points
C
C      This pattern can be repeated in one data file for multiple
C      groups of data per plot.  The number of read sections and
C      calculation sections must match the number of groups.
C
C      Following the read and calculation section is the plotting
C      sections.  The array LT is used to store legend titles for
C      each group of data.  Since not all groups of data will always
C      be plotted on every plot, as "construct the proper note" section
C      is included.  The desired elements of the LT array are
C      concatenated with the "//" operator.  INOTE must be set equal
C      to the number of LT elements included in the note.  Subsequent
C      to this is the actual plotting.  CHPLOT is used to plot the
C      individual markers and APOLIN is used to draw a line through
C      the data.  Again, since all groups of data are not always
C      desired on any particular plot, the undesired CHPLOT/APOLIN
C      combinations should be commented out.  Finally, each plotting
C      section includes code entitled "plot symbols with the notes".
C      This requires no adaptation and should work as written.
C-----------------------------------------------------------------------
      REAL*4 XMARK(1),YMARK(20)
      INTEGER MARK1(16),COLOR1(16)
      INTEGER MARK2( 8),COLOR2( 8)
      CHARACTER*30 LT(10),DUMB
      CHARACTER*182 NOTE
      CHARACTER*28 YTTL
      CHARACTER*1 ANS
      CHARACTER*14 NAME1(20),NAME2(2),NAME3(20),NAME4(20),NAME5(20),
     1 NAME6(20)
      REAL*4 REFX(2),REFY(2)
      REAL*4 T1(20),P1(20),TS1(20),KP1(20),K1(20),V1(20),N1(20),M1(20)
      REAL*4 T2(20),P2(20),TS2(20),KP2(20),K2(20),V2(20),N2(20),M2(20)
      REAL*4 T3(20),P3(20),TS3(20),KP3(20),K3(20),V3(20),N3(20),M3(20)
      REAL*4 T4(20),P4(20),TS4(20),KP4(20),K4(20),V4(20),N4(20),M4(20)
```

```
      REAL*4 T5(20),P5(20),TS5(20),KP5(20),K5(20),V5(20),N5(20),M5(20)
      REAL*4 T6(20),P6(20),TS6(20),KP6(20),K6(20),V6(20),N6(20),M6(20)
      REAL*4 H2O2(20)
      INTEGER ID(10)
      DATA MARK1 /1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8/
      DATA COLOR1/1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8/
      DATA MARK2 /1,2,3,4,5,6,7,8/
      DATA COLOR2/1,2,3,4,5,6,7,8/
C--- Read Data ---
      READ (1,100) DUMB
      READ (1,*) ID(1)
      READ (1,101) (NAME1(I),T1(I),P1(I),M1(I),KP1(I),TS1(I),V1(I),N1(I)
     1    ,I=1,ID(1))
      READ (1,100) DUMB
      READ (1,*) ID(2)
      READ (1,101) (NAME2(I),T2(I),P2(I),M2(I),KP2(I),TS2(I),V2(I),N2(I)
     1    ,I=1,ID(2))
      READ (1,100) DUMB
      READ (1,*) ID(3)
      READ (1,101) (NAME3(I),T3(I),P3(I),M3(I),KP3(I),TS3(I),V3(I),N3(I)
     1    ,I=1,ID(3))
      READ (1,100) DUMB
      READ (1,*) ID(4)
      READ (1,101) (NAME4(I),T4(I),P4(I),M4(I),KP4(I),TS4(I),V4(I),N4(I)
     1    ,I=1,ID(4))
      READ (1,100) DUMB
      READ (1,*) ID(5)
