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**DETERMINATION OF A KINETIC RATE EXPRESSION  
FOR THE OXIDATION OF CHLOROFORM  
OVER A 2% PLATINUM/ $\alpha$ -ALUMINA CATALYST**

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PREFACE

The work described in this report was authorized Contract No. DAAA15-91-C-0075, Improved Catalysts Materials and Modeling. The work was started in March 1991 and completed in August 1991.

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## CONTENTS

|   | Page |
|---|------|
| 1. INTRODUCTION .....                                 | 9    |
| 2. DATA ANALYSIS AND FIT PARAMETER ESTIMATION .....   | 11   |
| 3. EXPERIMENTAL METHODS .....                         | 13   |
| 3.1 Materials .....                                   | 13   |
| 3.2 Catalyst Pretreatment .....                       | 15   |
| 3.3 Equipment .....                                   | 15   |
| 3.4 Procedure .....                                   | 17   |
| 3.5 Spectroscopic Analyses .....                      | 19   |
| 4. RESULTS .....                                      | 20   |
| 4.1 Effects of Dew Point Temperature .....            | 20   |
| 4.2 Catalyst Induction and Deactivation .....         | 20   |
| 4.3 Reaction Products .....                           | 20   |
| 4.4 Reaction Kinetics .....                           | 25   |
| 4.5 Spectroscopic Analyses .....                      | 32   |
| 5. DISCUSSION .....                                   | 36   |
| 5.1 Effects of Dew Point Temperature .....            | 36   |
| 5.2 Catalyst Induction and Deactivation .....         | 36   |
| 5.3 Reaction Products .....                           | 39   |
| 5.4 Reaction Kinetics .....                           | 41   |
| 6. CONCLUSIONS .....                                  | 44   |
| LITERATURE CITED .....                                | 45   |
| APPENDIXES  |      |
| A. LIST OF SYMBOLS .....                              | 47   |
| B. COMPUTER CODES FOR ESTIMATING FIT PARAMETERS ..... | 49   |

## LIST OF FIGURES

|     |  |    |
|-----|--|----|
| 1.  | Schematic Representation of Fixed Bed Catalytic Reactor System .   | 16 |
| 2.  | Effects of Air Dew Point Temperature on Catalytic Activity .....   | 21 |
| 3.  | Conversion as a Function of Time-on-Stream for the Oxidation of<br>1,500 ppm Chloroform in Humid Air at 350 °C .....   | 22 |
| 4.  | Conversion as a Function of Time-on-Stream for the Oxidation of<br>1,500 ppm Chloroform in Humid Air at 400 °C .....   | 23 |
| 5.  | Conversion as a Function of Time-on-Stream for the Oxidation of<br>1,250 ppm Chloroform in Humid Air at 450 °C .....   | 24 |
| 6.  | Conversion as a Function of Residence Time for the Oxidation of<br>Chloroform at 300 °C .....  | 27 |
| 7.  | Conversion as a Function of Residence Time for the Oxidation of<br>Chloroform at 325 °C .....  | 29 |
| 8.  | Conversion as a Function of Residence Time for the Oxidation of<br>Chloroform at 350 °C .....  | 30 |
| 9.  | Conversion as a Function of Residence Time for the Oxidation of<br>Chloroform at 375 °C .....  | 30 |
| 10. | Conversion as a Function of Residence Time for the Oxidation of<br>Chloroform at 400 °C .....  | 31 |
| 11. | Conversion as a Function of Reaction Temperature for the<br>Oxidation of 1,250 ppm Chloroform in the Presence and Absence<br>of 5,000 ppm HCl .....  | 31 |
| 12. | Arrhenius Plot of the Rate Constant $k$ for the Decomposition of<br>Chloroform over a Platinum Alumina Catalyst .....  | 33 |
| 13. | Arrhenius Plots of the Adsorption Equilibrium Constants $K_a$ (A)<br>and $K_p$ (B) .....   | 34 |
| 14. | XPS Spectra of the Platinum 4d Photoelectron Region of the<br>2.15% Pt/Al <sub>2</sub> O <sub>3</sub> Catalyst Following Calcination at 450 °C,<br>and Following Deactivation Studies at 350 °C , 400 °C and<br>450 °C ..... | 35 |

## LIST OF TABLES

|    |  |    |
|----|--|----|
| 1. | Kinetic Rate Expressions Evaluated for the Oxidation of $\text{CHCl}_3$ ...          | 12 |
| 2. | Reactor Design Equations Corresponding to Rate Expressions<br>1 Through 5 .....      | 14 |
| 3. | Chlorine Balances for Selected Runs .....  | 25 |
| 4. | Percent Standard Deviations Calculated for Each Kinetic Rate<br>Expression .....     | 26 |
| 5. | Kinetic Fit Parameters Determined for Model 2 .....                                  | 32 |
| 6. | Atomic Ratios for Catalyst Samples Prior to and Following<br>Reaction Exposure ..... | 36 |

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## Determination of a Kinetic Rate Expression for the Oxidation of Chloroform over a 2% Platinum/ $\alpha$ -Alumina Catalyst

### 1. INTRODUCTION

Present air purification systems designed for removal of chemical warfare (CW) agents from air streams are based solely on activated, impregnated carbon, namely ASC whetlerite. Alternative air purification technologies are being investigated due to the loss of activity associated with the ASC whetlerite caused by reduction of the chromium(VI) impregnant<sup>1</sup>. The loss of activity imposes change-out requirements which may present logistical as well as disposal burdens. Several alternative filtration processes, such as pressure swing adsorption, temperature swing adsorption and catalytic oxidation, are candidate technologies which may alleviate the above mentioned burdens.

Catalytic oxidation is a means of removing CW agents from streams of air. Recently, Lester and Marinangeli<sup>2</sup> have demonstrated that low concentrations (less than 1,000 ppm; 1,200 mg/m<sup>3</sup>) of CW agents can be readily destroyed via catalytic oxidation. A study is currently underway aimed at developing kinetic rate expressions to describe the oxidation of toxic vapors in streams of humid air. The initial phase of this study involves developing rate expressions for CW agent model compounds, where a model compound is defined here as a compound which is less toxic but possess a molecular structure similar to that of the corresponding CW agent. For example, Rossin et al.<sup>3</sup> and Klinghoffer and Rossin<sup>4</sup> have previously reported a kinetic study involving the oxidation of chloroacetonitrile (ClCH<sub>2</sub>C≡N) over a supported platinum catalyst. Chloroacetonitrile was chosen as a model compound for cyanogen chloride because of the similarity in their respective molecular structures. Kinetic rate expressions provide information regarding how fast a compound is destroyed at a given set of process conditions. Kinetic rate expressions which describe experimental data over the desired range of process conditions are required if one is to estimate the size and energy requirements of a full scale catalytic filter.

In addition to determining reaction kinetics of model compounds, potential defeat mechanisms (specific to a catalytic filter) must also be evaluated. For example, it may be possible to challenge a catalytic filter with a compound of relatively low toxicity and produce toxic vapors. Further, it may also be possible to challenge a catalytic filter with a compound which will deactivate the catalytic filter, thereby reducing the performance of the catalytic filter against CW agents. Platinum catalysts are very nonselective, i.e., they completely oxidize a wide variety

of organic compounds<sup>5</sup>. However, the oxidation of halogenated organic compounds are reported to yield acid gases<sup>3,4,6</sup>, which above threshold levels may be regarded as toxic. Halogenated organic compounds are also potential catalyst poisons. Cullis and Willatt<sup>7</sup> have shown that halogenated organics inhibit the oxidation activity of supported platinum and palladium catalysts through the adsorption of the halogen atom onto the catalytic site. Their work also shows that the catalytic activity may be restored by removing the halogenated compound from the feed stream.

The literature involving catalytic oxidation of organic compounds over platinum catalysts is rather limited, and kinetic rate expressions have not been widely reported. Voltz et al.<sup>8</sup> performed a kinetic study involving the oxidation of propylene and carbon monoxide mixtures in streams of air. They were able to successfully correlate their data by assuming the reaction occurred between adsorbed oxygen and the adsorbed reactant. Hawkins and Wanke<sup>9</sup> followed a similar set of assumptions in developing a kinetic rate expression to describe the oxidation of ethylene. In studying the oxidation of methane over platinum and palladium catalysts, Cullis and Willatt<sup>10</sup> suggested a mechanism involving the reaction of methane with strongly adsorbed oxygen. Patterson and Kemball<sup>11</sup> suggested that the oxidation of ethylene and propylene over platinum and palladium films involved reaction between an adsorbed olefin molecule, with the olefin being adsorbed onto an oxygen-covered surface, and the adsorbed oxygen. The authors reported the reaction to be zeroth order in the olefin concentration. Klinghoffer and Rossin<sup>4</sup> developed a kinetic rate expression to describe the oxidation of chloroacetonitrile over a platinum catalyst. The rate expression took into account inhibition due to adsorption of both the reactant and acid gas products.

The objective of this study was to investigate chloroform as a potential compound which could defeat a catalytic filter by either deactivation or by generation of acid gases. Chloroform ( $\text{CHCl}_3$ ) was chosen for investigation in the present study because its oxidation products are expected to include acid gases, namely  $\text{HCl}$  and  $\text{Cl}_2$ . In addition, the chlorine atoms associated with chloroform could potentially poison the catalyst. Meeting this objective involved conducting deactivation studies, identifying reaction products and developing a kinetic rate expression to describe the oxidation of chloroform.

## 2. DATA ANALYSIS AND FIT PARAMETER ESTIMATION

The kinetic rate expressions evaluated in this study were derived from data collected in an isothermal, integral-flow fixed bed reactor. The design equation for said reactor is<sup>12</sup>:

$$\frac{W}{F_a^0} = \int_0^x \frac{dx}{\text{rate}} \quad (1)$$

where  $W$  is the mass of catalyst (g),  $F_a^0$  is the reactant flow rate (mols/sec),  $x$  is the fractional conversion (dimensionless) and rate is the rate of reactant disappearance (mols/s-g-cat). All rate expressions evaluated in this study can be derived from a generalized form of a kinetic rate expression for the reaction of hydrocarbons over metallic catalysts<sup>13</sup>:

$$\text{rate} = \frac{k_s \prod_i (K_i C_i)^\nu}{[1 + \sum_i (K_i C_i)^m]^n} \quad (2)$$

where  $k_s$  is the reaction rate constant (mols/s-g-cat),  $K$  is the adsorption equilibrium constant ( $\text{cm}^3/\text{mol}$ ) and  $C$  is the concentration of the reaction species ( $\text{mol}/\text{cm}^3$ ). Equation 2 was evaluated with  $\nu$  and  $m = 1$ , and  $n = 1$  or  $2$ . Five different kinetic rate expressions were evaluated for the oxidation of chloroform. These rate expressions are summarized in Table 1. Rate expressions 1 through 4 each contain a term for inhibition due to the adsorption of the reactant ( $K_a C_a$ ). Rate expressions 2, 4 and 5 each contain a term for inhibition due to the adsorption of reaction product(s) ( $K_p C_p$ ). Note that the product inhibition term may be a sum of inhibitions due to several reaction products, since the product concentrations are related through the reaction stoichiometry. All rate expressions reduce to first order (in  $C_a$ ) at low concentrations. At high concentrations (when the inhibition term become significant), rate expressions 1 and 2 become zeroth order in  $C_a$ , while rate expressions 3 and 4 become inverse order in  $C_a$ . Also of note regarding rate expressions 2, 4 and 5 is that at high concentrations and high conversions, the reaction rate will be strongly inhibited by the presence of the reaction product. For modeling purposes, the term  $k$  used with rate expressions 1 - 5 may be treated as a combination of the surface reaction rate constant,  $k_s$ , and the adsorption equilibrium constant,  $K_i$ . For rate expressions 2, 4 and 5, the concentration of reaction product(s),  $C_p$ , was calculated from the reaction stoichiometry.  $C_p$  was set equal to the conversion of chloroform times the chloroform feed concentration ( $C_p = C_a^0 x$ ).

**Table 1**  
**Kinetic Rate Expressions Evaluated for the Oxidation of  $\text{CHCl}_3$**

---

Rate Expression 1:      Rate =  $\frac{\frac{1}{\rho} k C_a}{1 + K_a C_a}$

Rate Expression 2:      Rate =  $\frac{\frac{1}{\rho} k C_a}{1 + K_p C_p + K_a C_a}$

Rate Expression 3:      Rate =  $\frac{\frac{1}{\rho} k C_a}{[1 + K_a C_a]^2}$

Rate Expression 4:      Rate =  $\frac{\frac{1}{\rho} k C_a}{[1 + K_p C_a + K_a C_a]^2}$

Rate Expression 5:      Rate =  $\frac{\frac{1}{\rho} k C_a}{1 + K_p C_p}$

---

The concentrations of oxygen and water present in the feed stream were nearly constant for all runs; consequently, terms for these molecules are not included in the rate expressions.

The five kinetic rate expressions were evaluated for quality of fit by incorporation into the fixed bed reactor design equation and integrating. In order to incorporate the rate expressions into the fixed bed reactor design equation, the concentration terms must be written in terms of the fractional conversion,  $x$ . This is accomplished by replacing  $C_a$  with  $C_a^0(1 - x)$  and  $C_p$  with  $C_a^0x$ . The results of making the above substitutions in rate expressions 1 through 5 and incorporating the rate expressions into the design equation (eq. 1) and integrating are reported in Table 2. Kinetic fit parameters were determined using a non-linear least squares routine which minimizes the sum of the error between the logarithm of the predicted and experimental values of  $W/F_a^0$ :

$$\text{Error} = \text{minimum} = \sum [\ln(W/F_a^0)_{\text{exp}} - \ln(W/F_a^0)_{\text{pred}}]^2 \quad (3)$$

It was decided to minimize the logarithm of  $W/F_a^0$  rather than  $W/F_a^0$  since  $W/F_a^0$  was varied over a wide range. Kinetic fit parameters were determined for each rate expression listed in Table 1 at each of the five reaction temperatures investigated in this study. The fit parameters were then correlated using the Arrhenius equation. The fortran programs which implement the algorithms for determining the kinetic fit parameters from the equations in Table 2 are presented in Appendix B.

### 3. EXPERIMENTAL METHODS

#### 3.1 *Materials.*

Chloroform (HPLC grade, 99.9 %) was obtained from Aldrich. Approximately 23.0 g of liquid chloroform were injected into a 1A compressed gas cylinder (volume = 43.8 L). The cylinder was then pressurized with UHP air to approximately 300 psig. The concentration of chloroform in the compressed gas cylinder was determined to be 5,050 ppm (26,898 mg/m<sup>3</sup>) based on an independent GC analysis. The 2% Pt/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalyst employed in this study was obtained from Engelhard as 60/80 mesh granules. An assay analysis of the catalyst showed it to be 2.15 wt% platinum. The support is reported to have a nominal BET surface area of 1-5 m<sup>2</sup>/g. The packing density of the catalyst was measured to be 0.95. Calibration gases (namely, CO<sub>2</sub> in air and CO in air) were obtained from Matheson.

Table 2  
Reactor Design Equations Corresponding to Rate Expressions 1 Through 5

---

$$W/F_{a0} = \frac{\rho}{kC_a^0} \ln\left(\frac{1}{1-x}\right) + \rho \frac{K_a}{k} x \quad (1)$$

$$W/F_{a0} = \rho \left\{ \frac{1}{kC_a^0} + \frac{K_p}{k} \right\} \ln\left(\frac{1}{1-x}\right) + \rho \left\{ \frac{K_a}{k} - \frac{K_p}{k} \right\} x \quad (2)$$

$$W/F_{a0} = \frac{\rho}{kC_a^0} \ln\left(\frac{1}{1-x}\right) + \rho \frac{2K_a}{k} x + \rho \frac{K_a^2}{k} C_a^0 x(1-x/2) \quad (3)$$

$$W/F_{a0} = \rho \left\{ \frac{1}{kC_a^0} + \frac{2K_p}{k} + \frac{2K_a}{k} + \frac{K_p C_a^0}{k} \right\} \ln\left(\frac{1}{1-x}\right) + \quad (4)$$

$$\rho \left\{ \frac{K_a^2 C_a^0}{k} - \frac{2K_p}{k} - \frac{2K_a}{k} - \frac{K_p^2 C_a^0}{k} \right\} x -$$

$$\rho \left\{ \frac{K_a^2}{k} + \frac{K_p^2}{k} - \frac{2K_a K_p}{k} \right\} \frac{C_a^0 x^2}{2}$$

$$W/F_{a0} = \rho \left\{ \frac{1}{kC_a^0} + \frac{K_p}{k} \right\} \ln\left(\frac{1}{1-x}\right) - \rho \left\{ \frac{K_p}{k} \right\} x \quad (5)$$


---

### 3.2 Catalyst Pretreatment.

The catalyst was pretreated prior to reaction exposure by calcining in flowing humid air within a quartz tube furnace. The calcination was performed by placing approximately 5.0 g catalyst in the quartz tube furnace. The catalyst was then exposed to humid air (dew point temperature = 20 °C) flowing at 1.0 Nl/min (Nl is defined as 1 liter of gas at 0 °C and 1 atm). The catalyst temperature was raised from room temperature to 450 °C in approximately 2 hours, with the final temperature being maintained for 16 hours. Several batches of catalyst were calcined and mixed together in order to provide a uniform batch of catalyst from which to conduct experiments.

### 3.3 Equipment.

Figure 1 shows a schematic representation of the fixed bed catalytic reactor system. Compressed air from an oil-free compressor was purified using a commercial PSA drier. Purified dry air was metered to the system using either a 0-2,000 Nml/min or a 0-50 Nml/min mass flow controller. The purified air stream was then blended with the air stream containing chloroform, which was delivered from the 5,050 ppm (26,898 mg/m<sup>3</sup>) chloroform in air compressed gas cylinder using a 0-50 Nml/min mass flow controller. By delivering the chloroform from the compressed gas cylinder, a stable chloroform concentration (to less than ±0.5%) could be achieved. Whenever operating at concentrations of 5,050 ppm (26,898 mg/m<sup>3</sup>), the feed was delivered to the reactor directly from the chloroform/air cylinder. Water was injected into the chloroform/air stream via a syringe pump. A temperature controller was used to maintain the temperature at the point of liquid injection at 110±1 °C. Following the water injection point, the feed stream was then sent to a 500 ml static mixer, which served to homogeneously blend the three streams. Following the static mixer, the entire feed stream entered a 1/8" Valco 6-port sampling valve. The valve was installed so that the feed concentration could be monitored during the course of a given run without switching the reactor off-line. Following the sampling valve, the feed was delivered to the catalytic reactor. The reactor was housed in a 7-cm diameter by 20-cm long aluminum block to ensure even heating of the catalyst bed. Reactor temperature was controlled by controlling the temperature of the aluminum block. This control scheme allowed for maintaining a stable catalyst bed temperature to within ±1 °C of the setpoint value. Following the reactor, the entire effluent stream was sent to a Hewlett-Packard 5790 gas chromatograph for on-line analysis. Following the gas chromatograph, the effluent stream was vented to a fume hood.

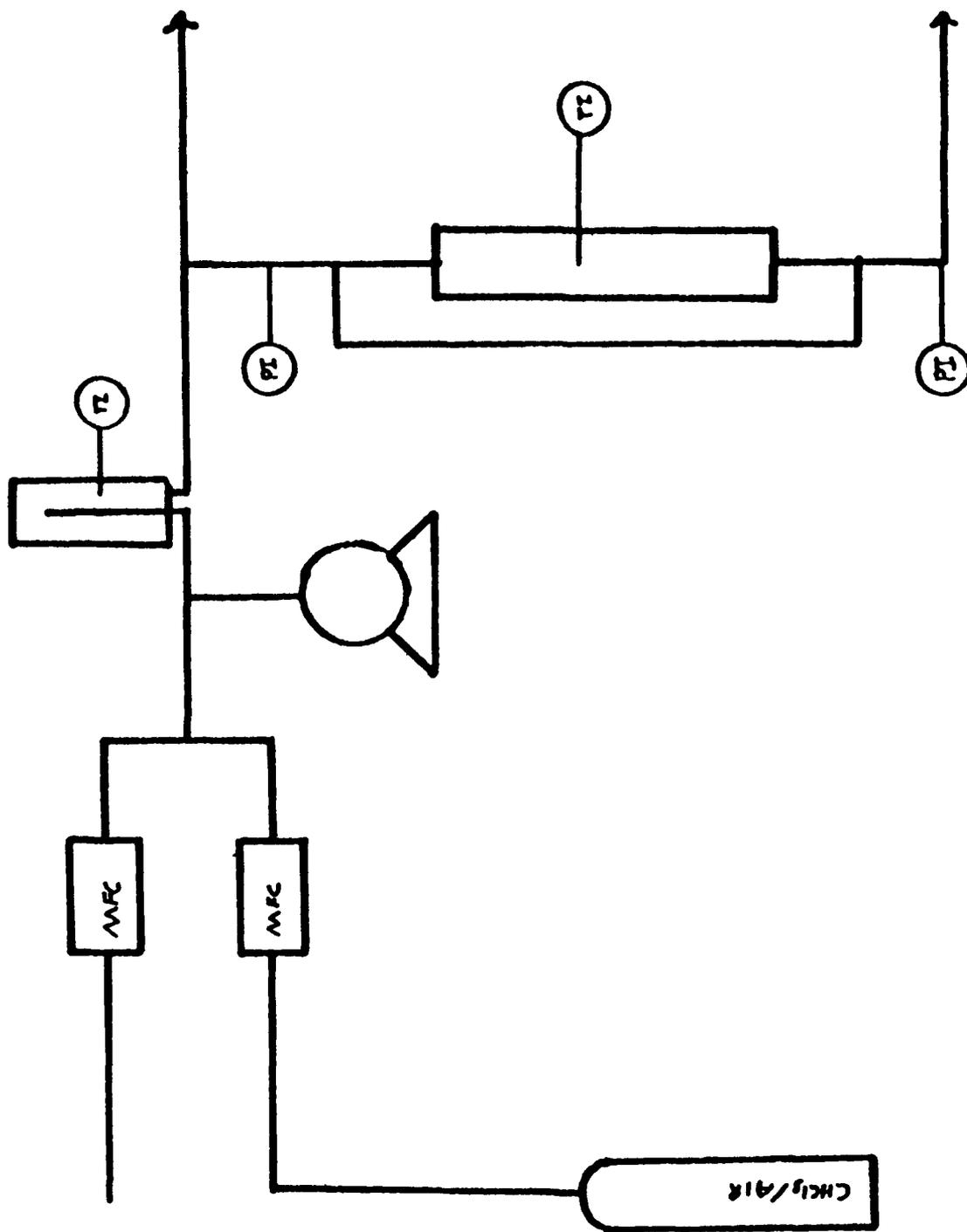


Figure 1: Schematic Representation of Fixed Bed Catalytic Reactor System.

