



A kinetic study of the pyrolysis reactions of acenaphthylene and bifuorenyl  
by Robert Andrew Currie

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of  
DOCTOR OF PHILOSOPHY in CHEMICAL ENGINEERING

Montana State University

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Abstract:

The underlying purpose of this study was to provide kinetic design information to the commercial coking technology. Specifically, the study developed kinetic - correlations with the Arrhenius model from thermal gravimetric pyrolysis data. The pyrolysis studies were conducted under non-isothermal conditions on acenaphthylene and bifuorenyl.

These two compounds were selected because of their probable similarity to coker feed stocks and because acenaphthylene forms a high quality graphite while bifuorenyl forms a relatively poor graphite.

Thermal gravimetric analysis experiments provided the desired pyrolysis data while temperature was increased at a constant rate.

To correlate the major reactions kinetically, it was necessary to obtain and analyze weight-loss data, light hydrocarbon gas evolution rate data, and thermal data. An IBM digital computer was used for data reduction and also for certain statistical programs. Linear regression was used to correlate the data to obtain activation energies and frequency factors. A PACE TR-48 analog computer was used to study thermal pyrolysis data when the reaction did not involve appreciable weight loss or gas evolution.

Bifuorenyl and acenaphthylene each undergo three major reactions that can be analyzed kinetically based on the TGA experimental evidence. Bifuorenyl first reacts in a disproportionation reaction to form volatile fluorene. The remaining reactive material again reacts to form the more volatile fluorene during a second reaction. Both of these reactions are second order. The third major reaction prior to dehydrogenation is first order and forms hydrogen and methane. Acenaphthylene undergoes a first order polymerization step followed by a second order reaction in which the more volatile acenaphthene is formed. The third major reaction prior to dehydrogenation is pseudo first order and forms hydrogen, methane, and ethane. The energy of activation and frequency factor for each reaction prior to dehydrogenation was also determined.

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by

ROBERT ANDREW CURRIE

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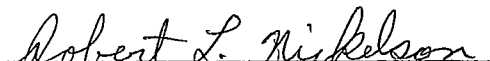
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Approved:



Head, Major Department

  
Chairman, Examining Committee

  
Graduate Dean

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## ABSTRACT

The underlying purpose of this study was to provide kinetic design information to the commercial coking technology. Specifically, the study developed kinetic correlations with the Arrhenius model from thermal gravimetric pyrolysis data. The pyrolysis studies were conducted under non-isothermal conditions on acenaphthylene and bifuorenyl. These two compounds were selected because of their probable similarity to coker feed stocks and because acenaphthylene forms a high quality graphite while bifuorenyl forms a relatively poor graphite.

Thermal gravimetric analysis experiments provided the desired pyrolysis data while temperature was increased at a constant rate. To correlate the major reactions kinetically, it was necessary to obtain and analyze weight-loss data, light hydrocarbon gas evolution rate data, and thermal data. An IBM digital computer was used for data reduction and also for certain statistical programs. Linear regression was used to correlate the data to obtain activation energies and frequency factors. A PACE TR-48 analog computer was used to study thermal pyrolysis data when the reaction did not involve appreciable weight loss or gas evolution.

Bifuorenyl and acenaphthylene each undergo three major reactions that can be analyzed kinetically based on the TGA experimental evidence. Bifuorenyl first reacts in a disproportionation reaction to form volatile fluorene. The remaining reactive material again reacts to form the more volatile fluorene during a second reaction. Both of these reactions are second order. The third major reaction prior to dehydrogenation is first order and forms hydrogen and methane. Acenaphthylene undergoes a first order polymerization step followed by a second order reaction in which the more volatile acenaphthene is formed. The third major reaction prior to dehydrogenation is pseudo first order and forms hydrogen, methane, and ethane. The energy of activation and frequency factor for each reaction prior to dehydrogenation was also determined.

## INTRODUCTION

In October of 1964, an agreement was entered into between Continental Oil Company and Montana State University, Bozeman, in which work was to be done at MSU on the kinetics of pyrolysis of certain high molecular weight aromatic hydrocarbons. It was intended that the research should provide additional technical information which could be pertinent to Conoco's commercial coke production process. To obtain the desired technical correlations, two pure compounds were selected which were representative constituents of coal and petroleum tars (1). The two compounds selected were acenaphthylene and bifuluorenyl. By using representative feed stock compounds the kinetic correlations obtained from pyrolysis data will have direct use for chemical reactor design purposes. As stated in Levenspiel's Chemical Reaction Engineering (2), "Chemical kinetics is simply the study of the factors that influence the rate of reaction and the explanations for the rate of reaction. For the chemical engineer the kinetics of a reaction must be known if he is to make a satisfactory design for equipment in which these reactions are to be effected on a technical scale." If the design engineer has kinetic correlations available, he then has information on how much time the reaction will require to produce a certain level of conversion. Also, when Arrhenius kinetic models are used, the design engineer can obtain an estimate for the most desirable temperature of operation.

(2)

The selection of acenaphthylene and bifluorenyl was also based on information contained in the literature. Union Carbide Corporation has published a series of pertinent documents under contract with the Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio. Most of their work applicable to the studies at MSU was brought up to date in a technical document published in September of 1964 (3). The earlier work done in 1962 was concerned with determining the coking value of various hydrocarbons and with the graphiticity of the resulting carbon (4,5). Later studies placed considerable emphasis on determining the mechanism of the reactions by electron spin resonance, nuclear magnetic resonance, and absorption spectroscopy (1,6). Two of the compounds consistently studied throughout Union Carbide's work were acenaphthylene and bifluorenyl. The studies reported in the literature were not concerned with the kinetics of the reactions involved in the coking sequence. However, the mechanisms reported have served as a guideline for developing the methods to be used in obtaining data for kinetic evaluation.

In the graphiticity studies conducted by Union Carbide (4,5) it was determined that the aromatic hydrocarbons could be placed in either category of "reactive" or "unreactive". The reactive hydrocarbons were thermally unstable and would react at one atmosphere pressure during pyrolysis to form new compounds, while unreactive compounds were simply distilled and did not undergo molecular structure changes. The reactive hydrocarbons were also studied to determine the quality of the carbon-

(3)

aceous residue and the coking value of the original compounds. To determine graphite quality, coke residues such as that produced in commercial coking processes are heated to approximately 3000°C before a quality determination is made.

The quality of graphite was determined by using x-ray diffraction equipment. The lattice spacing provides the desired information concerning the orientation of the graphite. The highly oriented synthetic graphite has a lattice spacing nearly the same as natural graphite. As the lattice spacing increases, the quality of graphite decreases since it becomes poorly oriented and nonplanar. Acenaphthylene produces a graphite in which the planes are well oriented and the lattice spacing is similar to natural graphite (3,7). Bifluorenyl produces a graphite that is highly nonplanar and is quite dissimilar from natural graphite.

Reactive compounds, by definition, leave a coke residue after pyrolysis. The amount of residue remaining at 700°C of the original weight determines the coking value. The properties of the final carbon and graphite depend to a large extent on the chemical constitution of the organic precursor. A listing of the thermally reactive hydrocarbons studied by Union Carbide has previously been reported (3,4,5). The coking value and the graphite quality are given for each reactive hydrocarbon.

(4)

The x-ray diffraction method for determining graphite quality is not sufficiently refined to report accurately variation of quality on a run-to-run basis. That is, on a set of pyrolysis experiments on a particular compound, the lattice spacings from run-to-run would not show sufficient deviation that meaningful correlations could be drawn. For this reason, no effort was made to obtain graphite quality determinations for the pyrolysis runs conducted at MSU. By selecting acenaphthylene and bifluorenyl, kinetic evaluation could be carried out for both a good and a poor graphite producing compound. Also, for this kinetic study it was desirable to choose compounds that produce sufficient volatile material so that weight loss data and gas evolution data could be obtained for use in kinetic evaluation.

During the initial planning phase it was decided to conduct the experimental work to obtain the most useful kinetic design information. In this connection, the pyrolysis was conducted at atmospheric pressure conditions while maintaining an inert environment around the reacting material and reaction products. The reacting material was heated from room temperature to essentially the same final temperature used in commercial coking operations. Because the temperature was continually increasing with time, the classical method of obtaining kinetic parameters under isothermal conditions could not be used. Instead, the temperature was increased at a constant rate and the theoretical kinetic expressions took temperature into consideration as an experimental variable. Data and correlations derived in this manner can then be used

for meaningful non-isothermal design relationships.

The data obtained for kinetic evaluation consisted of three general types. It was necessary to use differential thermal analysis data or similar thermal data to study reactions that were not characterized by weight loss or light hydrocarbon gas evolution. An example of this reaction would be vinyl type polymerization. For reactions that form volatile condensable intermediates, it was necessary to use thermal gravimetric data. For reactions that involve the formation of light-weight hydrocarbon gases, gas chromatography was used to obtain gas evolution rate data. By using all three data collection methods, it was possible to fully examine all the reactions of acenaphthylene and bifluorenyl over the temperature range normally associated with commercial coking processes.

