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A KINETIC STUDY OF THE UNCATALYZED HIGH PRESSURE OXIDATION OF PSEUDOCUMENE BY SULFUR DIOXIDE

A THESIS
SUBMITTED TO THE FACULTY OF GRADUATE STUDIES THROUGH
THE DEPARTMENT OF CHEMICAL ENGINEERING IN PARTIAL
FULFILMENT OF THE REQUIREMENTS OF THE DEGREE OF
MASTER OF APPLIED SCIENCE AT THE UNIVERSITY OF
WINDSOR

BY

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WINDSOR, ONTARIO

MAY, 1972.

DEDICATED TO :

CAROL AND PAMELA ANN

ABSTRACT

The oxidation of pseudocumene by sulfur dioxide at elevated temperatures and pressures was found to proceed according to the following expression,

$$-r_P = 1.85 (10^{28}) \cdot e^{-71,200/RT} \cdot C_P^{2.14}$$

where, $-r_P$ is the rate of consumption of pseudocumene in g.moles/liter/hour, 1.85 (10^{28}) is the frequency factor in $(\text{hr.})^{-1}(\text{g.moles/liter})^{-1.14}$, 71,200 is the activation energy in cal./g.mole, R is the gas constant (1.987 cal./ g.mole-°K), T is the temperature in °K, C_P is the concentration of pseudocumene in g.moles/liter, and 2.14 is the order of the reaction.

Pseudocumene was readily oxidized to its monocarboxylic acid derivatives, and, by increasing reaction time, to its dicarboxylic acid derivatives.

This study was carried out in the temperature range from 258 °C to 285 °C and for initial pressures of 260 atm. to 300 atm. Temperature control was maintained within ±3 °C of the reaction temperature for all experimental runs.

ACKNOWLEDGEMENTS

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E.E.M.

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I. INTRODUCTION

Commercial applications of trimellitic acid and trimellitic acid anhydride have encouraged a number of recent studies into their synthesis. Trimellitic acid has found use as an intermediate for coatings, plastics, polymers, and adhesives. Trimellitic anhydride is used in coatings, plasticizers and in the production of polyamide-imide resins.

The oxidation of pseudocumene to trimellitic acid is a logical consideration since its homologue, toluene, is readily oxidized to form benzoic acid. Pseudocumene, itself, is easily attainable from C_9 and C_{10} reformate streams. One (1) million pounds of this substance are produced annually.

The oxidation of pseudocumene by sulfur dioxide under high pressure and at elevated temperatures was the subject of a study by Shipman (10,11,12,13,14). In an exploratory study of the oxidation of a number of alkyl-substituted aromatics, he found the uncatalyzed oxidation of pseudocumene to trimellitic acid was feasible. Eighty (80) % yields of the acid were reported. The analysis of pressure-time data was used to find the rate of reaction proportional to the square of pseudocumene concentration. The activation energy was estimated in the range of

42 ± 2 kcal./mole. The validity of the analysis used by Shipman is not known, however, since little detail was available.

Morettin (9) designed a high pressure reactor for the purpose of studying this oxidation. No kinetic analysis resulted, but, for pressures approximately twice those used by Shipman, Morettin found the product of the oxidation was similar to the dicarboxylic acid derivatives of pseudocumene. Since only two (2) runs were performed, the results were not considered conclusive.

Considering the exploratory nature of these studies of the reaction, the present study was undertaken to :

(i) elucidate the reaction kinetics of the uncatalyzed oxidation of pseudocumene by sulfur dioxide for the temperature range from 258 °C to 285 °C and initial pressures of approx. 300 atm.

(ii) verify the nature of the product of the reaction.

II. LITERATURE SURVEY

The oxidation of pseudocumene to produce trimellitic acid has been reported by several researchers. The liquid phase oxidation process has received the attention of only a few investigations, however. The following is a brief review of the available information.

The use of chromic acid in glacial acetic acid or potassium permanganate and sodium hydroxide was reported to successfully oxidize pseudocumene to trimellitic acid in 1942 (4).

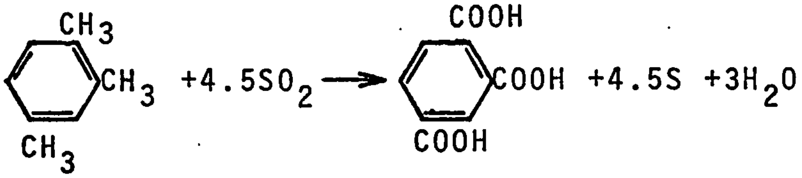
The oxidation of pseudocumene in the liquid phase was reported by Backlund (1, 2, 3). Addition of hot nitric acid to a water-pseudocumene mixture in the presence of HCl, HBr, NH_4Cl, and NH_4Br resulted in yields of 89% trimellitic acid for 1.5 hr. of reaction. Reaction temperatures of 200 to 250 ^{o}C were reported with pressures of 100 psig.

Kachurina et al (6) reported a catalyzed liquid phase process for this oxidation. An air oxidation under pressure with cobalt stearate catalyst was followed by the addition of water and nitric acid at 100-200 psig. in the presence of HCl and NH_4Cl. 97 % yields of trimellitic acid were cited.

Hofman et al (5) have studied the oxidation of pseudocumene by contacting with potassium t-butoxide or potassium hydroxide in hexamethylphosphoramide. The reaction was carried out at room temperature with oxygen passed through the mixture, but, only a 10 % yield of trimellitic acid was achieved in 3 hours.

Towle et al (16) reported the liquid phase oxidation of pseudocumene to trimellitic acid by the so-called " Mid-Century " process. This process makes use of a cobalt, molybdenum or manganese catalyst and a source of bromine for a regenerative source of chain-initiating free radicals. Reaction temperatures from 125 to 275 ^{o}C and 40 atm. pressure were employed. Excess oygen (5-15%) was found to prevent production of unwanted by-products.

Shipman (10,11,12,13,14) has reported the oxidation of a number of alkyl-substituted aromatics by sulfur dioxide under high pressure and at elevated temperatures. Pseudocumene was among those compounds studied. The overall reaction for pseudocumene was represented by the following,



(II-1)

As equation (II-1) indicates trimellitic acid was produced and Shipman reported yields of 80% for temperatures between 250 and 310 °C and for pressures from 100 to 500 atmospheres.

The experimental procedure commonly employed was to charge the reactor with a known weight of pseudocumene, assemble it into the furnace, heat to reaction temperature and pressurize with sulfur dioxide. As the reaction proceeded and the pressure fell, more sulfur dioxide was added to maintain reaction pressure. The best product recovery was achieved by cooling the reactor and dismantling it.

Trimellitic acid was recovered by water extraction. Acid recovered in this way was reported by Shipman to be 94 % pure.

Shipman reported the effect of reaction variables as follows :

(i) Temperature. The activation energy for the oxidation of pseudocumene was within the range of 42 ± 2 kcal./mole.

(ii) Concentration. The overall **rate** was proportional to the square of the pseudocumene concentration.

(iii) Pressure. The reaction rate decreases with increased pressure.

(iv) Purity of Reactants. Neither the reaction rate nor the product varied significantly with the purity of the reactants.

(v) Additives. The reaction was not affected by the presence of a few atmospheres of oxygen, free radical inhibitors and initiators, metal salts (sulfates, sulfites, sulfides of alkali and transition metals), metal oxides or chlorine compounds. The reaction was completely inhibited by the presence of metallic silver and copper. Bromine and iodine compounds catalyzed the reaction.

(vi) Solvents. Product quality was not improved significantly by use of benzene, acetic acid or water as solvents.

(vii) Product Yield. Yield may be limited by the formation of intermediate compounds and tars, and degradation to carbon. If the reaction were stopped before completion, small quantities of aldehydes were found. Even when the reaction is taken to completion, a small percentage of intermediate acids were present. In the case of pseudocumene, the major by- product was 4-methylphthalic acid.

Since aldehydes and hydrogen sulfide were found in significant quantities if the reaction were stopped before completion, Shipman proposed the following mechanism :

$$R\cdot CH_3 + SO_2 \longrightarrow R\cdot CHO + H_2O + S \qquad (II\text{-}2)$$

$$R\cdot CHO + 0.5SO_2 \longrightarrow R\cdot COOH + 0.5S \qquad (II\text{-}3)$$

$$R\cdot CH_3 + SO_2 \longrightarrow R\cdot COOH + H_2S \qquad (II\text{-}4)$$

$$H_2S + 0.5\,SO_2 \longrightarrow 1.5S + H_2O \qquad (II\text{-}5)$$

Shipman determined the reaction rate by measurement of pressure drop and elapsed time. Since the pressure fell due to the consumption of sulfur dioxide, pressure was intermittently restored by addition of sulfur dioxide. The mole fraction of pseudocumene was decreased as a result. Pressure drops were accumulated and plotted against time. The slope of this curve was assumed to be proportional to the reaction rate.

No mention was made of the method used to identify the products.

Morettin (9) carried out an exploratory study of the high pressure oxidation of pseudocumene by sulfur dioxide. Two (2) experimental runs at 252 °C and 273 °C were performed for pseudocumene concentrations of 1.19 and 3.72 g.moles/liter, respectively. Initial pressures were on the order of 10,500 psig. (approx. 700 atm.) and he allowed the pressure to decrease naturally during the reaction.

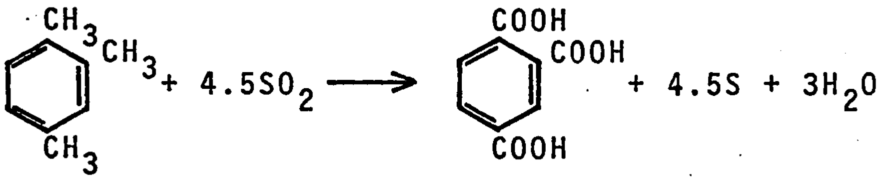
The product of this study was identified as a methyl-substituted carboxylic acid. The reaction rate was strongly dependent upon pseudocumene concentration. No kinetic analysis was attempted.

III. EXPERIMENTAL STRATEGY

According to the findings of Shipman (10), alkyl-substituted aromatics are oxidized to the corresponding carboxylic acid by sulfur dioxide at high pressure. The overall reaction was represented by the equation,

$$R \cdot CH_3 + 1.5SO_2 \longrightarrow R \cdot COOH + 1.5S + H_2O \qquad \text{(III-1)}$$

In the oxidation of pseudocumene by sulfur dioxide, the following was expected to apply,



(III-2)

Hence, the stoichiometric mole ratio of sulfur dioxide to pseudocumene was determined to be 4.5:1.0.

In order to evaluate the rate of consumption of pseudocumene, the following rate expression was proposed,

$$-r_P = k \cdot C_P^{\,A} \cdot C_S^{\,B} \qquad \text{(III-2)}$$

where $-r_P$ = the rate of consumption of pseudocumene in g.moles/liter,

k = the rate constant for the reaction in $(\text{hr.})^{-1}(\text{g.moles/liter})^{1-(A+B)}$,

C_P = the pseudocumene concentration in g.moles/l.,

A = the order of reaction with respect to pseudocumene, dimensionless,

C_S = the sulfur dioxide concentration in g.moles/l.

and, B = the order of reaction with respect to sulfur dioxide, dimensionless.

Experimental runs were then designed to evaluate the unknown quantities of equation (III-3). Stoichiometric and excess sulfur dioxide conditions were proposed for solution of the problem.

For stoichiometric conditions, the concentrations of pseudocumene and sulfur dioxide follow the expression,

$$4.5C_P = C_S \tag{III-4}$$

Substitution of (III-4) in (III-3) yielded,

$$-r_P = k_1 \cdot C_P^{\,n} \tag{III-5}$$

where $k_1 = 4.5^B k$ and $n = A + B$.

$$\text{But, } -r_P = -(dC_P/dt) \tag{III-6}$$

The combination of (III-5) and (III-6) yielded, upon integration,

$$C_{PO}^{\,1-n} - C_{PF}^{\,1-n} = (1-n)\cdot k_1 \cdot t \tag{III-7}$$

where the subscripts, 0 and F, denote initial and final conditions, respectively.

For excess sulfur dioxide conditions, the concentration of sulfur dioxide was assumed to be large enough to be essentially constant. Thus, at any time,

$$C_S = C_{SO} \qquad \text{(III-8)}$$

where C_{SO} is the initial concentration of sulfur dioxide in g.moles/liter.

Substitution of (III-8) in (III-3) and re-arrangement gives,

$$-(dC_P/dt) = k_2 \cdot C_P^{A} \qquad \text{(III-9)}$$

where $k_2 = k \cdot C_{SO}^{B}$.

Upon integration equation (III-9) becomes,

$$C_{PO}^{1-A} - C_{PF}^{1-A} = (1-A) \cdot k_2 \cdot t \qquad \text{(III-10)}$$

Therefore, two (2) runs for stoichiometric conditions and two (2) runs for excess conditions were required for solution of equations (III-7) and (III-10), respectively.

"Program GAUSHAUS " by Meeter (8), a non-linear least squares method, was chosen to evaluate the parameters. The program, itself, minimized the sum of the squares of the deviations in choosing the best values of the parameters. However, since two equations, (III-7) and (III-10), for stoichiometric and excess conditions, respectively, were required, the program was adjusted in order that the proper equation be associated with the proper data. Equations (III-7) and (III-10) were re-arranged for use in the program, as follows :

$$C_{PF} = (C_{PO}^{1-A-B} - ((1-A-B)\cdot 4.5^{B}\cdot k\cdot t))^{(1/(1-A-B))} \quad \ldots(III\text{-}11)$$

resulting from equation (III-7), stoichiometric conditions.

$$C_{PF} = (C_{PO}^{1-A} - ((1-A)\cdot C_{SO}^{B}\cdot k\cdot t))^{(1/(1-A))} \quad (III\text{-}12)$$

resulting from equation (III-10), excess sulfur dioxide conditions.

The input data were then tagged to allow the proper selection of working equation for each set of data.

Having established the order of the reaction for each reactant in this manner, several values of rate constant were to be evaluated for at least three (3) temperatures to determine the Arrhenius' activation energy (E) and the frequency factor (k_0). The Arrhenius' relationship for variation of the rate constant with temperature is expressed,

$$k = k_0\cdot e^{(-E/RT)} \quad (III\text{-}13)$$

where R = 1.987 cal./g.mole-^{o}K, and, T is the temperature in degrees Kelvin.

By taking natural logarithms of equation (III-13), the relationship becomes,

$$\ln k = \ln k_0 - (E/RT) \quad (III\text{-}14)$$

When plotted as ln k versus 1/T, equation (III-14) is a straight line with slope -E/R and intercept at the ln k axis of ln k_0. Hence, one can solve for the activation energy graphically. The frequency factor can be evaluated, subsequently, by graphical means or by solution of equation (III-13).

Mathematical determination of the line of best fit for the data was another possibility. In this analysis, the mathematic determination was chosen because this method was less arbitrary than the graphical technique. A method outlined by Volk (17) was selected to compute the slope = -E/R and the intercept = ln k_0. The coorelation coefficient for these data was also programmed to indicate the degree of fit of the data to the Arrhenius' relation.

Pressure was to be allowed to decrease naturally during the reaction to allow for simplication of the analysis. Otherwise, complications, resulting from the altered mole fraction of reactants as repressurization was accomplished, were encountered.

One further run was deemed necessary to properly satisfy the proposed study. The reaction was to be carried out for a period of time comparable to those used by Shipman in his study (10). The purpose of this run was to verify the product described and the yield reported. Therefore, a run of approximately twelve (12) hours duration was included in the proposal.