      READ (1,103) (NAME5(I),T5(I),P5(I),M5(I),KP5(I),TS5(I),V5(I),N5(I)
     1    ,H2O2(I),I=1,ID(5))
      READ (1,100) DUMB
      READ (1,*) ID(6)
      READ (1,101) (NAME6(I),T6(I),P6(I),M6(I),KP6(I),TS6(I),V6(I),N6(I)
     1    ,I=1,ID(6))
  100 FORMAT (A20)
  101 FORMAT (A14,F5.0,F6.0,F6.0,F8.0,F7.0,F7.0,I3)
  103 FORMAT (A14,F5.0,F6.0,F6.0,F8.0,F7.0,F7.0,I3,F8.0)
C--- Calculate K ---
      DO 1 I=1,ID(1)
      O2   = APOOXY(T1(I),P1(I))
      K1(I)= KP1(I)/SQRT(O2)
      T    = T1(I)
      T1(I)= 1./(T1(I)+273.15)
      TS1(I)=     O2 *TS1(I)
    1 WRITE (6,102)NAME1(I),T,T1(I),P1(I),TS1(I),KP1(I),O2,K1(I)
  102 FORMAT (1X,A14,F6.1,F9.5,F7.0,F8.5,F10.6,F09.6,F09.3)
      WRITE (6,*) ' '
      DO 2 I=1,ID(2)
      O2   = APOOXY(T2(I),P2(I))
      K2(I)= KP2(I)/SQRT(O2)
      T    = T2(I)
      TS2(I)=     O2 *TS2(I)
      T2(I)= 1./(T2(I)+273.15)
```

```
    2 WRITE (6,102)NAME2(I),T,T2(I),P2(I),TS2(I),KP2(I),O2,K2(I)
      WRITE (6,*) ' '
      DO 3 I=1,ID(3)
      O2   = APOOXY(T3(I),P3(I))
      K3(I)= KP3(I)/SQRT(O2)
      T    = T3(I)
      TS3(I)=     O2 *TS3(I)
      T3(I)= 1./(T3(I)+273.15)
    3 WRITE (6,102)NAME3(I),T,T3(I),P3(I),TS3(I),KP3(I),O2,K3(I)
      WRITE (6,*) ' '
      DO 4 I=1,ID(4)
      O2   = APOOXY(T4(I),P4(I))
      K4(I)= KP4(I)/SQRT(O2)
      T    = T4(I)
      TS4(I)=     O2 *TS4(I)
      T4(I)= 1./(T4(I)+273.15)
    4 WRITE (6,102)NAME4(I),T,T4(I),P4(I),TS4(I),KP4(I),O2,K4(I)
      WRITE (6,*) ' '
      DO 5 I=1,ID(5)
      O2   = APOOXY(T5(I),P5(I))
      K5(I)= KP5(I)/SQRT(O2)
      T    = T5(I)
      T5(I)= 1./(T5(I)+273.15)
    5 WRITE (6,102)NAME5(I),T,T5(I),P5(I),TS5(I),KP5(I),O2,K5(I)
      WRITE (6,*) ' '
      DO 6 I=1,ID(6)
      O2   = APOOXY(T6(I),P6(I))
      K6(I)= KP6(I)/SQRT(O2)
      T    = T6(I)
      T6(I)= 1./(T6(I)+273.15)
    6 WRITE (6,102)NAME6(I),T,T6(I),P6(I),TS6(I),KP6(I),O2,K6(I)
      WRITE (6,*) ' '
C--- Choose the plotting format ---
      IPLOT = 1
      GO TO (10,20),IPLOT
C---------------------------------------
C   k VS. 1/T Section
C---------------------------------------
   10 YTTL='k (1/min)*(ml/gm)**.5'
C---------------
      LT(1)= '    Xylene Alone,    E = 19.6;'
      LT(2)= '    Xylene/case "a", E = 18.7;'
      LT(3)= '    Xylene/case "b", E = 22.5;'
      LT(4)= '    Xylene/case "c", E = 30.0;'
      LT(5)= '    Xylene/H2O2,     E = 27.2;'
      LT(6)= '    Xylene/Soil,     E = 37.4;'
C
      LT(7)= '    Xylene Alone,    E = 24.2;'
      LT(8)= '    Xylene/H2O2,     E = 24.2;'
C
C     LT(7)= '    Xylene Alone              ;'
C     LT(8)= '    Xylene/H2O2               ;'
```

```
C     LT(9)= '    E = 24.2 kcal/mole       ;'
C
C----------------
C  Construct the proper note
      NOTE = LT(7) // LT(8) // LT(6)
      INOTE = 3
      NOTELN = INOTE * 30 - 1
C----------------
      XMIN=0.0018
      XMAX=0.0026
      YMIN=0.004
      YMAX=40.