The major reactions for both acenaphthylene and bifluorenyl are shown in Figure 1. This sequence of events is proposed because it is substantiated from MSU experimental results and from mechanism studies conducted by Union Carbide (4,5). The sequence of reactions for acenaphthylene and bifluorenyl provides a series of events as the temperature is increased. Furthermore, each compound has four major reactions. The fourth reaction in both cases involves only dehydrogenation. Dehydrogenation is initiated above temperatures of 550°C and continues to react at temperatures which exceed the capability of the TGA equipment. There is no corresponding measurable weight loss associated with the

(6)

dehydrogenation. This phase of pyrolysis is also very sensitive to temperature fluctuations. Since the temperature interval for the dehydrogenation exceeds the equipment capability, a kinetic study of this reaction was not feasible.

The three major reactions for both compounds shown in Figure 1 were studied in some detail. The proposed sequence does not mean that all of the reacting material must follow this set of reactions. As the pyrolysis proceeds, the exact composition of the reacting mass becomes more doubtful. The literature previously cited indicates that the pyrolysis products at higher temperatures have not been fully identified, although identification of the primary constituent was possible. The proposed reaction sequence was based on the identification of primary constituents and does not account for the formation of unidentified constituents. However, the probable molecular similarity between the identified and unidentified products gives the general reaction sequence additional significance.

## RESEARCH OBJECTIVES

In a general sense, the basic purpose of the project was to contribute to the technical knowledge of the coking process. More specifically, the study was to develop kinetic correlations on the reactions of certain aromatic hydrocarbons during pyrolysis. The kinetic evaluation was to employ the Arrhenius expression which replaces the rate constant with a temperature dependent exponential term. Three parameters for each reaction need to be determined to fully define all terms in this kinetic model. The three unknown parameters are the order of the reaction, the frequency factor, and the energy of activation. By analyzing pyrolysis weight loss data, gas evolution data, and thermal data, kinetic analyses of the various major reactions can be made.

As a secondary objective it was intended that the kinetic results for acenaphthylene be compared with the results for bifulorenyl. This comparison would point out noticeable differences in their behavior during coking. However, this analysis must be qualitative in nature because many factors besides kinetic behavior affect ultimate graphite quality.

## THEORETICAL DISCUSSION

### Arrhenius Kinetic Model:

In the early phases of this project it became evident that the pyrolysis reactions of acenaphthylene and bifulorenyl do not lend themselves to experiments conducted under isothermal conditions. Unfortunately, non-isothermal kinetic data cannot be analyzed by the classical technique of plotting various concentration functions versus time. Since the sequence of reactions for the two compounds studied extend over a considerable temperature range, it was necessary to consider temperature as a variable in the kinetic models.

As discussed in Perry's Chemical Engineers' Handbook (8), Arrhenius in 1889 was able to rationalize the simple exponential function which adequately accounted for temperature effects on the rate of reaction. He arrived at the final form of his exponential equation by assuming an equilibrium situation to which he applied the van't Hoff thermodynamic equation:

$$\frac{d(\ln K)}{dT} = \frac{\Delta E}{RT^2}$$

where K is the ratio of the forward and reverse reaction-rate constants. Arrhenius noted from experimental data that the individual specific reaction rates followed relations of the form  $k = k_0 e^{-E/RT}$  when the thermodynamic equation was integrated while holding E constant over the temperature interval of integration. This later equation is known as the

Arrhenius equation and  $E$  is the energy of activation and  $k_0$  is the frequency factor. As stated by Perry (8), this equation "represents the effect of temperature so accurately that when deviations occur they are usually taken as evidence that the reaction is a composite one or that physical processes are important." For a simple irreversible reaction, the rate of conversion is directly related to the concentration of the reacting material. This relationship involves a rate constant and the concentration term raised to some applicable power. The power of the concentration term is known as the order of the reaction. The order is usually taken as first or second order when the general reaction kinetics are studied unless reaction mechanisms or other physical evidence dictates selection of different orders. Because there was no justification for greater discrimination between reaction orders, orders of reaction other than first or second were not considered. Also, the kinetics for each reaction involves an analysis of the general reaction that best describes the behavior in the applicable temperature interval. Therefore, all reaction orders are to be considered as pseudo orders.

The concentration terms in the kinetic model are dependent upon the volume of the reacting material. Even if the concentration terms were converted to moles of reactant, the volume must be considered as a variable. Since it was impossible to obtain accurate estimates of the volume of the reacting material at any time during pyrolysis, an assumption was made to simplify this analysis. It was assumed that the volume in the reactor varied directly with the weight remaining in the reactor.

(10)

This is the same as assuming that the density in the reactor remains constant, since the volume is equal to the weight in the reactor divided by the density. The values used for the density were determined from experimental analysis. By permitting the volume to vary directly with the weight, experimental weight-loss data was used for a continuous variable in the kinetic model. Also, this permitted the use of concentrations in all the calculations which simplified certain mathematical relationships for data conversion and analysis.

To obtain a temperature dependent kinetic model, the rate constant is replaced by an Arrhenius exponential temperature term. The Arrhenius term involves two unknown parameters which are the frequency factor  $k_0$  and the energy of activation  $E$ . The kinetic model with the Arrhenius term has the form:

$$\frac{dC}{dt} = -k_0 e^{-E/RT} C^n$$

From experimental pyrolysis data the values for  $C$ ,  $dC/dt$ , and  $T$  can be determined. Consequently, for each reaction the parameters  $k_0$ ,  $E$ , and  $n$  must be determined. The exponential term also involves the universal gas constant  $R$ .

#### Linear Regression:

The general approach for obtaining values of frequency factor and energy of activation was to use linear regression. The rate equation employing the Arrhenius exponential term was put into a different form

(11)

by taking the natural logarithm of both sides of the equation. Upon rearranging, the following is obtained:

$$\ln\left(-\frac{dC_A}{dt}\right) - n \ln C_A = \ln k_0 - E/RT$$

By arranging the experimental data into this form and by selecting the order of reaction to be studied, the left hand side of this equation can be combined into a new variable, Y. The term  $1/RT$  can be converted into a new variable, X. In this manner the equation takes on the standard form for linear regression, which is  $Y = B_0 + B_1X$  where  $B_0$  is the intercept of the straight line and is the value for the logarithm of the frequency factor  $k_0$ . The slope of the straight line,  $B_1$ , is the value for the energy of activation E.

To perform the above regression analysis, an IBM 1620 digital computer program was used. This program permits rapid analysis of considerable quantities of experimental data which would be almost impossible to analyze if all the calculations were made by hand methods.

A multiple linear regression program was already written and available at Montana State University, consequently it was only necessary to program the computer to put the experimental data into the proper form for use in the regression program. This program determines the best fitting straight line by minimizing the sum of squares of the error. Once the computer fits the best fitting straight line, the desired values for the unknown parameters are defined.

Free Radical Reactions:

The reactions of acenaphthylene and bifuorenyl involve several major reactions besides the formation of some minor intermediate reaction products. Literature sources (3,5,6) indicate that all the major reactions involve free radicals. Lewis (5) indicates that the pyrolysis of reactive aromatic hydrocarbons is invariably accompanied by the formation of free radical species. It is felt that these radicals are transitory aromatic radicals formed by thermal dissociations of hydrogen at reactive ring sites by cleavage of substituent groups or by rearrangement. Energies of activation for some free radical reactions have been reported in the literature. Ethane has received considerable analysis over the past years. Recent references (9,10) give the energy of activation for the thermal decomposition of ethane to be greater than 70 K cal/mole. Steacie (11) indicates that energy required to get to the reactive transition state is dependent upon the singlet or triplet characteristics of the compound's transition state. If the  $\text{CH}_2$  is in the triplet state, the process will be endothermic and 125 to 150 K cal/mole is a reasonable estimate of the activation energy. If the  $\text{CH}_2$  reorganizes to the singlet state in the process, the reaction will be much less endothermic and 77 K cal/mole is not an unreasonable value. This argument shows that activation energies can vary over a large interval and that the mechanisms associated with the reaction are of considerable importance in explaining energy values.

TGA Thermal Data Analysis:

One reaction of acenaphthylene does not involve weight loss or gas evolution. This reaction is a vinyl type polymerization that is exothermic in nature. The kinetic study for this phase had to be based on thermal data from the TGA unit and from Conoco's DTA unit. The thermal data was obtained under non-isothermal conditions. The TGA data was analyzed by applying unsteady state heat transfer equations to the reacting mass. It was assumed that the material in the reactor behaved as a solid mass so that mixing effects were insignificant.

The partial differential equation relating the temperature to the time and position in a cylinder where end effects are negligible has the form:

$$\frac{\partial T}{\partial t} - \frac{k}{\rho C_p} \frac{\partial^2 T}{\partial r^2} - \frac{k}{\rho C_p r} \frac{\partial T}{\partial r} = \frac{1}{\rho C_p} \frac{\partial Q}{\partial t}$$

where  $k$  is the thermal conductivity,  $C_p$  is the heat capacity,  $\rho$  is the density, and  $\partial Q / \partial t$  is the rate of heat per unit volume generated by the reaction. This equation may be solved with appropriate boundary conditions to account for the heat transfer resistances at the boundary of the reacting mass.