The intention of the analysis of the product was to determine the pseudocumene concentration at a particular time and to separate and identify any acid products. Upon removal from the reactor the total product was weighed and this weight noted.

The first step in the treatment of this product was the separation of the solids by filtration. Both the solids and the liquid were then extracted with copious amounts of distilled water to separate any water-soluble acids. Following this, a second extraction of each with an approximately 10% solution of sodium bicarbonate was performed. The solids were then dried and weighed.

The water extract was heated to reduce the volume of water and allow crystallization of any product acid. Cooling of the remaining water solution was attempted to encourage crystallization. The last remaining water was allowed to evaporate at room temperature. In cases where the water extract showed colour impurity, activated carbon was used to render the solution colourless prior to crystallization.

The sodium bicarbonate extract was treated with activated carbon to purify the product and, subsequently, treated with a 50% solution of hydrochloric acid. Addition of HCl produced crystals of the product which were recovered by filtration, dried and weighed.

Melting point and equivalent weight determinations of the acid products were attempted to identify them. Infrared spectra were also determined.

The remaining solution contained pseudocumene and other products. The pseudocumene content was determined by distillation techniques. Two (2) consecutive distillations were performed to purify the pseudocumene when necessary. The final product of the distillation was weighed and then tested to assure purity by boiling point determination. The weight of pseudocumene and the weight of the residue solutions were noted.

IV. EXPERIMENTAL SET-UP AND PROCEDURE

Prior to the discussion of the procedure, a detailed description of the experimental apparatus is required.

Experimental Set-Up.

The schematic diagram of the apparatus, Figure IV-1, shows the basic components of the system employed. This set-up can be discussed in two (2) sections. These are:

(1) the sulfur dioxide feed system

(2) the autoclave, itself.

(1) Sulfur Dioxide Feed System. In this system, arrangements were made to feed sulfur dioxide in the liquid form into the reactor from an inverted gas cylinder. Flow into the reactor was unimpeded, but, backflow was prevented by a check valve. Liquid sulfur dioxide was allowed to flow under its own vapour pressure when possible. A liquid-handling pump was installed for the case where sufficient sulfur dioxide would not be charged by natural flow.

Provision for cooling the feed-lines ahead of the pump was made in order to condense sulfur dioxide vapours. An ice-water bath was used for this purpose. The gas cylinder was heated, on occasion, to increase the internal pressure and shift the vapour-liquid equilibrium to the

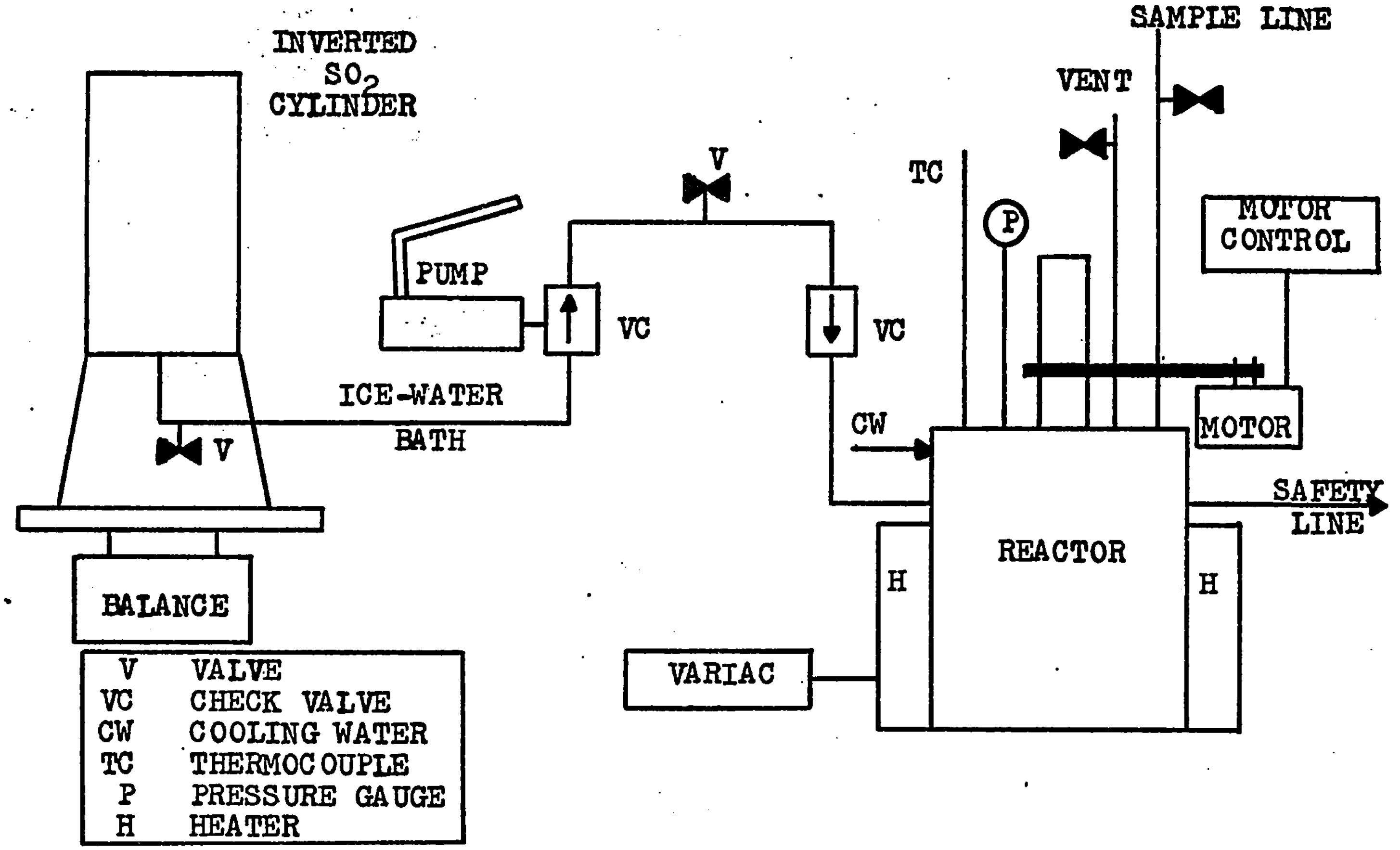


FIGURE IV-1 SCHEMATIC DIAGRAM OF THE EXPERIMENTAL SET-UP liquid side. Extreme caution was required in monitoring the heating of the gas cylinder as certain pressure and temperature limitations are placed upon its performance. The author does not recommend use of this procedure without consultation with the gas supplier regarding safe handling procedures.

To determine the amount of sulfur dioxide fed to the reactor, the cylinder was weighed continuously during the feeding period.

(2) The Autoclave. A standard one liter model AFP-1005 magnedrive packless autoclave was purchased from Autoclave Eng. Inc. Components of the autoclave are shown in Figure IV-2. This autoclave was designed for working pressures up to 5000 psi. at 650 °F and constructed of 316 stainless steel. Closure was achieved by bolting the reactor head to the body, thereby, compressing a 316 S.S. closure gasket.

The internals of the reactor included an impeller, cooling coil, and thermowell. The impeller was mounted on a shaft which extended through the reactor head. This shaft was rotated by the magnetic drive assembly shown in Figure IV-3. Temperature measurement was accomplished by insertion of a chromel-alumel thermocouple into the thermowell.

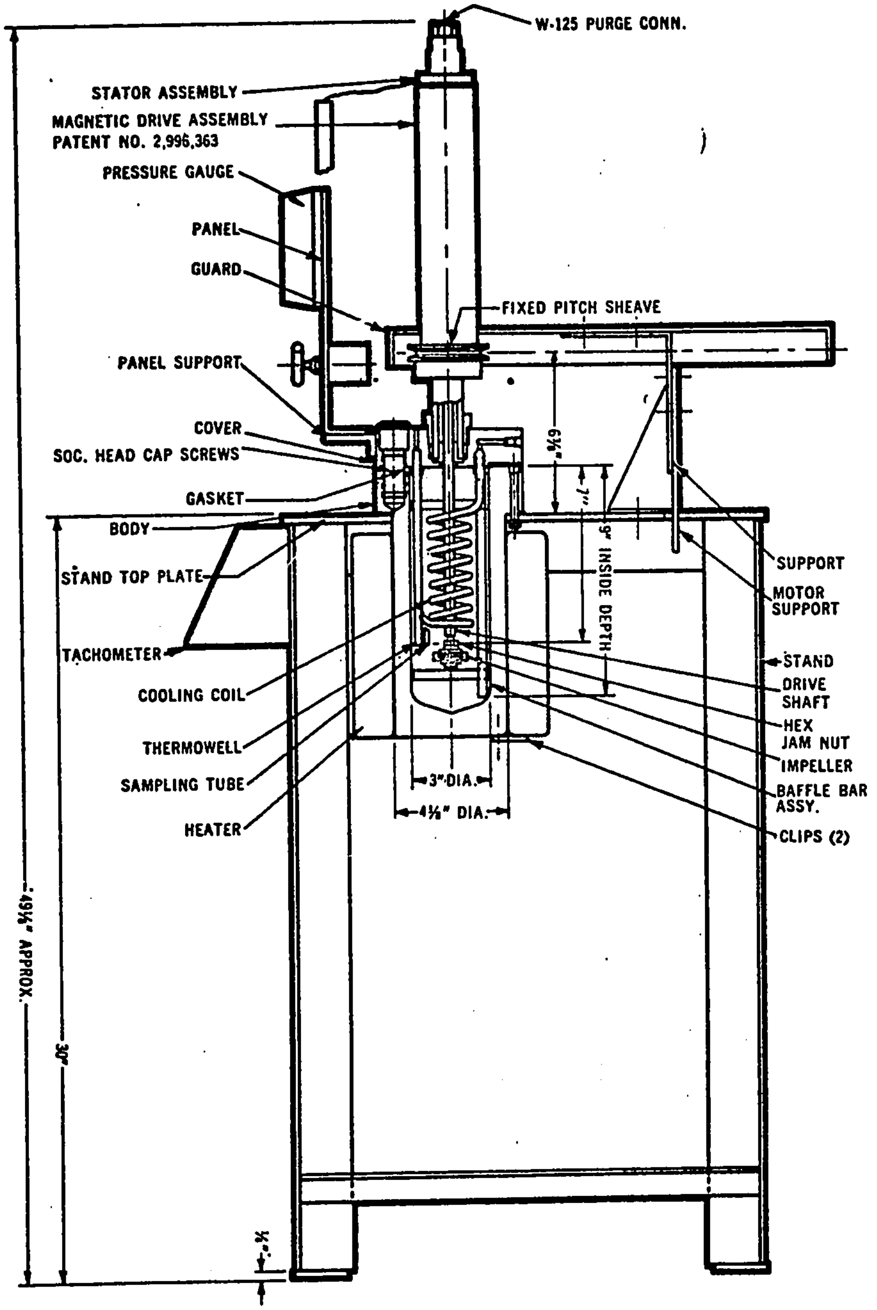


FIGURE IV-2 STANDARD ONE LITER AFP-1005 PACKLESS AUTOCLAVE(Autoclave Eng.)

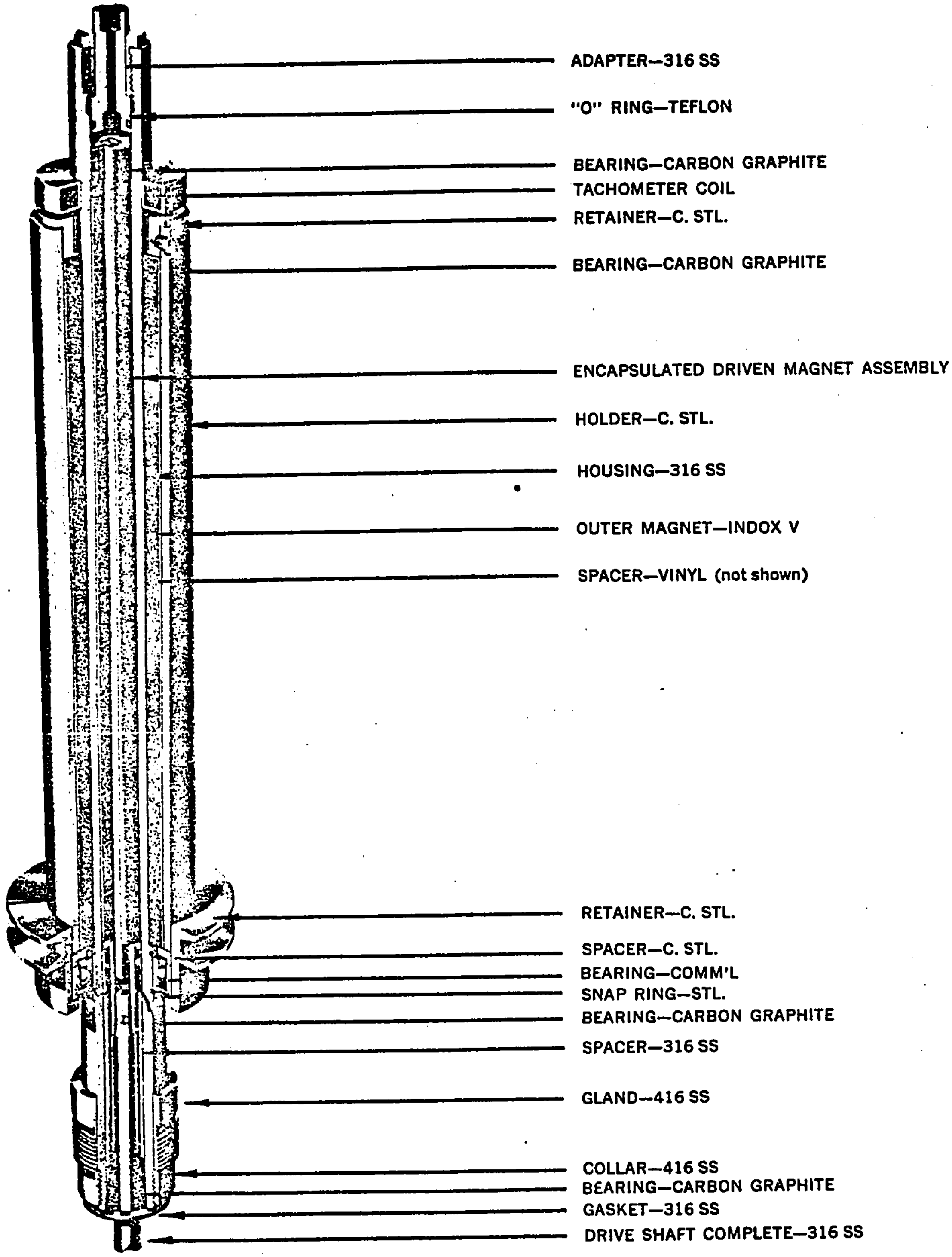


FIGURE IV-3 MAGNEDRIVE ASSEMBLY WITH ENCAPSULATED DRIVEN MAGNETS. (Autoclave Eng. Inc.)

Removable jacket-type heaters were supplied with the autoclave and controlled by use of a Variac.Seven (7) openings were provided in the cover for,

(i) the vent valve,

(ii) the sampling valve,

(iii) cooling coil input and output,

(iv) the thermowell,

(v) the charging port,and,

(vi) the pressure connections.