      CALL APOSP2 (YTTL,XMIN,XMAX,YMIN,YMAX)
      CALL CHMARK (16,MARK1)
      CALL CHCOL  (16,COLOR1)
      CALL CHSET ('BNOTE')
      CALL CHSET ('NBOX')
      CALL CHNOFF (52.,23.)
      CALL CHSET ('NDRAW')
C   Xylene alone
      CALL CHPLOT (1,ID(1),T1, K1)
C     CALL APOLIN (.0018  ,22.977   ,.00260 ,.0086387)
C   Xylene alone and with H2O2
      CALL APOLIN (.0018  ,37.226   ,.002550,.004    )
C   ALL H2O2 (various amount of hydrogen peroxide)
      CALL CHPLOT (1,ID(5),T5, K5)
C     CALL APOLIN (.001832,40.      ,.002503,.004    )
C   Xylene alone and with H2O2
      CALL APOLIN (.0018  ,37.226   ,.002550,.004    )
C   Xylene with 100% molar phenol
C     CALL CHPLOT (1,ID(2),T2, K2)
C     CALL APOLIN (.002003,40.      ,.00260 ,.1461   )
C   Xylene with 50% molar phenol
C     CALL CHPLOT (1,ID(3),T3, K3)
C     CALL APOLIN (.001968,40.      ,.00260 ,.031117 )
C   Xylene with 15% molar phenol
C     CALL CHPLOT (1,ID(4),T4, K4)
C     CALL APOLIN (.001928,40.      ,.00260 ,.0016038)
C   Xylene alone and with H2O2
C     CALL APOLIN (.0018  ,37.226   ,.002550,.004    )
C   Xylene with soil
      CALL CHPLOT (1,ID(6),T6, K6)
      CALL APOLIN (.0018  ,.04104   ,.001924,.004    )
C   Xylene alone and with H2O2
C     CALL APOLIN (.0018  ,37.226   ,.002550,.004    )
C
      CALL CHDRAX
      CALL CHNOTE ('C7',NOTELN,NOTE)
C  PLOT SYMBOLS WITH THE NOTES
      XFRAC= 0.73
      XMARK(1)= (XMAX-XMIN)*XFRAC + XMIN
      FRAC1 = 0.73
```

```
      FRAC2 = 0.034
      DO 30 I=1,INOTE
      FRAC = (INOTE-I)*FRAC2 + FRAC1
   30 YMARK(I) = EXP(FRAC*(ALOG(YMAX/YMIN)) + ALOG(YMIN))
      CALL CHSTRT
      CALL CHMARK (8,MARK2)
      CALL CHCOL  (8,COLOR2)
C
C     INOTE = INOTE - 1
      CALL CHPLOT (INOTE,1,XMARK,YMARK)
C
      CALL APOEP (1,ANS)
      STOP
C-----------------------------------------
C   Tstart * O2 VS. 1/T Section
C-----------------------------------------
   20 CONTINUE
      YTTL='tstart*O2 (min gm/ml)'
      LT(1)='    Xylene Alone,    E = 30.0;'
C     LT(1)='    E = 30.0 kcal/mole       ;'
      LT(2)='    Xylene/Case "a", E = 22.4;'
      LT(3)='    Xylene/Case "b", E = 21.4;'
      LT(4)='    Xylene/Case "c", E = 28.9;'
C----------------
C  Construct the proper note
      NOTE = LT(1) // LT(2) // LT(3) // LT(4)
      INOTE = 4
      NOTELN = INOTE * 30 - 1
C----------------
      XMIN=0.0018
      XMAX=0.0026
C     XMAX=0.0023
      YMIN=0.001
      YMAX=1.