The heat generated by the exothermic reaction is proportional to the rate of reaction. If the heat of reaction is known, the following substitution can be made in the differential equation:

(14)

$$\frac{\partial Q}{\partial t} = k_o e^{-E/RT} C_A^n \Delta H$$

where  $\Delta H$  is the heat of reaction on a mole basis.

To solve the partial differential equation the equation was transformed by using finite differences in the radial direction. Four radial increments were chosen so that cylinders were formed which had equal thickness of  $\Delta r$ . The partial differential equation under these transformations has the form:

$$\frac{\partial T_m}{\partial t} = \frac{k}{\rho C_p} \left[ \frac{T_{m+1} - 2T_m + T_{m-1}}{(\Delta r)^2} + \frac{1}{r_m} \frac{T_m - T_{m-1}}{\Delta r} \right]$$

$$= \frac{1}{\rho C_p} k_o e^{-E/RT_m} C_{A_m}^n \Delta H$$

and upon combining constants and rearranging, the equation becomes:

$$\frac{\partial T_m}{\partial t} = M T_{m+1} - M(2 - \frac{\Delta r}{r_m}) T_m + M(1 - \frac{\Delta r}{r_m}) T_{m-1} + \frac{\Delta H}{C_p} k_o e^{-E/RT_m} C_{A_m}^n$$

After the model for the reacting mass was divided into concentric cylinders, the equation was used on each cylinder by choosing the proper subscripts. Since four radial increments were chosen, there are four ordinary differential equations of the type above that must be solved simultaneously.

(15)

Estimates for the value of various constants also have to be made for conditions involved. The remaining terms must come from experimental data.

Finally, the values for the frequency factor  $k_0$  and the energy of activation were varied on an analog computer to best simulate the experimental temperature trace. An analog computer block diagram for this simulation is shown in Figure 2.

#### DTA Thermal Data Analysis:

The analysis of thermal data for evaluating reaction kinetics has been brought up to date recently by Reed, et al (12). This has proven to be of value in determining reaction kinetics from DTA data. Since DTA samples are very small and involve a large ratio of heat transfer area to sample volume, a perfectly mixed model can be assumed. This model again involves a heat balance where the exothermic reaction contributes heat based on the rate of reaction. The equation is:

$$\frac{dT}{dt} = \frac{hA}{\rho C_p V} (T_s - T) + \frac{k_0}{\rho C_p} e^{-E/RT} C_A^n \Delta H$$

where  $T_s$  is the reference temperature of the DTA unit and  $h$  is the heat transfer coefficient. The constants in this equation can be combined to simplify the form. The values for the combined constants were determined from experimental processes which involved simulation of the temperature on the analog computer. An analog block diagram for simulating the DTA curves is given in Figure 3.

## EXPERIMENTAL CONSIDERATIONS

### General:

After the first preliminary investigations on aromatic hydrocarbon pyrolysis, it became evident that a considerable amount of equipment had to be fabricated or purchased in order to obtain the necessary data for kinetic analysis. This equipment had to be able to operate at temperatures between ambient and 600°C, be able to monitor the weight loss of the pyrolysis sample, be able to collect and analyze all light hydrocarbon gaseous products, be able to monitor the temperature inside the reaction vessel, and also be able to maintain an inert atmosphere around the entire reaction chamber. The equipment used in this project generally consisted of a thermogravimetric analysis unit (TGA), differential thermal analysis (DTA), gas chromatograph, and miscellaneous support apparatuses.

### Thermogravimetric Analysis Unit (TGA):

The TGA unit was fabricated at Montana State University. The basic concept for this unit was first reported by Ewald (13), while certain useful modifications were obtained from an article by McAdie (14). The automatic recording balance as used by Ewald (13) was a modification to a model R Leeds & Northrup automatic recording mechanism. Figure 4 shows the modification made to a Leeds & Northrup mechanism at MSU to make an automatic recording balance useful for the pyrolysis experiments. The balance worked very well throughout the duration of the experiments.

The balancing chain was selected so that a weight loss of one gram would give a movement on the recording pen of about nine inches. The unit was calibrated to obtain an exact conversion factor. The balance proved to be sensitive to changes in weight of less than 0.01 grams. Tests were also made which proved that altering experimental conditions on temperature and inert sweep gas flow rate had essentially no effect on the accuracy of the balance.

The reaction chamber was placed directly below one arm of the automatic recording balance. The entire reaction chamber was custom fabricated to best serve the experimental objectives, and this assembly is shown in Figure 5. The reaction chamber refers to all the miscellaneous equipment necessary to perform the pyrolysis in the reactor, collect all gaseous products, preheat sweep gas and maintain an inert atmosphere around the reactor vessel.

The design of the reaction chamber had to take into consideration four major concepts. First, it was necessary to collect all components that were driven out of the reactor without destroying the automatic balancing capability. The reactor vessel was designed with a small gas exit tube which came out of the top of the reactor parallel to the shaft suspending the vessel from the arm of the balance. The exit tube telescoped into a larger tube fabricated into the lid of the heating chamber. The tube in the lid passed through a water-cooled condenser and into a gas collection system. As the pyrolysis reactions forced gaseous pro-

ducts out of the vessel, all the products were pulled off. The heavier reaction products condensed in the water-cooled condenser while light hydrocarbon gases continued to flow toward the gas collection system.

Second, an inert gas atmosphere had to be maintained at all times. Nitrogen was chosen for this because it was used as a chromatograph carrier gas and also because of its presence in air. Again, the inert atmosphere criterion could not interfere with the recording balance. Consequently, sweep gas had to be allowed to flow freely out of the hole in the heating element lid used by the shaft to the recording balance. This problem was handled by forcing more pre-heated nitrogen into the bottom of the heating element than was drawn off through the condenser. In this way, all the reaction products were swept through the condenser at a given flow rate with nitrogen making up the balance of the exit gas flow stream.

Third, the heating element which freely surrounds the reactor vessel had to be adjustable in all three axes. The element was vertically adjustable to govern the telescoping of the reactor vessel exit tube and the heating element lid. The element was horizontally adjustable in order to permit the reactor to hang freely inside the heating element and also to pass freely through the shaft hole in the heating element lid. The heating element is cylindrical in shape and is housed in a stainless steel can. The nitrogen sweep gas and the heating element electrical leads both enter the bottom of the can. The top is removable and houses the gas exit tubes previously discussed.

Finally, the reactor had to be machined for special features. The vessel was made of stainless steel and had to be designed to minimize its weight. The top of the vessel unscrews for sample insertion and for removing the coke residue after pyrolysis. A thermocouple well extends through the head of the reactor and comes within a quarter of an inch from the bottom of the reactor. By using a continuous strip chart recorder in conjunction with the reactor thermocouple, a continuous record of the reaction temperature was made. However, bringing the thermocouple leads off of the balance without destroying the balance sensitivity required special consideration. It was necessary to solder light, flexible number 34 copper leads to the thermocouple leads to span between the balance and the TGA cabinet. The connection to the cabinet for completing the circuit to the recorder was made by using two glass vials filled with mercury. The fine copper leads were inserted into the mercury before each pyrolysis run.

During each pyrolysis experiment a check of the accuracy of the reactor thermocouple was possible. This check was possible when the initial reactor sample reached the melting point of either acenaphthylene or bifuorenyl. The temperature trace would produce a constant temperature plateau as long as the sample was melting. The melting point temperature obtained from the TGA consistently was within  $\pm 2^{\circ}\text{C}$  of the melting point reported in the literature.

All of the equipment and parts that go together to make up the reactor assembly are housed in a cabinet just below the scales. Portions of the cabinet were water cooled. However, the main function of the cabinet was to provide an additional inert chamber around the reactor assembly. This additional nitrogen atmosphere was employed to minimize any oxygen diffusion around the balance shaft hole in the heating element lid. On early experiments it was noted that some oxygen diffused into the hot products gas stream causing carbon dioxide and water to be formed. As an additional precaution, the head of the heating element can was made of a stainless steel block 1-1/4 inches thick. The balance shaft hole was drilled through the block so that oxygen would have to diffuse a greater distance before coming into contact with the hot reaction products. After these modifications were made, oxygen contamination was not a problem. The diffusion block is shown in Figure 5.

The nitrogen used for sweep gas was first metered through a rotameter and then heated prior to entering the bottom of the heating element can. The heating element around the reactor vessel and the nitrogen pre-heater were controlled by Variacs. The head of the heating element can was clamped onto the can by two large C-clamps. An aluminum foil gasket was placed between the lid and the stainless steel can to minimize the amount of oxygen that could enter between these two pieces. The gas collection system used to pull a given flow rate of gas out of the reactor was controlled by a positive displacement pump. The pump

(21)

removed water from a large jar at a controllable rate. The water removed caused the gaseous reaction products and the nitrogen sweep gas to be drawn through the condenser and through a solenoid-operated, automatic sampling valve on the chromatograph. The sampling valve was actuated periodically to inject a sample into the chromatograph for analysis.