The fixed bed reactor consisted of a 0.95-cm o.d. glass tube, approximately 25-cm in length. The catalyst bed was supported on a plug of glass wool located approximately 8 cm from the bottom of the reactor tube. The catalyst bed was prepared by diluting between 0.20 and 2.00 g of catalyst with 60/80 mesh crushed glass in order to achieve a bed volume of approximately 2 cm<sup>3</sup>. The catalyst bed was diluted in an effort to minimize any axial temperature gradients. Lower catalyst loadings were used with increasing reaction temperatures. When operating at 400 °C, the catalyst bed was diluted approximately 10:1 (diluent:catalyst) on a volume basis. 12/20 mesh crushed glass was placed above the catalyst bed to serve as a pre-heat zone for the incoming feed gas. The glass reactor had a single thermocouple which extended from the top of the reactor to approximately one-third of the way into the catalyst bed. Although the temperature profile in the catalyst bed could not be monitored, by comparing the temperature of the catalyst bed to that of the aluminum heating block, deviations from isothermal operating conditions could be assessed.

#### 3.4 Procedure.

*Effects of Dew Point Temperature:* 0.5035 g of catalyst (60/80 mesh) were diluted with crushed glass (60/80 mesh) to achieve a reactor volume of 2.0 cm<sup>3</sup>. The catalyst plus diluent were then loaded into the reactor and heated to 400 °C. Once at temperature, the catalyst was exposed to 1,250 ppm (6,658 mg/m<sup>3</sup>) chloroform in dry air ( $T_{\text{dew}} < -10$  °C). The residence time (calculated at 0 °C and 1 atmosphere pressure) was 0.30 seconds and the run was conducted at atmospheric pressure. The reactor temperature of 400 °C was maintained for 2 hours, after which, the reactor temperature was decreased at a rate of 30 °C/hr to a final temperature of 290 °C. Reactor effluent was sampled every 15 minutes (7.5 °C temperature intervals) for chloroform. Following completion of the run, the flow of chloroform was discontinued and the reactor was again heated to 400 °C at a rate of 30 °C/hr in flowing humid air. The final temperature was maintained overnight. The run was then repeated in the morning under the same conditions as before, but with humid air ( $T_{\text{dew}} = 28$  °C).

*Catalyst Deactivation:* Catalyst deactivation studies were performed at temperatures of 350 °C, 400 °C and 450 °C using 0.675g, 0.40g and 0.20 g catalyst, respectively. The catalyst was used as 60/80 mesh granules and diluted with crushed glass (60/80 mesh) so as to achieve a reactor bed volume of 2.0 cm<sup>3</sup>. The runs conducted at 350 °C and 400 °C employed feed concentrations of 1,500 ppm (7,990 mg/m<sup>3</sup>), while the run conducted at 450 °C employed a feed concentration of 1,250 ppm (6,658 mg/m<sup>3</sup>). All runs were conducted in humid air with a dew point

temperature of 28 ° C at atmospheric pressure. The runs were initiated by first heating the catalyst to reaction temperature and then introducing the chloroform feed to the catalyst bed. Process conditions were maintained continuously for up to 160 hours on stream. Reactor effluent was sampled every 20 minutes for the first 5 hours of the run, then every hour thereafter.

*Kinetic Studies:* Kinetic rate data were recorded at temperatures of 300 ° C, 325 ° C, 350 ° C, 375 ° C and 400 ° C at a pressure of  $1.5 \pm 1$  psig. 60/80 mesh catalyst particles were used when operating at all reaction temperatures. Four feed concentrations were employed in generating the kinetic data for all the runs. These concentrations were 100 ppm, 300 ppm, 1,000 ppm and 5,050 ppm ( $533 \text{ mg/m}^3$ ,  $1,598 \text{ mg/m}^3$ ,  $5,326 \text{ mg/m}^3$  and  $26,898 \text{ mg/m}^3$ ; respectively). All runs were conducted in humid air with a dew point temperature of 28 ° C. The residence time (based on the packed catalyst volume and calculated at 0 ° C, 1 atm) was adjusted in an effort to keep conversions between 20 and 90 %. Air flow rates were typically varied between 10 and 250 Nml/min. Air flow rates greater than 250 Nml/min could not be employed due to an excessive pressure drop across the catalyst bed. Rarely was the catalyst on stream for more than 72 hours of operation. All process conditions were maintained for a minimum of 2 to 3 hours to insure the achievement of steady-state operation. On-line GC analysis, which measured the concentration of chloroform using a flame ionization detector (FID), was performed every 20 minutes during the run. Remote GC analysis of the the reactor effluent for CO and CO<sub>2</sub> were performed approximately one hour into the run, and at the end of the run for each set of process conditions evaluated. Effluent samples were transferred to the remote GC using a gas tight syringe. The analytical procedure will be described in detail later in this text. The conversion of chloroform was calculated from the concentration of chloroform in the reactor effluent.

Due to the effects of concentrations on conversion, two or three different catalyst loadings were employed at each reactor temperature investigated. Each run was initiated using a feed concentration of 1000 ppm ( $5,326 \text{ mg/m}^3$ ) and adjusting the residence time so that the conversion would be approximately 50 % to 60 %. These conditions were typically maintained overnight. By initiating each run (constant temperature) at a similar set of process conditions (concentration, residence time), a point of continuity could be established between the different catalyst loadings which were employed at each reaction temperature. Further, following this procedure serves as a test for external mass transfer resistances (same residence time with a different linear velocity).

**Effluent Analysis:** Reactor effluent was analyzed on-line using a Hewlett - Packard 5790 gas chromatograph equipped with flame ionization detector (FID). Chloroform was separated using a 6' x 1/8" glass column filled with 10% OV-210 on Supelcoport which was operated at 75 °C. Remote GC analysis of the reactor effluent was performed using a Hewlett-Packard 5971 gas chromatograph/mass spectroscopy system. Permanent gases were separated using a 6' x 1/8" Porapak Q column and analyzed using a thermal conductivity detector of the gas chromatograph. Peak identification was performed using the mass spectroscopy unit.

A set of experiments was performed in an effort to analyze the reactor effluent for acid gases. These experiments were performed at reaction temperatures of 300 °C, 350 °C and 400 °C using a chloroform feed concentration of 1,250 ppm (6,658 mg/m<sup>3</sup>) in humid air. Residence times were adjusted so that the conversion of chloroform was between 65 and 95 %. Reactor effluent was collected in a cold trap submerged in a dry ice/acetone bath placed just downstream of the reactor. The distance between the reactor and the cold trap was minimized to lessen the effects of accumulation onto the transfer lines. Reactor effluent was collected in the cold trap over discrete time periods (collection times varied between 2 and 16 hours) and analyzed for total acid content by titration with sodium hydroxide. The titration was performed by first diluting the contents of the cold trap to 50 ml with distilled water. The solution was then placed in a 100 ml TFE jar and titrated to neutrality using a 0.0413N solution of NaOH. A total acid balance was performed by assuming all the Cl associated with the chloroform (either as Cl<sub>2</sub> or HCl) was dissolved into solution.

### 3.5 *Spectroscopic Analyses.*

Catalyst samples were analyzed using X-ray photoelectron spectroscopy (XPS) for Pt, Al, O, Cl and C as-received, following calcination and following various reaction exposures. XPS spectra of the catalyst samples were recorded using a Perkin-Elmer Phi 570 ESCA/SAM surface analysis instrument employing Mg-K<sub>α</sub> X-rays. Catalyst samples which were analyzed following reaction exposures were separated from the glass diluent by "pressing" the contents of the catalyst bed through a fine mesh sieve. The glass diluent could not be pushed through the sieve. Atomic ratios were calculated using sensitivity factors supplied by the manufacturer.

## 4. RESULTS

### 4.1 *Effects of Dew Point Temperature.*

Figure 2 shows the effects of temperature on the conversion of chloroform in the presence of dry and humid ( $T_{\text{dew}} = 28^{\circ}\text{C}$ ) air. Both sets of data were recorded using a chloroform feed concentration of approximately 1,500 ppm ( $7,990\text{ mg/m}^3$ ) with a reactor pressure of 1 psig and a residence time ( $\tau$ ) of 0.30 seconds. As the data show, the presence of water in the feed stream did not have a significant effect on the conversion of chloroform. For the run conducted in humid air, the apparent activation energy was calculated to be 25,500 cal/mol, which compared to an activation energy of 26,300 cal/mol for the run conducted in dry air. The apparent activation energies were calculated from data collected over the temperature range of  $350^{\circ}\text{C}$  to  $400^{\circ}\text{C}$ .

### 4.2 *Catalyst Induction and Deactivation.*

Figures 3, 4 and 5 report conversion as a function of time-on-stream for the oxidation of chloroform in humid ( $T_{\text{dew}} = 28^{\circ}\text{C}$ ) air at  $350^{\circ}\text{C}$ ,  $400^{\circ}\text{C}$  and  $450^{\circ}\text{C}$ , respectively. For the runs conducted at  $350^{\circ}\text{C}$  and  $400^{\circ}\text{C}$ , the concentration of chloroform was 1,500 ppm ( $7,990\text{ mg/m}^3$ ), while the concentration of chloroform was 1,250 ppm ( $6,658\text{ mg/m}^3$ ) for the run conducted at  $450^{\circ}\text{C}$ . For the run conducted at  $350^{\circ}\text{C}$ , conversion decreased from 92 % to 83 % over the 62 hours of operation. Over the course of this run, the catalyst was exposed to 204 moles of chlorine per mole of platinum. For the run conducted at  $400^{\circ}\text{C}$ , conversion decreased from about 75 % at the start of the run to 65 % over the 62 hours of operation. Over the course of this run, the catalyst was exposed to 1,352 moles of chlorine per mole of platinum. Upon raising the catalyst temperature to  $450^{\circ}\text{C}$ , a significant decrease in the conversion of chloroform was observed over the first 70 to 80 hours of operation. Over this time period, conversion decreased from 91 % to about 30 %. During the 164 hours of operation, the catalyst was exposed to 8,685 moles of chlorine per mole of platinum.

### 4.3 *Reaction Products.*

The only reaction product identified via gas chromatograph analysis of the reactor effluent was  $\text{CO}_2$ . No chlorine gas nor chlorine containing products were detected using the gas chromatographic technique. Carbon balances were typically greater than 90% for all runs. Results of the chlorine balances, using the acid gas collection technique, are reported in Table 3.

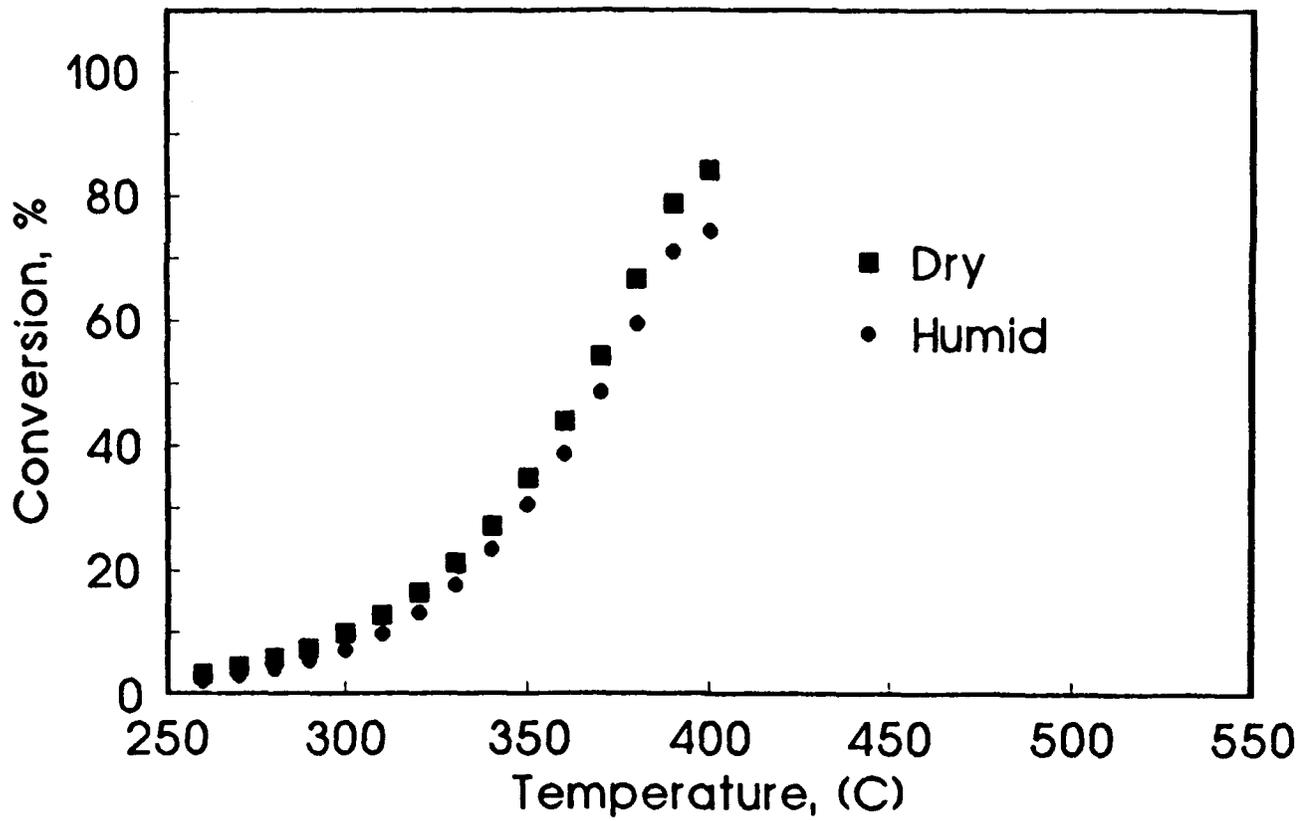


Figure 2: Effects of Air Dew Point Temperature on Catalytic Activity.

Run 7-12b-91, Deactivation of CHCL3 at 350 C

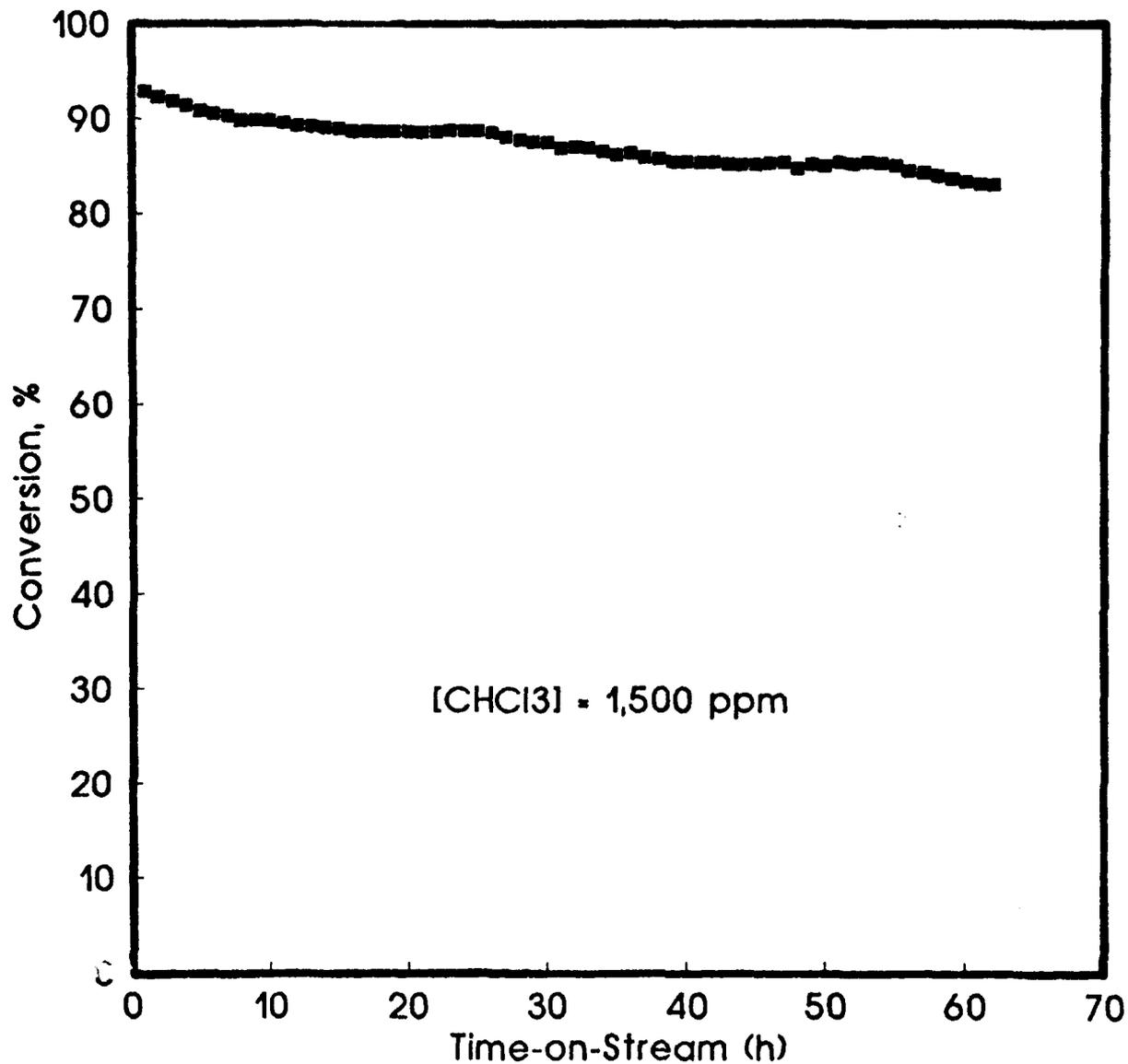


Figure 3: Conversion as a Function of Time-on-Stream for the Oxidation of 1,500 ppm Chloroform in Humid Air at 350 °C.

Run 7-19-91, Deactivation of CHCL3 at 400 C

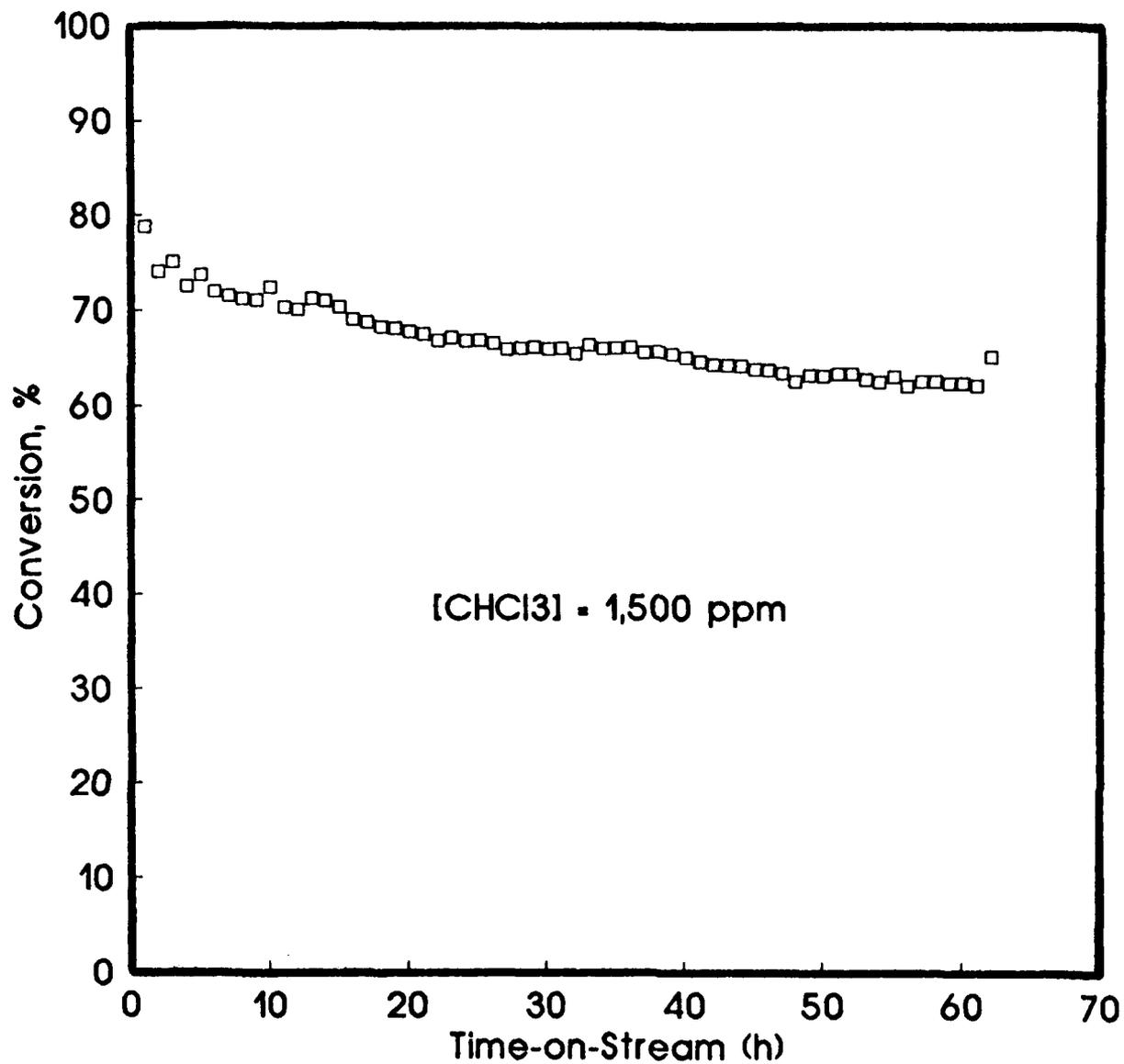


Figure 4: Conversion as a Function of Time-on-Stream for the Oxidation of 1,500 ppm Chloroform in Humid Air at 400 ° C.