      CALL APOSP2 (YTTL,XMIN,XMAX,YMIN,YMAX)
      CALL CHMARK (16,MARK1)
      CALL CHCOL  (16,COLOR1)
      CALL CHSET ('BNOTE')
      CALL CHSET ('NBOX')
      CALL CHNOFF (52.,12.)
      CALL CHSET ('NDRAW')
C   Xylene alone
      CALL CHPLOT (1,ID(1),T1,TS1)
      CALL APOLIN (.0018  ,.002199  ,.002206, 1.     )
C   Xylene with 100% molar phenol
      CALL CHPLOT (1,ID(2),T2,TS2)
      CALL APOLIN (.001993,.001     ,.002606, 1.     )
C   Xylene with  50% molar phenol
      CALL CHPLOT (1,ID(3),T3,TS3)
      CALL APOLIN (.001935,.001     ,.002577, 1.     )
C   Xylene with  15% molar phenol
      CALL CHPLOT (1,ID(4),T4,TS4)
```

```
      CALL APOLIN (.001982,.001      ,.002457, 1.      )
C
      CALL CHDRAX
      CALL CHNOTE ('C7',NOTELN,NOTE)
C  PLOT SYMBOLS WITH THE NOTES
      XFRAC= 0.73
      XMARK(1)= (XMAX-XMIN)*XFRAC + XMIN
      FRAC1 = 0.25
      FRAC2 = 0.034
      DO 40 I=1,INOTE
      FRAC = (INOTE-I)*FRAC2 + FRAC1
   40 YMARK(I) = EXP(FRAC*(ALOG(YMAX/YMIN)) + ALOG(YMIN))
      CALL CHSTRT
      CALL CHMARK (8,MARK2)
      CALL CHCOL  (8,COLOR2)
      CALL CHPLOT (INOTE,1,XMARK,YMARK)
C
      CALL APOEP (1,ANS)
      STOP
      END
```

Program Name: XYLEN

```
C-----------------------------------------------------------------
C   Program Description: m-Xylene results--enhancement number
C
C   Programmer: Scott Willms
C
C   Usage: This program is used to generate semi-log plots of En
C      versus 1/T
C-----------------------------------------------------------------
      INTEGER MARK(20),COLOR(20),NATT(4)
      CHARACTER*20 LED(20)
      CHARACTER*28 YTTL
      CHARACTER*1 ANS
      CHARACTER*14 NAME1(20),NAME2(20),NAME3(20),NAME4(20)
      REAL*4 T(500),K1(500),K2(500),K3(500),K4(500)
      DATA NATT/0,0,0,80/
C
      LED(1)='Case "a"'
      LED(2)='Case "b"'
      LED(3)='Case "c"'
      DO 1 I=1,201
      T(I)=(I-1)/200.*0.0005  + 0.00205
      K1(I) =         EXP(-12190.*T(I) + 25.559)
      K2(I) =         EXP(-8835.2*T(I) + 21.182) / K1(I)
      K3(I) =         EXP(-11335.*T(I) + 26.001) / K1(I)
      K4(I) =         EXP(-15074 *T(I) + 32.757) / K1(I)
C     WRITE (6,*) T(I),K1(I),K2(I),K3(I),K4(I)
    1 CONTINUE
C
      YTTL='           En    '
      CALL APOSP2 (YTTL,0.0020,0.0026,0.1,100.)