The sampling valve could be connected with an internal tube for withdrawal of samples at any depth in the reactor. The sampling tube was omitted in this study since the exploratory runs showed it was easily blocked. Two (2) openings in the reactor body were provided for gas connections.

The reactor body also provided a safety head connection port. A safety head assembly, containing a rupture disc of inconel, rated at 5300 psi. at 72°F was connected here. This device protected the reactor and accessories from exposure to extreme pressures by accident. A vent pipe was connected to this assembly to protect personnel from exposure to hot, and possibly, lethal doses of reactants and products in the event of an accident.

The reactor, as described, was located behind a shield of ¼" boiler plate as a further precaution against explosion. The shield and reactor were shrouded by a plastic sheet. This enclosure was ventilated by a fan and duct assembly to protect against exposure to sulfur dioxide vapours.

Experimental Procedure.

The reactor was charge with a known weight of pseudocumene and closed. All external connections, for cooling water, etc., were made and the reactor head insulated. The reactor was now prepared for charging with sulfur dioxide.

The sulfur dioxide cylinder was accurately weighed. It was then connected to the feeding system. Weight, while feeding, was measured using a pan balance as support for the cylinder. Sulfur dioxide was admitted by opening the feed system to the reactor and pumping when necessary until the desired amount was charged. The cylinder was then disconnected, reweighed and the weight determined to the nearest gram.

The reactor and contents were then heated to reaction temperature and pressure. Reaction temperature was controlled by manipulation of the heater temperature. Heater current, and subsequently heater temperature, was controlled by a Variac. In this way, it was possible to maintain reaction temperature within ±3°C. Starting time for the reaction was noted when the desired reaction temperature was reached. The reaction was then allowed to proceed for the time designated.

Termination of the reaction was achieved by the admission of cooling water to the cooling coil and removal of the jacket-type heaters. Cooling was aided by removal of the insulation from the reactor head.

Once cooled to room temperature, the remaining sulfur dioxide was vented slowly. When sulfur dioxide removal was complete, the reactor was opened and the contents removed. Contents of the reactor were then subjected to the treatment outlined in Chapter III, Experimental Strategy.

V.EXPERIMENTAL RESULTS

Several experimental runs were accomplished in accordance with the strategy outlined in Chapter III. Figure V-1 shows the results typical of runs performed for stoichiometric conditions. Figure V-2 was the typical pressure-time plot resulting from runs at excess sulfur dioxide conditions. Pressure versus time curves for all runs can be found in Appendix I.

The data given in Table V-1 were collected to elucidate the kinetics of the oxidation of pseudocumene by sulfur dioxide. Analysis of the reaction mixture by methods outlined in Chapter III resulted in the data of Table V-2, concerning reaction products.

Equivalent weight determinations of all sodium bicarbonate extracts were found and the results are given in Table V-3. The equivalent weight of the water extracts were evaluated and found to average 154 grams/equivalent.

Infrared spectra of the extracted products showed responses characteristic of carboxylic acids. Appendix II contains the infrared spectra of the reaction product and the spectrum of a known carboxylic acid, trimellitic acid, for comparison. Table V-4 compares the results of the infrared spectra of the reaction product to the infrared spectrum expected of a carboxylic acid (15).

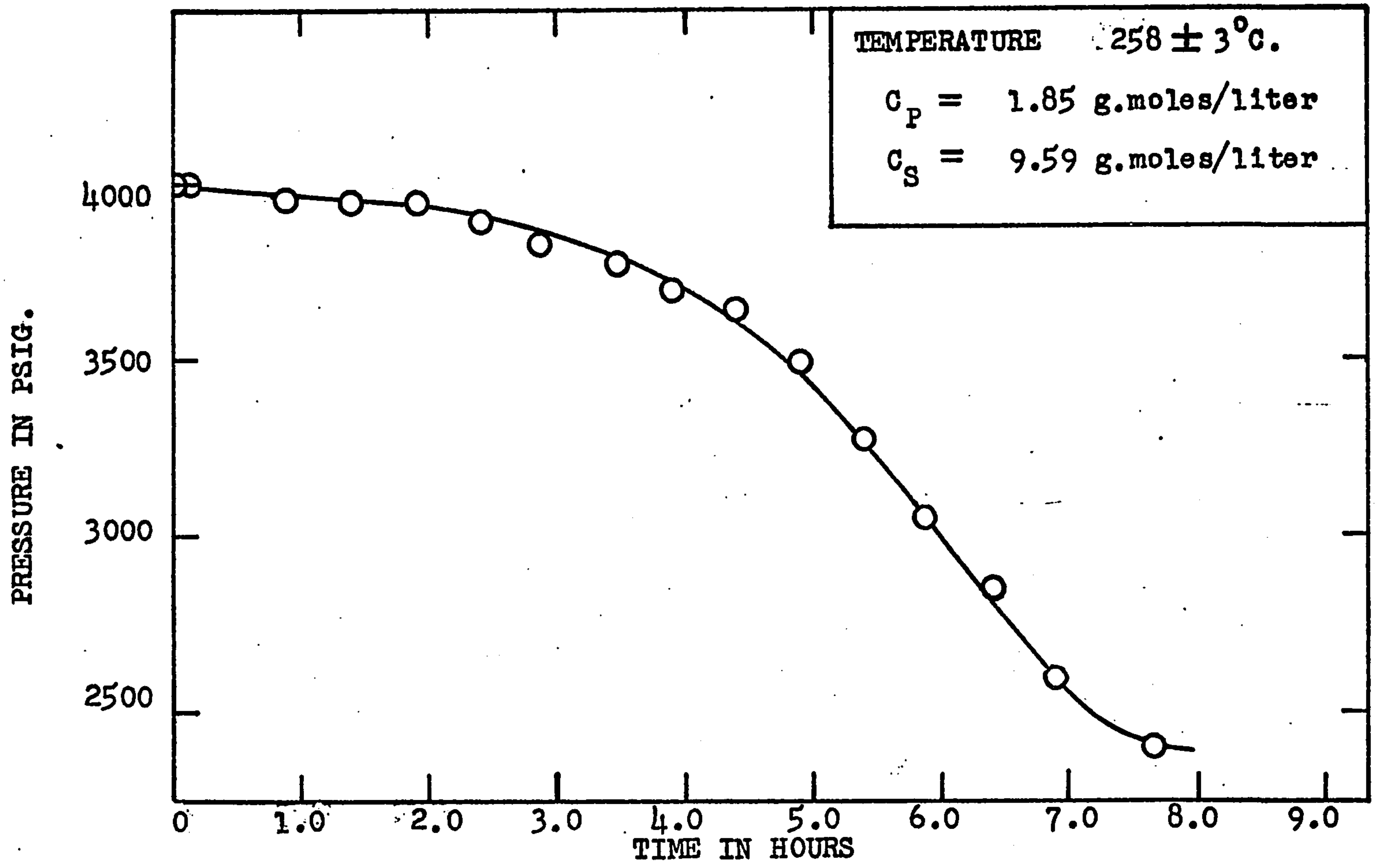


FIGURE V-1 PRESSURE-TIME PLOT FOR STOICHIOMETRIC CONDITIONS (RUN 9).

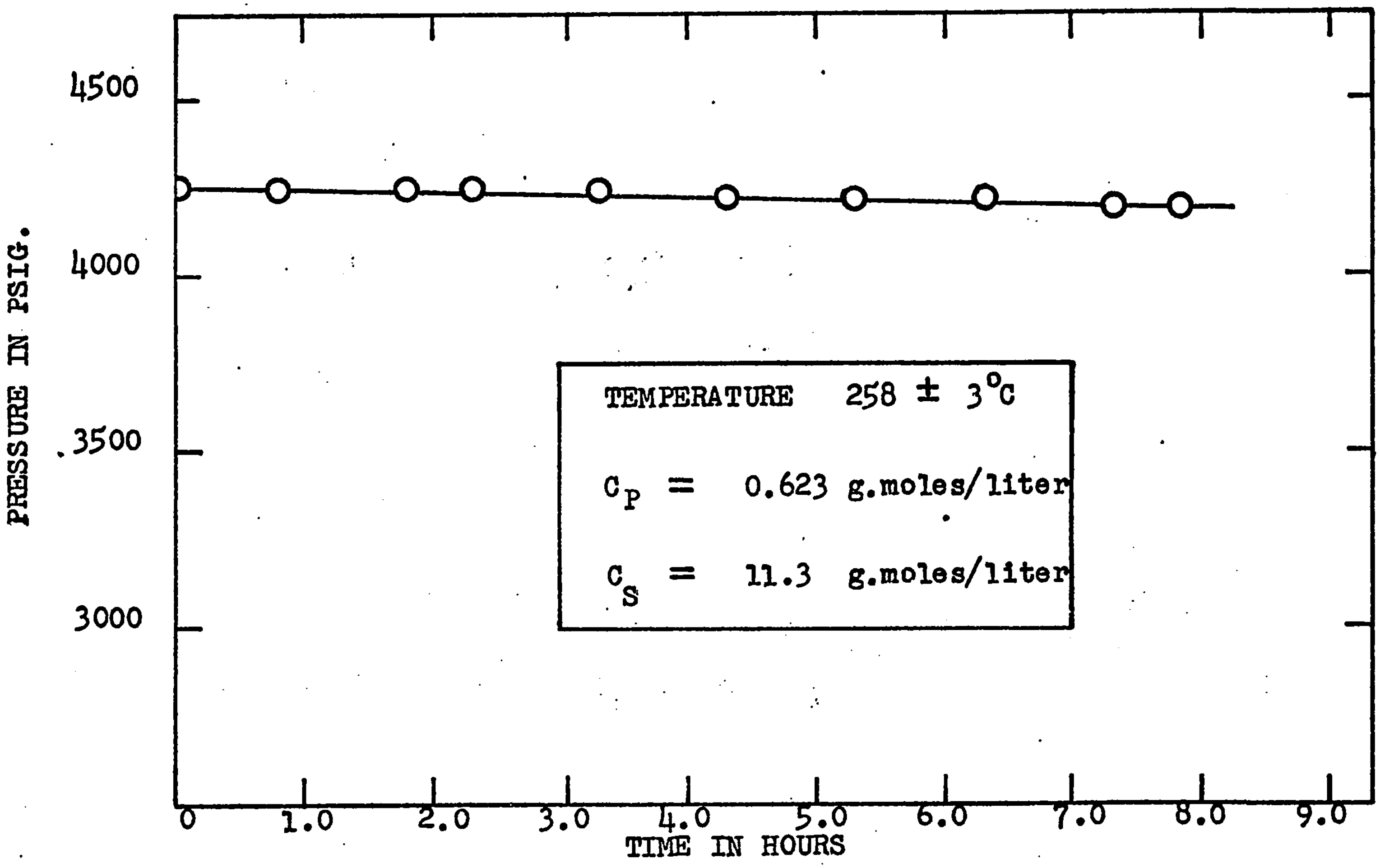


FIGURE IV-2 PRESSURE-TIME PLOT FOR EXCESS SULFUR DIOXIDE CONDITIONS (RUN 3)

TABLE V-1 PSEUDOCUMENE CONCENTRATION DATA FOR USE IN THE KINETIC ANALYSIS OF THE OXIDATION.

RUN NUMBER	PSEUDOCUMENE CONCENTRATION (G.MOLES/LITER)		CONVERSION (%)	TIME (HR.)	TEMPERATURE (°C)
	INITIAL	FINAL			
1	2.065	1.25	39.5	4.2	258
2	2.036	0.875	57.0	6.0	258
3	0.623	0.50	19.7	7.8	258
4	0.624	0.49	21.5	7.7	258
5	0.622	0.417	33.0	9.9	258
6	0.631	0.167	73.5	6.4	275
7	0.630	0.25	60.3	2.4	280
8	0.621	0.167	73.1	2.3	285

TABLE V-2 RESULTS OF THE GRAVIMETRIC ANALYSIS OF THE REACTION PRODUCT OF THE OXIDATION OF PSEUDOCUMENE BY SULFUR DIOXIDE.

RUN NUMBER	WATER EXTRACT (g.)	SODIUM BICARBONATE EXTRACT (g.)	SOLIDS (g.)	UNIDENTIFIED PRODUCTS (g.)	HANDLING LOSSES (%)	TEMPERATURE (°C)
1	0.3	25.4	17.8	45.2	4.2	258
2	2.4	72.1	35.5	60.0	2.7	258
3	—[1]	1.4	1.3	11.2	0.5	258
4	—[1]	1.7	1.0	12.5	-2.6	258
5	—[1]	7.5	3.3	17.6	6.1	258
6	0.7	21.9	27.0	20.0	4.1	275
7	0.4	12.3	15.7	12.8	6.5	280
8	0.6	19.2	25.4	14.1	3.9	285
9	2.6	—[2]	62.9	—[2]	—[2]	258

[1] not detectable [2] not measured

TABLE V-3 EQUIVALENT WEIGHT OF SODIUM BICARBONATE EXTRACTS *.

RUN NUMBER	EQUIVALENT WEIGHT (grams / equivalent)
1	146
2	152
3	153
4	154
5	153
6	149
7	153
8	148

* phenolthalein indicator

TABLE V-4 COMPARISON OF INFRARED SPECTRA OF PRODUCT WITH CARBOXYLIC ACID SPECTRA.

TYPE OF VIBRATION (15)	WAVENUMBER (cm.$^{-1}$)	
	CARBOXYLIC ACID	REACTION PRODUCT
O - H STRETCHING	3520 3300-2500	3250-2500
C = H STRETCHING	1760 1720-1680	1750-1650
O - H BENDING	1440-1395	1460-1400
C - O STRETCHING; C - O - H IN-PLANE BENDING	1320-1210	1350-1180
O - H OUT-OF-PLANE BENDING	920	950-910

In addition to the runs already mentioned, an excess sulfur dioxide run at 280 °C was performed. Reaction time for this run was 12.8 hours.Product analysis resulted in 36 grams of product from water extraction, 16 grams of product from sodium bicarbonate extraction and 105 grams of solids. No pseudocumene was detected.

Equivalent weight of the water extract was 86 grams per equivalent. Infrared spectrum of this product was similar to the expected results of the spectrum of a carboxylic acid. The sodium bicarbonate extract had an equivalent weight of 95 grams/equivalent. Its infrared spectrum was also typical of that of a carboxylic acid.

VI. DATA ANALYSIS AND DISCUSSION OF RESULTS

A total of ten (10) runs are reported in this study of the oxidation of pseudocumene by sulfur dioxide at high pressure. The following is a detailed discussion of the treatment of the data and the results of such treatment.

The determination of the reaction time was of critical importance to the study of this reaction. The starting or zero time for the experimental runs was selected as the time at which reaction temperature was reached. The heat-up period required to raise the temperature from room temperature to that at which the reaction was to take place was usually between 2.0 and 2.5 hours. Some error is introduced into the analysis because of this time interval. The magnitude of this error is relative to the rate at which the reaction takes place, however. Thus, for slow reactions, timing errors are smaller than for very fast reactions. The oxidation of pseudocumene was found to take place over a period of several hours by Shipman (10) and Morettin (9). This error in starting time was, therefore, assumed to be negligible. Subsequently, experimental runs at 258°C showed that consumption of pseudocumene was, indeed, slow and the assumption was assumed valid.

For reactions carried out at higher temperatures, the rate of reaction was increased. The timing error was assumed small for these runs because of the relatively short time required to raise the temperature another thirty (30) degrees, from 258 °C to approximately 285 °C.