Run 8-30-91, Deactivation of CHCl<sub>3</sub> at 450 C

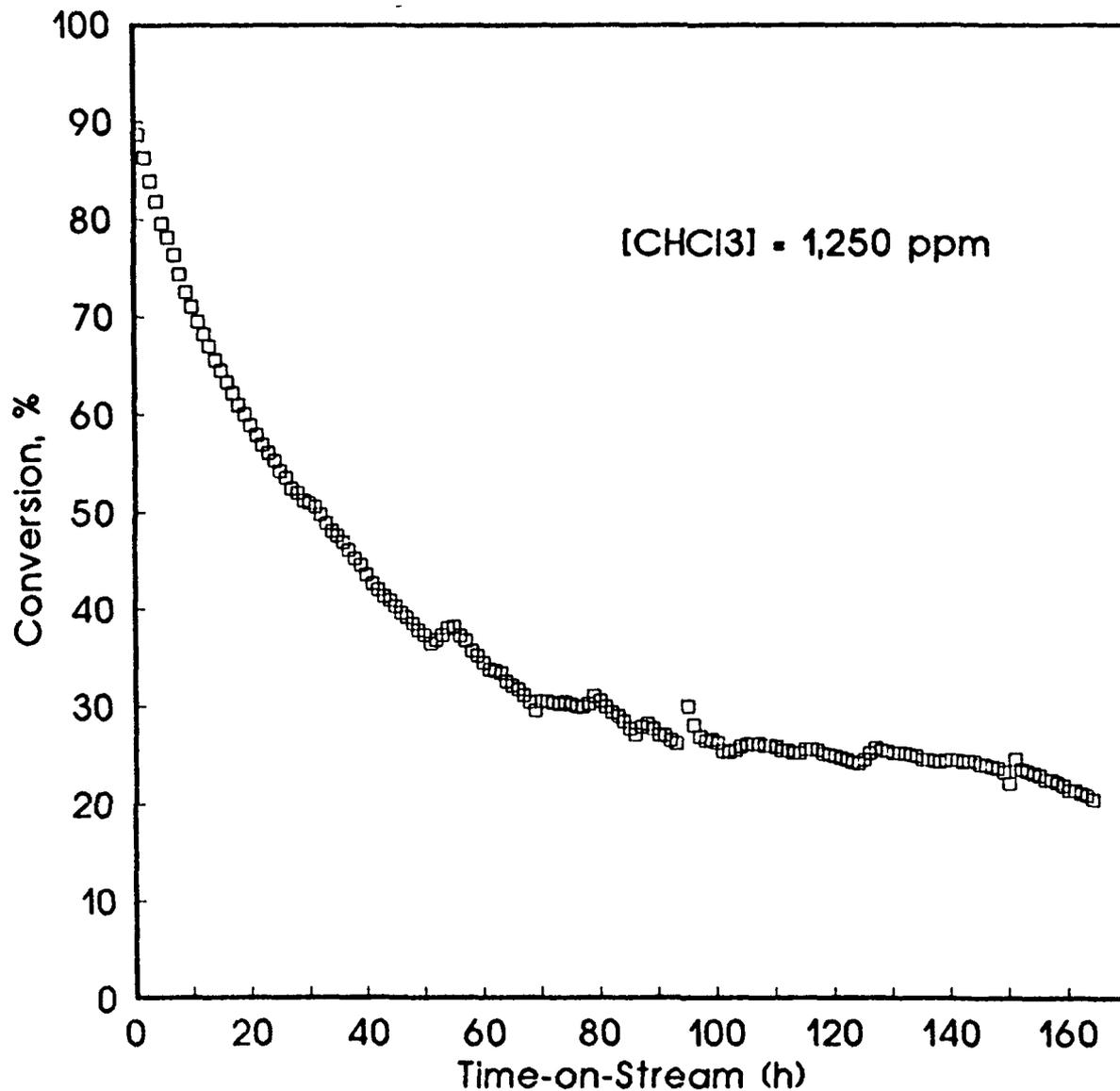


Figure 5: Conversion as a Function of Time-on-Stream for the Oxidation of 1,250 ppm Chloroform in Humid Air at 450 °C.

Table 3  
Chlorine Balances for Selected Runs

| Temperature | Conversion | Time-on-Stream | Cl-Balance |
|-------------|------------|----------------|------------|
| 300 °C      | 66.0 %     | 0.0 - 4.0 h    | 59.8 %     |
| 300 °C      | 66.0 %     | 22. - 29.5h    | 79.2 %     |
| 300 °C      | 87.0 %     | 30. - 45. h    | 78.0 %     |
| 350 °C      | 94.5 %     | 10. - 25. h    | 80.0 %     |
| 400 °C      | 97.4 %     | 0.0 - 3.0 h    | 57.1 %     |
| 400 °C      | 97.4 %     | 3.5 - 6.5 h    | 76.8 %     |
| 400 °C      | 97.4 %     | 7.0 - 22. h    | 80.9 %     |
| 400 °C      | 80.8 %     | 23. - 26. h    | 64.0 %     |

The conversions reported in Table 3 were the average of several GC analyses, and the time-on-stream heading refers to the interval over which the chlorine balance was performed. A fresh catalyst batch was used at each reaction temperature. Data reported in Table 3 illustrate the effects of conversion, reaction temperature and time-on-stream on the chlorine balances. Chlorine balances are calculated as the percent of chlorine recovered in the cold trap as determined by NaOH titration divided by the moles of chlorine reacted. In calculating the chlorine balances this way, the unreacted chloroform does not figure into the calculations.

#### 4.4 *Reaction Kinetics.*

Catalytic deactivation was assessed during each run. Prior to the termination of a run, an initial set of process conditions were repeated, and the conversion recorded at this time was compared to that recorded early into the run. Typically, the deviation in the conversions was less than 3%, indicating that catalytic deactivation was not significant.

The effects of external mass transfer resistances were evaluated by repeating a set of process conditions (identical residence times, concentration and temperature) while employing a different linear velocity. Results of this experiment indicated that linear velocity, and hence external mass transfer resistances, had no effect on the conversion of chloroform. For example, at 375 °C and a feed concentration of 1,000 ppm (5,326 mg/m<sup>3</sup>), doubling the linear velocity had an insignificant effect on conversion; 59.98 % versus 58.27 % at double the linear velocity. Intraparticle mass transfer resistances were evaluated by calculating effectiveness

factors. At 400 ° C, effectiveness factors were calculated to be greater than 0.98 for all concentrations evaluated. The results presented above indicate that the kinetic data reported here were not influenced by either external or intraparticle mass transfer resistances.

Table 4 reports the standard deviations calculated for each kinetic rate expression at the five reaction temperatures investigated. The standard deviation is defined as the norm of the error between the predicted and experimental values of  $W/F_a^0$ .

Table 4  
Percent Standard Deviations Calculated for Each Kinetic Rate Expression

| Temperature | Model 1 | Model 2 | Model 3 | Model 4 | Model 5 |
|-------------|---------|---------|---------|---------|---------|
| 300 ° C     | 5.97%   | 3.41%   | 7.65%   | 4.80%   | 8.91%   |
| 325 ° C     | 6.09%   | 3.54%   | 6.87%   | 4.27%   | 8.14%   |
| 350 ° C     | 5.76%   | 1.76%   | 7.51%   | 3.58%   | 9.02%   |
| 375 ° C     | 6.54%   | 3.44%   | 8.07%   | 5.12%   | 6.46%   |
| 400 ° C     | 6.92%   | 2.60%   | 8.84%   | 5.25%   | 8.94%   |

Figures 6a through e show plots of the kinetic data recorded at 300 ° C and correlated with rate expressions 1 through 5; respectively. Kinetic data recorded at 325 ° C, 350 ° C, 375 ° C and 400 ° C are reported in Figures 7 through 10, respectively. From the data reported in these figures, it is evident that the reaction is not first order, and that conversion is a strong function of both residence time and concentration of chloroform. The solid lines in Figures 7 - 10 represents the data as predicted by rate expression 2 using the fit parameters as calculated from the Arrhenius equations.

Table 5 reports the kinetic fit parameters corresponding to rate expression 2 determined at each of the five reaction temperature. Frequency factors, the activation energy and heats of reaction for the fit parameter are also reported in the table. Figure 11 reports conversion as a function of temperature for the oxidation of chloroform in humid air in the presence and absence of 5,000 ppm (8,143 mg/m<sup>3</sup>) HCl. The effects of HCl on the conversion of chloroform was performed in an effort

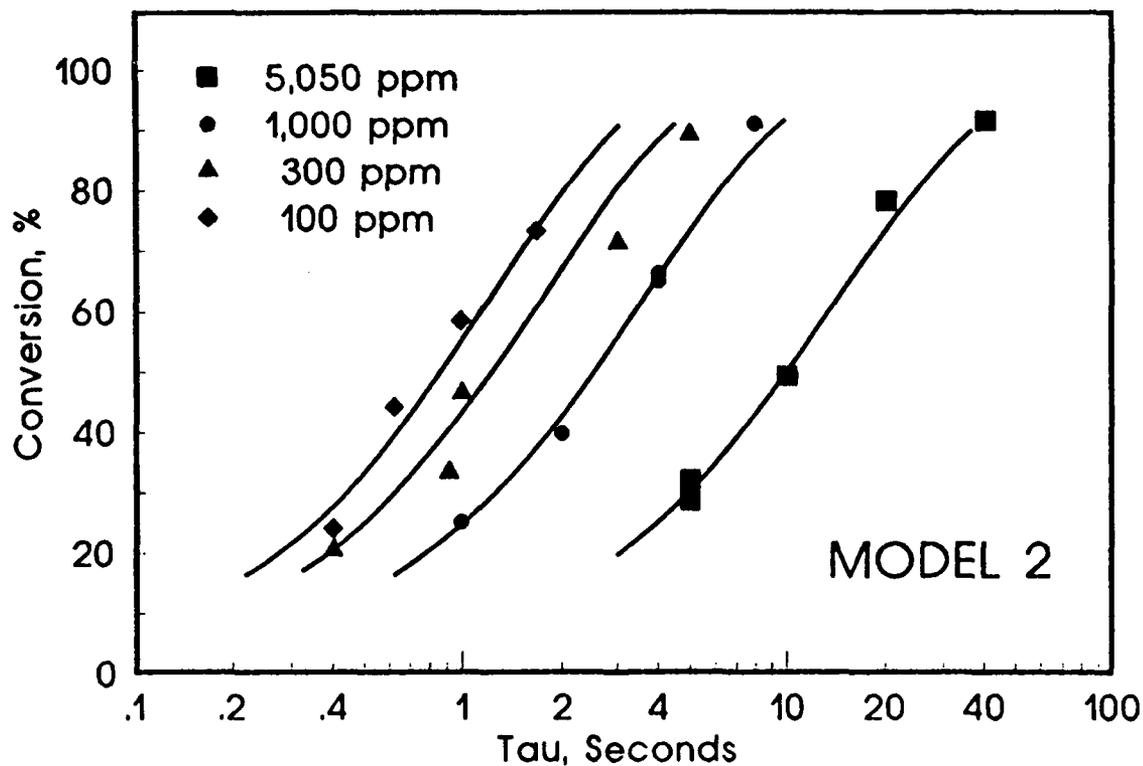
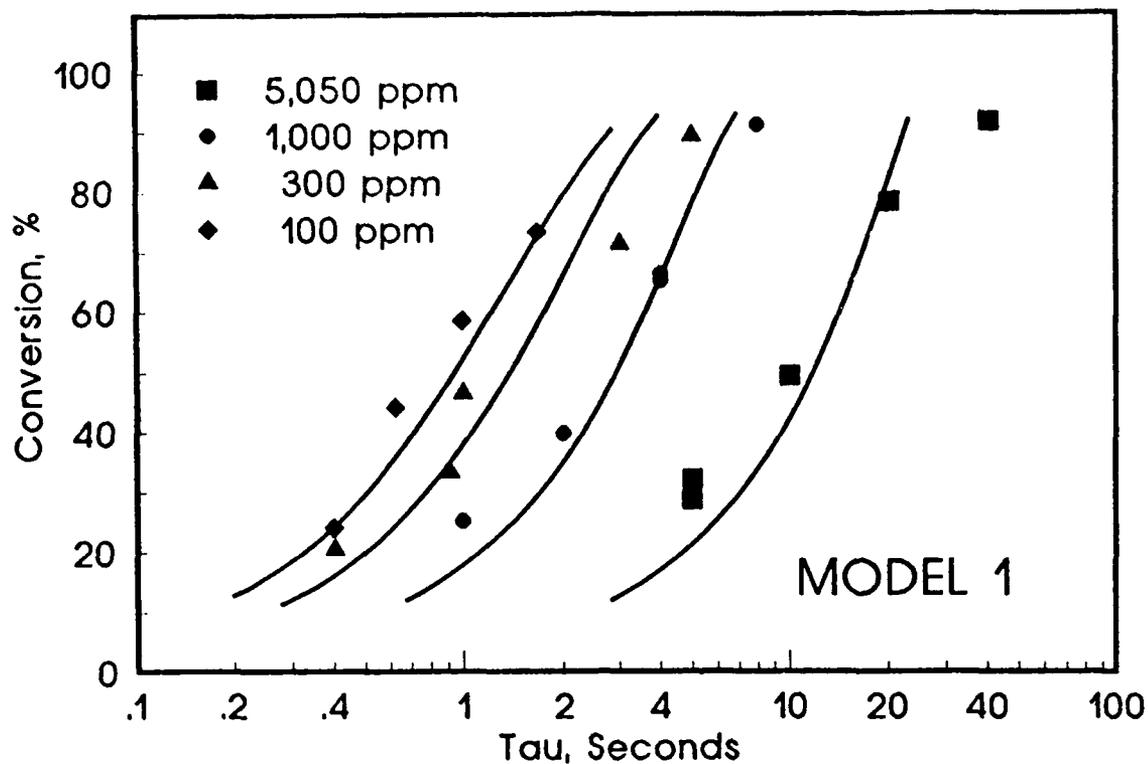


Figure 6: Conversion as a Function of Residence Time for the Oxidation of Chloroform at 300 °C. (A) Data correlated using rate expression 1; (B) data correlated using rate expression 2; (C) data correlated using rate expression 3; (D) data correlated using rate expression 4; (E) data correlated using rate expression 5.

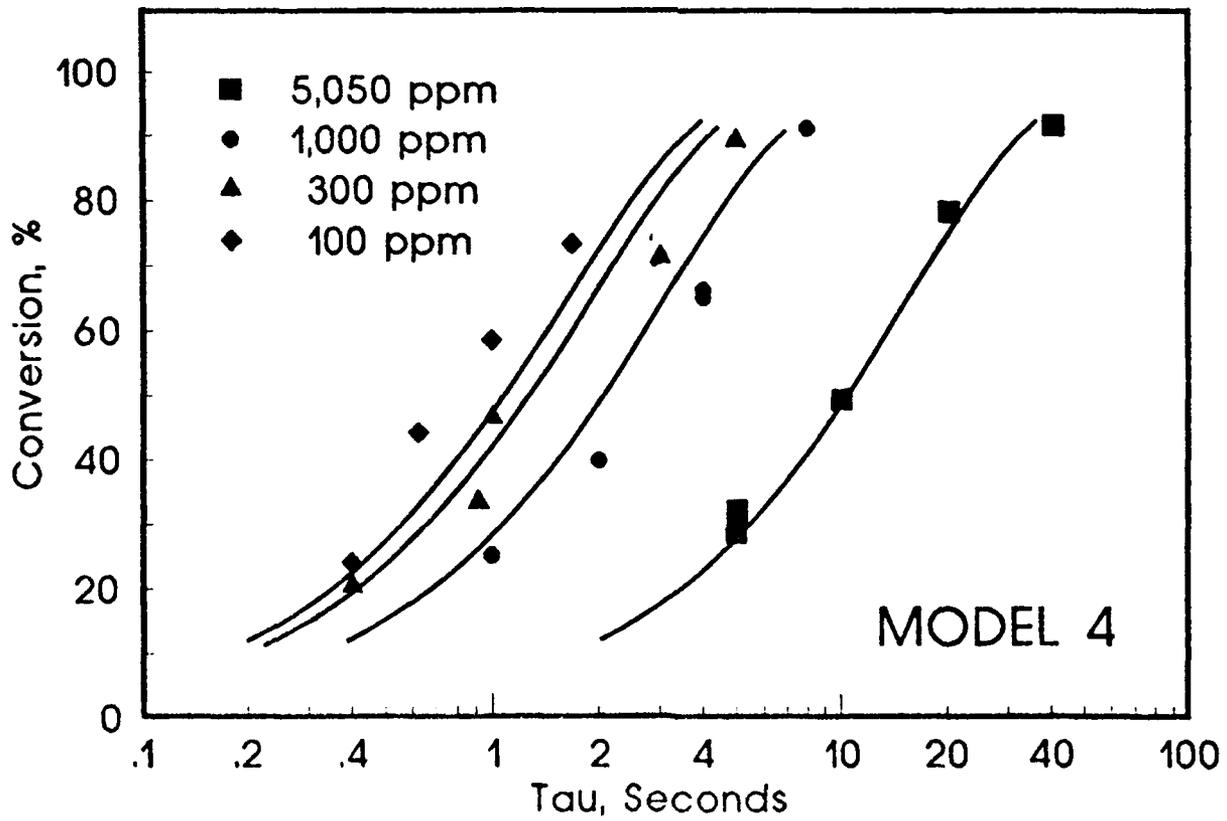
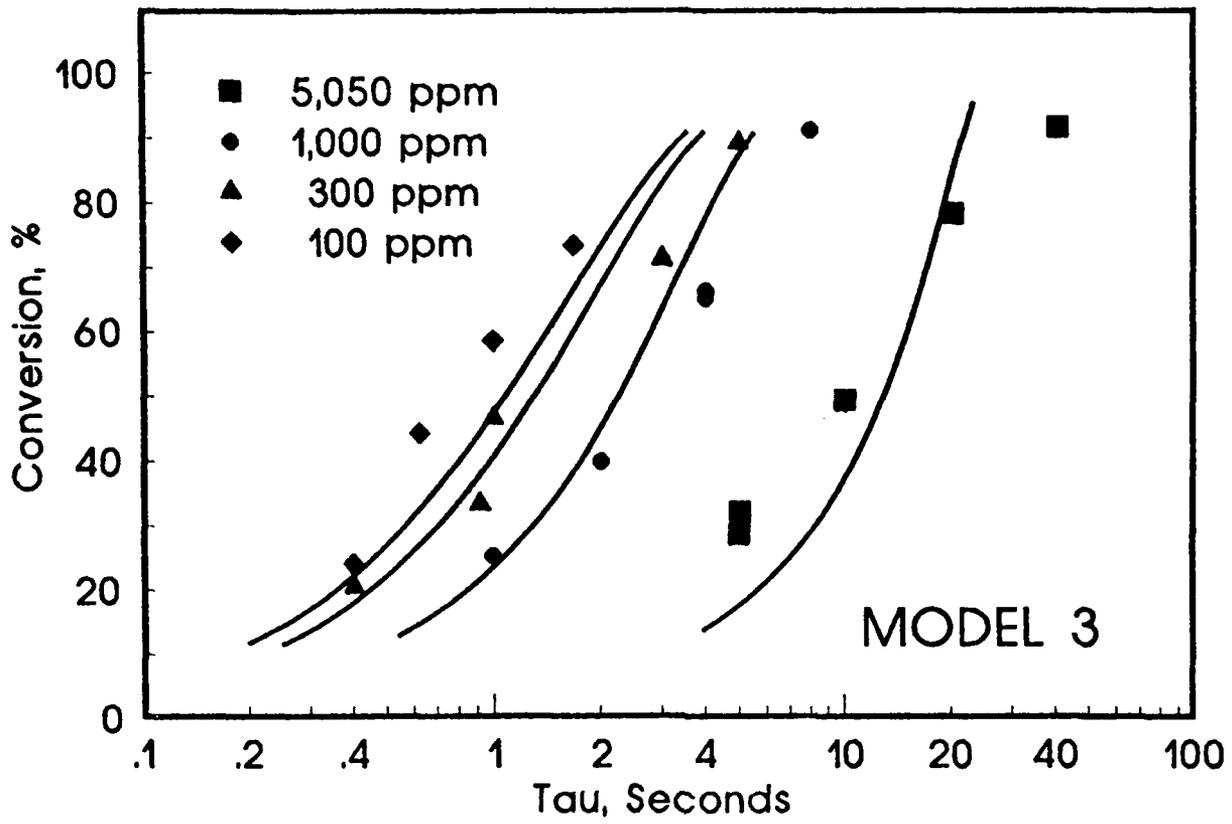


Figure 6 (con't):

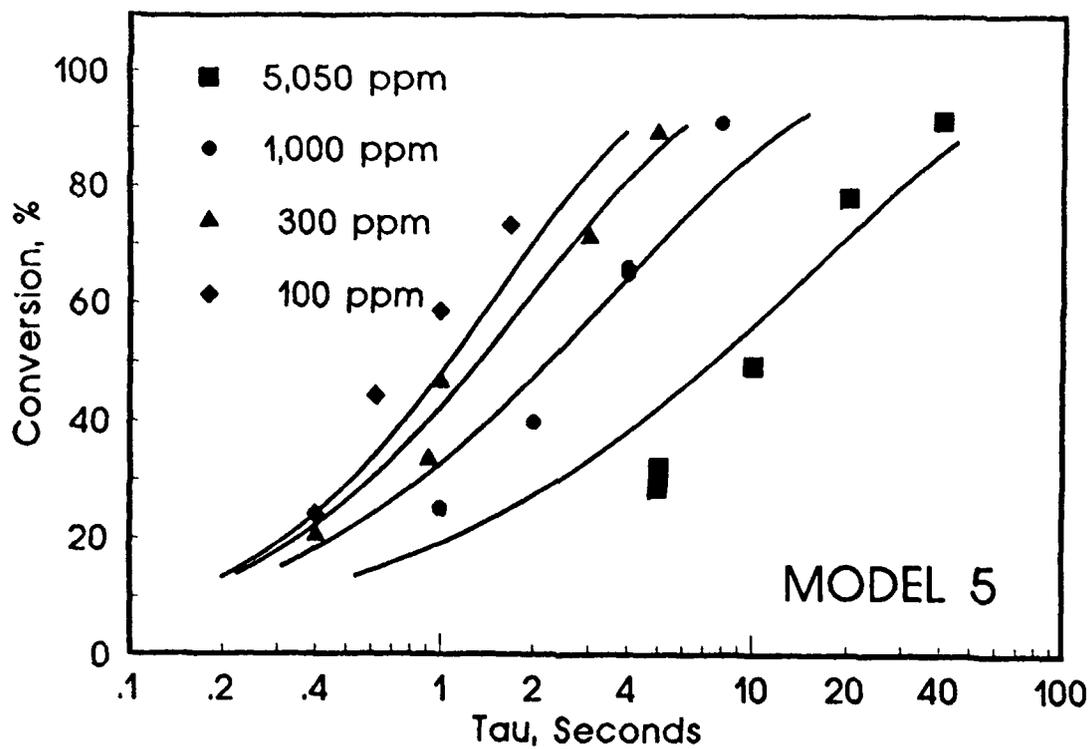


Figure 6 (con't):