#### Gas Chromatograph:

During the planning phases for this project, it was anticipated that various hydrocarbon gases from methane to n-pentane would have to be analyzed as part of the pyrolysis products. After consulting literature sources it became evident that hydrogen and light hydrocarbon gases up through C<sub>5</sub> could not be analyzed at one time, with one sample, on one column. From information contained in chromatography catalogs it was decided to use a 24-foot partition column of 30% Bis (2-(2-methoxyethoxy) ethyl) ether on chromosorb. This partition column can separate most of the hydrocarbon gases between methane and n-pentane but does not separate hydrogen from methane. Since hydrogen and methane were known to be pyrolysis products, an additional column had to be used. Hydrogen can be separated from methane by using just molecular sieve in a six-foot column. However, the columns can not be used in series because hydrocarbon gases above ethane will not pass through the molecular sieve. Finally, a thermal conductivity chromatograph was modified by a series of quick-opening valves to permit one sample to be injected on molecular sieve for methane-hydrogen separation and analysis and then a second

sample could be injected on the partition column for hydrocarbon gas analysis. As it turned out, the pyrolysis of bifuorenyl only produced appreciable quantities of methane and hydrogen so that the sieve column was sufficient. On acenaphthylene, besides hydrogen and methane, significant quantities of ethane appeared. For this analysis the samples of gas were alternated between the sieve column and the partition column.

To determine the gas evolution rate from the pyrolysis reactions, peak heights on the chromatogram were used. To calibrate the column a gas mixture containing known percentages of hydrogen, methane, and ethane was ordered. These three gases each made up about five percent of the mixture, with the remainder being nitrogen. Since samples were injected into the columns by an automatic gas sampling valve, it was decided to obtain a peak height calibration curve by changing the sample loop size. Sample loops were obtained which had volumes of 1/4, 1, 2, and 4 ml. As each loop was used, a different concentration of standard gas was injected into the chromatograph. In this way it was possible to determine peak heights versus volume percent. Since the reaction products were passing through the system at a known flow rate metered by the gas collection system, the experimental peak heights represented gas evolution rate. A standard sweep gas flow rate of 65 cc/min was chosen. By using the ideal gas law, the calibration curve was plotted as gas evolution rate in moles per minute versus chromatogram peak height in strip chart recorder units.

The chromatograph used nitrogen as a carrier gas, since this carrier works well when hydrogen detection is required. Also, nitrogen was used as the reactor sweep gas and is quite inexpensive compared to most other carriers. The detector and columns were operated at 50°C, and the current to the detector was 200 milli-amperes. The carrier gas flow rate was approximately 110 cc/min at room temperature and 640 mm Hg. The peak heights were recorded on a Brown strip chart recorder at approximately five-minute intervals.

#### Differential Thermal Analysis, (DTA):

One reaction of acenaphthylene was characterized by an exothermic reaction that did not result in weight loss or gas evolution. To analyze this reaction, three DTA runs were made on Conoco's unit. The DTA unit was a Dupont 900 Differential Thermal Analyzer. This apparatus is capable of heating a sample under inert conditions at various heating rates from zero to 30°C per minute. The temperature of the reacting material is measured against the temperature of an inert sample and the temperature difference  $\Delta T$  is monitored.

#### TGA Operating Procedures:

The stainless steel vessel reactor has a volume of just over 10 cubic centimeters. However, pyrolysis runs generally used only about one-third of this volume for the sample. Larger samples had a tendency to bubble out of the reactor as gaseous products were formed. Of importance in this connection was the free volume in the water-cooled condenser for

precipitating the condensable products. By keeping the samples small, plugging was not a problem. Also, the volume of light gaseous products did not exceed the gas collection sweep capability. Pyrolysis runs produced the best results when the voltage to the reactor heating element was increased at a given, predetermined rate. This procedure proved to be extremely important in obtaining reproducible, accurate, meaningful data.

By increasing temperature linearly at some determined rate, several errors are minimized. In this respect, the thermocouple temperature lag is kept approximately constant. The heat applied to the reactor maintains a more constant driving force and minimizes transient behavior. Reaction products are driven off at a constant rate providing smooth weight-loss traces and gas evolution curves for better analysis. To aid in maintaining a constant temperature rate, power was drawn from a constant voltage transformer to prevent line fluctuations. Data obtained in this manner proved to be more reliable and much easier to analyze.

The voltage rates used had to be determined from experience based on the compound under study. If the increase was too slow, the reaction took far too long to go to completion. If the increase was too rapid, the automatic balance could not keep up with the actual weight loss. Also, the rate of gas evolution would be increased causing the volume of the gas to exceed the capability of the gas collection system.

Early experiments were conducted without preheating the nitrogen sweep gas. It was later determined that the sweep gas did not become hot enough on passing through the reactor heating element. As the colder nitrogen came in contact with the volatile reaction products, the products tended to precipitate to the nearest surface. Often the condensed products remained in the telescoping gas exit tubes causing an inaccurate weight-loss trace. Upon preheating the nitrogen, all the volatile material was carried well into the condenser before condensing. The preheated nitrogen never exceeded 320°C prior to entering the reactor area.

#### Post-Pyrolysis Procedures:

After a pyrolysis experiment, the coke in the reactor is scraped out. The condensed products in the condenser are washed out with acetone and the solution is collected in a beaker. From the data available, a check is made on the overall material balance. The coke, condensed products, and light gases are all considered in the weight balance. After some early equipment modifications it was possible to obtain a material balance that accounted for 96 to 98% of the original sample weight. The major part of the missing material is lost from the condensable products during the acetone wash of the condenser. This is quite important since the weight-loss curve is then quite accurate for data correlation. That is, as long as the condensable products leave the reactor zone, the weight-loss trace will show the true pyrolysis weight data.

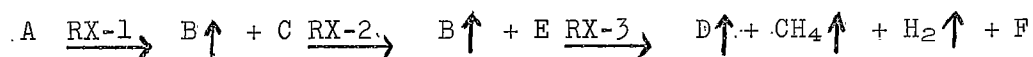
## DISCUSSION AND RESULTS

### General:

The sequence of reactions for acenaphthylene and bifluorenyl provides a natural series of events as temperature increases. Each compound has three major reactions that can be kinetically analyzed from TGA data. These three reactions for both acenaphthylene and bifluorenyl will be considered in some detail. The reactions of bifluorenyl will be discussed in sequence followed by a sequential analysis of acenaphthylene. Certain comparisons between the two compounds will be discussed last.

### Kinetics of Bifluorenyl:

The mechanism studies reported in the literature were very valuable in planning and executing pyrolysis experiments. A set of pyrolysis mechanisms is contained in a Union Carbide Corporation report (3). Figure 6 shows the pyrolysis reactions of bifluorenyl which includes the formation of the bifluorylidene radical. In the pyrolysis of bifluorenyl three separate reactions make up the significant reactions prior to dehydrogenation. Figure 1 shows this main sequence of events as it applies to the kinetic study. The thermal gravimetric data (TGA) substantiates that three reactions are kinetically significant prior to high temperature dehydrogenation. The general reaction sequence and the compound designations are as follows:



In this equation, A represents bifluorenyl, B is fluorene, C is bifluorylidene, D is predominately tetrabenzonaphthalene, E is unreacted tetrabenzonaphthalene or one of its homologs, and F is the carbonaceous material. The molecular structures for these compounds are given in Figure 6. Tetrabenzonaphthalene is shown in this sequence of reactions because Union Carbide was able to identify this compound as part of the reacting mass. A pyrolysis weight-loss trace is depicted in Figure 7, which shows the weight loss associated with each sequence of the pyrolysis. The corresponding temperature trace is also shown on Figure 7.

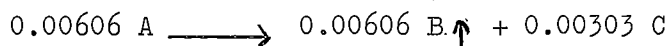
There is one alternate possibility for the third reaction which will be discussed later. Also, more exacting equations with stoichiometric coefficients will be presented with the discussion of each reaction. Table I is a complete listing of all the pyrolysis experiments conducted on bifluorenyl. A brief description of the applicability of each experiment is also given in this table.

The yield of carbonaceous material for bifluorenyl pyrolysis runs conducted at MSU average about 28%. The yield for each run is given in Table I. This yield is comparable to the yield reported in a Union Carbide document (1), which was about 30%. In other work performed by Union Carbide (4) the yield was reported to be as low as 5.8%; however, experimental conditions were not discussed. The carbon yields resulting from MSU pyrolysis runs indicate that the run-to-run variations are quite low.