Termination of the reaction at any point in time was accomplished by the rapid cooling of the reactor and contents. Removal of the external heaters and cooling with cold water was found to quite effectively stop the reaction. Pressure was observed to decrease by 2000 psi. and temperature decreased by 150 °C or more in a few minutes following completion of the termination procedure described. The rapid fall of temperature was expected to indicate the termination was effective almost immediately and the time was noted after the termination procedure was completed.

Temperature of the reaction mixture was controlled by control of the heater temperature. Overheating of the contents because of energy released during reaction was not a problem in any of the runs reported. Temperature control was maintained within ± 3 °C of reaction temperature for all runs and, in some cases, ±2.0 °C control was achieved.

Heat of reaction for this oxidation was a cause of some concern for reactions at temperatures above 258 °C and for stoichiometric conditions. For this reason, excess sulfur dioxide runs were performed to maintain temperature control within ± 3 ^{o}C. This limit was considered essential for a meaningful kinetic analysis.

As mentioned previously, two (2) different types of experimental runs were performed. Type I runs were for stoichiometric amounts of reactants while type II runs were for excess sulfur dioxide conditions. Type I and II runs are shown in Figures V-1 and V-2, respectively. The pressure-time curves for these two types of runs showed some distinct differences.

Run 9, which was typical of type I conditions, showed three (3) distinct regions of pressure behaviour. Figure V-1 showed these areas clearly. Initially, there was a constant pressure region. This was followed by a period of almost-linear pressure drop. The final stage was another constant pressure region. Examination of the pressure-time plots for runs 1 and 2 in Appendix I, showed the characteristic regions of a stoichiometric run, with the exception of the final stage. The last portion of the curve was not encountered because the reaction times were too short.

Pressure versus time curves for runs at excess sulfur dioxide conditions, on the other hand, were all approximately linear. Runs 3 through 8, inclusive, were the result of type II runs (refer to Appendix I). Slopes of the pressure-time curves were observed to increase as temperature increased.

Of particular interest were the relatively pressure-invariant pressure-time curves obtained for excess sulfur dioxide runs at 258 °C. Runs 3, 4 and 5 showed that the pressure changed relatively little during reaction. This observation has a direct bearing on the assumption of constant sulfur dioxide concentration made in outlining the experimental strategy. This pressure-invariance indicated that the sulfur dioxide concentration was not changing significantly with respect to the pseudocumene concentration. The validity of the experimental strategy was, thus, enhanced.

Reaction orders and the rate constant at 258 °C were evaluated using the data gathered from runs 1 to 5, inclusive, given in Table V-1.

These data were fitted to the derived equations by use of the subroutine, " Program GAUSHAUS " by Meeter (8). This program performed a non-linear least squares fit using minimization of the sum of the squares of the deviations as criterion.

As a result of this treatment, the order of reaction with respect to pseudocumene was 2.15, the order with respect to sulfur dioxide was $3.87 \cdot (10^{-4})$ and the rate constant at 258 ^{o}C was 0.085 $(hr.)^{-1}(g.moles/liter)^{-1.15}$. Output of the program indicated, however, that the model was poorly conditioned. The ratio of the eigenvalues, i.e. highest to lowest, gave a negative value. Meeter (8) suggested that this was often encountered when more parameters than are necessary to explain the data are included in the model. With this in mind, and because the value of the order with respect to sulfur dioxide was very small, the program was re-applied for the case of zero order for sulfur dioxide. This resulted in an order with respect to pseudocumene of 2.14 and no change in the value of the rate constant equal to 0.085 $(hr.)^{-1}\cdot(g.moles/liter)^{-1.14}$. The ratio of the eigenvalues for this case was 1.0, indicating the suitability of the model. Remaining calculations were performed with these values.

Runs 6, 7 and 8 were next used to evaluate the rate constant for temperatures of 275, 280 and 285 ^{o}C, respectively. Pressure-time curves for these runs are given in Appendix I. These curves were linear but showed increased slopes for increased temperatures. As mentioned earlier, the order of reaction was found to be zero with respect to sulfur dioxide. Thus, the rate expression could be re-written with the sulfur dioxide concentration deleted. Now that the rate is independent of sulfur dioxide concentration, the assumption of constant sulfur dioxide concentration for type II runs is not required for a valid kinetic analysis. As such, the pressure-time plot for an excess sulfur dioxide run need not show pressure-invariant behaviour.

The data from runs 6, 7 and 8, given in Table V-1, were used with the following equation to evaluate the rate constant at the corresponding temperatures,

$$k\cdot(1-A)\cdot t = (C_{PO}^{\,1-A} - C_{PF}^{\,1-A}) \qquad \text{(VI-1)}$$

where A = 2.14, the order with respect to pseudocumene,

C_{PO} = the initial concentration of pseudocumene in g.moles/liter,

C_{PF} = the final concentration of pseudocumene in g.moles/liter, and,

t = the reaction time in hr.

Results of the evaluation of the rate constant at various temperatures are given in Table VI-1. Values of ln k and the reciprocal of temperature in $^{\circ}$K are also given as they were required for determination of the Arrhenius' activation energy and frequency factor. These data were plotted and resulted in the straight line shown in Figure VI-1. The slope and intercept of this straight line were determined by fitting the best line

TABLE VI-1 VARIATION OF RATE CONSTANT WITH TEMPERATURE.

RATE CONSTANT k $(hr.)^{-1}(g.moles/liter)^{-1.14}$	NATURAL LOGARITHM OF k	TEMPERATURE T (°C)	$(1/T)\cdot(10^3)$ (°C)
0.085	-2.465	258	1.88
0.839	-0.176	275	1.82
1.167	0.154	280	1.80
2.305	0.835	285	1.79

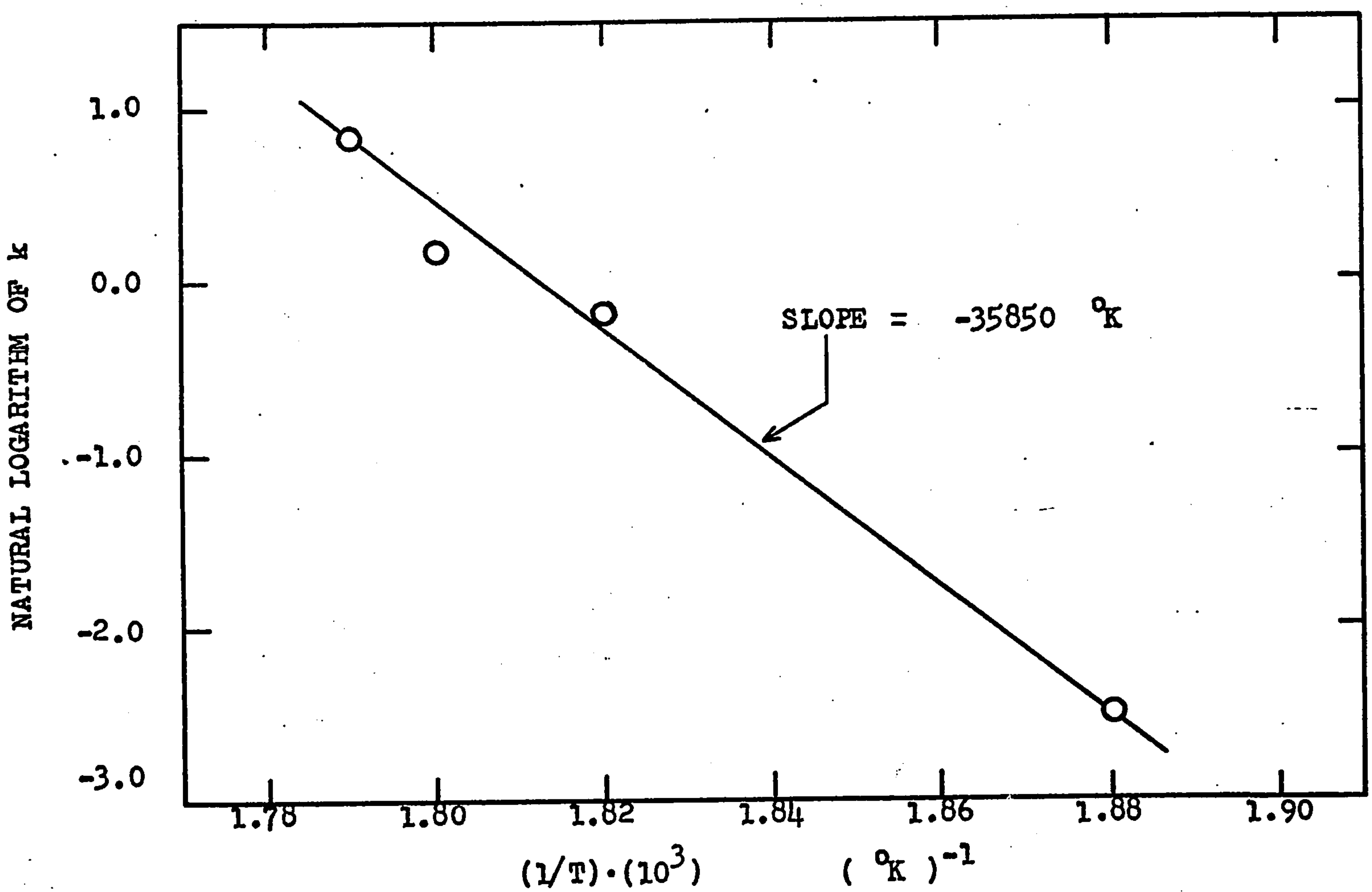


FIGURE VI-1 ARRHENIUS' PLOT FOR THE OXIDATION OF PSEUDOCUMENE BY SO_2.

to the data using a method described by Volk (17). The slope found in this manner was -35850 ^{o}K while the frequency factor, k_0, was $1.85 \cdot (10^{28})$ (hr.)(g.moles/l)$^{-1.14}$

As discussed in Chapter III, the Arrhenius' relationship is expressed,

$$k = k_0 \cdot e^{(-E/RT)} \qquad \text{(VI-2)}$$

Taking natural logarithms of equation (VI-2) yielded,

$$\ln k = \ln k_0 - (E/RT) \qquad \text{(VI-3)}$$

Thus, the slope of the ln k versus 1/T plot is -E/R, where R = 1.987 cal./g.mole-^{o}K. The activation energy was determined as follows,

$$E = -(-35850) \cdot (1.987)$$

Therefore, E = 71.2 kcal./mole.

Correlation coefficient for the data was 0.9959. According to Volk (17), this indicated that there was only 0.01 chance that there was no coorelation for these data.

The high pressure oxidation of pseudocumene by sulfur dioxide was found to proceed according to the following expression,

$$-r_p = 1.85(10^{28}) \cdot e^{(-71,200/RT)} \cdot C_p^{2.14} \qquad \text{(VI-4)}$$

where $-r_p$ = the rate of consumption of pseudocumene in g.moles/liter/hour,

$1.85(10^{28})$ = Arrhenius' frequency factor in $(\text{ hr. })^{-1}$ $(\text{ g.moles/liter })^{-1.14}$

71,200 = Arrhenius' activation energy in cal./g.mole,

R = the gas constant = 1.987 cal./g.mole-^{o}K,

T = the temperature in ^{o}K,

C_p = the concentration of pseudocumene in g.moles /liter, and,

2.14 = the order of the reaction.

The ability of the rate expression to predict the concentration of pseudocumene was indicated by the final function values given by the program used to fit the data. Table VI-2 gives the result of the comparison of observed and predicted pseudocumene concentrations.

Deviations between observed and predicted values were attributed to errors incurred in the gravimetric analysis of the reaction product. Table V-2 gave some indication of the losses due to handling alone. To this error, the error encountered in properly separating the pseudocumene from other products must be added. A more rigorous method of analysis of the product, i.e. chromatography, may have alleviated this problem, but development of such a technique is subject to a number of complications dictated by the nature of the reaction products. The gravimetric technique was found to be quite acceptable for the purposes of this study.

TABLE VI-2 ABILITY OF THE PROPOSED RATE EXPRESSION, EQU'N (VI-4), TO PREDICT PSEUDOCUMENE CONCENTRATION.

PSEUDOCUMENE CONCENTRATION g.moles/liter		PERCENT DEVIATION (%)
OBSERVED	PREDICTED	
1.25	1.164	6.8
0.875	0.975	-11.4
0.50	0.453	9.4
0.417	0.422	-1.25

This oxidation has also been studied by Shipman (10) for similar conditions. Shipman maintained reaction pressure within 10 to 15 atm. of the initial pressure throughout the reaction, however. Results of his study showed,

(1) the order with respect to sulfur dioxide was zero,

(2) the order with respect to pseudocumene was 1.8,

and, (3) the activation energy was in the range of 42±2 kcal./mole.

In obtaining these results, Shipman interpreted pressure versus time data. However, pressure-time data is not always interchangeable with concentration-time data for the purpose of kinetic analysis. Shipman does not indicate the validity of this approach to the study of the pseudocumene oxidation, in particular. In this instance, pressure-time response of the reaction need not be simply related to the concentration-time response. The results obtained by this technique cannot be considered conclusive without some proof of the validity of the approach. The nature of the study undertaken by Shipman was exploratory, however, and, as such, requires further investigation.

The present study has employed concentration versus time information in the kinetic analysis. The result was a value for the order of the reaction which was 19% higher than that predicted by Shipman and an activation energy approximately 39% higher. This indicated that the interpretation of pressure-time data used by Shipman was not completely valid for the pseudocumene oxidation, at least.

The major implication of the results of the present study was a significantly slower rate for the oxidation of pseudocumene than reported by Shipman. This was illustrated by the much greater energy requirements found by the present investigation.

The product of this reaction was analyzed with the specific aim of identifying any carboxylic acids formed. Equivalent weight determinations of the products of runs 1 through 9, inclusive, consistently indicated that the product had an equivalent weight of approximately 150 grams/equivalent.

Infrared spectra of the products were also examined. These spectra showed significant similarity to that determined for trimellitic acid (refer to Appendix II). Table V-4 indicated the favourable comparison of the spectra of the product with that spectrum typical of carboxylic acids, as described by Silverstein and Bassler (15).

Considering these results, the major acid product of the first nine (9) runs would appear to be a monocarboxylic acid derivative of pseudocumene. There are three (3) such derivatives of pseudocumene having equivalent weights of 150 grams/equivalent. These acids are :

(1) 3,4-dimethyl-benzenecarboxylic acid,
(2) 2,5-dimethyl-benzenecarboxylic acid,
(3) 2,4-dimethyl-benzenecarboxylic acid.

Melting point determination proved useless in the identification of these acids. This was attributed to poor product purity. It appears likely that a mixture of these three (3) acids makes up the product of the reaction.

On the basis of existing evidence, the product was assumed to be the monocarboxylic acid derivative of pseudocumene. Using an equivalent weight of 150 grams/equivalent, yields and selectivities for runs 1 through 9 were calculated. The results are given in Table VI-3. The following definitions applied, for the purpose of these calculations, ,

$$\text{yield} = \frac{(\text{ moles of acid })\cdot(\text{ 100 })}{(\text{ moles of pseudocumene initially })} \qquad \text{...(VI-5)}$$

TABLE VI-3 YIELD AND SELECTIVITY FOR THE MONOCARBOXYLIC ACID.