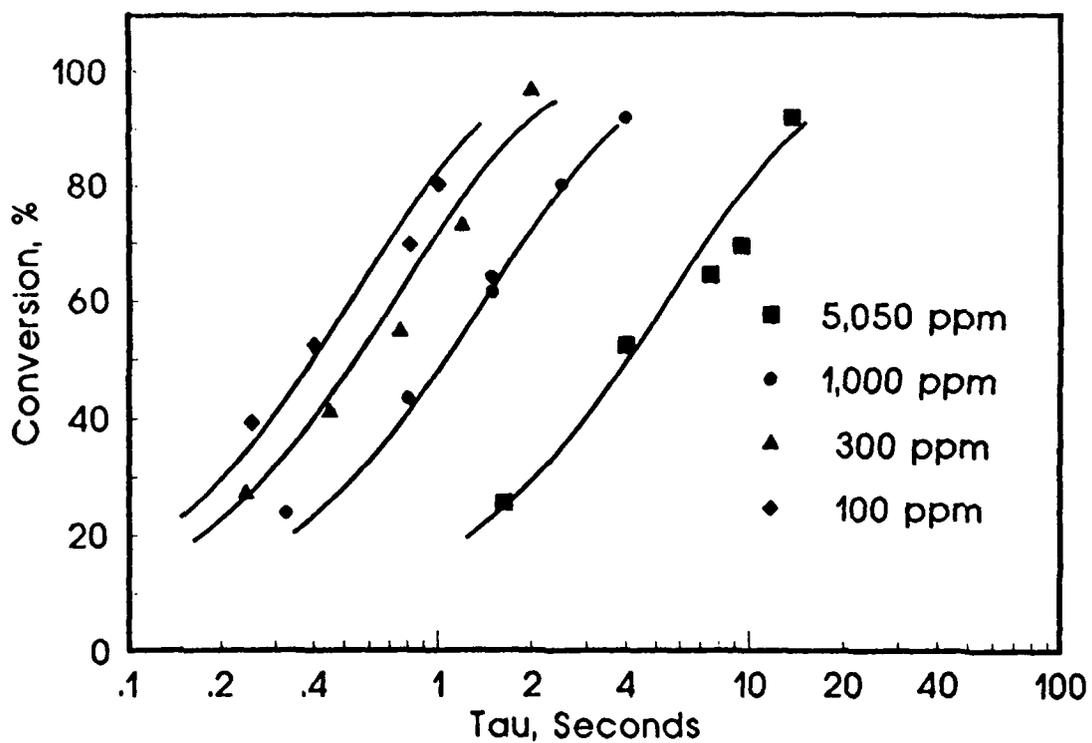


Figure 7: Conversion as a Function of Residence Time for the Oxidation of Chloroform at 325 °C. The solid lines represent the kinetic data correlated with rate expression 2.

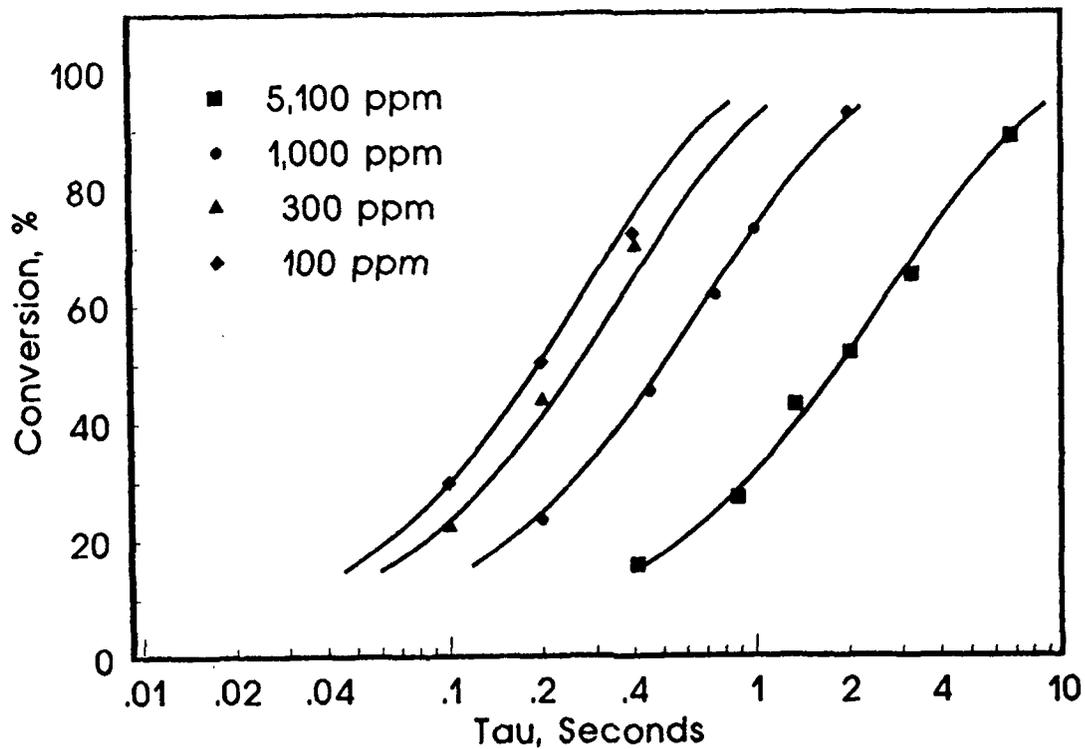


Figure 8: Conversion as a Function of Residence Time for the Oxidation of Chloroform at 350 °C. The solid lines represent the kinetic data correlated with rate expression 2.

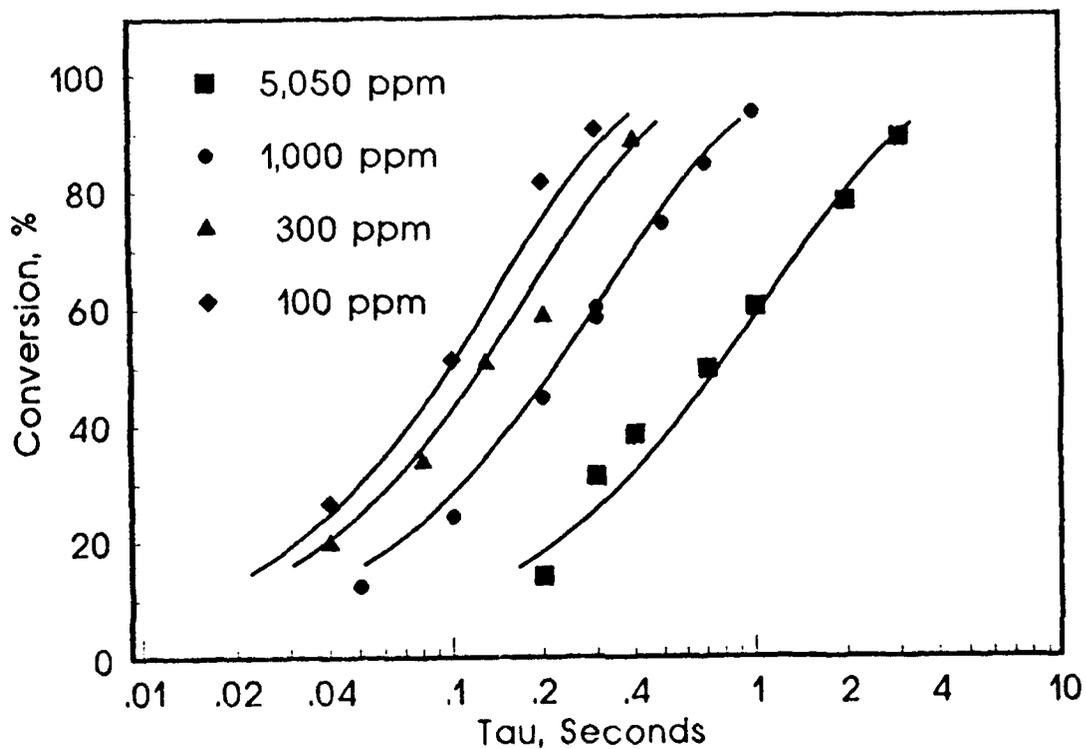


Figure 9: Conversion as a Function of Residence Time for the Oxidation of Chloroform at 375 °C. The solid lines represent the kinetic data correlated with rate expression 2.

Oxidation of  $\text{CHCl}_3$ : 2% Pt/ $\text{Al}_2\text{O}_3$ , 400 C

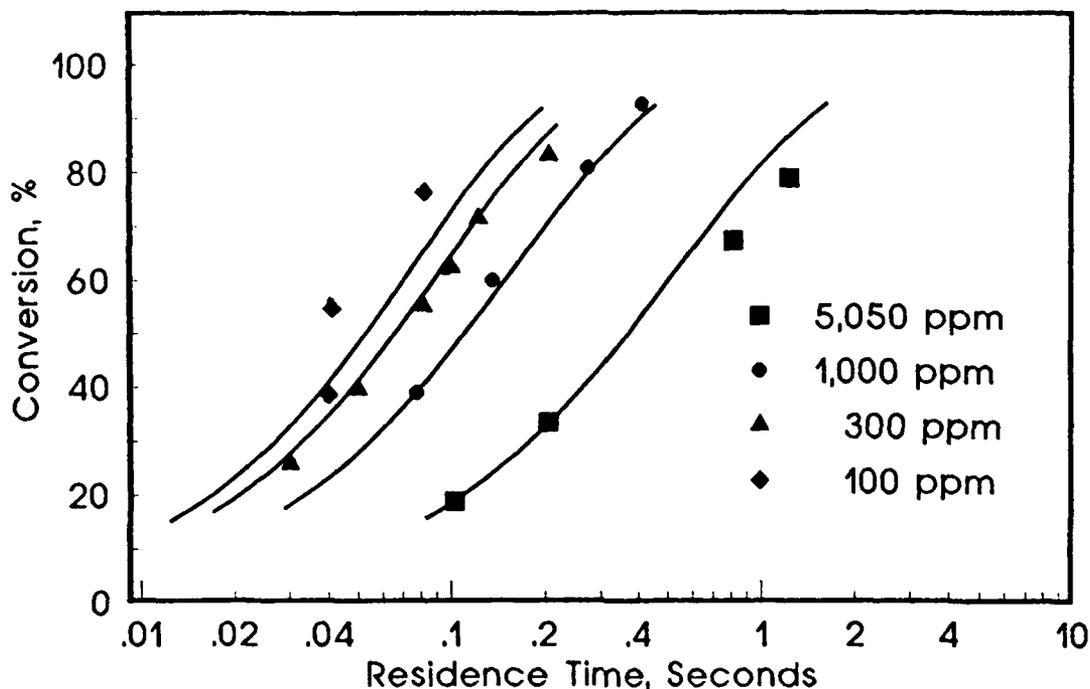


Figure 10: Conversion as a Function of Residence Time for the Oxidation of Chloroform at 400 °C. The solid lines represent the kinetic data correlated with rate expression 2.

Effects of HCl on Conversion of  $\text{CHCl}_3$

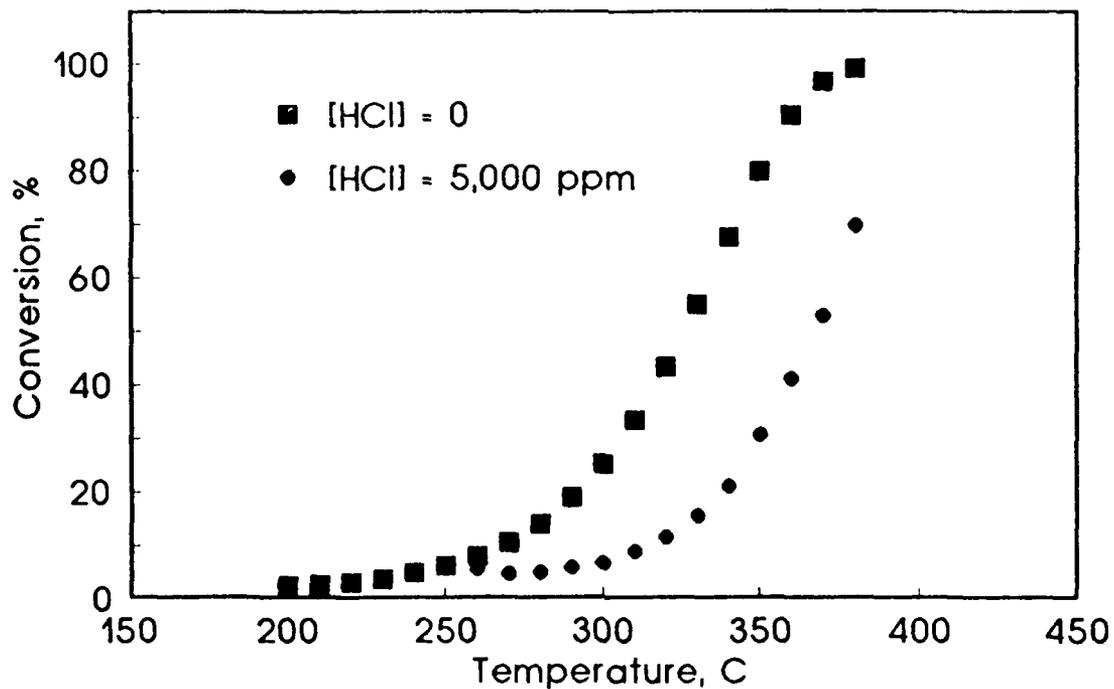


Figure 11: Conversion as a Function of Reaction Temperature for the Oxidation of 1,250 ppm Chloroform in the Presence and Absence of 5,000 ppm HCl.

to assess the physical significance of the product inhibition term present in rate expression 2. Arrhenius plots corresponding to the rate constant,  $k$ , and adsorption equilibrium constants,  $K_a$  and  $K_p$ , are shown in Figures 12 and 13, respectively.

Table 5  
Kinetic Fit Parameters Determined for Model 2

| Temperature                                 | $k, s^{-1}$ | $K_p, cm^3/mol$ | $K_a, cm^3/mol$ |
|---|-------------|-----------------|-----------------|
| 300 ° C                                     | 2.17        | 0.1517(9)       | 0.1302(9)       |
| 325 ° C                                     | 4.72        | 0.1293(9)       | 0.1070(9)       |
| 350 ° C                                     | 9.75        | 0.1399(9)       | 0.9634(8)       |
| 375 ° C                                     | 18.78       | 0.1206(9)       | 0.7613(8)       |
| 400 ° C                                     | 36.74       | 0.1052(9)       | 0.6460(8)       |
| $k = .3720(9) \text{ EXP } \{-21,610/RT\}$  |             | $r^2 = .9999$   |                 |
| $K_p = .1785(8) \text{ EXP } \{+2,435/RT\}$ |             | $r^2 = .8942$   |                 |
| $K_a = .1229(7) \text{ EXP } \{+5,328/RT\}$ |             | $r^2 = .9926$   |                 |

#### 4.5 Spectroscopic Analyses.

Figure 14 reports the XPS spectra of the platinum 4d photoelectron region for the catalyst following calcination at 450 ° C in humid air, and following the deactivation tests at 350 ° C, 400 ° C and 450 ° C. The XPS spectra reported in Figure 14 corresponds to the data presented in Figures 3, 4 and 5. The XPS spectrum corresponding to the as-received catalyst was very similar to that of the catalyst following calcination, and is therefore not shown. The binding energy of the platinum 4d<sub>3/2</sub> peak corresponding to the calcined catalyst (314.7 eV) is consistent with platinum in the zero valent oxidation state<sup>14,15,16</sup>. Following reaction exposure at 350 ° C and 400 ° C, the binding energy of the platinum 4d<sub>3/2</sub> photoelectron peak has increased to approximately 315.9 eV. Following reaction exposure at 450 ° C, the binding energy of the platinum 4d<sub>3/2</sub> photoelectron peak has increased to 316.8 eV, which is indicative of platinum in the +4 oxidation state<sup>14,16</sup>.

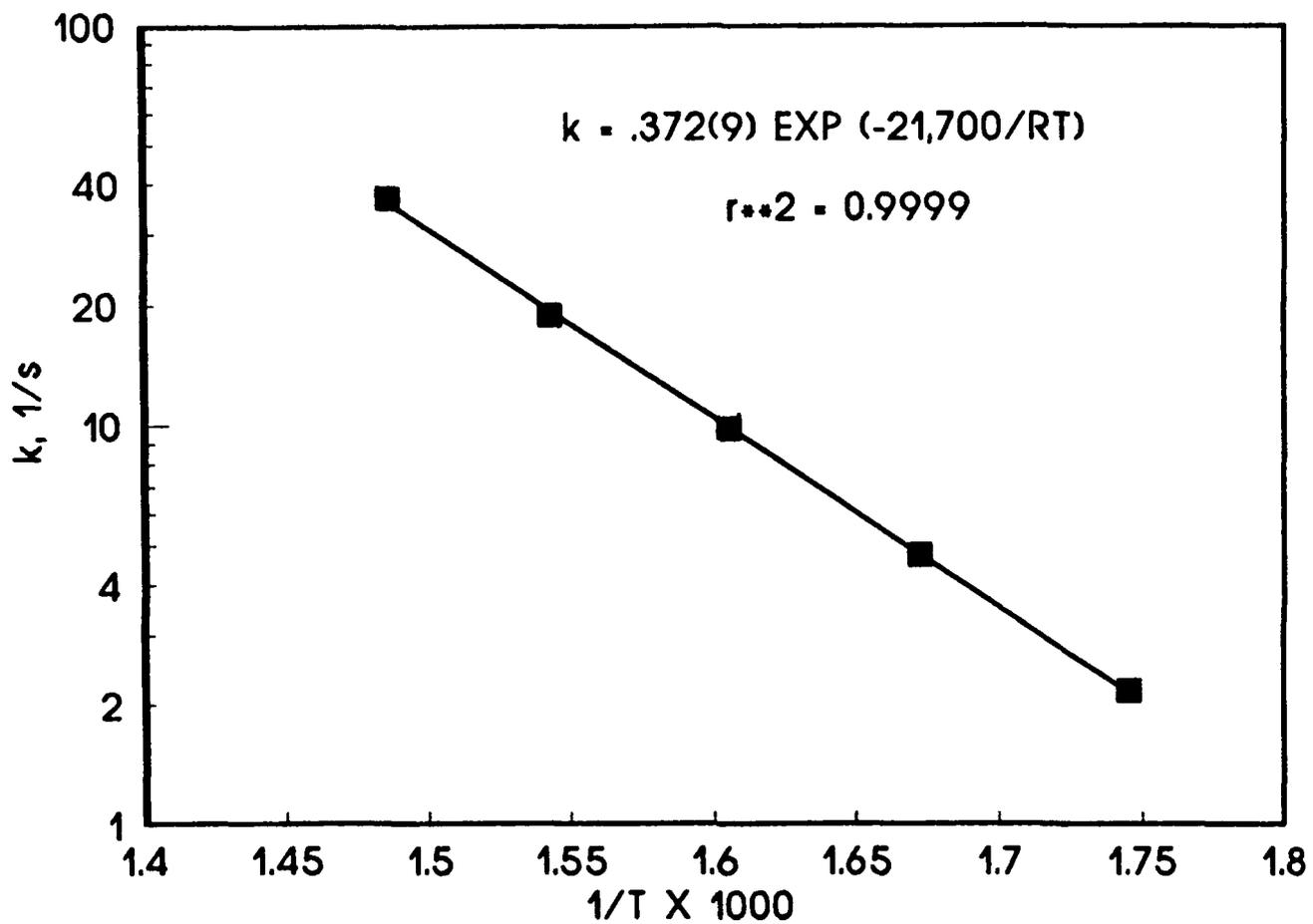


Figure 12: Arrhenius Plot of the Rate Constant  $k$  for the Decomposition of Chloroform over a Platinum Alumina Catalyst.