      CALL CHSET ('LINE')
      CALL CHSET ('NOMARK')
      CALL CHPLOT (1,201,T,K2)
      CALL CHPLOT (1,201,T,K3)
      CALL CHPLOT (1,201,T,K4)
C
      CALL CHNATT (4,NATT)
      CALL CHSET ('NONBOX')
      CALL CHSET ('BNOTE')
      CALL CHNOFF (T(100),K2(100))
      CALL CHNOTE ('Z5',8,LED(1))
      CALL CHNOFF (T(100),K3(100))
      CALL CHNOTE ('Z5',8,LED(2))
      CALL CHNOFF (T(100),K4(100))
      CALL CHNOTE ('Z5',8,LED(3))
      CALL APOEP (1,ANS)
      STOP
      END
```

Program Name: XYLORDER

```
C-----------------------------------------------------------------------
C   Program Description: m-Xylene reaction order analysis
C
C   Programmer: Scott Willms
C
C   Usage: This program is similar to XYLARRH, but is used to analyse
C      reaction orders with respect to oxygen in the active and
C      induction periods.  Different markers are used on the Arrhenius
C      plots for different pressures.  The plot which collapses all
C      markers on one line is the true reaction order.  The input data
C      (described in XYLARRH) is read from unit 1.
C-----------------------------------------------------------------------
      REAL*4 XMARK(1),YMARK(20)
      INTEGER MARK1(16),COLOR1(16)
      INTEGER MARK2( 8),COLOR2( 8)
      CHARACTER*13 LT(10),DUMB
      CHARACTER*182 NOTE
      CHARACTER*28 YTTL
      CHARACTER*1 ANS
      CHARACTER*14 NAME1(20),NAME2(2),NAME3(20),NAME4(20),NAME5(20),
     1 NAME6(20)
      REAL*4 REFX(2),REFY(2)
      REAL*4 T1(20),P1(20),TS1(20),KP1(20),K1(20),V1(20),N1(20),M1(20)
      REAL*4 T1000(10),K1000(10),TS1000(10)
      REAL*4 T1500(10),K1500(10),TS1500(10)
      REAL*4 T2000(10),K2000(10),TS2000(10)
      INTEGER ID(10)
      DATA MARK1 /1,2,3,4,3,3,4,4,5,5,6,6,7,7,8,8/
      DATA COLOR1/1,2,3,4,3,3,4,4,5,5,6,6,7,7,8,8/
      DATA MARK2 /1,2,3,4,5,6,7,8/
      DATA COLOR2/1,2,3,4,5,6,7,8/
C--- Read Data ---
      READ (1,100) DUMB
      READ (1,*) ID(1)
      READ (1,101) (NAME1(I),T1(I),P1(I),M1(I),KP1(I),TS1(I),V1(I),N1(I)
     1    ,I=1,ID(1))
  100 FORMAT (A20)
  101 FORMAT (A14,F5.0,F6.0,F6.0,F8.0,F7.0,F7.0,I3)
  103 FORMAT (A14,F5.0,F6.0,F6.0,F8.0,F7.0,F7.0,I3,F8.0)
C--- Calculate K ---
      DO 1 I=1,ID(1)
      O2   = APOOXY(T1(I),P1(I))
C     K1(I)= KP1(I)/SQRT(O2)
      K1(I)= KP1(I)/    (O2)
      T    = T1(I)
      T1(I)= 1./(T1(I)+273.15)
      TS1(I)=     O2 *TS1(I)
    1 WRITE (6,102)NAME1(I),T,T1(I),P1(I),TS1(I),KP1(I),O2,K1(I)
```

```
  102 FORMAT (1X,A14,F6.1,F9.5,F7.0,F8.5,F10.6,F09.6,F09.3)
C--- Divide results into pressure groups ---
      I1000 = 0
      I1500 = 0
      I2000 = 0
      DO 2 I=1,ID(1)
      IF (P1(I).EQ.1000) THEN
         I1000 = I1000 + 1
         T1000(I1000) = T1(I)
         K1000(I1000) = K1(I)
         TS1000(I1000)= TS1(I)
      END IF
      IF (P1(I).EQ.1500) THEN
         I1500 = I1500 + 1
         T1500(I1500) = T1(I)
         K1500(I1500) = K1(I)
         TS1500(I1500)= TS1(I)
      END IF
      IF (P1(I).EQ.2000) THEN
         I2000 = I2000 + 1
         T2000(I2000) = T1(I)
         K2000(I2000) = K1(I)
         TS2000(I2000)= TS1(I)
      END IF
    2 CONTINUE
      WRITE (6,*) '1000 PSI'
      WRITE (6,*) (T1000(I),I=1,I1000)
      WRITE (6,*) '1500 PSI'
      WRITE (6,*) (T1500(I),I=1,I1500)
      WRITE (6,*) '2000 PSI'
      WRITE (6,*) (T2000(I),I=1,I2000)
C--- Choose the plotting format ---
      IPLOT = 2
      GO TO (10,20),IPLOT
C-------------------------------------------
C   k VS. 1/T Section
C-------------------------------------------
   10 CONTINUE
C     YTTL='k (1/min)*(ml/gm)**.5'
      YTTL='k (1/min)*(ml/gm)**1.'