RUN NUMBER	TIME (hr.)	TEMPERATURE (°C)	YIELD (%)	SELECTIVITY (%)
1	4.2	258	8.3	21.0
2	6.0	258	24.4	42.7
3	7.8	258	1.44	7.3
4	7.7	258	1.76	8.2
5	9.9	258	8.04	24.4
6	6.4	275	23.9	32.5
7	2.4	280	13.5	22.4
8	2.3	285	21.3	29.1

$$\text{selectivity} = \frac{(\text{ moles of acid })\cdot(\text{ 100 })}{(\text{ moles of pseudocumene consumed })} \qquad \ldots(\text{VI-6})$$

Runs 1 and 2, for stoichiometric conditions at 258 ^{o}C, showed an increase in yield and selectivity of the monocarboxylic acid for increased reaction time. Reference to the pressure-time plots for these runs, in Appendix I, showed that the higher yield and selectivity occurred when the reaction was terminated during the latter stages of the linear pressure drop region. The lower yield and selectivity were achieved when the reaction was terminated in the earlier stages of this region. Yield and selectivity appear to be dependent upon the region of pressure behaviour during which termination occurs.

Runs 3, 4 and 5 were performed for excess sulfur dioxide conditions. The dependence of yield and selectivity upon pseudocumene concentration was indicated by the comparison of excess sulfur dioxide runs (low C_p) and to stoichiometric runs (higher C_p).

Comparison of run 3 and 4 with run 5 showed a significant increase in yield and selectivity. For an increase in the reaction time of 30%, the yield was increased by 600% and the selectivity by 200%.

In both the type I and type II runs, a period of increased yield and selectivity was preceded by a period during which these values were relatively low. Shipman (10) also noted a period of apparently little activity and referred to it as an induction period. The runs for stoichiometric conditions show the period which Shipman called the induction period as a pressure-invariant region at the beginning of the run.

Temperature dependence of the yield and selectivity was shown by runs 6, 7 and 8. Both yield and selectivity increased as the temperature increased. In Table VI-3 comparable yields and selectivities required proportionally longer reaction times as temperature decreased.

The pressure versus time plots for the higher temperature runs showed steeper slopes for increasing temperatures and appear to show no induction period as the pressure drops linearly from the beginning of the reaction.

In an attempt to achieve the same product as Shipman indicated, a tenth run was performed with the reaction time increased to the order of Shipman's runs. The reaction was carried out at 280 ^{o}C for 12.8 hours.

The product's equivalent weight was found to be approximately 90 grams/equivalent for both the water and sodium bicarbonate extracts.

The dicarboxylic acid derivative of pseudocumene has a molecular weight of 180.07 grams/mole and, since it has two (2) replacable hydrogens, an equivalent weight of 90 grams/equivalent, approximately. Trimellitic acid, on the other hand, has a molecular weight of 210.14 grams/mole and an equivalent weight of approximately 70 grams/equivalent, since it has three (3) replacable hydrogens. The reaction product, therefore, appears to resemble the dicarboxylic acid derivative of pseudocumene more than the other derivative acids.

There is also the possibility that products of run 10 consisted of a mixture of the mono-, di- and tricarboxylic acid derivatives of pseudocumene. Based on the evidence presented in the analysis of this product thus far, it would be impossible to suggest what fraction of each was present. Since the equivalent weight was approximately 90 g./equivalent, however, the presence of dicarboxylic and tricarboxylic acid derivatives is very likely.

There are three (3) dicarboxylic acid derivatives of pseudocumene. They are :

(1) 4-methyl-1,2-benzenedicarboxylic acid,
(2) 4-methyl-1,3-benzenedicarboxylic acid,
(3) 2-methyl-1,4-benzenedicarboxylic acid.

Of the three (3) dicarboxylic acids mentioned, only 4-methyl-1,2-benzenedicarboxylic acid is soluble in water to any extent. Thus, the water extract may contain this acid to some extent. As shown in the first nine (9) runs only relatively small amounts of the monocarboxylic acid were recovered from the water extraction. Only one of three monocarboxylic acid derivatives of pseudocumene is soluble in water and then it is only slightly soluble. Thus, the water extract was expected to be largely composed of the dicarboxylic acid derivative. Small amounts of the mono- and tri-carboxylic acid derivatives are also likely to be present, however.

The sodium bicarbonate extract was also expected to contain a large amount of the dicarboxylic product, as well, since trimellitic acid was removed in the water extraction and the equivalent weight was almost exactly 90 g./equivalent. Had this phase contained appreciable amounts of monocarboxylic acid the equivalent weight should have been higher, approaching the 150 g./equiv. of the monocarboxylic acids.

Shipman has claimed 80 % yields of trimellitic acid from this oxidation while Morettin (9) found that the product was a methyl-substituted carboxylic acid. The results of this study indicate that the monocarboxylic acid derivatives of pseudocumene are readily obtained. Lengthening the reaction time produced a product which appeared to be largely the dicarboxylic acid derivative. Although small amounts of trimellitic acid were likely to be present in this product, the high yields of trimellitic acid claimed by Shipman were not achieved.

Since the monocarboxylic acid derivatives of pseudocumene were found to dominate the products of the runs used in the kinetic analysis, a stoichiometric mole ratio of 1.5 for the reaction is indicated. The analysis performed previously involved the assumption of a stoichiometric mole ratio of 4.5. Therefore, further analysis was required to check the effect of this factor on the results reported.

A general expression of the rate equation was written in terms of conversion and time. The rate equation was integrated by numerical techniques. The integration was performed for each set of parameter values generated by the non-linear least squares program previously described. The best parameter values resulting from this treatment were in good agreement with those reported earlier. The order with respect to pseudocumene was 2.169, the order with respect to SO_2 was $6.3 \cdot (10^{-6})$ and the rate constant was 0.0842 $(\text{hr.})^{-1}(\text{g.moles/liter})^{-1.169}$. The low value of the order with respect to SO_2 indicated that the rate was virtually independent of SO_2 concentration. The results reported in this study have been double checked and found valid.

VII. CONCLUSIONS AND RECOMMENDATIONS

The rate of consumption of pseudocumene in the oxidation reaction with sulfur dioxide was found to proceed according to the following expression,

$$-r_P = 1.85(10^{28}) \cdot e^{(-71{,}200/RT)} \cdot C_P^{2.14} \qquad \text{(VIII-1)}$$

where $-r_P$ = the rate of consumption of pseudocumene in g.moles/liter/hour,

$1.85(10^{28})$ = Arrhenius' frequency factor in $(\text{hour})^{-1}$ $(\text{g.moles/liter})^{-1.14}$,

71,200 = Arrhenius' activation energy in calories/g.mole,

R = the gas constant = 1.987 calories/g.mole-^{o}K,

T = the temperature in ^{o}K,

C_P = the concentration of pseudocumene in g.moles/liter, and,

2.14 = the order of the reaction, dimensionless.

The temperature range from 258 ^{o}C to 285 ^{o}C was covered. Initial pressures were between 260 and 300 atm. Temperature was controlled within ±3 ^{o}C and the reaction carried out in a one liter, stirred autoclave.

Pseudocumene was successfully oxidized to its monocarboxylic acid derivative and, by increasing the reaction time, to its dicarboxylic acid derivative. No trimellitic acid was detected in any of the reaction products.

In regard to the oxidation of pseudocumene, further studies could include determination of the optimum reaction temperature and the effects of various catalysts upon the reaction rate. Analysis of the reaction product could be made more rigorous to identify more of the species present in an attempt to uncover the mechanism of the reaction.

More generally, a large number of alkyl-substituted aromatics could be studied using the existing equipment. The reactor might also be used to study oxidations by gases other than sulfur dioxide, i.e. carbon dioxide,etc.

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IX. NOMENCLATURE

SYMBOLS

A	the order with respect to pseudocumene
B	the order with respect to sulfur dioxide
C	concentration in g.moles/liter
^{o}C	degrees centigrade
E	Arrhenius' activation energy in cal./g.mole
k	the rate constant in (hr.)$^{-1}$(g.moles/liter)$^{1-A-B}$
k_o	the frequency factor in the Arrhenius' relation in (hr.)$^{-1}$(g.moles/liter)$^{1-A-B}$
^{o}K	degrees Kelvin
n	the overall order of the reaction
r	the rate of reaction in g.moles/liter/hour
R	the gas constant = 1.987 cal./g.mole-^{o}K
t	the reaction time in hours
T	the temperature in appropriate units

SUBSCRIPTS

O	denotes initial conditions
F	denotes final conditions
P	denotes pseudocumene
S	denotes sulfur dioxide

APPENDIX I

PRESSURE VERSUS TIME CURVES

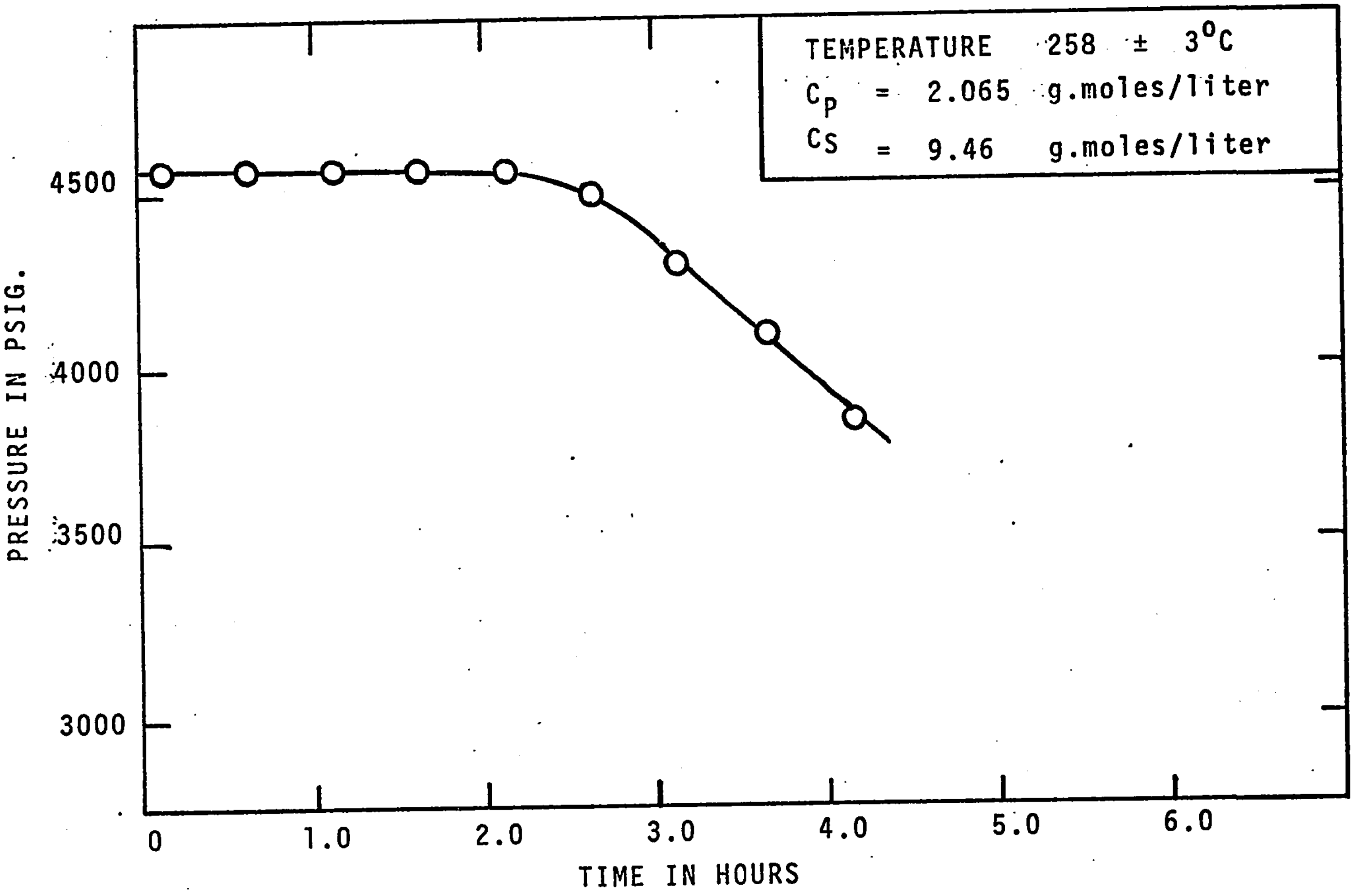

FIGURE AI-1 RUN 1 PRESSURE-TIME PLOT FOR THE OXIDATION OF PSEUDOCUMENE BY SULFUR DIOXIDE.