First Reaction of Bifluorenyl (RX-B-1):

The first reaction of bifluorenyl is a disproportionation to yield reactive fluorene radicals which can abstract hydrogen atoms to form volatile fluorene or dimerize to bifluorylidene. From experimental data the disproportionation begins at about 347°C. The final temperature for this reaction overlaps with the beginning of the second pyrolysis reaction. This overlapping occurs at temperatures greater than approximately 405°C. The volatile fluorene is condensed as a solid in the condenser during pyrolysis. Chromatography has been used to compare a known fluorene sample with the condensate from pyrolysis. Fluorene has thus been identified as the major constituent in the condenser after pyrolysis.

Since the first reaction of bifluorenyl involves disproportionation, the stoichiometric equation in moles based on a two-gram initial sample is:



where A, B, and C are bifluorenyl, fluorene, and bifluorylidene, respectively. The one-to-one mole ratio between A and B simplifies the data conversion equations for concentration. The exact form of the data conversion equations are given later with the applicable computer program.

The kinetic correlations were first studied using a PACE TR-48 analog computer. The general approach was to place the experimental data on the analog function generators and also simulate the desired

kinetic model on the computer. Certain parameters of the chosen model could be varied by adjusting potentiometers. When the simulated model agreed well with the experimental data, the potentiometer settings were recorded. From the settings, best values for the various parameters could be determined.

Considerable effort was spent to make use of mathematical techniques suggested for use on the analog computer in an article by Steinmetz (15). The method employed the concept of steepest descent to provide the optimum values for the unknown parameters. This method did not work well when a kinetic model was anything but simple in nature. The Arrhenius expression presented several problems when this technique was used. The method requires almost twice as much analog equipment as less sophisticated programs. The TR-48 computer at MSU did not have sufficient equipment for the Arrhenius steepest descent program. Secondly, the steepest descent program was quite complicated and consequently lost its versatility rather quickly. Each time a slight change was made in the model or the anticipated value for certain parameters, the program needed considerable revision. Finally, error introduced within the analog equipment also made the results questionable. However, this method made use of some analog techniques that worked very well when combined with other programs. One of the most useful analog techniques that was incorporated in other programs was the use of repetitive operation.

The analog program which proved to be most successful for non-isothermal data required manual adjustment of potentiometers to obtain the best data simulation. Experimental data from Run EX-B-12 was chosen for simulation because of the smooth increase in the temperature during the weight loss. The weight-loss data was placed on one variable diode function generator (VDFG) and the corresponding temperature placed on the second VDFG. A complete analog block diagram for this simulation is shown as Figure 8. For better usage on the analog computer, the Arrhenius equation was put into a form using logarithms to the base ten. The following equations indicate how the Arrhenius expression was handled.

$$\frac{1}{V} \frac{dN_A}{dt} = -k_0 e^{-E/RT} \left( \frac{N_A}{V} \right)^n$$

Assume constant density in the reactor so that  $V = \frac{W_r}{\rho_0}$

where:  $\rho_0 = .957$  grams/cc (from experimental data)

$W_0 = 2.00$  grams bifluorenyl

M.W. fluorene = 166

M.W. bifluorenyl = 330

$E = \alpha E_0$  (for computer reasons) calories/mole

$R = 1.987$  calories/mole °K

$W_r$  = weight in reactor at any time

$k_0 = \text{sec}^{-1}$  1st order; cc/mole sec. 2nd order

$N_A = W_0/330 - (W_0 - W_r)/166 = W_r/166 - 0.00599$

(moles bifluorenyl)

$r$  = scaling factor for analog

(31)

$$\text{Let: } \frac{k}{r} = \frac{k_0}{r} e^{\alpha E_0/RT}$$

For analog usage:

$$\frac{1}{2} \log 100 \left( \frac{k}{r} \right) = \frac{1}{2} \log \frac{100}{r} (k_0) - \frac{40 \left( \frac{\alpha}{80} \right) E_0 / 400}{2.303 R (T/400)}$$

The scaled differential equations solved by the computer were:

1st Order:

$$\left[ \frac{dN_A}{.01 dt} \right] = -r \left[ \frac{k}{r} \right] \left[ \frac{N_A}{.01} \right]$$

2nd Order:

$$\left[ \frac{dN_A}{.01 dt} \right] = - .005 \rho_{or} \left[ \frac{k}{r} \right] \left[ \frac{N_A}{.01} \right]^2 / \left[ \frac{W_r}{2} \right]$$

The optimization is carried out by adjusting the potentiometers for the terms  $(1/20)(\log 100/r)(k_0)$  and  $-40 (\alpha/80)/2.3 R$ . However, the computer introduces a certain amount of error when certain analog components are used. The VDFG units which are used for the experimental data memory can use only ten experimental data points. The VDFG unit then puts a straight line segment between each consecutive pair of data points. This means that a smooth continuous function like a weight-loss curve is simulated by ten consecutive straight line segments. Also, the logarithm generator works on essentially the same idea as the VDFG unit and, consequently, this unit also introduces a certain amount of error. In addition to the above two potentiometers, a third one had to be ad-

justed to provide the scaling factor  $r$ . The adjustment of the factor made changes in the error from the logarithm generator. The optimization is dependent upon matching the segmented curve to the theoretical concentration curve, consequently varying the scaling factor does not affect the optimization. The use of a third potentiometer considerably complicates finding the true minimum error.

The error term is generated by taking the difference between the experimental concentration curve (stored on the VDFG) and the theoretical concentration curve (generated from the Arrhenius expression). This term is squared and integrated over the applicable time period to produce a final value for the total error. The value for the total error is read on a voltmeter.

The weight loss data for the Run EX-B-12 was tried using this method for both first and second order kinetics. The procedure worked quite well within the capability of the equipment. The exact point at which a minimum value of the error occurred could not be determined; instead it was necessary to determine an interval within which the minimum error occurred. For example, the first order reaction gave minimum error values between an energy of activation of 42,500 and 48,200 cal/mole. It was necessary to treat the second order reaction in the same manner. After determining kinetic values for EX-B-12, Run EX-B-2 was chosen because of its different temperature profile. The minimum error range was determined for this run and the results of this

study are given in Table II. From this analog study it was not possible to determine if a first or second order kinetic model fit the data best. Neither visual comparisons nor the final value for the error made it possible to distinguish the proper order of reaction.

After studying Run EX-B-12 and Run EX-B-2 data on the analog computer, it was decided to investigate the possibilities of programming the IBM 1620 digital computer to perform the desired data analysis. Changing computers became necessary when the analog provided a range of acceptable values for each set of data instead of the best value. Besides being a slow, time-consuming analysis, the error generated in the analog equipment may have affected the results to the point of losing the true optimum value.

The general approach for the digital computer was to convert experimental data to applicable concentration and temperature data, obtain rate of reaction data, combine terms and then use linear regression to determine the best values for kinetic parameters. The experimental data was punched directly onto IBM cards in the units used by the strip chart recorders. The computer was then programmed to use conversion factors and stoichiometric equations to convert the experimental data to units of concentration (moles/cc), temperature ( $^{\circ}\text{K}$ ), and time (sec). However, the Arrhenius expression also requires rate data (moles/cc sec). To obtain rate data, the computer was used to fit a polynomial to the concentration and time data. After trying polynomial orders of three

through seven, a sixth order polynomial gave the best fit. The polynomial program provides a value for the sum of squares of the errors and this value was used to determine the degree of the polynomial to use. A print out of the polynomial data was also checked against each set of pyrolysis data. Once the coefficients of the sixth order polynomial were determined, the derivative of the polynomial was taken for each experimental data point (one minute intervals). After this program, the computer rearranged the experimental data into a form for use in a linear regression program. The linear regression program then provided the best values for the energy of activation and the frequency factor. The regression program was run twice, once for a first order reaction and once for a second order reaction. A simplified flow diagram of this procedure is given in Figure 9. A listing of the computer programs for data conversion and rearrangement is given in Table III. The linear regression concept was previously discussed in the Theoretical Considerations section of this thesis.

Five weight-loss pyrolysis experiments were correlated using the digital computer. The experimental data for these five TGA runs are listed in Tables IV through VIII. Table IX lists the five runs and the corresponding results obtained from the regression analysis. Also given is the correlation coefficient for each regression analysis. The correlation coefficient is an indication of the goodness of fit between the regression line and the experimental data. Correlations above 0.90 are

considered good correlations with a perfect correlation being equal to unity.

By analyzing the results of the analog and digital computers, Tables II and IX, several conclusions can be drawn. First, it can be seen that first order results obtained from the analog and the digital computers are similar. The second order results can not be compared because the analog program did not permit values for frequency factor above approximately  $10^{17}$ . Second, by using the digital, it was possible to get results on five pyrolysis runs. Four of these runs showed excellent results as far as comparability. All five runs indicate that a second order fit is consistently better than a first order fit. This can be seen from the correlation coefficient and from the fact that there is very little scatter in the second order results. For example, if we tentatively delete Run EX-B-10, the value for first order energy of activation varies by 6,000 cal/mole while second order varies by only 2,000 cal/mole. The relative error would even improve the argument for second order kinetics. The consistent results obtained indicate that a high degree of reproducibility exists between pyrolysis runs.