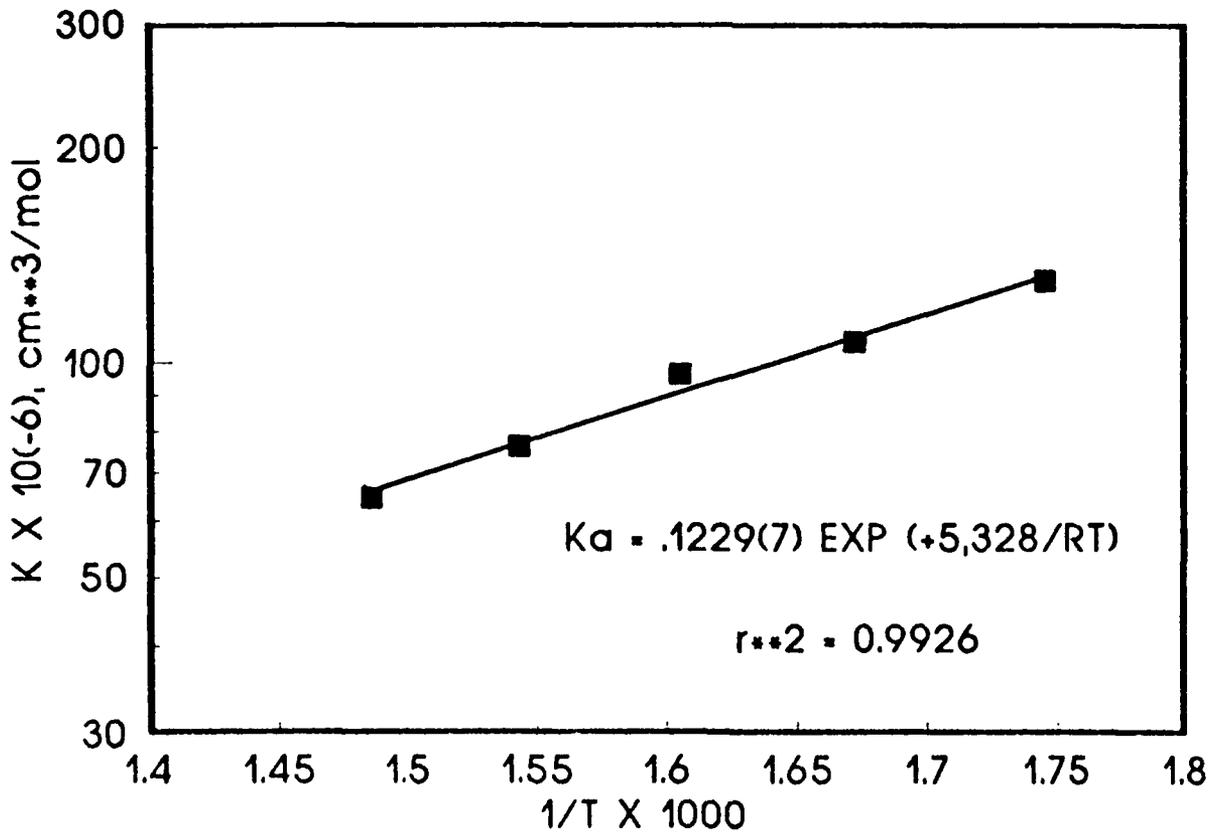
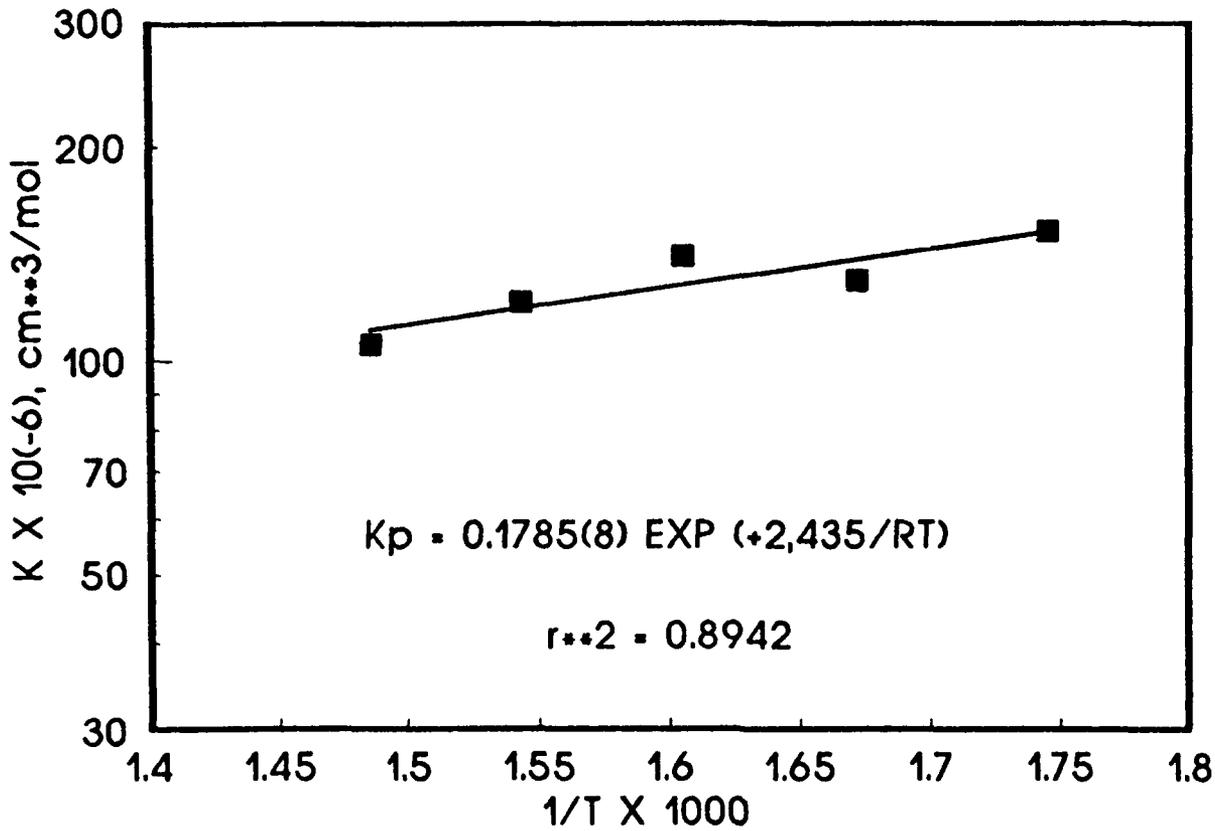


Figure 13: Arrhenius Plots of the Adsorption Equilibrium Constants  $K_a$  (A) and  $K_p$  (B).

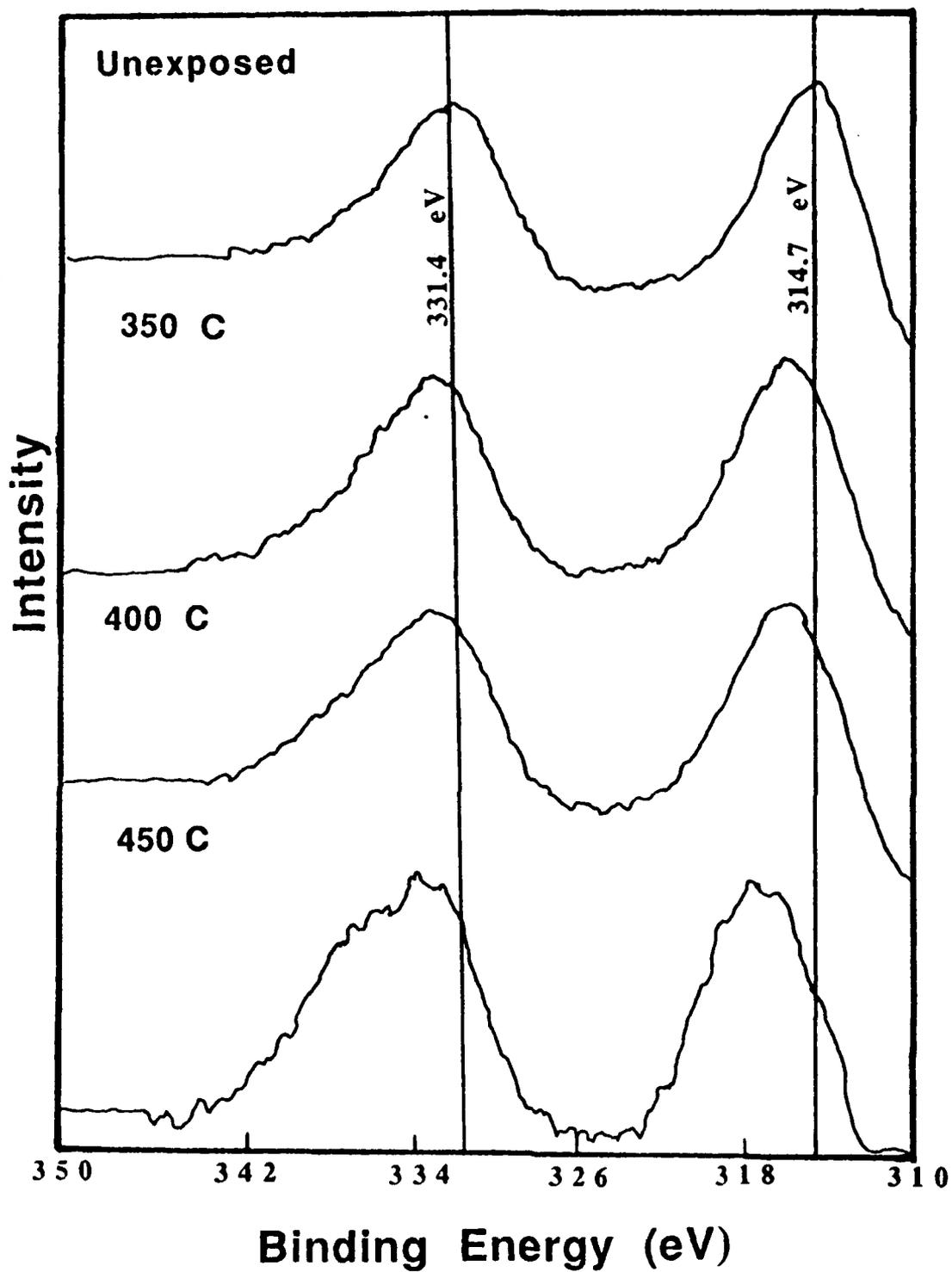


Figure 14: XPS Spectra of the Platinum 4d Photoelectron Region of the 2.15% Pt/Al<sub>2</sub>O<sub>3</sub> Catalyst Following Calcination at 450 °C, and Following Deactivation Studies at 350 °C, 400 °C and 450 °C.

Table 6 reports atomic ratios as calculated from the integrated peak areas for the catalyst samples examined above. The heading "calcined" refers to the catalyst following calcination, while the temperature headings correspond to the temperature at which the catalyst was exposed to chloroform.

Table 6  
Atomic Ratios for Catalyst Samples Prior to and Following Reaction Exposure

| Atomic Ratio | Calcined | 350 ° C | 400 ° C | 450 ° C |
|--------------|----------|---------|---------|---------|
| Pt/Al        | 0.0242   | 0.0254  | 0.0234  | 0.0140  |
| Cl/Al        | 0.0000   | 0.0236  | 0.0247  | 0.0284  |
| Cl/Pt        | 0.0000   | 0.93    | 1.06    | 2.03    |

## 5. DISCUSSION

### 5.1 *Effects of Dew Point Temperature.*

The presence of water in the feed stream had a minimal effect on the catalytic activity, as illustrated by the data reported in Figure 2. The conversion of chloroform in the presence of water was slightly less than that obtained when water was present in the feed stream, suggesting that water has a slight inhibition effect. Rossin et al.<sup>3</sup> presented data which indicated that water had a minimal effect on the activity of a platinum/alumina catalyst during the oxidation of chloroacetonitrile. The results of Rossin et al. are consistent with those reported here.

### 5.2 *Catalyst Induction and Deactivation.*

Following exposure of a catalyst to reactant, the catalytic activity may change with time-on-stream, eventually achieving a steady-state activity. This behavior is referred to as an induction effect, with the induction period being defined as the time required for the catalyst to achieve steady-state activity. No induction effects were observed during any of the tests. At 350 ° C, the decrease in the catalytic activity with time-on-stream was minimal during the 62 hour run (Figure 3). The same was true for the run conducted at 400 ° C (Figure 4). At 450 ° C, the decrease in catalytic activity with time-on-stream was significant during the first 70 hours (Figure 5). After the 70 hours of operation, the decrease in the catalytic activity was minimal. It is interesting to note, however, that the activity of the catalyst at 450 ° C is at all times greater than the activity at 400 ° C.

Following the deactivation runs, spent catalysts were analyzed using X-ray photoelectron spectroscopy (XPS). XPS analysis of the spent catalyst revealed similar levels of chlorine associated with each catalyst. Surprisingly, only a minimal amount of carbon was detected, as one might expect some coking due to the acidic nature of the alumina support. No change in the binding energy of the platinum  $4d_{3/2}$  photoelectron peak was observed following the calcination step. This indicates that the calcination step did not affect the oxidation state of the platinum (i.e. platinum metal was not oxidized to platinum(IV) oxide). Changes in the binding energy of the platinum  $4d_{3/2}$  photoelectron peak following reaction exposure were evident (see Figure 14). XPS analysis of the spent catalyst following the deactivation tests at 350 °C and 400 °C showed an increase in the binding energy of the platinum  $4d_{3/2}$  photoelectron peak; from 314.7 eV to 315.9 eV. The increase in binding energy indicates that the oxidation state of platinum has increased, likely from 0 to +2, as a result of the reaction exposure. Lieske et al.<sup>17</sup> have demonstrated that the addition of chlorine (as HCl) to a platinum catalyst can result in the formation of platinum-chloride complexes. It is possible that the increase in the platinum binding energy may be due to the formation of a platinum chloride complex. Although there is a change in the platinum speciation based on the platinum binding energy, the loss in catalytic activity was minimal for the runs conducted at 350 °C and 400 °C. This suggests that if the increase in the platinum binding energy is due to adsorption of chlorine, the adsorbed chlorine atom does not significantly affect the activity of the platinum catalyst over the duration of the runs reported here. One possible explanation for the slight decrease in conversion observed at 350 °C and 400 °C could be due to the particle size distribution of the supported platinum being altered by the reaction environment. Guo et al.<sup>18</sup> have shown that treatment of a Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst in chloroform and trichloroethylene (in oxygen) environments affect the platinum crystallite size, resulting in simultaneous sintering and redispersion of platinum. The net result is reported to produce a very bimodal particle size distribution. Chlorine gas and hydrochloric acid (likely reaction products of chloroform) are reported to be useful in the redispersion of platinum<sup>18,19</sup>.

For the run conducted at 450 °C, the binding energy of the platinum  $4d_{3/2}$  photoelectron peak increased from 314.7 eV to 316.8 eV. The position of this peak is consistent with platinum in the +4 oxidation state<sup>14,16</sup>. For this run, the conversion decreased sharply over the first 70 to 80 hours on-stream. It is possible that the decrease in conversion with time-on-stream observed at 450 °C was due to the metallic platinum becoming oxidized to platinum(IV). Lieske et al.<sup>17</sup> have shown that although it is very difficult to transform platinum metal crystallites into crystallites of platinum(IV) oxide, it is not difficult to accomplish this transformation provided one proceeds through a platinum chloride intermediate.

The results presented in Table 6 indicate that chlorine is present on all catalyst samples following reaction exposure. It is interesting to note that the Cl/Al atomic ratio is virtually the same for all catalyst samples exposed to chloroform. This would indicate that the chlorine accumulation onto the catalyst sample is independent of the reaction temperature, which is not what one would expect. The Cl/Pt ratio provides some information regarding the location of the chlorine. For the catalysts reacted at 350 ° C and 400 ° C, the Cl/Pt ratio is very close to 1.0, while for the catalyst reacted at 450 ° C, the Cl/Pt ratio is very close to 2.0. The whole number ratios obtained from the quantitative XPS analyses suggest that the chlorine is associated with the platinum, likely forming a platinum chloride complex. This result suggests that for the catalyst samples reacted at 400 ° C and below, a complex was formed which contained a platinum to chlorine ratio of one. This would be consistent with the increase in the binding energy of platinum as illustrated in Figure 14. For the catalyst reacted at 450 ° C, the chlorine to platinum ratio suggests that a platinum chloride complex different than the one formed at 350 ° C and 400 ° C has been formed. Further, the shift in the platinum binding energy suggests that the presence of the additional chlorine atom has increased the oxidation state of platinum. It should be noted, however, that the binding energy reported for the catalyst reacted at 450 ° C corresponds very well to platinum in the +4 oxidation state. Since the oxidation state of chlorine is -1, the platinum chloride complex which was formed by reaction with chloroform at 450 ° C would have to have other atoms associated with it in order to account for the +4 oxidation state. Likely, the additional atoms would be either oxygen or hydroxide ions.

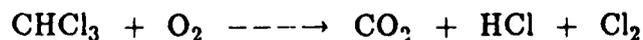
The Pt/Al ratio is presented to provide an indication regarding changes in the dispersion of platinum. The higher the ratio, the greater platinum dispersion one would expect for catalyst samples with similar platinum loadings. At reaction temperatures of 400 ° C and below, the Pt/Al ratio as determined by XPS is consistent with that of the calcined catalyst, indicating that the dispersion of the platinum has not changed as a result of the reaction exposure. At 450 ° C, the Pt/Al ratio has decreased significantly from that of the calcined catalyst. It is possible that the change in platinum dispersion may contribute to the deactivation observed when operating at 450 ° C. However, for 2 % platinum supported on a low surface area catalyst, the dispersion would be expected to be low initially, consequently, further changes in dispersion may not have a significant impact on the catalyst activity. It is also possible that the decrease in the Pt/Al ratio was a result of chlorine "shielding" the platinum from detection, or that platinum has been lost from the catalyst via the volatilization of platinum chloride complexes. Changes in the platinum metal content have not been examined.

One possible explanation for the deactivation data reported here is as follows. At temperatures of 400 °C and below, the metallic platinum is transformed into a platinum(II) chloride complex. The activity of this complex is similar to that of platinum metal and the complex is stable; hence, the rate of catalytic deactivation resulting from exposure to chloroform is minimal (Figures 3 and 4). Upon increasing the reaction temperature to 450 °C, the platinum is transformed into platinum(IV), possibly through a chloride intermediate. Assuming the activity of the platinum(IV) to be less than that of the metallic platinum, the catalytic activity decreases. At a certain point in time, all the platinum has been transformed into platinum(IV), and the catalytic activity stabilizes. This behavior is consistent with the data reported in Figure 5, where following 70 to 80 hours on stream, the catalytic activity begins to stabilize.

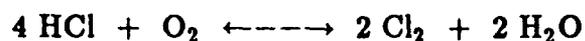
Chloroform contains the hetroatom chlorine which is a potential catalyst poison. In addition, oxidation of chloroform yields chlorine and hydrochloric acid, which can potentially degrade the catalyst support. As was stated earlier, rapid deactivation of the catalytic material would be a potential method for defeating a catalytic filter. However, results indicate that any deactivation of the catalyst resulting from exposure to chloroform will be minimal despite the large chlorine dose the catalyst was exposed to. Based on the deactivation study, it would not be possible to defeat a catalytic filter with chloroform via a deactivation mechanism.

### 5.3 *Reaction Products.*

The only reaction product identified in the reactor effluent via GC analysis was CO<sub>2</sub>. No carbon monoxide was present, indicating that the chloroform was not being partially oxidized to carbon monoxide. No chlorine containing products were detected in the reactor effluent using the GC technique. Carbon balances were typically 90% or better for all runs conducted in this study. Results of the acid gas analysis provided an indication as to what percent of the chlorine associated with the chloroform were transformed into acid gases. The oxidation of chloroform would be expected to proceed according to:



Because of the presence of H<sub>2</sub>O, HCl and Cl<sub>2</sub>, the Deacon reaction must be considered. The Deacon reaction proceeds according to:



Equilibrium constants were calculated for the Deacon reaction using the relationship provided by Arnold and Kobe<sup>20</sup> and were determined to be between 93.1 (400 °C) and 3,575 (300 °C) for the temperature range investigated in this study. These values indicate that the reaction equilibrium would be shifted towards the formation of chlorine. We were unable to find any indications in the literature as to whether or not (or how significantly) the Deacon reaction is catalyzed over supported platinum. However, analysis of the Deacon reaction indicates that for the temperature range investigated in this study, chlorine (Cl<sub>2</sub>) would be the favored reaction product, formed in stoichiometric yields at a minimum.

Chlorine balances (based on the *reacted* chloroform) were between 60 and 80 % for all conditions investigated, as reported in Table 3. Due to the quantity of chloroform that the catalyst had been exposed to, it is unlikely that the discrepancies in the chlorine balances could be attributed simply to the accumulation of chlorine on the catalyst. Discrepancies in the chlorine balance were attributed to the inefficiency of the cold trap in capturing chlorine gas.

From the data reported in Table 3, conversion and temperature had little effect on the chlorine balance. The chlorine balance was, however, observed to increase with increasing time-on-stream. For example, at 400 °C the chlorine balance was 57 % during the first three hours of the run. The chlorine balance increased to 77 % during the following three hour period, and remained essentially constant for the sample collected overnight. The same trend was observed for the run conducted at 300 °C. The increase in the chlorine balance with time-on-stream was attributed to the accumulation of chlorine onto the catalyst support during the initial catalyst exposure.

As stated earlier, the generation of toxic vapors from low toxicity compounds is a potential mechanism for defeating a catalytic filter. Exposure of a catalytic filter to chloroform will yield HCl and Cl<sub>2</sub> in unacceptable levels. Acid gases are, however, reactive and therefore may be easily removed by either reaction with the filter construction material, or by the design of a down stream acid gas scrubbing system.

#### 5.4 Reaction Kinetics.

The five kinetic rate expressions evaluated in this study are reported in Table 2. None of the rate expressions evaluated in this study took into account the concentration of oxygen. This is because the concentration of oxygen was constant and in great excess for all runs, and as a constant the term would only divide out of the rate expression. A term accounting for inhibition due to the presence of water in the feed stream was also omitted from the above rate expressions. The inhibition effect of water was found to be constant, to within experimental error, for feed streams with dew point temperatures greater than 6 °C. Therefore, slight changes in the air dew point temperature would not be expected to influence the results.

Rate expressions 1 through 5 were evaluated for their ability to correlate the kinetic data. Rate expressions 1 and 2 are similar, with rate expression 2 containing an additional term in the denominator to account for inhibition due to adsorption of the reaction product(s). The term  $K_p C_p$  was added to the denominator of rate expression 2 because acid gases, likely HCl and Cl<sub>2</sub>, were detected in the reactor effluent and are potential catalytic inhibitors. Rate expression 5 accounts for only the inhibition due to the adsorption of the reaction product(s). Rate expressions 1, 2 and 5 may be derived by assuming the reaction occurs between adsorbed oxygen and gas phase chloroform (Eley-Rideal mechanism), or that the reaction occurs via adsorption and decomposition of the chloroform onto an oxidized platinum surface. Mechanistic assumptions similar to those listed above have been proposed in an effort to describe the oxidation of organic molecules over platinum catalysts<sup>3,4,10,11,21</sup>. Rate expressions 3 and 4 are similar, with rate expression 4 containing a product(s) inhibition term in the denominator. Rate expressions 3 and 4 may be derived by assuming the reaction occurs between an adsorbed chloroacetonitrile molecule and an adsorbed oxygen atom (Langmuir-Hinshelwood mechanism). In rate expression 4, the term  $K_p C_p$  has been added to the denominator to account for inhibition due to adsorption of reaction product(s) onto active sites. Voltz et al.<sup>8</sup>, and Hawkins and Wanke<sup>9</sup> developed kinetic rate expressions following the above assumptions to describe the oxidation of propylene and carbon monoxide, and ethylene, respectively, over supported platinum catalysts.