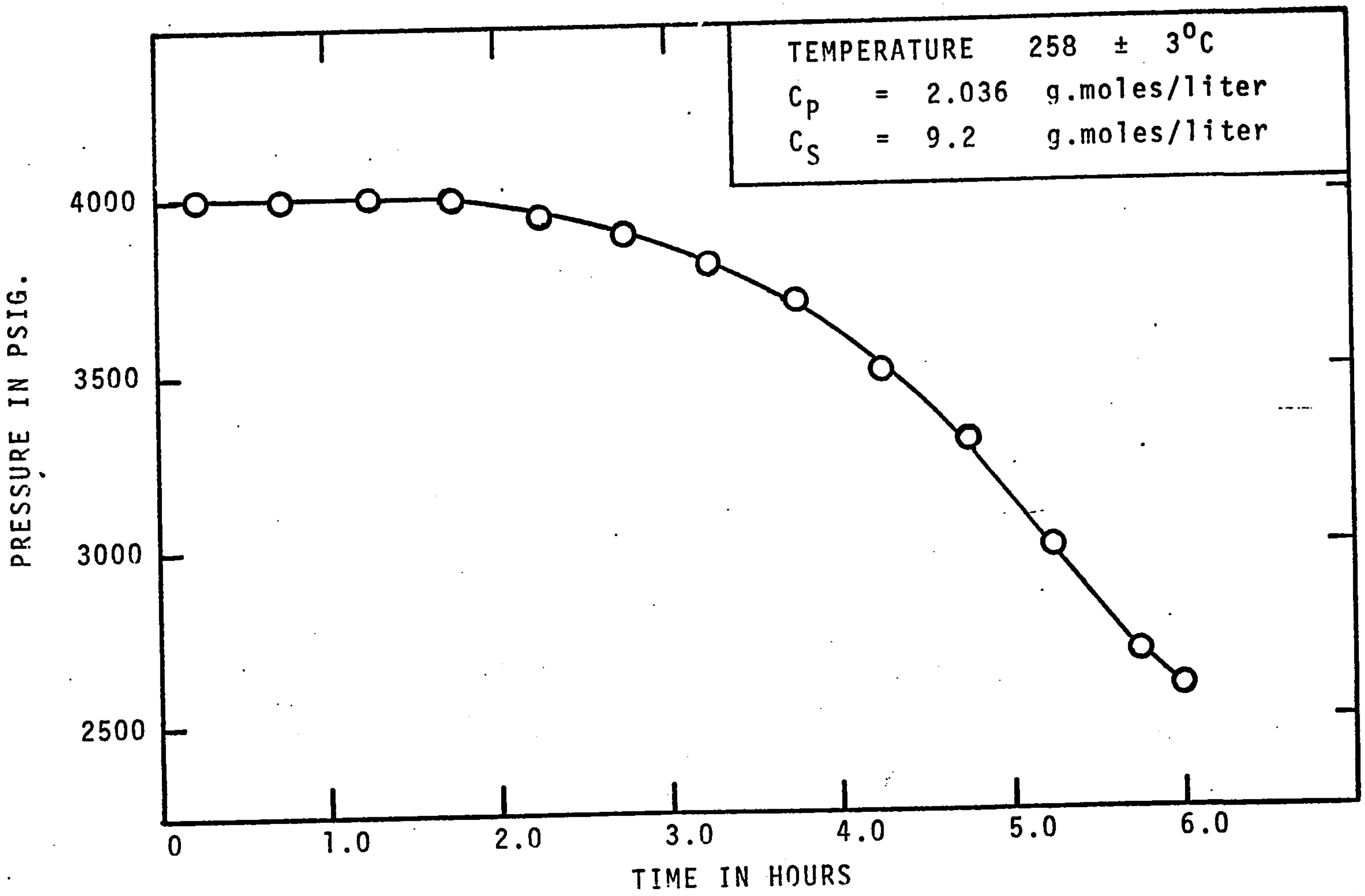

FIGURE AI-2 RUN 2 PRESSURE-TIME PLOT FOR THE OXIDATION OF PSEUDOCUMENE BY SULFUR DIOXIDE

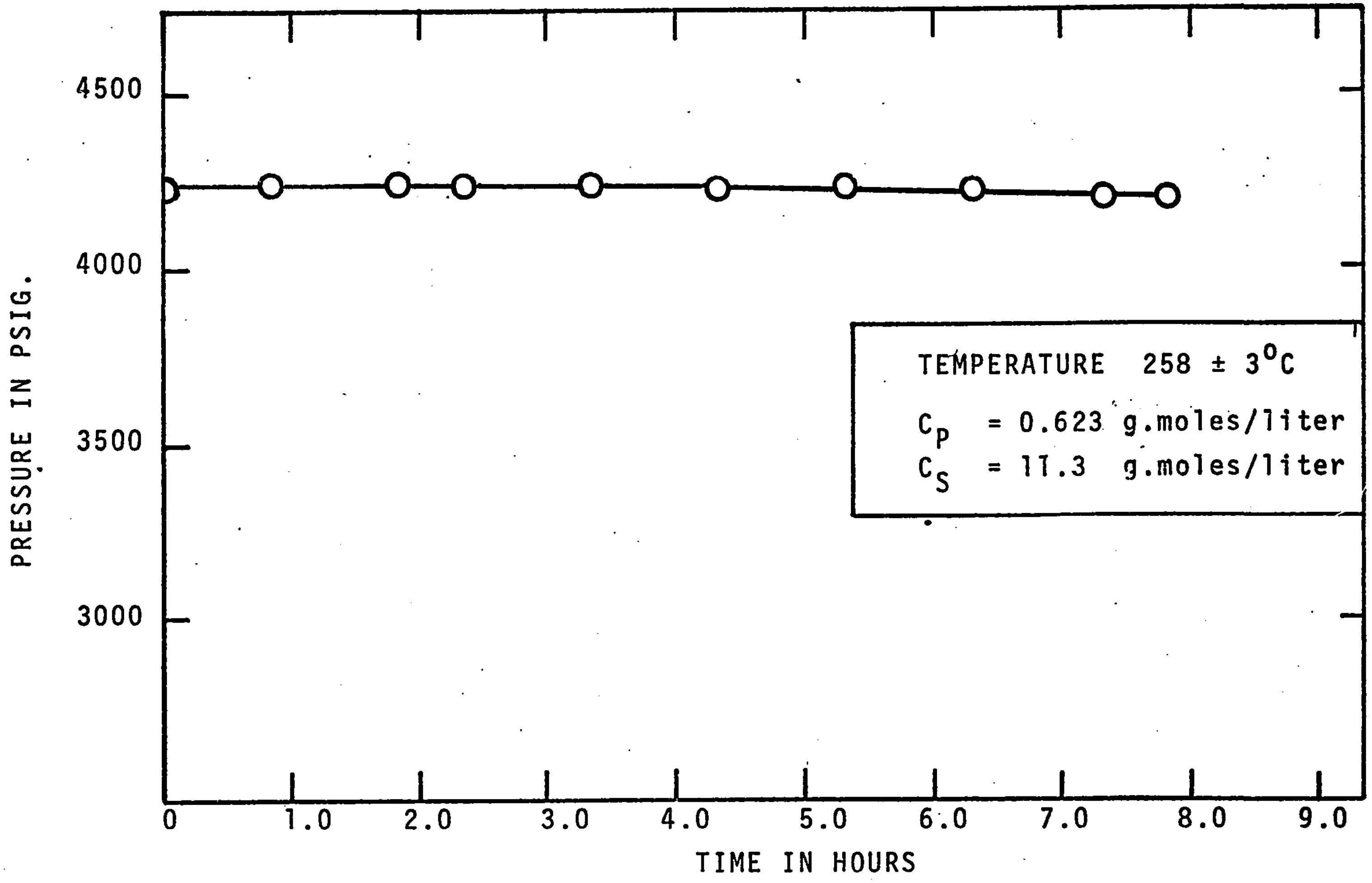

FIGURE AI-3 RUN 3 PRESSURE-TIME PLOT FOR THE OXIDATION OF PSEUDOCUMENE BY SULFUR DIOXIDE.

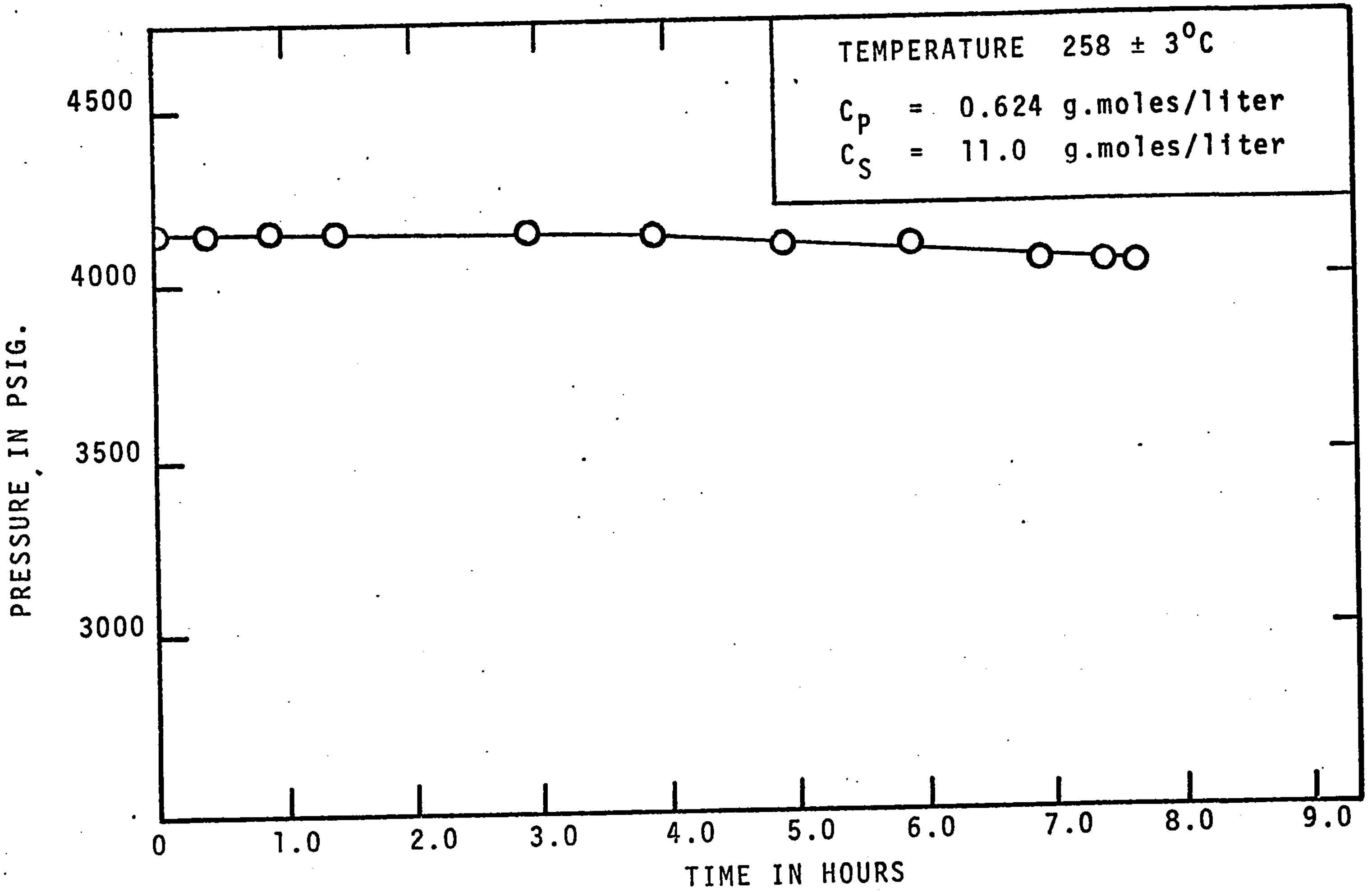

FIGURE AI-4 RUN 4 PRESSURE-TIME PLOT FOR THE OXIDATION OF PSEUDOCUMENE BY SULFUR DIOXIDE.

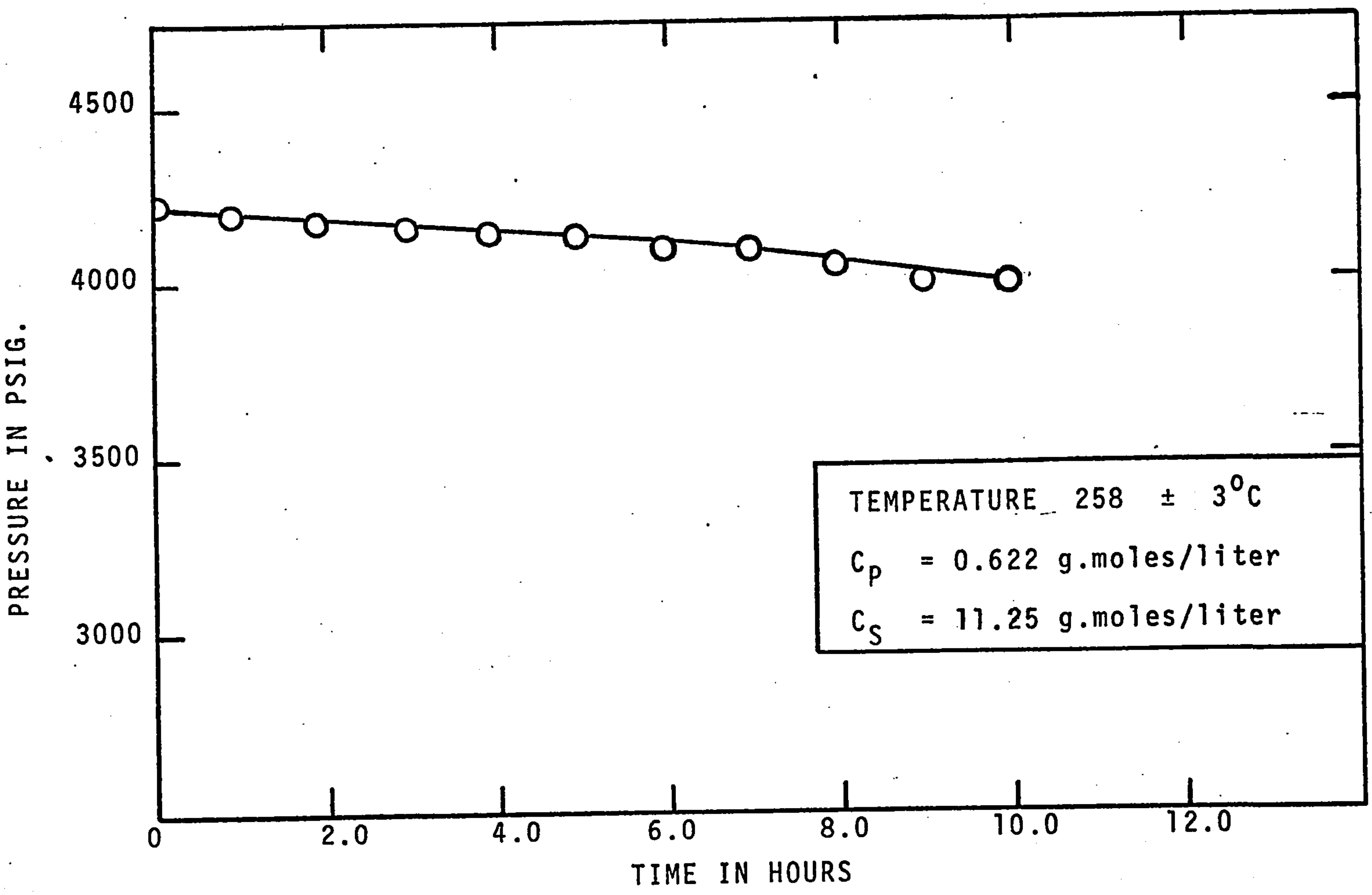

FIGURE AI-5 RUN 5 PRESSURE-TIME PLOT FOR THE OXIDATION OF PSEUDOCUMENE BY SULFUR DIOXIDE.

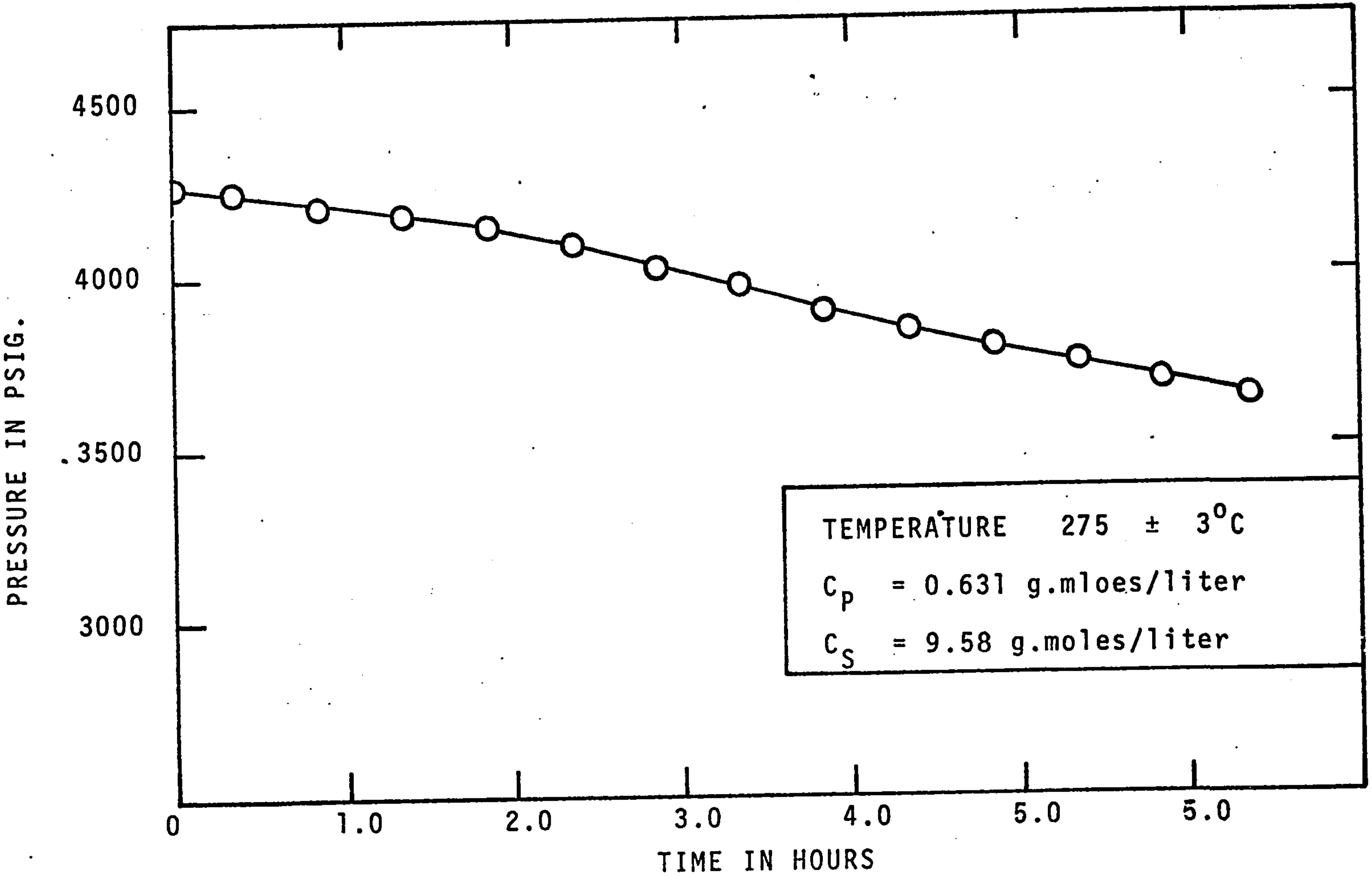

FIGURE AI-6 RUN 6 PRESSURE-TIME PLOT FOR THE OXIDATION OF PSEUDOCUMENE BY SULFUR DIOXIDE.