The results indicate, also, that selection of a single value for the frequency factor and energy of activation would be difficult to make. This same situation is encountered with the analysis of all the reactions of acenaphthylene and bifuorenyl. However, selection of a single value may be entirely misleading if certain physical and math-

emational considerations are not observed. In determining the error, the Arrhenius temperature correction term should be examined for its effect on the rate of reaction.

In isothermal kinetics the rate equation has the form  $dc_A/dt = kC_A^n$  where  $k$  is the rate constant. The Arrhenius exponential term replaces the rate constant with a term that is temperature dependent. In this form,  $k$  is equal to  $k_0 e^{-E/RT}$ . The effect upon the rate constant  $k$  caused by variations in frequency factor and energy of activation was examined. The digital computer was programmed to calculate values for  $k$  at temperature increments of two degrees centigrade. The program was run once using the frequency factor and activation energy from the lower end of the reported values. Then the same program was run using values from the higher end of the interval. The results of this comparison for the first pyrolysis reaction are given in Table X. This analysis shows that for any given temperature the rate constant is not greatly altered. In fact, the average percentage deviation over a temperature range from 349 to 401°C is 17.4 percent. This indicates that the overall effect on the rate constant is not severe because the frequency factor tends to offset the effects of the activation energy in the Arrhenius expression. However, for design purposes it is recommended that corresponding values of frequency factor and energy of activation be used. Should averaged values for these parameters be used, the canceling effect between the energy of activation and frequency factor may be destroyed so that larger errors would be introduced.

Reporting Arrhenius parameters within an interval is also advisable because of physical considerations associated with the experiments. A discussion of equipment variables was included in the Experimental Considerations section of this thesis.

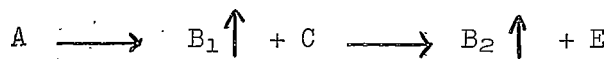
For this reaction, the analysis shows that a second order Arrhenius kinetic model fits the data best. The values for the energy of activation vary from 56,675 cal/mole to 67,330 cal/mole. The frequency factor varies from  $10^{18.2}$  to  $10^{21.8}$  cc/mole sec. Because of disproportionation, the reacting mass loses approximately half of its original weight. Formation of light hydrocarbon gases was not evident; consequently, the kinetic analysis was made entirely on weight-loss data.

#### Second Reaction of Bifluorenyl (RX-B-2):

The second pyrolysis sequence of bifluorenyl is concerned with the continued reaction of bifluorylidene. Previous studies have shown that fluorene is a pyrolysis product of bifluorylidene (4). Since bifluorylidene is a reaction product of bifluorenyl, the formation of more fluorene from bifluorylidene must be considered. Two aspects of this reaction made the experimental data considerably more difficult to handle.

The first problem was that the second reaction appears to start forming more fluorene while the tail end of the first disproportionation reaction was still producing fluorene. Consequently, the analysis had to take into consideration a type of series reaction such as:

(38)



The second problem was that only weight-loss data was available to make this analysis. The amount of fluorene formed by this reaction was quite low. In fact, the weight-loss data to be analyzed makes up only 3.1% of the weight of the initial sample. In the process of analysis when such small numbers are involved in subtractive terms, considerable error can be introduced.

Even with the above handicap a satisfactory IBM program was developed to handle this reaction. The first step was to use the kinetic information previously obtained on the first reaction to predict the nature of the weight-loss data for the first reaction when carried to near 100% completion. That is, the known value of the frequency factor and energy of activation for each pyrolysis run was used with the corresponding temperature data to predict the weight-loss at any time for the first reaction. This means that if concentrations are used (instead of actual weight-loss data), and if the disproportionation reaction was  $2A \longrightarrow 2B_1 \uparrow + C$ , the Arrhenius expression would be:

$$\frac{dC_A}{dt} = -k_0 e^{-E/RT} C_A^n$$

$k_0$  -- obtained from previous analysis for each pyrolysis run

$E$  -- obtained from previous analysis for each pyrolysis run

$n$  -- previously determined to be second order

T -- known from pyrolysis temperature trace

t -- one-minute intervals

$C_A$  -- known from weight-loss data and stoichiometry at all points prior to the beginning of the second reaction

$\frac{dC_A}{dt}$  -- dependent variable for the equation to be solved by numerical solution of differential equation

The idea behind this is that if all the information prior to initiation of the second reaction is known, an approximation (extrapolation) can be made to determine  $C_A$  and  $dC_A/dt$  for each minute interval after the second reaction begins. For this, it was found that the Adams-Bashforth method for the numerical solution of differential equations worked best (16). Both the open formula (prediction of a new value) and the closed formula (refinement of the prediction) were used. In fact, the computer was programmed to use the refinement formula four times prior to moving to the next prediction. Milne's method (16) was also tried but proved to become unstable over the range of the numerical solution. The Adams-Bashforth method was also recommended because of its computer adaptability and the corresponding accuracy that can be obtained.

To continue the analysis the rate of reaction of bifluorylidene (C) is defined by the following statement: The rate of change of concentration of C is equal to the rate of formation of C from the first reaction minus the rate of reaction of C from the second reaction.

(40)

In terms of the Arrhenius model:

$$\frac{dC_C}{dt} = 1/2 k_{oA} e^{-E_A/RT} C_A^2 - k_{oC} e^{-E_C/RT} C_C^n$$

In this equation the one-half comes from the stoichiometry of the first reaction and the values for  $C_A$  have been obtained by using the Adams method. By rearranging terms, it becomes possible to put this equation into a form such that linear regression can be used.

$$-\frac{dC_C}{dt} + 1/2 k_{oA} e^{-E_A/RT} C_A^2 = k_{oC} e^{-E_C/RT} C_C^n$$

$$\ln \left[ \left( -\frac{dC_C}{dt} \right) + 1/2 k_{oA} e^{-E_A/RT} C_A^2 \right] = \ln k_{oC} - E_C/RT + n \ln C_C$$

$$\ln \left[ \left( -\frac{dC_C}{dt} \right) + 1/2 k_{oA} e^{-E_A/RT} C_A^2 \right] - n \ln C_C = \ln k_{oC} - E_C/RT$$

If the terms are summed so that the entire left side of the equation is one variable and the other variable is  $1/RT$ , the resulting terms will fit into a linear regression program. The regression program then provides the best values for  $\ln k_{oC}$  and  $E_C$  and also gives certain statistical information concerning the goodness of fit.

In the above equation the values for  $dC_C/dt$  and  $C_C$  must still be determined from experimental weight-loss data. To obtain the two desired values, an approach similar to the analysis of the first reaction

(41)

was used. That is, the value for  $C_C$  was determined from the weight-loss and stoichiometric data. Once this was obtained, all the values for  $C_C$  were fit to a sixth order polynomial. The IBM computer fits this data versus time and gives the desired coefficients of the best sixth order polynomial. The IBM then takes the derivative of the polynomial to determine values of  $dC_C/dt$  at each corresponding point of  $C_C$ . Once the desired order of reaction is chosen (either first or second), all the information is available to permit the computer to determine the desired X, Y regression data.

The relationship between the stoichiometry, weight-loss data and  $C_C$  is not a simple expression. The development of the equation for the concentration of  $C_C$  assumes that the density in the reactor is constant; therefore, the volume varies directly with the weight of the sample in the reactor. The development of the equation is as follows:

The amount of bifluorylidene (C) formed at any time is related to the amount of bifluorenyl (A) reacted at any time.

$$C_C \text{ formed} = \frac{\rho_o}{2W_r} (N_{A_0} - N_A) = 1/2 \left( \frac{\rho_o N_{A_0}}{W_r} - C_A \right)$$

where:  $W_r$  = weight in reactor at any time  
 $N_{A_0}$  = moles of bifluorenyl initially  
 $N_A$  = moles of bifluorenyl unreacted at any time  
and must be determined from the numerical solution of the differential equation for the first reaction

(42)

$\rho_o$  = constant density

1/2 = first reaction stoichiometric coefficient

The amount of bifluorylidene (C) reacted is related to the weight-loss trace by the stoichiometry of the second reaction. The second reaction has the form  $mC \longrightarrow nB_2 \uparrow + E$  where m and n are the stoichiometric coefficients of bifluorylidene (C) and fluorene (B), respectively.

The amount of  $C_C$  present at any time is given by:

$$C_C = C_{C \text{ formed}} - m/n C_{B_2}$$

The amount of fluorene formed is related also to the first reaction in which fluorene is the major product:

$$C_{B_2} = \left( \frac{\rho_o}{W_r} \right) \left( \frac{W_o - W_r}{166} \right) - \left( \frac{N_{A_o} \rho_o}{W_r} - C_A \right)$$

where:  $C_{B_2}$  is the difference between total fluorene evolved and the amount produced by the first reaction.