The standard deviations calculated at each of the five reaction temperatures are reported in Table 5. All kinetic fit parameters determined for rate expressions 1 through 5 were positive in sign and followed the expected trends, i.e., the rate constant increased with increasing temperature, and the adsorption equilibrium constants decreased with increasing temperature. The use of rate expressions 1, 3 and 5 resulted in a very poor data correlation. The inability of these correlations to describe the data are illustrated in Figures 6a, 6c and 6e, respectively. Rate

expressions 1 and 3 were able to provide a somewhat accurate correlation of the lower concentration data (100 to 1,000 ppm, 533 to 5,326 mg/m<sup>3</sup>), but were unable to correlate the experimental data at the higher challenge concentrations (1,000 to 5,050 ppm, 5,326 to 26,898 mg/m<sup>3</sup>), most notably whenever the conversion exceeded 50%. Addition of the product(s) inhibition term to rate expressions 1 and 3 resulted in improving the data correlation (see Table 5). The improved data correlation may be observed by comparing the data correlation presented in Figure 6a (rate expression 1) to the data correlation presented in Figure 6b (rate expression 2). The reason for the improved data correlation obtained with rate expression 2 may be deduced from the form of the rate expression. As conversion increases, rate expression 1 predicts a decreased inhibition effect (the term  $K_a C_a$  no longer dominates the denominator). Consequently, the conversion versus residence time curve becomes very sharp as conversion increases above 50% (Figure 6b). With rate expression 2, the decrease in the inhibition effect of the reactant with increasing conversion is offset by an increase in the inhibition resulting from the reaction product(s). Thus the conversion versus residence time curve becomes much smoother in the region where conversion exceeds 50%. Both rate expressions 2 and 4 were able to correlate the experimental data better than rate expressions 1, 3 and 5. A comparison of the data correlation obtained with equations 2 and 4 may be made by comparing figures 6b and 6d. Note from this figure that rate expression 2 provides a better data correlation than rate expression 4; i.e. the correlation in the region of high concentration and high conversions more closely follows the data. The standard deviations calculated for rate expression 2 was between 1.5 to 2 times less than that calculated for rate expression 4. Based on a comparison of Figures 6a through 6e and the standard deviations reported in Table 2, rate expression 2 provided the best data correlation and was therefore used to describe the kinetic data for the oxidation of chloroform.

Figures 7 through 10 report conversion as a function of residence time for reaction temperatures of 325 °C, 350 °C, 375 °C and 400 °C. The solid lines in the figures represent the conversion obtained by incorporation of kinetic rate expression 2 into the fixed bed reactor design equation. The kinetic fit parameters used in generating all curves were obtained from the Arrhenius equations corresponding to the reaction rate constant and adsorption equilibrium constants. These results demonstrate that rate expression 2 provides an accurate data correlation over the wide range of concentrations and temperatures investigated in this study.

To assess the physical significance of the product inhibition term,  $K_p C_p$ , the catalyst activity was evaluated in the presence and absence of 5,000 ppm HCl in the feed stream. The results shown in Figure 11 indicate that the addition of HCl to the feed stream results in a greater reaction temperature being required to achieve a

similar chloroform conversion. These results indicate that HCl is a strong catalytic inhibitor and is consistent with previously reported studies<sup>3,4</sup>. A similar test with chlorine gas was not performed. Because of the inhibition effects of HCl, physical significance may be assigned to the product inhibition term.

The rate constant and the adsorption equilibrium constants were determined at each reaction temperature, and then correlated using the Arrhenius equation. An Arrhenius plot of the rate constant,  $k$ , is reported in Figure 12.  $k$  was calculated to be  $0.3720 \times 10^9 \exp(-21,700/RT) \text{ s}^{-1}$ . Arrhenius plots of the adsorption equilibrium constants,  $K_a$  and  $K_p$ , are reported in Figures 13a and 13b, respectively.  $K_p$  was calculated to be  $0.1785 \times 10^8 \exp(+2,435/RT) \text{ cm}^3/\text{mol}$ , while  $K_a$  was calculated to be  $0.1229 \times 10^7 \exp(+5,328/RT) \text{ cm}^3/\text{mol}$ . The activation energy reported for the rate constant is consistent with values reported for oxidation of organic compounds over platinum catalysts<sup>3,4,8,9,11,22</sup>. The values for the heats of reaction are lower than one would expect, however, values of this magnitude have been reported by Weldon and Senkan for the oxidation of methylchloride over a chromium/alumina catalyst<sup>23</sup>. The adsorption equilibrium constants follow the trend one would expect, i.e., the constants decrease with increasing reaction temperature and are positive in sign.

Weldon and Senkan<sup>23</sup> determined a kinetic rate expression for the oxidation of methylchloride using a chromium/alumina catalyst operating at temperatures between 340 °C and 470 °C. Weldon and Senkan recorded reaction rates using a differential reactor, keeping conversions between 5 and 20 %. Data were correlated using a rate expression which accounted for inhibition due to the adsorption of methylchloride onto the catalyst. Their equation was similar in form to equation 3 reported here. Of note is that the authors do not include a term in their rate expression to take into account any inhibition effects due to the adsorption of HCl and  $\text{Cl}_2$  (observed reaction products). However, under differential conversions, the concentrations of HCl and  $\text{Cl}_2$  would be low compared to that of methylchloride, and therefore, a product inhibition term would be difficult to justify statistically from their data. Klinghoffer and Rossin<sup>2,3</sup> conducted a kinetic study involving the oxidation of chloroacetonitrile over a supported platinum catalyst. In this study, integral conversions were studied, and the authors found it necessary to employ a rate expression which included terms in the denominator which accounted for the inhibition due to adsorption of both reactants and products (namely HCl and  $\text{HNO}_3$ ). The form of the rate expression employed in modeling the kinetic data was identical to equation 2.

It was not the objective of this study to determine a reaction mechanism for the oxidation of chloroform, however, certain mechanistic observations may be made based on the form of the rate expression. The form of rate expression 2 suggests that the reaction proceeds via either decomposition of chloroform onto an oxidized platinum surface or via reaction between adsorbed oxygen and gas phase chloroform. The form of the rate expression also indicates that the reaction is strongly inhibited by both the reactant and the reaction product(s). The present study does not necessarily show that the reactions corresponding to rate equation 2 describe the true mechanism. However, rate equation 2 was found to accurately correlate the experimental data over a wide range of concentrations and temperatures.

## 6. CONCLUSIONS

For a supported platinum catalyst operating below 400°C, deactivation of the catalyst due to poisoning by chloroform would be insignificant. Acid gas reaction products, likely chlorine gas and hydrochloric acid, are present in the reactor effluent. These acid gases are not retained on the catalytic filter. Kinetic rate expression 2 provides an accurate correlation of the kinetic data recorded over a wide range of conditions. The rate expression takes into account inhibition by both the reactant and the reaction product(s).

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## APPENDIX A: LIST OF SYMBOLS

|         |  |
|---------|--|
| $C_a^0$ | Feed concentration of chloroacetonitrile, mols/cm <sup>3</sup> .         |
| $C_a$   | Concentration of chloroacetonitrile, mols/cm <sup>3</sup>                |
| $C_p$   | Concentration of product, mol/cm <sup>3</sup>                            |
| $F_a^0$ | Chloroacetonitrile flow rate, mols/s                                     |
| $k$     | Reaction rate constant, s <sup>-1</sup>                                  |
| $k_s$   | Reaction rate constant, mol/s-g-cat                                      |
| $K_a$   | Chloroacetonitrile adsorption equilibrium constant, cm <sup>3</sup> /mol |
| $K_p$   | Product(s) adsorption equilibrium constant, cm <sup>3</sup> /mol         |
| Rate    | Rate of chloroacetonitrile oxidation, mols/s-g-cat                       |
| $W$     | Catalyst weight, g   |
| $x$     | Fractional conversion, dimensionless                                     |
| $\rho$  | Catalyst density, g/cm <sup>3</sup>                                      |
| $\tau$  | Residence time, s  |

**Blank**

## APPENDIX B: COMPUTER CODES FOR ESTIMATING FIT PARAMETERS

---

```

c
c
c   This routine determines the fit parameters from a given
c   data set for the rate equation:
c
c
c           A*Ca
c   Rate =  -----
c           1 + B*Cp + D*Ca
c
c   Where: A, B, and D are the fit parameters
c           Ca is the concentration of reactant a
c           Cp is the concentration of product p
c
c   This rate equation is incorporated into the design
c   equation for a fixed bed reactor operating in the integral
c   mode. The integrated form of the design equation is:
c
c   W/F = (1/A*Ca0)*ln(1/1-x) + (B/A)*ln(1/1-x) + (D - B)*x/A
c
c   Where: W is the catalyst weight in grams
c           F is the reactant flow rate, mols/sec
c           Ca0 is the reactant feed concentration, mols/cm**3
c           x is the fractional conversion
c
c   The fit parameters are solved using either a linear or nonlinear
c   least squares routine.

```

---

```

IMPLICIT REAL*8 (A-H,O-Z)
CHARACTER*12 FNAME
DIMENSION CA0(25), WF(25), X(25), Z(3,4), U(3)
DATA ZERO /0.0D00/, ONE /1.0D00/, TWO /2.0D00/, NCOUNT /0/
WRITE(*,1)
READ(*,2) FNAME
1 FORMAT(2X,'INPUT NAME OF DATA FILE:')
2 FORMAT(A12)
OPEN (1,FILE=FNAME)
REWIND(1)
Write(*,11)
READ(*,14) T
14 FORMAT(D12.6)
11 FORMAT(2X,'INPUT REACTION TEMPERATURE, C')
DO 10 J = 1, 25
  READ(1,15,END=20) WF(J), CA0(J), X(J)
  IF(X(J).GT.ONE) X(J) = X(J)/1.0D02
  NCOUNT = NCOUNT + 1
10 CONTINUE
15 FORMAT(3D15.6)
20 CONTINUE
29 CONTINUE
WRITE(*,32)
READ(*,31) K3
32 FORMAT(2X,'DO YOU WISH TO DETERMINE THE FIT PARAMETERS USING',/,
1 2X,'A LINEAR OR NON-LINEAR METHOD?',/,
2 2X,'LINEAR FIT ENTER 1',/,

```

```

3 2X,'NON-LINEAR FIT ENTER 2',/)
31 FORMAT(I2)
   IF(K3.EQ.1) GOTO 99
   IF(K3.EQ.2) GOTO 199
   GOTO 29
99 CONTINUE

```

---

c This loop computes the sums for the least squares approximation.

---

```

DO 100 J = 1, NCOUNT
  SUMWF = SUMWF + WF(J)
  SMWFX = SMWFX + WF(J)*X(J)
  SMWFXX = SMWFXX + WF(J)*X(J)*X(J)
  Q = DLOG(ONE/(ONE - X(J)))
  QC = Q/CA0(J)
  SUM1 = SUM1 + QC
  SUM1X = SUM1X + QC*X(J)
  SUM1XX = SUM1XX + QC*X(J)*X(J)
  SUM2 = SUM2 + Q
  SUM2X = SUM2X + Q*X(J)
  SUM2XX = SUM2XX + Q*X(J)*X(J)
  SUMX = SUMX + X(J)
  SUMXX = SUMXX + X(J)*X(J)
  SUMXXX = SUMXXX + X(J)*X(J)*X(J)
100 CONTINUE
  Z(1,1) = SUM1
  Z(2,1) = SUM1X
  Z(3,1) = SUM1XX
  Z(1,2) = SUM2
  Z(2,2) = SUM2X
  Z(3,2) = SUM2XX
  Z(1,3) = SUMX
  Z(2,3) = SUMXX
  Z(3,3) = SUMXXX
  Z(1,4) = SUMWF
  Z(2,4) = SMWFX
  Z(3,4) = SMWFXX
  KORD = 3
  KORD1 = 4
  CALL GAUSS(KORD,KORD1,Z,U)
  A = ONE/U(1)
  B = U(2)*A
  D = A*U(3) + B
  WRITE(*,109) A, B, D
109 FORMAT(2X,'A= ',D12.6,5X,'B = ',D12.6,5X,'D = ',D12.6)
  WRITE(*,112)
  READ(*,114) ISTART
112 FORMAT(2X,'DO YOU WISH TO USE THESE VALUES AS INITIAL',/,
1 2X,'GUESSES FOR THE NON-LINEAR LEAST SQUARES?',/,
2 2X,'0 - NO, 1 - YES',/)
114 FORMAT(I2)
   IF(ISTART.EQ.1) GOTO 199
   GOTO 501
199 CONTINUE

```

c This loop computes the sums for the non-linear least squares  
 c method.

```

IF(ISTART.EQ.1) GOTO 41
WRITE(*,30)
READ(*,40) A, B, D
30 FORMAT(2X,'INPUT INITIAL VALUES OF A B, D:')
40 FORMAT(D12.6,/,D12.6,/,D12.6)
41 CONTINUE
TOL = 1.0d-07
44 FORMAT(D12.6)
DO 500 K = 1, 1000
ICOUNT = ICOUNT + 1
AOLD = A
BOLD = B
DOLD = D
A1 = A*1.00001D00
B1 = B*1.00001D00
D1 = D*1.00001D00
F1 = ZERO
F1A = ZERO
F1B = ZERO
F1D = ZERO
F2 = ZERO
F2A = ZERO
F2B = ZERO
F2D = ZERO
F3 = ZERO
F3A = ZERO
F3B = ZERO
F3D = ZERO
F4 = ZERO
F4A = ZERO
F4B = ZERO
F4D = ZERO
F5 = ZERO
F5A = ZERO
F5B = ZERO
F5D = ZERO
F6 = ZERO
F6A = ZERO
F6B = ZERO
F6D = ZERO
DO 101 J = 1, NCOUNT
Q = DLOG(ONE/(ONE - X(J)))
Y = (ONE/(A*CA0(J)) + B/A)*Q + (D - B)*X(J)/A
YA = (ONE/(A1*CA0(J)) + B/A1)*Q + (D - B)*X(J)/A1
YB = (ONE/(A*CA0(J)) + B1/A)*Q + (D - B1)*X(J)/A
YD = (ONE/(A*CA0(J)) + B/A)*Q + (D1 - B)*X(J)/A
DWDA = ((-ONE/(A*A*CA0(J)) - B/(A*A))*Q - (D - B)*X(J)/(A*A))/Y
DWDA1 = ((-ONE/(A1*A1*CA0(J)) - B/(A1*A1))*Q
1 - (D - B)*X(J)/(A1*A1))/YA
DWDA2 = ((-ONE/(A*A*CA0(J)) - B1/(A*A))*Q

```

```

1      - (D - B1)*X(J)/(A*A))/YB
DWDAD = ((-ONE/(A*A*CA0(J)) - B/(A*A))*Q
1      - (D1 - B)*X(J)/(A*A))/YD
DWDB = (Q/A - X(J)/A)/Y
DWDBA = (Q/A1 - X(J)/A1)/YA
DWDBB = (Q/A - X(J)/A)/YB
DWDBD = (Q/A - X(J)/A)/YD
DWDD = X(J)/(A*Y)
DWDDA = X(J)/(A1*YA)
DWddb = X(J)/(A*YB)
DWDDD = X(J)/(A*YD)
F1 = DLOG(WF(J))*DWDA + F1
F1A = DLOG(WF(J))*DWDA + F1A
F1B = DLOG(WF(J))*DWDA + F1B
F1D = DLOG(WF(J))*DWDA + F1D
F2 = DLOG(Y)*DWDA + F2
F2A = DLOG(YA)*DWDA + F2A
F2B = DLOG(YB)*DWDA + F2B
F2D = DLOG(YD)*DWDA + F2D
F3 = DLOG(WF(J))*DWDB + F3
F3A = DLOG(WF(J))*DWDBA + F3A
F3B = DLOG(WF(J))*DWDBB + F3B
F3D = DLOG(WF(J))*DWDBD + F3D
F4 = DLOG(Y)*DWDB + F4
F4A = DLOG(YA)*DWDBA + F4A
F4B = DLOG(YB)*DWDBB + F4B
F4D = DLOG(YD)*DWDBD + F4D
F5 = DLOG(WF(J))*DWDD + F5
F5A = DLOG(WF(J))*DWDDA + F5A
F5B = DLOG(WF(J))*DWddb + F5B
F5D = DLOG(WF(J))*DWDDD + F5D
F6 = DLOG(Y)*DWDD + F6
F6A = DLOG(YA)*DWDDA + F6A
F6B = DLOG(YB)*DWddb + F6B
F6D = DLOG(YD)*DWDDD + F6D
101 CONTINUE
F1 = TWO*F1 - TWO*F2
F1A = TWO*F1A - TWO*F2A
F1B = TWO*F1B - TWO*F2B
F1D = TWO*F1D - TWO*F2D
F2 = TWO*F3 - TWO*F4
F2A = TWO*F3A - TWO*F4A
F2B = TWO*F3B - TWO*F4B
F2D = TWO*F3D - TWO*F4D
F3 = TWO*F5 - TWO*F6
F3A = TWO*F5A - TWO*F6A
F3B = TWO*F5B - TWO*F6B
F3D = TWO*F5D - TWO*F6D
Z(1,1) = (F1 - F1A)/(A - A1)
Z(2,1) = (F2 - F2A)/(A - A1)
Z(3,1) = (F3 - F3A)/(A - A1)
Z(1,2) = (F1 - F1B)/(B - B1)
Z(2,2) = (F2 - F2B)/(B - B1)
Z(3,2) = (F3 - F3B)/(B - B1)

```

```

Z(1,3) = (F1 - F1D)/(D - D1)
Z(2,3) = (F2 - F2D)/(D - D1)
Z(3,3) = (F3 - F3D)/(D - D1)
Z(1,4) = - F1
Z(2,4) = - F2
Z(3,4) = - F3
KORD = 3
KORD1 = 4
CALL GAUSS(KORD,KORD1,Z,U)
A = AOLD + U(1)
B = BOLD + U(2)
D = DOLD + U(3)
110 FORMAT(2X,'A=',D12.6,3X,'B=',D12.6,3X,'D=',D12.6,
1 3X,'ERR=',d12.6)
ERRA = (DABS((A - AOLD)/A))**TWO
ERRB = (DABS((B - BOLD)/B))**TWO
ERRD = (DABS((D - DOLD)/D))**TWO
ERR = DSQRT(ERRA + ERRB + ERRD)/TWO
WRITE(*,110) A, B, D, ERR
IF(ERR.LE.TOL) GOTO 501
500 CONTINUE
501 CONTINUE

```

---

c Computes conversion based on fit parameters a, b, and d

---

```

TOLN = 1.0D-05
OPEN(4,FILE='MODEL1.OUT',STATUS='NEW')
DO 200 J = 1, NCOUNT
  X1 = 0.1
  DO 210 K = 1, 15
    XOLD = X1
    IF(X1.GT.ONE) X1 = .95D00
    IF(X1.LT.ZERO) X1 = .05D00
    F = WF(J) - (ONE/(A*CA0(J)))*DLOG(ONE/(ONE - X1))
1    - (B/A)*DLOG(ONE/(ONE - X1)) - (D-B)*X1/A
    FP = - (ONE/A)*(ONE/CA0(J) + B)*(ONE/(ONE-X1))
1    - (D-B)/A
    X1 = X1 - F/FP
    EPS = DABS(X1 - XOLD)
    IF(EPS.LE.TOLN) GOTO 220
210 CONTINUE
220 CONTINUE
XC = CA0(J)*(T + 273.15d00)*1.0d06*82.054d00
IC = INT(XC)
WF1 = ONE/(A*CA0(J))*DLOG(ONE/(ONE - X(J)))
1  + (B/A)*DLOG(ONE/(ONE - X(J))) + (D-B)*X(J)/A
WNORM = DABS(WF1 - WF(J))*DABS(WF1 - WF(J))/(WF(J)*WF(J))
1  + WNORM
XNORM = DABS(X1 - X(J))*DABS(X1 - X(J)) + XNORM
WRITE(*,225) X1, X(J), IC
WRITE(4,225) X1, X(J), IC
200 CONTINUE
225 FORMAT(2X,'Xpred = ',f8.4,4x,'Xexp = ',f8.4,4x,'[C] = ',i5)
XNORM = XNORM**0.5d00/dble((NCOUNT - 1))

```

```

WNORM = WNORM**0.5D00/DBLE((NCOUNT - 1))
WRITE(4,226) XNORM, WNORM
WRITE(*,226) XNORM, WNORM
WRITE(*,110) A, B, D, ERR
WRITE(4,110) A, B, D, ERR
OPEN(1,FILE='MODEL1.OUT',STATUS='NEW')
226 FORMAT(/,17X,'XNORM = ',F8.4/,17X,'WNORM + ',F8.4)
STOP
END

```

```

SUBROUTINE GAUSS(KORD,KORD1,A,P5)
IMPLICIT REAL*8 (A-H,O-Z)
DIMENSION A(3,4), P5(3)
KORD1 = KORD + 1
KORD2 = KORD - 1
DO 100 N1 = 1,KORD
  N3 = N1 + 1
  DO 101 N2 = N3,KORD
    IF(DABS(A(N2,N1)).GT.DABS(A(N1,N1))) GOTO 105
    GOTO 101
105  DO 106 I = 1,KORD1
      SAVE1 = A(N2,I)
      SAVE2 = A(N1,I)
      A(N1,I) = SAVE1
106  A(N2,I) = SAVE2
101  CONTINUE
  DO 115 N = N1,KORD
    ASAVE = A(N,N1)
    IF(DABS(ASAVE).LE.1.0D-50) GOTO 115
    DO 116 M = N1,KORD1
      A(N,M) = A(N,M)/ASAVE
116  CONTINUE
115  CONTINUE
    IF(N1.EQ.KORD) GOTO 100
    NEQ = N1 + 1
    DO 120 N = NEQ,KORD
      IF(DABS(A(N,N1)).LE.1.0D-50) GOTO 120
      DO 121 N2 = N1,KORD1
        IF(DABS(A(N1,N)).LE.1.0D-50) GOTO 121
        A(N,N2) = A(N1,N2) - A(N,N2)
121  CONTINUE
120  CONTINUE
100 CONTINUE
  P5(KORD) = A(KORD,KORD1)
  DO 200 N = 1,KORD2
    RHS = 0.0D00
    DO 210 I = 1,N
210  RHS = P5(KORD1-I)*A(KORD-N,KORD1-I) + RHS
200  P5(KORD-N) = A(KORD-N,KORD1) - RHS
  RETURN
END

```

---

c  
c This routine determines the fit parameters from a given  
c data set for the rate equation:  
c  
c 
$$\text{Rate} = \frac{A \cdot C_a}{1 + D \cdot C_a}$$
  
c  
c Where: A, and D are the fit parameters  
c  $C_a$  is the concentration of reactant a  
c  
c This rate equation is incorporated into the design  
c equation for a fixed bed reactor operating in the integral  
c mode. The integrated form of the design equation is:  
c  
c 
$$W/F = (1/A \cdot C_{a0}) \cdot \ln(1/1-x) + D \cdot x/A$$
  
c  
c Where: W is the catalyst weight in grams  
c F is the reactant flow rate, mols/sec  
c  $C_{a0}$  is the reactant feed concentration, mols/cm<sup>3</sup>  
c x is the fractional conversion  
c  
c The fit parameters are solved using either a linear or nonlinear  
c least squares routine.