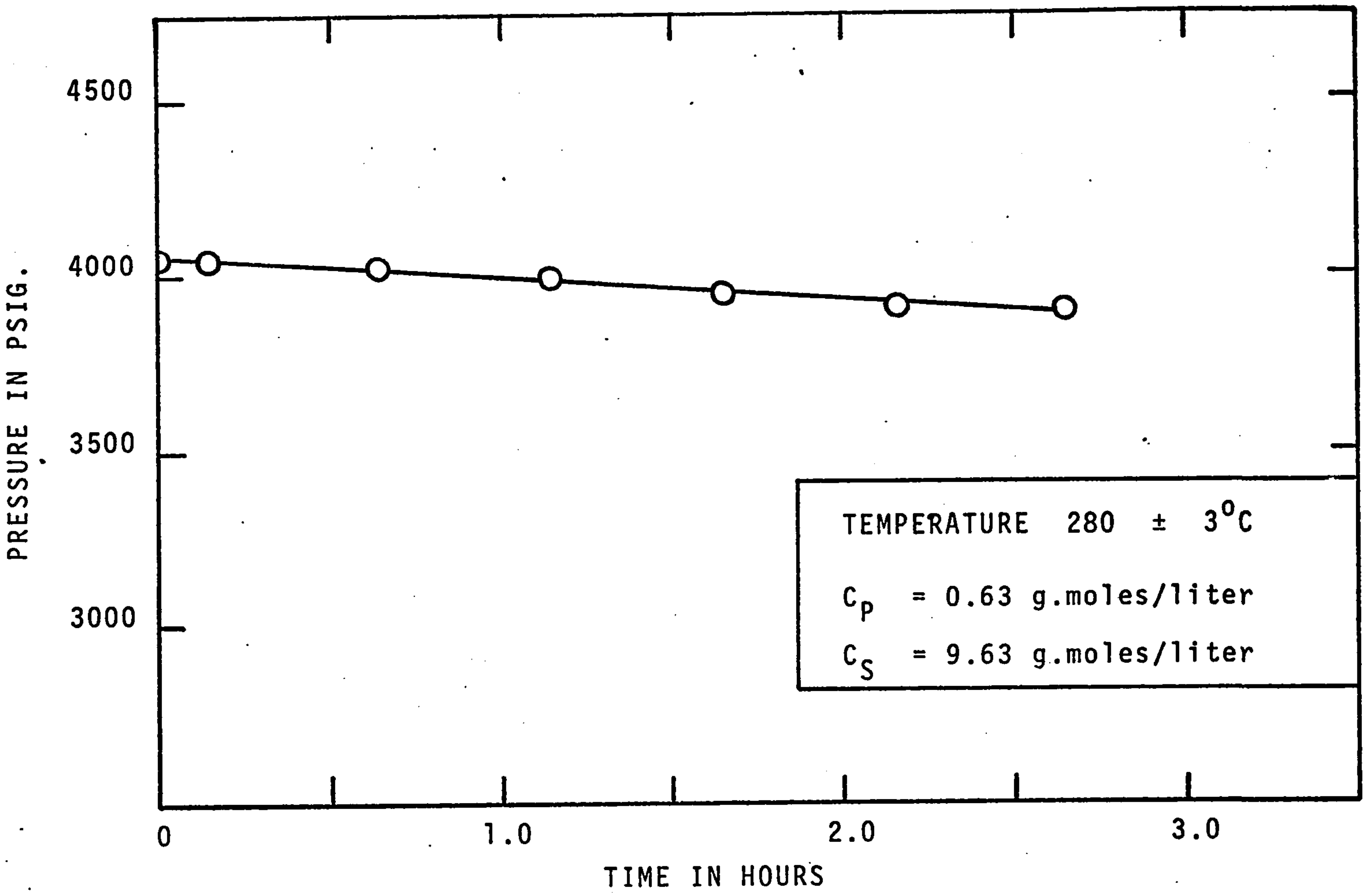

FIGURE AI-7 RUN 7 PRESSURE-TIME PLOT FOR THE OXIDATION OF PSEUDOCUMENE BY SULFUR DIOXIDE.

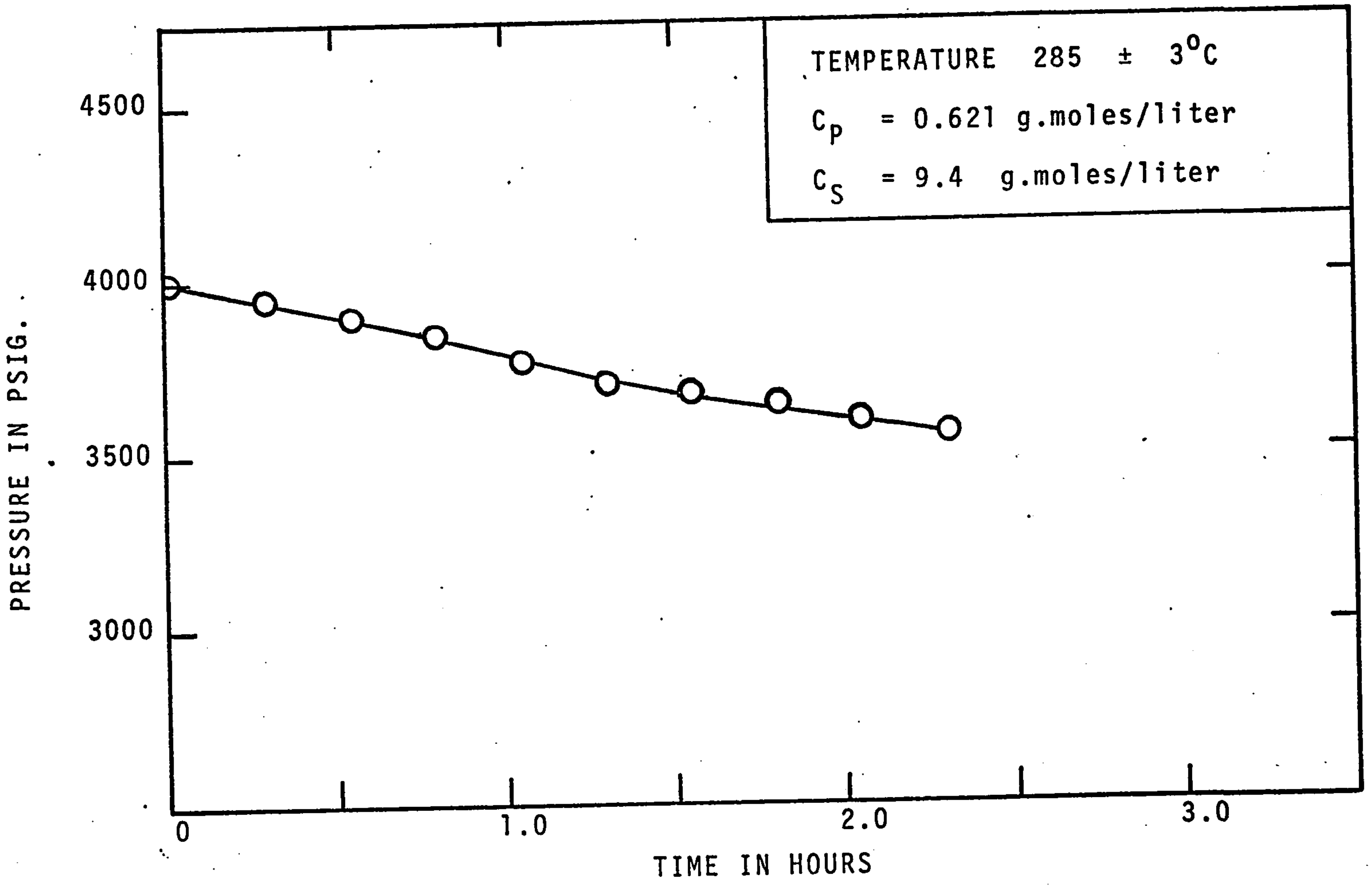

FIGURE AI-8 RUN 8 PRESSURE-TIME PLOT FOR THE OXIDATION OF PSEUDOCUMENE BY SULFUR DIOXIDE.

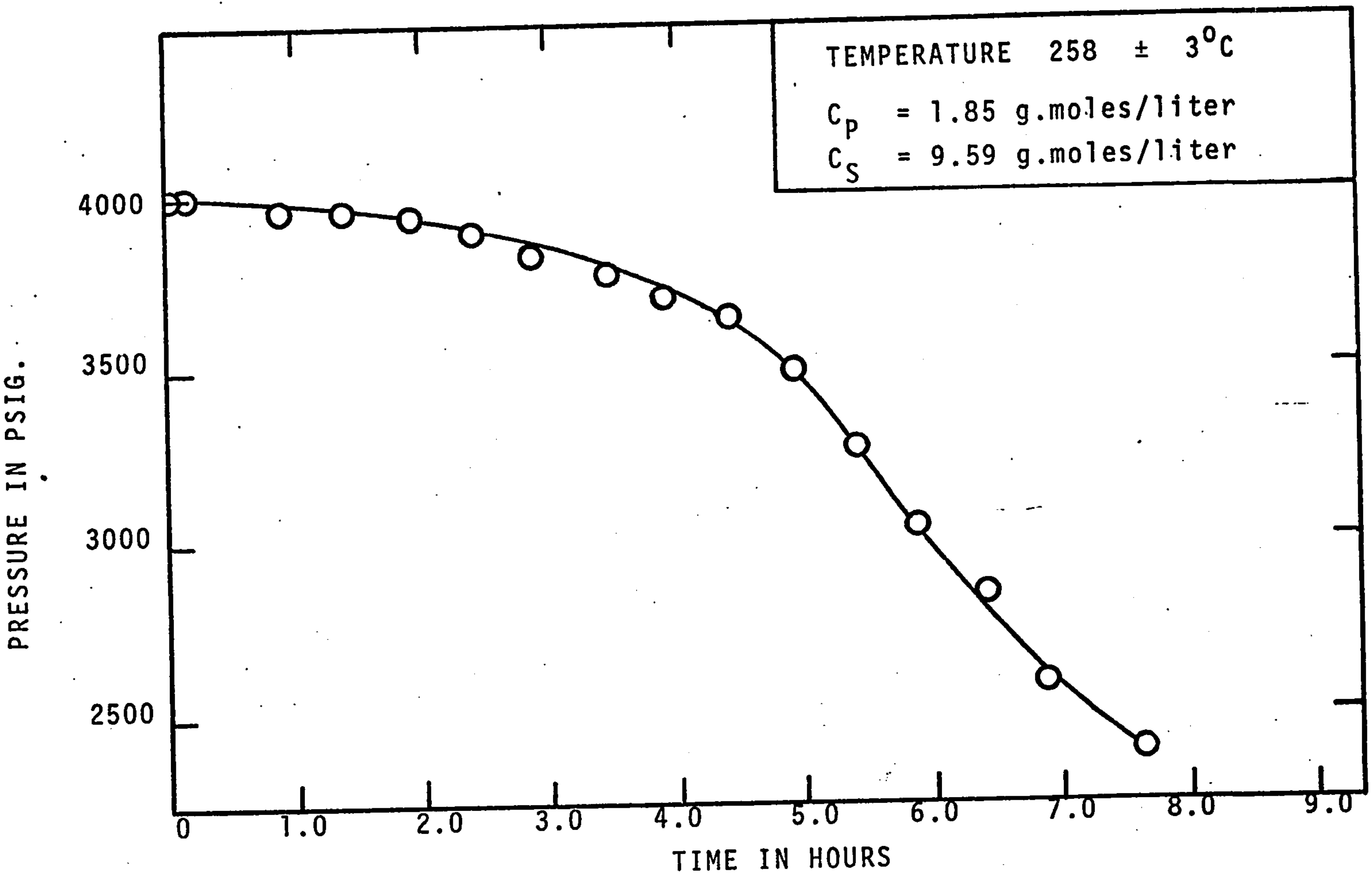

FIGURE AI-9 RUN 9 PRESSURE-TIME PLOT FOR THE OXIDATION OF PSEUDOCUMENE BY SULFUR DIOXIDE.

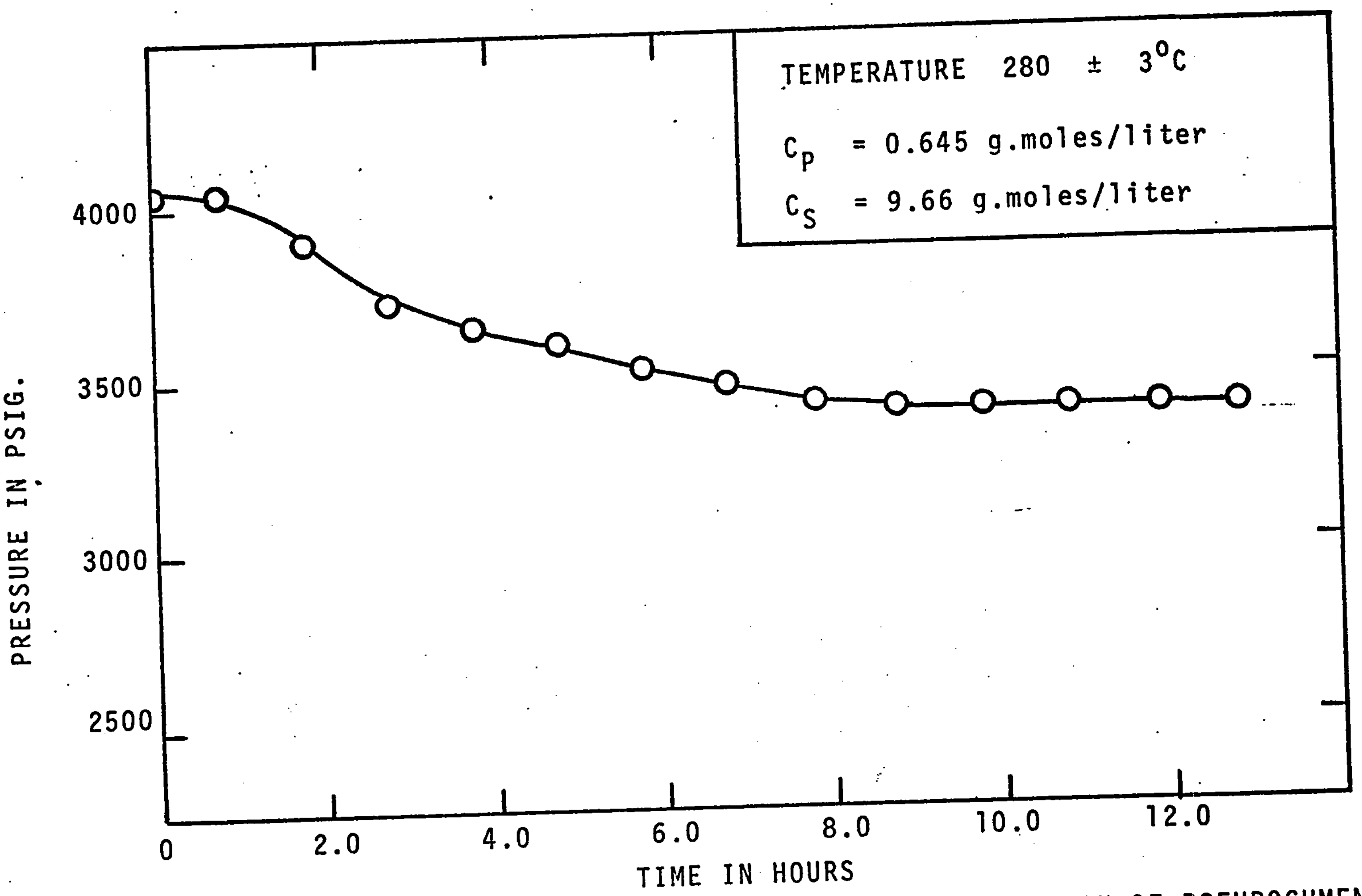

FIGURE AI-10 RUN 10 PRESSURE-TIME PLOT FOR THE OXIDATION OF PSEUDOCUMENE BY SULFUR DIOXIDE.