C----------------
      LT(1)= '    E = 19.6;'
C----------------
C  Construct the proper note
      NOTE = '    1000 psi;    1500 psi;    2000 psi;' // LT(1)
C     INOTE = 4
      INOTE = 3
      NOTELN = INOTE * 13 - 1
C----------------
      XMIN=0.0018
```

```
      XMAX=0.0023
C     YMIN=0.1
C     YMAX=10.
      YMIN=10.
      YMAX=1000.
      CALL APOSP2 (YTTL,XMIN,XMAX,YMIN,YMAX)
      CALL CHMARK (16,MARK1)
      CALL CHCOL  (16,COLOR1)
      CALL CHSET ('BNOTE')
      CALL CHSET ('NBOX')
      CALL CHNOFF (52.,23.)
      CALL CHSET ('NDRAW')
C   Xylene alone
      CALL CHPLOT (1,I1000,T1000,K1000)
      CALL CHPLOT (1,I1500,T1500,K1500)
      CALL CHPLOT (1,I2000,T2000,K2000)
C     CALL APOLIN (.0018   ,22.977    ,.00260 ,.0086387)
C
      CALL CHDRAX
      CALL CHNOTE ('C7',NOTELN,NOTE)
C  Plot symbols with the notes
      XFRAC= 0.73
      XMARK(1)= (XMAX-XMIN)*XFRAC + XMIN
      FRAC1 = 0.73
      FRAC2 = 0.034
      DO 30 I=1,INOTE
      FRAC = (INOTE-I)*FRAC2 + FRAC1
   30 YMARK(I) = EXP(FRAC*(ALOG(YMAX/YMIN)) + ALOG(YMIN))
      CALL CHSTRT
      CALL CHMARK (8,MARK2)
      CALL CHCOL  (8,COLOR2)
      CALL CHPLOT (3    ,1,XMARK,YMARK)
C
      CALL APOEP (1,ANS)
      STOP
C------------------------------------------
C   Tstart * O2 VS. 1/T Section
C------------------------------------------
   20 CONTINUE
      YTTL='TSTART*O2 (min gm/ml)'
C---------------
      LT(1)= '    E =     ;'
C---------------
C  Construct the proper note
      NOTE = '    1000 psi;    1500 psi;    2000 psi;' // LT(1)
C     INOTE = 4
      INOTE = 3
      NOTELN = INOTE * 13 - 1
C---------------
      XMIN = 0.0018
      XMAX = 0.0026
      YMIN = 0.001
```

```
      YMAX = 1.
      CALL APOSP2 (YTTL,XMIN,XMAX,YMIN,YMAX)
      CALL CHMARK (16,MARK1)
      CALL CHCOL  (16,COLOR1)
      CALL CHSET ('BNOTE')
      CALL CHSET ('NBOX')
      CALL CHNOFF (52.,23.)