---

```

IMPLICIT REAL*8 (A-H,O-Z)
CHARACTER*12 FNAME
DIMENSION CA0(25), WF(25), X(25), Z(3,4), U(3)
DATA ZERO /0.0D00/, ONE /1.0D00/, TWO /2.0D00/, NCOUNT /0/
WRITE(*,1)
READ(*,2) FNAME
1 FORMAT(2X,'INPUT NAME OF DATA FILE:')
2 FORMAT(A12)
OPEN (1,FILE=FNAME)
REWIND(1)
DO 10 J = 1, 25
  READ(1,15,END=20) WF(J), CA0(J), X(J)
  IF(X(J).GT.ONE) X(J) = X(J)/1.0D02
  NCOUNT = NCOUNT + 1
10 CONTINUE
15 FORMAT(3D15.6)
20 CONTINUE
29 CONTINUE
WRITE(*,32)
READ(*,31) K3
32 FORMAT(2X,'DO YOU WISH TO DETERMINE THE FIT PARAMETERS USING',/,
1 2X,'A LINEAR OR NON-LINEAR METHOD?',/,
2 2X,'LINEAR FIT ENTER 1',/,
3 2X,'NON-LINEAR FIT ENTER 2',/)
31 FORMAT(I2)
IF(K3.EQ.1) GOTO 99
IF(K3.EQ.2) GOTO 199
GOTO 29

```

99 CONTINUE

---

c This loop computes the sums for the least squares approximation.

---

```
DO 100 J = 1, NCOUNT
  SUMWF = SUMWF + WF(J)
  SMWFX = SMWFX + WF(J)*X(J)
  Q = DLOG(ONE/(ONE - X(J)))
  QC = Q/CA0(J)
  SUM1 = SUM1 + QC
  SUM1X = SUM1X + QC*X(J)
  SUMX = SUMX + X(J)
  SUMXX = SUMXX + X(J)*X(J)
100 CONTINUE
  Z(1,1) = SUM1
  Z(2,1) = SUM1X
  Z(1,2) = SUMX
  Z(2,2) = SUMXX
  Z(1,3) = SUMWF
  Z(2,3) = SMWFX
  KORD = 2
  KORD1 = 3
  CALL GAUSS(KORD,KORD1,Z,U)
  A = ONE/U(1)
  D = U(2)*A
  WRITE(*,110) A, D
110 FORMAT(2X,'A = ',D12.6,5X,'D = ',D12.6)
  WRITE(*,112)
  READ(*,114) ISTART
112 FORMAT(2X,'DO YOU WISH TO USE THESE VALUES AS INITIAL',/,
  1 2X,'GUESSES FOR THE NON-LINEAR LEAST SQUARES?',/,
  2 2X,'0 - NO, 1 - YES',/)
114 FORMAT(I2)
  IF(ISTART.EQ.1) GOTO 199
  GOTO 501
199 CONTINUE
```

---

c This loop computes the sums for the non-linear least squares  
c method.

---

```
IF(ISTART.EQ.1) GOTO 41
WRITE(*,30)
READ(*,40) A, D
30 FORMAT(2X,'INPUT INITIAL VALUES OF A, D:')
40 FORMAT(D12.6,/,D12.6)
41 CONTINUE
WRITE(*,42)
READ(*,44) TOL
42 FORMAT(2X,'INPUT ERROR TOL. FOR NEWTON:')
44 FORMAT(D12.6)
DO 500 K = 1, 1000
  ICOUNT = ICOUNT + 1
  AOLD = A
  DOLD = D
```

```

A1 = A*1.00001D00
D1 = D*1.00001D00
F1 = ZERO
F1A = ZERO
F1D = ZERO
F2 = ZERO
F2A = ZERO
F2D = ZERO
F3 = ZERO
F3A = ZERO
F3D = ZERO
F4 = ZERO
F4A = ZERO
F4D = ZERO
DO 101 J = 1, NCOUNT
  Q = DLOG(ONE/(ONE - X(J)))
  Y = Q/(A*CA0(J)) + D*X(J)/A
  YA = Q/(A1*CA0(J)) + D*X(J)/A1
  YD = Q/(A*CA0(J)) + D1*X(J)/A
  DWDA = (Q/(A*A*CA0(J)) - D*X(J)/(A*A))/Y
  DWDA A = (Q/(A1*A1*CA0(J)) - D*X(J)/(A1*A1))/YA
  DWDA D = (Q/(A*A*CA0(J)) - D1*X(J)/(A*A))/YD
  DWDD = X(J)/(A*Y)
  DWDDA = X(J)/(A1*YA)
  DWDDD = X(J)/(A*YD)
  F1 = DLOG(WF(J))*DWDA + F1
  F1A = DLOG(WF(J))*DWDA A + F1A
  F1D = DLOG(WF(J))*DWDA D + F1D
  F2 = DLOG(Y)*DWDA + F2
  F2A = DLOG(YA)*DWDA A + F2A
  F2D = DLOG(YD)*DWDA D + F2D
  F3 = DLOG(WF(J))*DWDD + F3
  F3A = DLOG(WF(J))*DWDDA + F3A
  F3D = DLOG(WF(J))*DWDDD + F3D
  F4 = DLOG(Y)*DWDD + F4
  F4A = DLOG(YA)*DWDDA + F4A
  F4D = DLOG(YD)*DWDDD + F4D
101 CONTINUE
  F1 = TWO*F1 - TWO*F2
  F1A = TWO*F1A - TWO*F2A
  F1D = TWO*F1D - TWO*F2D
  F2 = TWO*F3 - TWO*F4
  F2A = TWO*F3A - TWO*F4A
  F2D = TWO*F3D - TWO*F4D
  Z(1,1) = (F1 - F1A)/(A - A1)
  Z(2,1) = (F2 - F2A)/(A - A1)
  Z(1,2) = (F1 - F1D)/(D - D1)
  Z(2,2) = (F2 - F2D)/(D - D1)
  Z(1,3) = - F1
  Z(2,3) = - F2
  KORD = 2
  KORD1 = 3
  CALL GAUSS(KORD,KORD1,Z,U)
  A = AOLD + U(1)

```

```

      D = DOLD + U(2)
119  FORMAT(2X,'A=',D12.6,3X,'D=',D12.6,
1     3X,'ERR=',d12.6)
      ERR = (DABS((A - AOLD)/A))**TWO
      ERRD = (DABS((D - DOLD)/D))**TWO
      ERR = DSQRT(ERRA + ERRD)
      WRITE(*,119) A, D, ERR
      IF(ERR.LE.TOL) GOTO 501
500  CONTINUE
501  CONTINUE
c-----
c  Computes conversion based on fit parameters a and d
c-----
      TOLN = 1.0D-05
      DO 200 J = 1, NCOUNT
          X1 = X(J)
          DO 210 K = 1, 15
              XOLD = X1
              IF(X1.GT.ONE) X1 = 0.95D00
              IF(X1.LT.ZERO) X1 = 0.05D00
              F = WF(J) - (ONE/(A*CA0(J)))**DLOG(ONE/(ONE - X1))
1             - D*X1/A
              FP = - ONE/(A*CA0(J))*(ONE/(ONE-X1)) - D/A
              X1 = X1 - F/FP
              EPS = DABS(X1 - XOLD)
              IF(EPS.LE.TOLN) GOTO 220
210   CONTINUE
220   CONTINUE
          WF1 = ONE/(A*CA0(J))*DLOG(ONE/(ONE - X(J))) + D*X(J)/A
          WNORM = (DABS(WF1 - WF(J))/WF(J))**TWO + WNORM
          XNORM = (DABS(X1 - X(J)))**TWO + XNORM
          WRITE(*,225) X1, X(J), K
200  CONTINUE
225  FORMAT(2X,'Xpred = ',f8.4,4x,'Xexp = ',f8.4,4x,'K = ',i5)
      XNORM = DSQRT(XNORM)/(NCOUNT - 1)
      WNORM = DSQRT(WNORM)/(NCOUNT - 1)
      WRITE(*,226) XNORM, WNORM
226  FORMAT(/,17X,'NORM = ',F8.4,/,17X,'WNORM = ',F8.4)
      STOP
      END

      SUBROUTINE GAUSS(KORD,KORD1,A,P5)
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION A(3,4), P5(3)
      KORD1 = KORD + 1
      KORD2 = KORD - 1
      DO 100 N1 = 1,KORD
          N3 = N1 + 1
          DO 101 N2 = N3,KORD
              IF(DABS(A(N2,N1)).GT.DABS(A(N1,N1))) GOTO 105
              GOTO 101
105   DO 106 I = 1,KORD1
              SAVE1 = A(N2,I)
              SAVE2 = A(N1,I)

```

```

      A(N1,I) = SAVE1
106      A(N2,I) = SAVE2
101      CONTINUE
      DO 115 N = N1,KORD
      ASAVE = A(N,N1)
      IF(DABS(ASAVE).LE.1.0D-50) GOTO 115
      DO 116 M = N1,KORD1
      A(N,M) = A(N,M)/ASAVE
116      CONTINUE
115      CONTINUE
      IF(N1.EQ.KORD) GOTO 100
      NEQ = N1 + 1
      DO 120 N = NEQ,KORD
      IF(DABS(A(N,N1)).LE.1.0D-50) GOTO 120
      DO 121 N2 = N1,KORD1
      IF(DABS(A(N1,N)).LE.1.0D-50) GOTO 121
      A(N,N2) = A(N1,N2) - A(N,N2)
121      CONTINUE
120      CONTINUE
100      CONTINUE
      P5(KORD) = A(KORD,KORD1)
      DO 200 N = 1,KORD2
      RHS = 0.0D00
      DO 210 I = 1,N
210      RHS = P5(KORD1-I)*A(KORD-N,KORD1-I) + RHS
200      P5(KORD-N) = A(KORD-N,KORD1) - RHS
      RETURN
      END

```

---

```

c
c
c This routine determines the fit parameters from a given
c data set for the rate equation:
c
c
c      A*Ca
c      Rate = -----
c      (1 + B*Cp)**2
c
c Where: A, B, and D are the fit parameters
c      Ca is the concentration of reactant a
c
c This rate equation is incorporated into the design
c equation for a fixed bed reactor operating in the integral
c mode. The integrated form of the design equation is:
c
c W/F = (1/A*Ca0)*ln(1/1-x) + (2B/A)x + B*B*Ca0*x*(1-x/2)/A
c
c Where: W is the catalyst weight in grams
c      F is the reactant flow rate, mols/sec
c      Ca0 is the reactant feed concentration, mols/cm**3
c      x is the fractional conversion
c
c The fit parameters are solved using either a linear or nonlinear
c least squares routine.

```

---

```

IMPLICIT REAL*8 (A-H,O-Z)
CHARACTER*12 FNAME
DIMENSION CA0(25), WF(25), X(25), Z(2,3), U(2)
DATA ZERO /0.0D00/, ONE /1.0D00/, TWO /2.0D00/, NCOUNT /0/
WRITE(*,1)
READ(*,2) FNAME
1 FORMAT(2X,'INPUT NAME OF DATA FILE:')
2 FORMAT(A12)
OPEN (1,FILE=FNAME)
REWIND(1)
DO 10 J = 1, 25
  READ(1,15,END=20) WF(J), CA0(J), X(J)
  IF(X(J).GT.ONE) X(J) = X(J)/1.0D02
  NCOUNT = NCOUNT + 1
10 CONTINUE
15 FORMAT(3D15.6)
20 CONTINUE

```

---

```

c This loop computes the sums for the non-linear least squares
c method.

```

---

```

WRITE(*,30)
READ(*,40) A, B
30 FORMAT(2X,'INPUT INITIAL VALUES OF A, B:')
40 FORMAT(D12.6,/,D12.6)
41 CONTINUE
WRITE(*,42)
READ(*,44) TOL

```

```

42 FORMAT(2X,'INPUT ERROR TOL. FOR NEWTON:')
44 FORMAT(D12.6)
DO 500 K = 1, 1000
ICOUNT = ICOUNT + 1
AOLD = A
BOLD = B
A1 = A*1.00001D00
B1 = B*1.00001D00
F1 = ZERO
F1A = ZERO
F1B = ZERO
F2 = ZERO
F2A = ZERO
F2B = ZERO
F3 = ZERO
F3A = ZERO
F3B = ZERO
F4 = ZERO
F4A = ZERO
F4B = ZERO
DO 101 J = 1, NCOUNT
  Q = DLOG(ONE/(ONE - X(J)))
  Y = Q/(A*CA0(J)) + TWO*B*X(J)/A
1  + B*B*CA0(J)*X(J)*(ONE - X(J)/TWO)/A
  YA = Q/(A1*CA0(J)) + TWO*B*X(J)/A1
1  + B*B*CA0(J)*X(J)*(ONE - X(J)/TWO)/A1
  YB = Q/(A*CA0(J)) + TWO*B1*X(J)/A
1  + B1*B1*CA0(J)*X(J)*(ONE - X(J)/TWO)/A
  DWDA = - Q/(A*A*CA0(J)) - TWO*B*X(J)/(A*A)
1  - B*B*CA0(J)*X(J)*(ONE - X(J)/TWO)/(A*A)
  DWDA = DWDA/Y
  DWDAA = - Q/(A1*A1*CA0(J)) - TWO*B*X(J)/(A1*A1)
1  - B*B*CA0(J)*X(J)*(ONE - X(J)/TWO)/(A1*A1)
  DWDAA = DWDAA/YA
  DWDAB = - Q/(A*A*CA0(J)) - TWO*B1*X(J)/(A*A)
1  - B1*B1*CA0(J)*X(J)*(ONE - X(J)/TWO)/(A*A)
  DWDAB = DWDAB/YB
  DWDB = (TWO*X(J)/A + TWO*B*CA0(J)*X(J)*(ONE - X(J)/TWO)/A)/Y
  DWDBA = (TWO*X(J)/A1 +
1  TWO*B*CA0(J)*X(J)*(ONE - X(J)/TWO)/A1)/YA
  DWDBB = (TWO*X(J)/A +
1  TWO*B1*CA0(J)*X(J)*(ONE - X(J)/TWO)/A)/YB

  F1 = DLOG(WF(J))*DWDA + F1
  F1A = DLOG(WF(J))*DWDAA + F1A
  F1B = DLOG(WF(J))*DWDAB + F1B
  F2 = DLOG(Y)*DWDA + F2
  F2A = DLOG(YA)*DWDAA + F2A
  F2B = DLOG(YB)*DWDAB + F2B
  F3 = DLOG(WF(J))*DWDB + F3
  F3A = DLOG(WF(J))*DWDBA + F3A
  F3B = DLOG(WF(J))*DWDBB + F3B
  F4 = DLOG(Y)*DWDB + F4
  F4A = DLOG(YA)*DWDBA + F4A

```

```

      F4B = DLOG(YB)*DWDBB + F4B
101 CONTINUE
      F1 = TWO*F1 - TWO*F2
      F1A = TWO*F1A - TWO*F2A
      F1B = TWO*F1B - TWO*F2B
      F2 = TWO*F3 - TWO*F4
      F2A = TWO*F3A - TWO*F4A
      F2B = TWO*F3B - TWO*F4B
      Z(1,1) = (F1 - F1A)/(A - A1)
      Z(2,1) = (F2 - F2A)/(A - A1)
      Z(1,2) = (F1 - F1B)/(B - B1)
      Z(2,2) = (F2 - F2B)/(B - B1)
      Z(1,3) = - F1
      Z(2,3) = - F2
      KORD = 2
      KORD1 = 3
      CALL GAUSS(KORD,KORD1,Z,U)
      A = AOLD + U(1)
      B = BOLD + U(2)
110 FORMAT(2X,'A=',D12.6,3X,'B=',D12.6,3X,'ERR=',d12.6)
      ERRA = (DABS((A - AOLD)/A))**TWO
      ERRB = (DABS((B - BOLD)/B))**TWO
      ERR = DSQRT(ERRA + ERRB)
      WRITE(*,110) A, B, ERR
      IF(ERR.LE.TOL) GOTO 501
500 CONTINUE
501 CONTINUE

```

---

c Computes conversion based on fit parameters a, b, and d

---

```

      TOLN = 1.0D-05
      DO 200 J = 1, NCOUNT
          X1 = X(J)
          DO 210 K = 1, 15
              XOLD = X1
              IF(X1.GT.ONE) X1 = .95D00
              IF(X1.LT.ZERO) X1 = .05D00
              F = WF(J) - (ONE/(A*CA0(J)))*DLOG(ONE/(ONE - X1))
                - TWO*B*X1/A - B*B*CA0(J)*X1*(ONE - X1/TWO)/A
              FP = - (ONE/A)*(ONE/CA0(J) + B)*(ONE/(ONE-X1))
                - TWO*B/A - B*B*CA0(J)*(ONE - X1)/A
              X1 = X1 - F/FP
              EPS = DABS(X1 - XOLD)
              IF(EPS.LE.TOLN) GOTO 220
210 CONTINUE
220 CONTINUE
          WF1 = (ONE/(A*CA0(J)))*DLOG(ONE/(ONE - X(J)))
            + TWO*B*X(J)/A + B*B*CA0(J)*X(J)*(ONE - X(J)/TWO)/A
          XNORM = (DABS(X1 - X(J)))**TWO + XNORM
          WNORM = (DABS(WF1 - WF(J))/WF(J))**TWO + WNORM
          C = CA0(J)*628.15D00*82.054D00*1.0D06
          IC = INT(C)
          WRITE(*,225) X1, X(J), IC
200 CONTINUE

```

```

225 FORMAT(2X,'Xpred = ',f8.4,4x,'Xexp = ',f8.4,4x,'[C] = ',i7)
   XNORM = DSQRT(XNORM)/(NCOUNT - 1)
   WNORM = DSQRT(WNORM)/(NCOUNT - 1)
   WRITE(*,226) XNORM, WNORM
226 FORMAT(/,17X,'NORM = ',F8.4,/,17X,'WNORM = ',F8.4)
STOP
END

```

```

SUBROUTINE GAUSS(KORD,KORD1,A,P5)
IMPLICIT REAL*8 (A-H,O-Z)
DIMENSION A(2,3), P5(2)
KORD1 = KORD + 1
KORD2 = KORD - 1
DO 100 N1 = 1,KORD
   N3 = N1 + 1
   DO 101 N2 = N3,KORD
      IF(DABS(A(N2,N1)).GT.DABS(A(N1,N1))) GOTO 105
      GOTO 101
105   DO 106 I = 1,KORD1
      SAVE1 = A(N2,I)
      SAVE2 = A(N1,I)
      A(N1,I) = SAVE1
106   A(N2,I) = SAVE2
101   CONTINUE
      DO 115 N = N1,KORD
         ASAVE = A(N,N1)
         IF(DABS(ASAVE).LE.1.0D-50) GOTO 115
         DO 116 M = N1,KORD1
            A(N,M) = A(N,M)/ASAVE
116   CONTINUE
115   CONTINUE
         IF(N1.EQ.KORD) GOTO 100
         NEQ = N1 + 1
         DO 120 N = NEQ,KORD
            IF(DABS(A(N,N1)).LE.1.0D-50) GOTO 120
            DO 121 N2 = N1,KORD1
               IF(DABS(A(N1,N)).LE.1.0D-50) GOTO 121
               A(N,N2) = A(N1,N2) - A(N,N2)
121   CONTINUE
120   CONTINUE
100  CONTINUE
      P5(KORD) = A(KORD,KORD1)
      DO 200 N = 1,KORD2
         RHS = 0.0D00
         DO 210 I = 1,N
            210  RHS = P5(KORD1-I)*A(KORD-N,KORD1-I) + RHS
            200  P5(KORD-N) = A(KORD-N,KORD1) - RHS
      RETURN
END

```

c  
c  
c This routine determines the fit parameters from a given  
c data set for the rate equation:

$$\text{Rate} = \frac{A \cdot C_a}{(1 + B \cdot C_p + D \cdot C_a)^{**2}}$$

c  
c Where: A, B, and D are the fit parameters  
c C<sub>a</sub> is the concentration of reactant a  
c C<sub>p</sub> is the concentration of product p

c  
c This rate equation is incorporated into the design  
c equation for a fixed bed reactor operating in the integral  
c mode. The integrated form of the design equation is:

$$\begin{aligned} W/F = & (1/A \cdot C_{a0} + 2B/A + B \cdot B \cdot C_{a0}/A) \cdot \ln(1/1-x) + \\ & (D \cdot D \cdot C_{a0}/A - 2B/A + 2D/A - B \cdot B \cdot C_{a0}/A) \cdot x - \\ & (D \cdot D/A - 2B \cdot D/A + B \cdot B/A) \cdot x \cdot x \cdot C_{a0}/2 \end{aligned}$$

c  
c Where: W is the catalyst weight in grams  
c F is the reactant flow rate, mols/sec  
c C<sub>a0</sub> is the reactant feed concentration, mols/cm<sup>3</sup>  
c x is the fractional conversion

c  
c The fit parameters are solved using a linear least  
c squares routine.

---

```

IMPLICIT REAL*8 (A-H,O-Z)
CHARACTER*12 FNAME
DIMENSION CA0(25), WF(25), X(25), Z(3,4), U(3)
DATA ZERO /0.0D00/, ONE /1.0D00/, TWO /2.0D00/, NCOUNT /0/
WRITE(*,1)
READ(*,2) FNAME
1 FORMAT(2X,'INPUT NAME OF DATA FILE:')
2 FORMAT(A12)
OPEN (1,FILE=FNAME)
REWIND(1)
DO 10 J = 1, 25
  READ(1,15,END=20) WF(J), CA0(J), X(J)
  IF(X(J).GT.ONE) X(J) = X(J)/1.0D02
  NCOUNT = NCOUNT + 1
10 CONTINUE
15 FORMAT(3D15.6)
20 CONTINUE

```

c  
c This loop computes the sums for the non-linear least squares  
c method.