APPENDIX II

INFRARED SPECTRA OF REACTION PRODUCTS

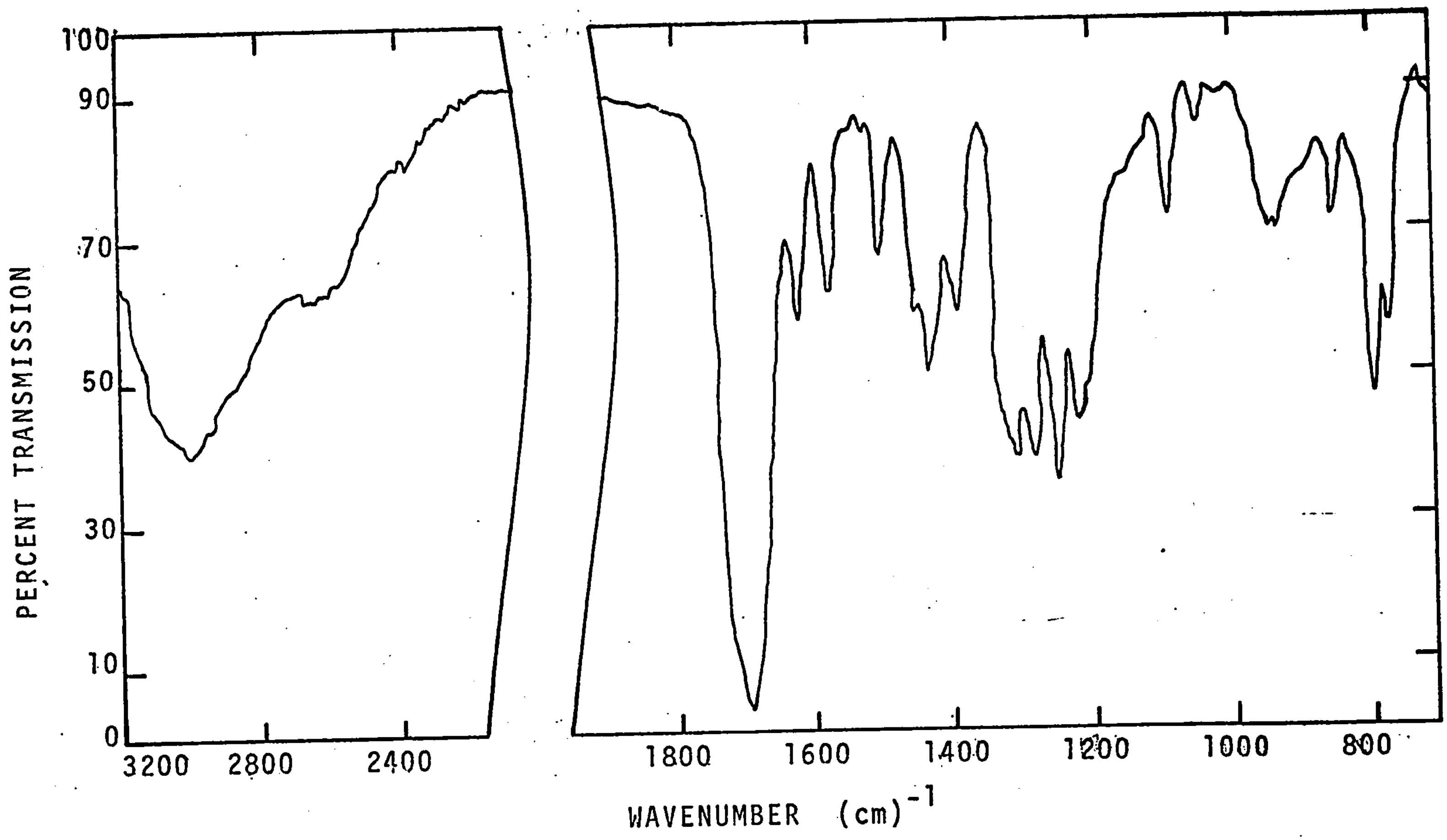

FIGURE AII-1 Infrared Spectra of the Water Extract of Run 10,

Equivalent Weight = 86 grams/equivalent.

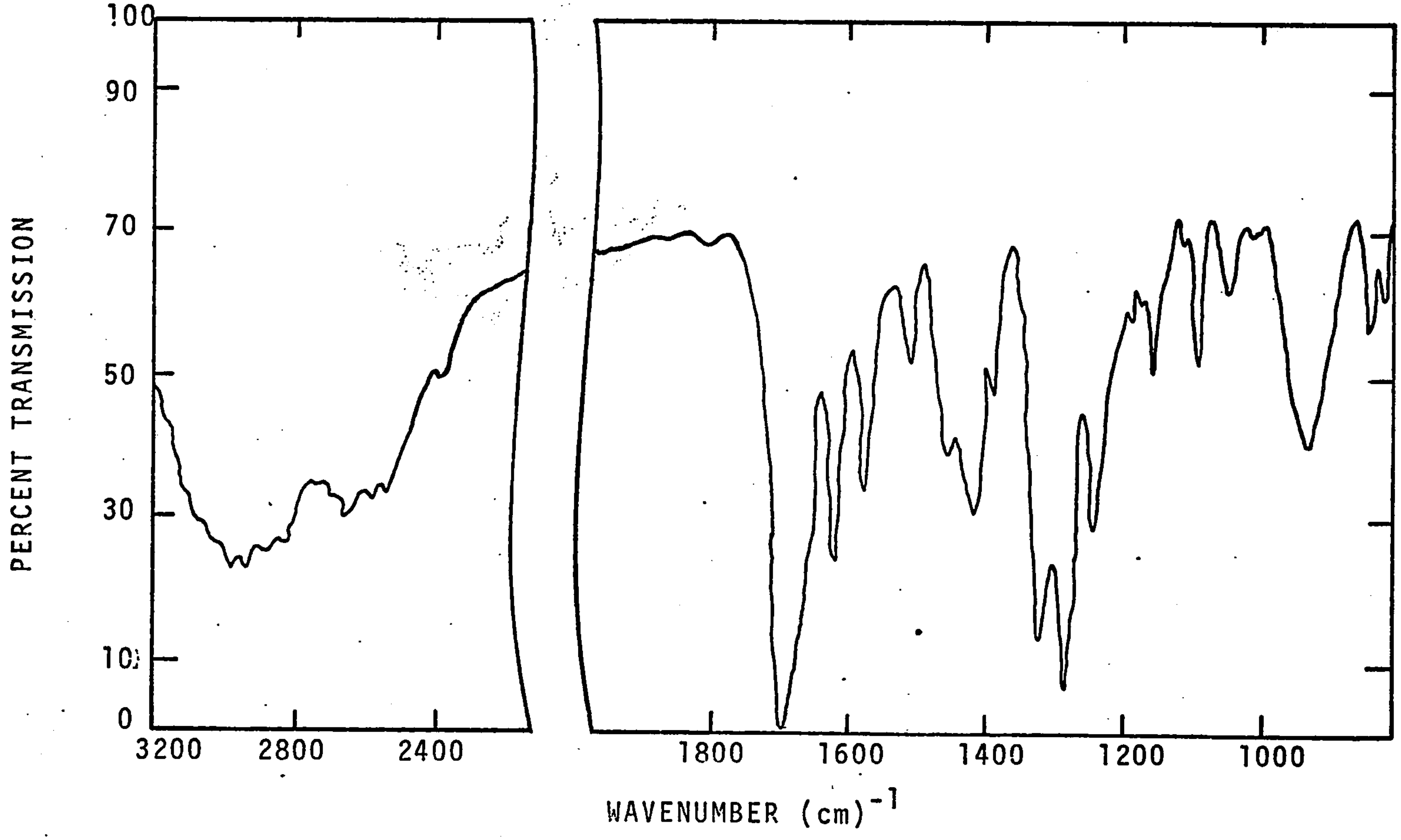

FIGURE AII-2 Typical Infrared Spectra of the Sodium Bicarbonate Extract of Runs 1 through 9, inclusive, Equivalent Weight = approximately 150 grams/equivalent.

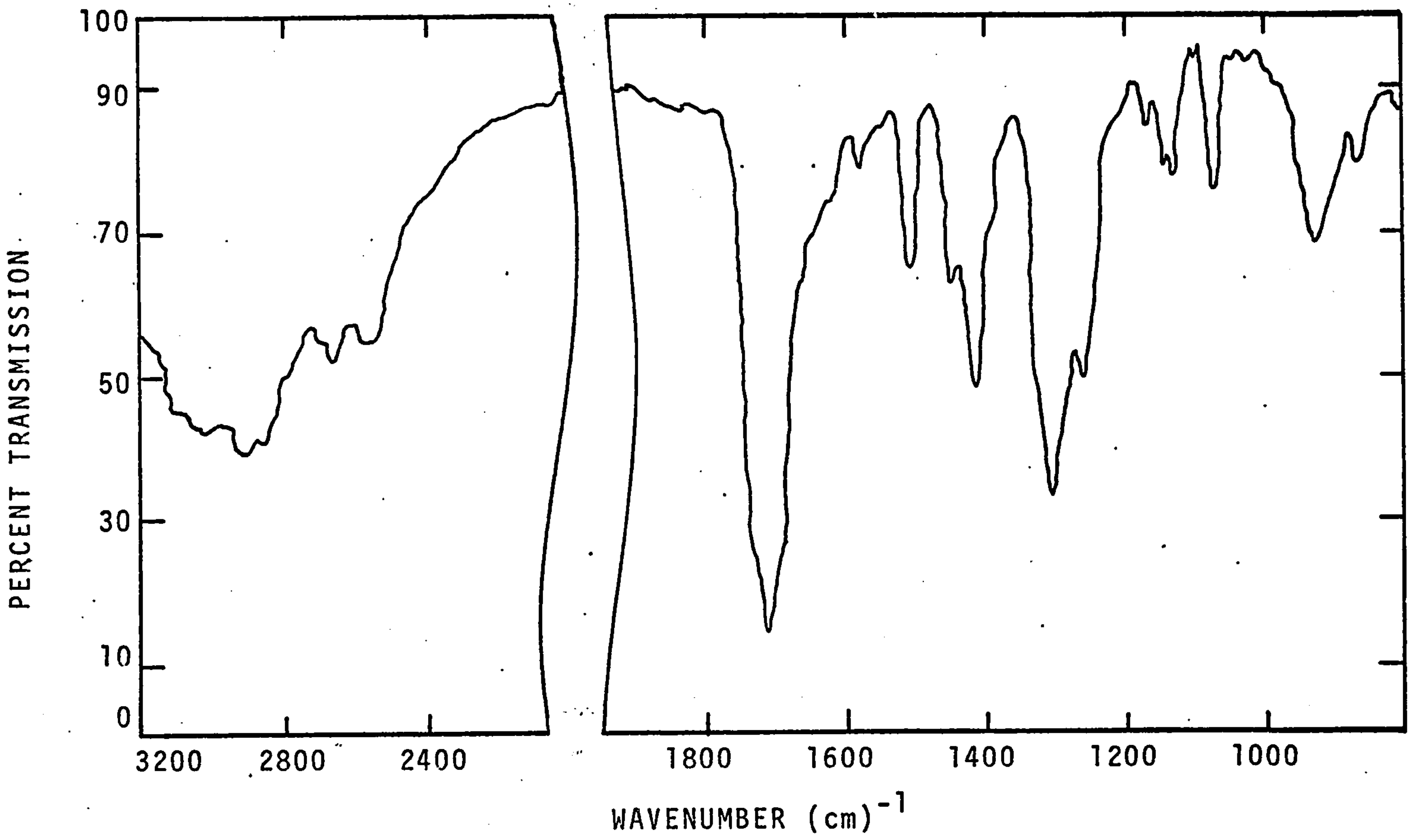

FIGURE AII-3 Infrared Spectrum of Trimellitic Acid to be used as the Standard Spectrum for Carboxylic Acids.

APPENDIX III

PHYSICAL PROPERTIES AND CALIBRATION DATA

TABLE AIII-1 Physical Properties of Pseudocumene 1,2,4-trimethylbenzene.

molecular formula	C_9H_{12}
molecular weight	120.2
melting point	-60.5 °C
boiling point	169.5 °C @ 1 atm.
density	0.889 g./cm^3
insoluble in water	
soluble in alcohol, acetone, ether, and benzene.	

TABLE AIII-2 Physical Properties of Sulfur Dioxide

molecular formula	SO_2
molecular weight	64.07
boiling point	-10.0 °C
specific gravity, gas 1 atm., 0°C, air = 1	2.264
specific gravity, liquid @ 0°C	1.434
vapour pressure @ 70 °F	34.4 psig.
specific volume @ 70 °F	5.9 ft^3/lb.

TABLE AIII-3 Pressure Gauge Calibration.

GAUGE PRESSURE PSIG.	TRUE PRESSURE PSIG.
1000	950
2000	1975
3000	2975
4000	3975
5000	5025

TABLE AIII-4 Thermocouple Calibration.

MERCURY THERMOMETER (±0.1 °C)	CHROMEL-ALUMEL THERMOCOUPLE (°C)
98.5	99.2
78.3	78.7
65.7	65.8
50.4	49.9
35.5	35.1

VITA AUCTORIS

1946	Born in Windsor, Ontario, Canada.
1964	Completed High School at Patterson C.I. in Windsor.
1965	Graduated from one-year program at Windsor Teachers' College.
1970	Received Bachelor of Applied Science Degree from the University of Windsor.
1972	Candidate for the Degree of Master of Applied Science in Chemical Engineering at the University of Windsor.