      CALL CHSET ('NDRAW')
C    Xylene alone
      CALL CHPLOT (1,I1000,T1000,TS1000)
      CALL CHPLOT (1,I1500,T1500,TS1500)
      CALL CHPLOT (1;I2000,T2000,TS2000)
C     CALL APOLIN (.0018  ,22.977   ,.00260 ,.0086387)
C
      CALL CHDRAX
      CALL CHNOTE ('C7',NOTELN,NOTE)
C  Plot symbols with the notes
      XFRAC= 0.73
      XMARK(1)= (XMAX-XMIN)*XFRAC + XMIN
      FRAC1 = 0.73
      FRAC2 = 0.034
      DO 40 I=1,INOTE
      FRAC = (INOTE-I)*FRAC2 + FRAC1
   40 YMARK(I) = EXP(FRAC*(ALOG(YMAX/YMIN)) + ALOG(YMIN))
      CALL CHSTRT
      CALL CHMARK (8,MARK2)
      CALL CHCOL  (8,COLOR2)
      CALL CHPLOT (3    ,1,XMARK,YMARK)
C
      CALL APOEP (1,ANS)
      STOP
      END
```

Program Name: XYLSEN

```
C-----------------------------------------------------------------------
C   Program Description: m-Xylene/Soil results--enhancement number
C
C   Programmer: Scott Willms
C
C   Usage: This program is used to generate semi-log plots of En
C      versus 1/T for the m-xylene/soil system.
C-----------------------------------------------------------------------
      CHARACTER*28 YTTL
      CHARACTER*1 ANS
      REAL*4 T(500),K1(500),K2(500)
C
      DO 1 I=1,201
      T(I)=(I-1)/200.*0.0002  + 0.0018
      K1(I) =         EXP(-12190.*T(I) + 25.559)
      K2(I) =         EXP(-18824.*T(I) + 30.690) / K1(I)
      WRITE (6,*) T(I),K1(I),K2(I)
    1 CONTINUE
C
      YTTL='                 En  '
      CALL APOSP2 (YTTL,0.0017,0.0021,0.00001,1.,0.00005)
      CALL CHSET ('LINE')
      CALL CHSET ('NOMARK')
      CALL CHPLOT (1,201,T,K2)
      CALL APOEP (1,ANS)
      STOP
      END
```

VITA

Richard Scott Willms, the son of Dr. Richard Kenneth and Mrs. Wilda Jane Willms, was born in San Bernardino, California, on February 26, 1957. He was raised in Jacksonville, Texas, where he attended East Side Elementary School and Jacksonville High School, from which he graduated in May, 1975.

He graduated from Louisiana State University in December, 1980, receiving a Bachelor of Science degree in Chemical Engineering. Upon entering graduate school at Louisiana State University the following year, he received the Paul M. Horton Scholastic Achievement Award. In May, 1983, he received his Master of Science degree in Chemical Engineering. During 1983 and 1984 he was an instructor in the Department of Chemical Engineering at Louisiana State University, teaching a course in FORTRAN.

His industrial experience includes one year with Georgia-Pacific, two summers with an engineering position at Pro-Serve, Inc. (Memphis, Tennessee), and two consulting jobs.

The author is a member of Tau Beta Pi, Phi Lambda Upsilon, the American Institute of Chemical Engineers, and the American Chemical Society. In 1985 he received a special award from the LSU Department of Chemical Engineering for extraordinary service to the department.

The author is presently starting a postdoctoral position at Los Alamos National Laboratory in Los Alamos, New Mexico. He is married to the former Mary Patricia Hurstell of New Orleans, Louisiana, and they reside in Los Alamos, New Mexico.

DOCTORAL EXAMINATION AND DISSERTATION REPORT

Candidate: Richard Scott Willms

Major Field: Chemical Engineering

Title of Dissertation: Aqueous Phase Oxidation Of Organics

Approved:

Douglas P Harrison
Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

Kerry Dooley

F. R. Groves Jr.

Date of Examination:

October 9, 1985