Figure 7 shows a sketch of the weight-loss trace for this reaction. By combining terms and solving for the desired concentration of bifluorylidene (C) at any time, the following is obtained:

(43)

$$C_C = 1/2 \left[ \frac{\rho_o N_{A_o}}{W_r} - C_A \right] - (m/n) \left[ \left( \frac{\rho_o}{W_r} \right) \left( \frac{W_o - W_r}{166} \right) - \frac{N_{A_o} \rho_o}{W_r} - C_A \right]$$

where:  $C_A$  must come from predicted values (numerical solution)  
 $m$  and  $n$  must come from the weight-loss trace and are  
the total moles reacted and produced, respectively.

$W_o$  is the initial sample size in grams

$N_{A_o}$  is the initial number of moles of bifluorenyl at the  
beginning of the run

166 is the molecular weight of fluorene

A computer flow diagram for this reaction is shown in Figure 10.  
This figure is oversimplified to show the general sequence of events.  
In the actual computer program several steps were combined to improve  
computer efficiency; consequently not all the intermediate data was  
repeatedly punched on IBM cards. Tables XI and XII give the actual  
computer program for this analysis.

From the above analysis it would appear that each set of data from  
one pyrolysis experiment would only have to be run once to determine the  
desired kinetic parameters. However, certain difficulties are involved  
that made it necessary to run each set of data several times to deter-  
mine the best set of conditions and statistics. It was determined that  
the following variables had to be considered:

- 1) The first consideration was the stoichiometry of the second reaction that produces  $n$  moles of fluorene. This value could not be determined accurately enough from the experimental data since so little weight loss is involved in the reaction. The value for  $n$  had to be varied slightly to improve the goodness of fit.
- 2) The second consideration was the starting point from which the numerical solution to the differential equation was begun. Starting several minutes prior to the initiation of the second reaction introduced error in the approximation.
- 3) The third consideration was the use of  $X, Y$  data after the maximum concentration of bifluorylidene had been obtained. The kinetic models for the decay of  $C_G$  did not fit the data when the concentration of  $C_G$  was still increasing. This problem may have been caused because the sixth order polynomial failed to fit accurately the data over this interval. The rising concentration portion of the data was consequently not used in the polynomial or linear regression.

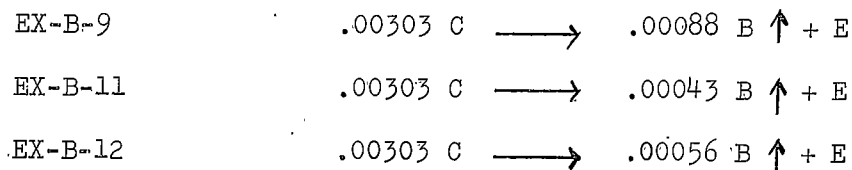
Table XIII gives the pertinent results from this study. It is easily shown that the order of this reaction is of the second order. The first order Arrhenius model did not fit the data at all well. In Table XIII the various values for the stoichiometric coefficients that were tried are also listed. From this table it becomes apparent that only a slight

change in stoichiometry has a considerable effect on the kinetic parameters. Also, the starting point for the solution to the differential equation has an effect upon the kinetic results. It may appear from Table XIII that a thorough analysis of first order kinetics was not made. However, about six additional IBM runs were made on each set of data which fully indicated the order of reaction. The values reported were runs to improve the accuracy of the correlation and stoichiometric values.

To summarize this reaction, Table XIV has been included which takes into consideration the correlation coefficient, the accuracy of the solution to the differential equation and the weight-loss data available for determining stoichiometry. Also, the applicability of the pyrolysis run in general should be considered. In this connection, Run EX-B-11 should be looked upon as doubtful. The temperature associated with the second reaction is poor in that the temperature was quite erratic during this phase of weight-loss. This can be seen in the correlation coefficient which is rather poor compared to the other two runs. Too, this run appeared to be affected more by the starting point of the numerical approximation than did other runs.

It should also be pointed out that since it was necessary to have kinetic parameters for the first reaction to be used in the second reaction, only those runs which were previously studied could be used in this analysis. The three following equations give the stoichiometry for a two-gram initial sample of bifluorenyl, as based on experimental weight-loss data.

(46)



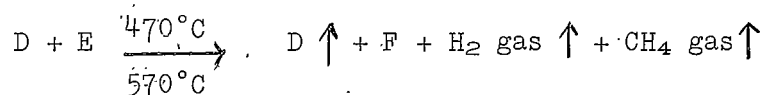
As stated previously, the second reaction is characterized by a second order kinetic expression. The values for the energy of activation varied from 47,007 to 66,415 cal/mol and the frequency factor varied from  $10^{14.4}$  to  $10^{20.6}$  cc/mol sec. Even though it is necessary to report a range of values, this appears to be sufficient when all the analysis problems are considered along with the variations introduced from conducting each pyrolysis run in a slightly different manner.

Third Reaction of Bifluorenyl (RX-B-3):

The third reaction of bifluorenyl begins above a temperature of 470°C and is generally completed by 570°C. This reaction is characterized by both a weight loss and light hydrocarbon gas evolution. There is a separation between the second and third reaction of bifluorenyl so that it is not necessary to consider this phase under the conditions of a series reaction. However, two possibilities exist for this pyrolysis data based on literature information and laboratory experience. Literature sources indicate that bifluorylidene reacts to form two stable compounds (5,6). The first thermally stable compound formed is fluorene. The second thermally stable compound formed is tetrabenzonaphthalene. Lewis (5) reports the boiling point of this compound to be approximately 565°C based on TGA work. Since the boiling point is above the tempera-

ture at which most of the weight-loss occurs for the third reaction, two possibilities must be considered.

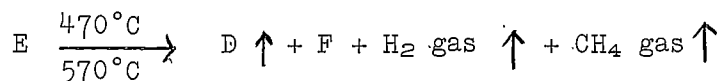
- a) The tetrabenzonaphthalene type compounds are formed at lower temperatures, perhaps even simultaneously with the formation of fluorene in the second reaction of bifluorenyl. If so, the weight-loss trace of the third reaction is only a distillation curve and not indicative of the reaction kinetics. If so, the evolution of light hydrocarbon gases is the only information to be used for kinetic analysis. Under this assumption the reaction would take on the form:



where D is tetrabenzonaphthalene formed in previous reactions but distilled at higher temperatures. E would be the thermally unstable compounds formed during the second reaction previously discussed. F would be the condensed polynuclear aromatic compounds that remain in the reactor as coke and later undergo dehydrogenation.

- b) Tetrabenzonaphthalene is formed in the third reaction along with the evolution of hydrogen and methane. Under this condition, it is possible that tetrabenzonaphthalene is driven out of the reactor as fast as it is formed. Consequently, the weight-loss would be of kinetic nature and

could be analyzed. There is a possibility that the gas-evolution and the weight-loss occur from the same reaction (not just simultaneous reactions). If so, the kinetic results should indicate this similarity. Under the assumptions of this second model, a general reaction form would be:



where E is the entire quantity of material remaining in the reactor after the second reaction of bifuorenyl. D would be the tetrabenzonaphthalene type compounds that are formed and immediately driven out of the reactor. F would again be the product that later forms the coke. A typical weight-loss trace for this phase is also included in Figure 7.

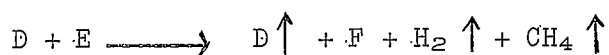
#### Third Reaction, Model (a):

The kinetics for Model (a) are determined from the hydrogen gas evolution while the weight-loss data is taken into consideration only as a volume change parameter. The assumption of constant density was again made; therefore, the volume varies directly with the weight remaining in the reactor. The gas evolution curve for hydrogen from pyrolysis Run EX-B-12 is shown in Figure 11; the corresponding temperature is also shown.

Since the second reaction (previously discussed) is completed before gas evolution begins, it is not necessary to consider a series

reaction. The weight-loss data is used to determine the number of moles of tetrabenzonaphthalene that were previously formed and which are distilled under the assumptions of this model. The remaining weight is the material which reacts to form the coke material, hydrogen and methane. Consequently, the number of moles of starting material is known for each pyrolysis run once a molecular weight is determined. From Union Carbide studies of bifluorylidene (compound "C" in previous discussions) the average molecular weight for remaining material at 400°C is 565 and 450°C is 604. Since this material was essentially formed by the time the temperature was 450°C, the value of 604 for molecular weight was used for the thermally reactive material of reaction three.

The experimental data was again transformed into the necessary form for regression analysis. However, the data from the chromatograph is rate of evolution and not total evolution as in the case of weight-loss data. The general reaction expression for the third reaction under model one is:



therefore:

$$\frac{dC_E}{dt} = -k_{oE} e^{-E_E/RT} C_E^n$$

Values of  $dN_{H_2}/dt$  are known from chromatograph data for each five-minute interval. For this analysis a smooth curve was drawn through all

(50)

the evolution data and values of  $dN_{H_2}/dt$  obtained for minute intervals. From the stoichiometry of the reaction the corresponding values for  $dC_E/dt$  were obtained for each  $dN_{H_2}/dt$  value.