---

```

WRITE(*,30)
READ(*,40) A, B, D
30 FORMAT(2X,'INPUT INITIAL VALUES OF A, B, D:')
40 FORMAT(D12.6,/,D12.6,/,D12.6)

```

```

41 CONTINUE
  WRITE(*,42)
  READ(*,44) TOL
42 FORMAT(2X,'INPUT ERROR TOL. FOR NEWTON:')
44 FORMAT(D12.6)
  DO 500 K = 1, 1000
  ICOUNT = ICOUNT + 1
  AOLD = A
  BOLD = B
  DOLD = D
  A1 = A*1.00001D00
  B1 = B*1.00001D00
  D1 = D*1.00001D00
  F1 = ZERO
  F1A = ZERO
  F1B = ZERO
  F1D = ZERO
  F2 = ZERO
  F2A = ZERO
  F2B = ZERO
  F2D = ZERO
  F3 = ZERO
  F3A = ZERO
  F3B = ZERO
  F3D = ZERO
  F4 = ZERO
  F4A = ZERO
  F4B = ZERO
  F4D = ZERO
  F5 = ZERO
  F5A = ZERO
  F5B = ZERO
  F5D = ZERO
  F6 = ZERO
  F6A = ZERO
  F6B = ZERO
  F6D = ZERO
  DO 101 J = 1, NCOUNT
    Q = DLOG(ONE/(ONE - X(J)))
    Y = (ONE/(A*CA0(J)) + TWO*B/A + B*B*CA0(J)/A)*Q
  1   + (D*D*CA0(J)/A - TWO*B/A + TWO*D/A - B*B*CA0(J)/A)*X(J)
  2   - (D*D - TWO*B*D + B*B)*CA0(J)*X(J)*X(J)/(A*TWO)
    YA = (ONE/CA0(J) + TWO*B + B*B*CA0(J))*Q/A1
  1   + (D*D*CA0(J) - TWO*B + TWO*D - B*B*CA0(J))*X(J)/A1
  2   - (D*D - TWO*B*D + B*B)*CA0(J)*X(J)*X(J)/(A1*TWO)
    YB = (ONE/CA0(J) + TWO*B1 + B1*B1*CA0(J))*Q/A
  1   + (D*D*CA0(J) - TWO*B1 + TWO*D - B1*B1*CA0(J))*X(J)/A
  2   - (D*D - TWO*B1*D + B1*B1)*CA0(J)*X(J)*X(J)/(A*TWO)
    YD = (ONE/CA0(J) + TWO*B + B*B*CA0(J))*Q/A
  1   + (D1*D1*CA0(J) - TWO*B + TWO*D1 - B*B*CA0(J))*X(J)/A
  2   - (D1*D1 - TWO*B*D1 + B*B)*CA0(J)*X(J)*X(J)/(A*TWO)
    DWDA = ((- ONE/CA0(J) - TWO*B - B*B*CA0(J))*Q/(A*A)
  1   + (-D*D*CA0(J) + TWO*B - TWO*D + B*B*CA0(J))*X(J)/(A*A)
  2   + (D*D - TWO*B*D + B*B)*CA0(J)*X(J)*X(J)/(A*A*TWO))/Y

```

$DWDA = ((- ONE/CAO(J) - TWO*B - B*B*CAO(J))^Q/(A1*A1)$   
1  $+ (-D*D*CAO(J) + TWO*B - TWO*D + B*B*CAO(J))^X(J)/(A1*A1)$   
2  $+ (D*D - TWO*B*D + B*B)*CAO(J)*X(J)*X(J)/(A1*A1*TWO))/YA$   
 $DWDAB = ((- ONE/CAO(J) - TWO*B1 - B1*B1*CAO(J))^Q/(A*A)$   
1  $+ (-D*D*CAO(J) + TWO*B1 - TWO*D + B1*B1*CAO(J))^X(J)/(A*A)$   
2  $+ (D*D - TWO*B1*D + B1*B1)*CAO(J)*X(J)*X(J)/(A*A*TWO))/YB$   
 $DWDAD = ((- ONE/CAO(J) - TWO*B - B*B*CAO(J))^Q/(A*A)$   
1  $+ (-D1*D1*CAO(J) + TWO*B - TWO*D1 + B*B*CAO(J))^X(J)/(A*A)$   
2  $+ (D1*D1 - TWO*B*D1 + B*B)*CAO(J)*X(J)*X(J)/(A*A*TWO))/YD$   
 $DWDB = ((TWO/A + TWO*B*CAO(J)/A)*Q$   
1  $+ (-TWO/A - TWO*B*CAO(J)/A)*X(J)$   
2  $- (B - D)*CAO(J)*X(J)*X(J)/A)/Y$   
 $DWDBA = ((TWO/A1 + TWO*B*CAO(J)/A1)*Q$   
1  $+ (-TWO/A1 - TWO*B*CAO(J)/A1)*X(J)$   
2  $- (B - D)*CAO(J)*X(J)*X(J)/A1)/YA$   
 $DWDBB = ((TWO/A + TWO*B1*CAO(J)/A)*Q$   
1  $+ (-TWO/A - TWO*B1*CAO(J)/A)*X(J)$   
2  $- (B1 - D)*CAO(J)*X(J)*X(J)/A)/YB$   
 $DWDBD = ((TWO/A + TWO*B*CAO(J)/A)*Q$   
1  $+ (-TWO/A - TWO*B*CAO(J)/A)*X(J)$   
2  $- (B - D1)*CAO(J)*X(J)*X(J)/A)/YD$   
 $DWDD = ((TWO*D*CAO(J) + TWO)*X(J)/A$   
1  $- (D - B)*CAO(J)*X(J)*X(J)/A)/Y$   
 $DWDDA = ((TWO*D*CAO(J) + TWO)*X(J)/A1$   
1  $- (D - B)*CAO(J)*X(J)*X(J)/A1)/YA$   
 $DWddb = ((TWO*D*CAO(J) + TWO)*X(J)/A$   
1  $- (D - B1)*CAO(J)*X(J)*X(J)/A)/YB$   
 $DWDDD = ((TWO*D1*CAO(J) + TWO)*X(J)/A$   
1  $- (D1 - B)*CAO(J)*X(J)*X(J)/A)/YD$   
 $F1 = DLOG(WF(J))*DWDA + F1$   
 $F1A = DLOG(WF(J))*DWDA + F1A$   
 $F1B = DLOG(WF(J))*DWDAB + F1B$   
 $F1D = DLOG(WF(J))*DWDAD + F1D$   
 $F2 = DLOG(Y)*DWDA + F2$   
 $F2A = DLOG(YA)*DWDA + F2A$   
 $F2B = DLOG(YB)*DWDAB + F2B$   
 $F2D = DLOG(YD)*DWDAD + F2D$   
 $F3 = DLOG(WF(J))*DWDB + F3$   
 $F3A = DLOG(WF(J))*DWDBA + F3A$   
 $F3B = DLOG(WF(J))*DWDBB + F3B$   
 $F3D = DLOG(WF(J))*DWDBD + F3D$   
 $F4 = DLOG(Y)*DWDB + F4$   
 $F4A = DLOG(YA)*DWDBA + F4A$   
 $F4B = DLOG(YB)*DWDBB + F4B$   
 $F4D = DLOG(YD)*DWDBD + F4D$   
 $F5 = DLOG(WF(J))*DWDD + F5$   
 $F5A = DLOG(WF(J))*DWDDA + F5A$   
 $F5B = DLOG(WF(J))*DWddb + F5B$   
 $F5D = DLOG(WF(J))*DWDDD + F5D$   
 $F6 = DLOG(Y)*DWDD + F6$   
 $F6A = DLOG(YA)*DWDDA + F6A$   
 $F6B = DLOG(YB)*DWddb + F6B$   
 $F6D = DLOG(YD)*DWDDD + F6D$

101 CONTINUE

```

F1 = TWO*F1 - TWO*F2
F1A = TWO*F1A - TWO*F2A
F1B = TWO*F1B - TWO*F2B
F1D = TWO*F1D - TWO*F2D
F2 = TWO*F3 - TWO*F4
F2A = TWO*F3A - TWO*F4A
F2B = TWO*F3B - TWO*F4B
F2D = TWO*F3D - TWO*F4D
F3 = TWO*F5 - TWO*F6
F3A = TWO*F5A - TWO*F6A
F3B = TWO*F5B - TWO*F6B
F3D = TWO*F5D - TWO*F6D
Z(1,1) = (F1 - F1A)/(A - A1)
Z(2,1) = (F2 - F2A)/(A - A1)
Z(3,1) = (F3 - F3A)/(A - A1)
Z(1,2) = (F1 - F1B)/(B - B1)
Z(2,2) = (F2 - F2B)/(B - B1)
Z(3,2) = (F3 - F3B)/(B - B1)
Z(1,3) = (F1 - F1D)/(D - D1)
Z(2,3) = (F2 - F2D)/(D - D1)
Z(3,3) = (F3 - F3D)/(D - D1)
Z(1,4) = - F1
Z(2,4) = - F2
Z(3,4) = - F3
KORD = 3
KORD1 = 4
CALL GAUSS(KORD,KORD1,Z,U)
A = AOLD + U(1)
B = BOLD + U(2)
D = DOLD + U(3)
110 FORMAT(2X,'A=',D12.6,3X,'B=',D12.6,3X,'D=',D12.6,
1      3X,'ERR=',d12.6)
ERRA = (DABS((A - AOLD)/A))**TWO
ERRB = (DABS((B - BOLD)/B))**TWO
ERRD = (DABS((D - DOLD)/D))**TWO
ERR = DSQRT(ERRA + ERRB + ERRD)/TWO
WRITE(*,110) A, B, D, ERR
IF(ERR.LE.TOL) GOTO 501
500 CONTINUE
501 CONTINUE

```

---

c Computes conversion based on fit parameters a, b, and d

---

```

TOLN = 1.0D-05
DO 200 J = 1, NCOUNT
  X1 = X(J)
  DO 210 K = 1, 15
    XOLD = X1
    IF(X1.GT.ONE) X1 = .95D00
    IF(X1.LT.ZERO) X1 = .05D00
    Q = DLOG(ONE/(ONE - X1))
    QP = ONE/(ONE - X1)
    F = WF(J) - (ONE/CA0(J) + TWO*B + B*B*CA0(J))*Q/A
1      - ((D*D - B*B)*CA0(J) - TWO*(B-D))*X1/A

```

```

2      + (D*D - two*B*D + B*B)*CA0(J)*X1*X1/(TWO*A)
FP = - (ONE/CA0(J) + TWO*B + B*B*CA0(J))*QP/A
1      - ((D*D - B*B)*CA0(J) - TWO*(B-D))/A
2      + (D*D - TWO*B*D + B*B)*CA0(J)*X1/A
X1 = X1 - F/FP
EPS = DABS(X1 - XOLD)
IF(EPS.LE.TOLN) GOTO 220
210  CONTINUE
220  CONTINUE
      Q = DLOG(ONE/(ONE - X(J)))
      WF1 = (ONE/CA0(J) + TWO*B + B*B*CA0(J))*Q/A
1      + ((D*D - B*B)*CA0(J) - TWO*(B-D))*X(J)/A
2      - (D*D - TWO*B*D + B*B)*CA0(J)*X(J)*X(J)/(TWO*A)
WNORM = WNORM + (DABS(WF1 - WF(J))/WF(J))**TWO
XNORM = XNORM + (DABS(X1 - X(J)))**TWO
WRITE(*,225) X1, X(J), K
200  CONTINUE
225  FORMAT(2X,'Xpred = ',f8.4,4x,'Xexp = ',f8.4,4x,'K = ',i5)
XNORM = DSQRT(XNORM)/(NCOUNT - 1)
WNORM = DSQRT(WNORM)/(NCOUNT - 1)
WRITE(*,226) XNORM,WNORM
226  FORMAT(/,17X,'NORM = ',F8.4,/, 'WNORM = ',F8.4)
STOP
END

```

```

SUBROUTINE GAUSS(KORD,KORD1,A,P5)
IMPLICIT REAL*8 (A-H,O-Z)
DIMENSION A(3,4), P5(3)
KORD1 = KORD + 1
KORD2 = KORD - 1
DO 100 N1 = 1,KORD
  N3 = N1 + 1
  DO 101 N2 = N3,KORD
    IF(DABS(A(N2,N1)).GT.DABS(A(N1,N1))) GOTO 105
    GOTO 101
105   DO 106 I = 1,KORD1
      SAVE1 = A(N2,I)
      SAVE2 = A(N1,I)
      A(N1,I) = SAVE1
106   A(N2,I) = SAVE2
101  CONTINUE
      DO 115 N = N1,KORD
        ASAVE = A(N,N1)
        IF(DABS(ASAVE).LE 1.0D-50) GOTO 115
        DO 116 M = N1,KORD1
          A(N,M) = A(N,M)/ASAVE
116  CONTINUE
115  CONTINUE
      IF(N1.EQ.KORD) GOTO 100
      NEQ = N1 + 1
      DO 120 N = NEQ,KORD
        IF(DABS(A(N,N1)) LE 1.0D-50) GOTO 120
        DO 121 N2 = N1,KORD1
          IF(DABS(A(N1,N2)).LE.1.0D-50) GOTO 121

```

```
      A(N,N2) = A(N1,N2) - A(N,N2)
121      CONTINUE
120      CONTINUE
100      CONTINUE
      P5(KORD) = A(KORD,KORD1)
      DO 200 N = 1,KORD2
        RHS = 0.0D00
        DO 210 I = 1,N
          210      RHS = P5(KORD1-I)*A(KORD-N,KORD1-I) + RHS
          200      P5(KORD-N) = A(KORD-N,KORD1) - RHS
      RETURN
      END
```

c-----  
c PRODUCT INHIBITION ONLY  
c  
c This routine determines the fit parameters from a given  
c data set for the rate equation:

$$\text{Rate} = \frac{A \cdot C_a}{1 + B \cdot C_p}$$

c  
c Where: A, B are the fit parameters  
c Ca is the concentration of reactant a  
c Cp is the concentration of product p

c This rate equation is incorporated into the design  
c equation for a fixed bed reactor operating in the integral  
c mode. The integrated form of the design equation is:

$$W/F = (1/A \cdot C_{a0}) \cdot \ln(1/1-x) + (B/A) \cdot \ln(1/1-x) - B \cdot x/A$$

c  
c Where: W is the catalyst weight in grams  
c F is the reactant flow rate, mols/sec  
c Ca0 is the reactant feed concentration, mols/cm\*\*3  
c x is the fractional conversion

c The fit parameters are solved using nonlinear  
c least squares routine.

c-----  
IMPLICIT REAL\*8 (A-H,O-Z)  
CHARACTER\*12 FNAME  
DIMENSION CA0(25), WF(25), X(25), Z(2,3), U(2)  
DATA ZERO /0.0D00/, ONE /1.0D00/, TWO /2.0D00/, NCOUNT /0/  
WRITE(\*,1)  
READ(\*,2) FNAME  
1 FORMAT(2X,'INPUT NAME OF DATA FILE:')  
2 FORMAT(A12)  
OPEN (1,FILE=FNAME)  
REWIND(1)  
Write(\*,11)  
READ(\*,14) T  
14 FORMAT(D12.6)  
11 FORMAT(2X,'INPUT REACTION TEMPERATURE, C')  
DO 10 J = 1, 25  
READ(1,15,END=20) WF(J), CA0(J), X(J)  
IF(X(J).GT.ONE) X(J) = X(J)/1.0D02  
NCOUNT = NCOUNT + 1  
10 CONTINUE

15 FORMAT(3D15.6)

20 CONTINUE

c

c This loop computes the sums for the non-linear least squares  
c method.

c

WRITE(\*,30)

READ(\*,40) A, B, D

30 FORMAT(2X,'INPUT INITIAL VALUES OF A, B, D:')

40 FORMAT(D12.6,/,D12.6,/,D12.6)

TOL = 1.0d-07

44 FORMAT(D12.6)

DO 500 K = 1, 100

ICOUNT = ICOUNT + 1

AOLD = A

BOLD = B

DOLD = D

A1 = A\*1.00001D00

B1 = B\*1.00001D00

D1 = D\*1.00001D00

F1 = ZERO

F1A = ZERO

F1B = ZERO

F2 = ZERO

F2A = ZERO

F2B = ZERO

F3 = ZERO

F3A = ZERO

F3B = ZERO

F4 = ZERO

F4A = ZERO

F4B = ZERO

F5 = ZERO

F5A = ZERO

F5B = ZERO

F6 = ZERO

F6A = ZERO

F6B = ZERO

DO 101 J = 1, NCOUNT

Q = DLOG(ONE/(ONE - X(J)))

Y = (ONE/(A\*CA0(J)) + B/A)\*Q - B\*X(J)/A

YA = (ONE/(A1\*CA0(J)) + B/A1)\*Q - B\*X(J)/A1

YB = (ONE/(A\*CA0(J)) + B1/A)\*Q - B1\*X(J)/A

DWDA = ((-ONE/(A\*A\*CA0(J)) - B/(A\*A))\*Q + B\*X(J)/(A\*A))/Y

DWDA1 = ((-ONE/(A1\*A1\*CA0(J)) - B/(A1\*A1))\*Q

1 + B\*X(J)/(A1\*A1))/YA

DWDA2 = ((-ONE/(A\*A\*CA0(J)) - B1/(A\*A))\*Q

```

1      + B1*X(J)/(A*A))/YB
      DWDB = (Q/A - X(J)/A)/Y
      DWDBA = (Q/A1 - X(J)/A1)/YA
      DWDBB = (Q/A - X(J)/A)/YB
      F1 = DLOG(WF(J))*DWDA + F1
      F1A = DLOG(WF(J))*DWDA + F1A
      F1B = DLOG(WF(J))*DWDA + F1B
      F2 = DLOG(Y)*DWDA + F2
      F2A = DLOG(YA)*DWDA + F2A
      F2B = DLOG(YB)*DWDA + F2B
      F3 = DLOG(WF(J))*DWDB + F3
      F3A = DLOG(WF(J))*DWDBA + F3A
      F3B = DLOG(WF(J))*DWDBB + F3B
      F4 = DLOG(Y)*DWDB + F4
      F4A = DLOG(YA)*DWDBA + F4A
      F4B = DLOG(YB)*DWDBB + F4B
101  CONTINUE
      F1 = TWO*F1 - TWO*F2
      F1A = TWO*F1A - TWO*F2A
      F1B = TWO*F1B - TWO*F2B
      F2 = TWO*F3 - TWO*F4
      F2A = TWO*F3A - TWO*F4A
      F2B = TWO*F3B - TWO*F4B
      Z(1,1) = (F1 - F1A)/(A - A1)
      Z(2,1) = (F2 - F2A)/(A - A1)
      Z(1,2) = (F1 - F1B)/(B - B1)
      Z(2,2) = (F2 - F2B)/(B - B1)
      Z(1,3) = - F1
      Z(2,3) = - F2
      KORD = 2
      KORD1 = 3
      CALL GAUSS(KORD,KORD1,Z,U)
      A = AOLD + U(1)
      B = BOLD + U(2)
110  FORMAT(2X,'A=',D12.6,3X,'B=',D12.6,3X,
1      3x,'ERR=',d12.6)
      ERRA = (DABS((A - AOLD)/A))**TWO
      ERRB = (DABS((B - BOLD)/B))**TWO
      ERR = DSQRT(ERRA + ERRB)
      WRITE(*,110) A, B, ERR
      IF(ERR.LE.TOL) GOTO 501
500  CONTINUE
501  CONTINUE
c-----
c   Computes conversion based on fit parameters a, and b
c-----
      TOLN = 1.0D-05

```

```

OPEN(4,FILE='MODEL1.OUT',STATUS='NEW')
DO 200 J = 1, NCOUNT
  X1 = X(J)
  DO 210 K = 1, 15
    XOLD = X1
    IF(X1.GT.ONE) X1 = .95D00
    IF(X1.LT.ZERO) X1 = .05D00
    F = WF(J) - (ONE/(A*CA0(J)))*DLOG(ONE/(ONE - X1))
1    - (B/A)*DLOG(ONE/(ONE - X1)) + B*X1/A
    FP = - (ONE/A)*(ONE/CA0(J) + B)*(ONE/(ONE-X1))
1    + B/A
    X1 = X1 - F/FP
    EPS = DABS(X1 - XOLD)
    IF(EPS.LE.TOLN) GOTO 220
210 CONTINUE
220 CONTINUE
    XC = CA0(J)*(T + 273.15d00)*1.0d06*82.054d00
    IC = INT(XC)
    WF1 = ONE/(A*CA0(J))*DLOG(ONE/(ONE - X(J)))
1    + (B/A)*DLOG(ONE/(ONE - X(J))) - B*X(J)/A
    WNORM = DABS(WF1 - WF(J))*DABS(WF1 - WF(J))/(WF(J)*WF(J))
1    + WNORM
    XNORM = DABS(X1 - X(J))*DABS(X1 - X(J)) + XNORM
    WRITE(*,225) X1, X(J), IC
    WRITE(4,225) X1, X(J), IC
200 CONTINUE
225 FORMAT(2X,'Xpred = ',f8.4,4x,'Xexp = ',f8.4,4x,'[C] = ',i5)
    XNORM = XNORM**0.5d00/dbl((NCOUNT - 1))
    WNORM = WNORM**0.5D00/DBLE((NCOUNT - 1))
    WRITE(4,226) XNORM, WNORM
    WRITE(*,226) XNORM, WNORM
    WRITE(*,110) A, B, D, ERR
    WRITE(4,110) A, B, D, ERR
    OPEN(1,FILE='MODEL1.OUT',STATUS='NEW')
226 FORMAT(/,17X,'XNORM = ',F8.4,/,17x,'WNORM + ',F8.4)
    STOP
    END

```

```

SUBROUTINE GAUSS(KORD,KORD1,A,P5)
IMPLICIT REAL*8 (A-H,O-Z)
DIMENSION A(2,3), P5(2)
KORD1 = KORD + 1
KORD2 = KORD - 1
DO 100 N1 = 1,KORD
  N3 = N1 + 1
  DO 101 N2 = N3,KORD
    IF(DABS(A(N2,N1)).GT.DABS(A(N1,N1))) GOTO 105

```