The relationships are:

$$N_{E_0} - N_E = (q/r) N_{H_2}$$

$$-\frac{dN_E}{dt} = (q/r) \frac{dN_{H_2}}{dt}$$

converting units:

$$-\frac{dC_E}{dt} = (q/r) (\rho_0/W_r) \left( \frac{dN_{H_2}}{dt} \right)$$

where:

$q$  is the moles of E initially (stoichiometry)

$r$  is the total moles of hydrogen evolved through the reaction under study (stoichiometry)

$\rho_0$  is constant density

$W_r$  is the weight in the reactor at any time  
(volume correction)

To obtain values of  $C_E$  at any time it is necessary to integrate the area under the  $dN_{H_2}/dt$  versus time curve. Since very little error is introduced upon integration, a simple trapezoid integration over one-minute intervals was performed. The IBM computer was programmed to provide the total moles of hydrogen evolved after each new minute incre-

(51)

ment. Using the same initial equation as before:

$$N_E = N_{E_0} - (q/r)(N_{H_2})$$

$$C_E = (N_{E_0})(\rho_o/w_r) - (q/r)(\rho_o/w_r)(N_{H_2})$$

Since  $N_{E_0}$  is equal to  $q$  from the stoichiometry:

$$C_E = (N_{E_0})(\rho_o/w_r)(1 - N_{H_2}/r)$$

where:  $N_{E_0}$  is obtained from weight data

$N_{H_2}$  is provided by incremental integration

$r$  is the total number of moles of hydrogen evolved  
and is the final value for the incremental integration

Once all the values have been determined, the necessary information is available for linear regression analysis. A simplified flow diagram for this sequence is depicted in Figure 12. Table XV gives a listing of the actual computer program. The analysis of the third reaction was based on four pyrolysis runs. The TGA experimental data for the four runs are given in Tables XVI through XIX.

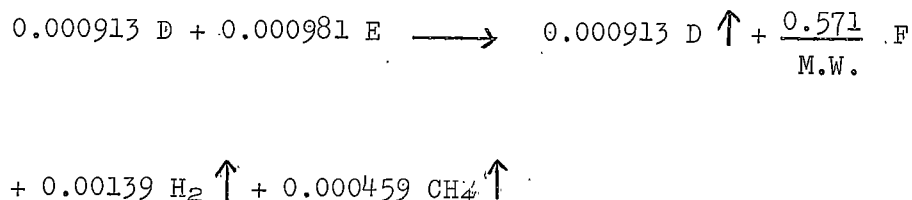
The third reaction was not as difficult to analyze as the second reaction because the stoichiometry is fixed to a single value, derivative data was directly available, the polynomial fit program was not used, and a numerical solution of a differential equation was not re-

quired. Each set of data was run only once. The results of this analysis are given in Table XX. The values listed for stoichiometric coefficients came from experimental data.

From the data of Table XX several things become evident. The third reaction is best described by first order kinetics. In fact, the first order kinetics consistently gave a very good fit as indicated by the correlation coefficient. The values for the frequency factor and the energy of activation again produced an interval of values. Also, the values are higher than on earlier reactions. Literature sources indicate that there are free radicals present during reaction which tend to cause high values for  $E$  and  $k_0$ . Also, it has been previously noted that this reaction is extremely sensitive to temperature fluctuation. This is the reason EX-B-2 data was not considered for analysis. However, EX-B-8 could be used since the third reaction is not affected by difficulties encountered at lower temperatures. Some of the variables which affect the results have been previously discussed.

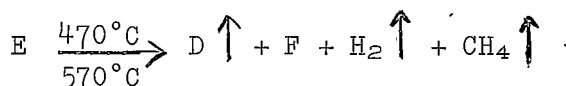
The results shown in Table XX indicate that model (a) of the third reaction is first order and that the values for frequency factor vary from  $10^{13.4}$  to  $10^{22.7} \text{ sec}^{-1}$ , while the activation energies vary from 62,287 to 96,874 cal/mole. An average stoichiometric equation for this reaction would be:

(53)



Third Reaction Model (b) (RX-B-3):

The kinetics for model (b) are determined from weight-loss data. With this model it is assumed that tetrabenzonaphthalene is formed during the third pyrolysis reaction and that it is driven out of the reactor as fast as it is formed. Under these assumptions the general equation for the second model would be:



where E is the entire quantity of material remaining in the reactor after the second reaction of bifluorenyl. D is the tetrabenzonaphthalene type compounds that are driven out of the reactor and condensed. F is the material that later undergoes dehydrogenation to form the coke residue.

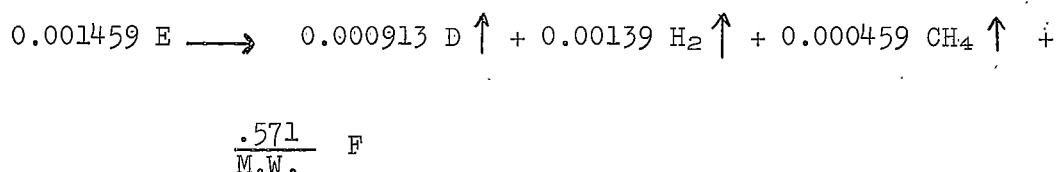
The analysis of this weight-loss data was very similar to the analysis of the first bifluorenyl reaction. The equation which relates the concentration of the reacting material to the weight-loss data is:

$$C_E = \frac{\rho_{\circ} N_{E_{\circ}}}{W_r} \left[ 1 - \frac{W_{E_{\circ}} - W_r}{328 N_D} \right]$$

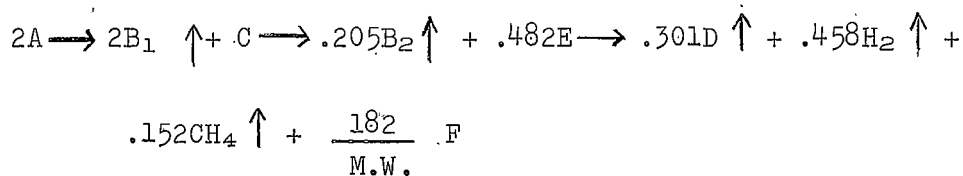
where  $C_E$  is the concentration of reaction material,  $N_{E_0}$  is the initial moles of reacting material,  $W_P$  is the weight in the reactor at any time,  $W_{E_0}$  is the initial weight of E in the reactor and  $N_D$  is the total number of moles of tetrabenzonaphthalene formed. The actual IBM computer program for this sequence is given in Table XXI. A sixth order polynomial was used to fit the data and to obtain concentration rate data. The results from linear regression are given in Table XXII. Also listed are the values that were used for  $W_{E_0}$ ,  $N_{E_0}$ , and  $N_D$ .

The kinetic analysis for the weight-loss data indicates that a first order Arrhenius expression fits the data best. Consequently, both models of reaction three predict first order kinetics. The range of values for the activation energy were 49,810 to 75,069 cal/mole. This compares with the first model values which were 62,287 to 96,874 cal/mole. The frequency factors for the first and second model, respectively, were  $10^{13.4}$  to  $10^{22.7}$  and  $10^{10.3}$  to  $10^{17.2}$   $\text{sec}^{-1}$ . The results of the second model suggest that weight-loss of the third reaction is not a simple distillation of tetrabenzonaphthalene and therefore the first model as proposed is not entirely correct. However, the kinetic analysis of model (a) under the equation  $D + E \longrightarrow D \uparrow + F + H_2 + CH_4$  is synonymous with the analysis of the equation  $E \longrightarrow D \uparrow + F + H_2 + CH_4$  provided gas evolution data is simulated. This happens because the entire kinetic analysis is based on the shape of the hydrogen evolution curve which is the same curve for both equations.

Because the distillation model appears doubtful by the analysis of model (b), only the formation behavior of tetrabenzonaphthalene needs to be considered. The gas evolution data and the weight-loss data both gave better first order kinetics than second order. The high correlation associated with the second order indicates that for design purposes both orders come close to describing the reaction. Since the values for frequency factor and activation energies were within reasonable magnitude of each other, it is felt that the formation of tetrabenzonaphthalene is first order and is simultaneous with the formation of hydrogen and methane. This means that the average stoichiometric equation for the third reaction of bifluorenyl has the form:



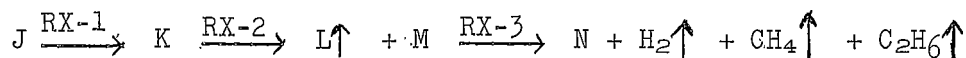
The stoichiometric equations for the separate reactions of bifluorenyl can be combined into one overall stoichiometric equation. Starting with two moles of bifluorenyl the general stoichiometric equation is:



In this equation a molecular weight for the coke residue F was not assigned.

Kinetics of Acenaphthylene:

Figure 13 shows the pyrolysis sequences of acenaphthylene as reported by Union Carbide (3). This sequence also shows the formation of a minor constituent decacyclene and the presence of a reactive radical. These intermediates are not significant in developing kinetic expressions for the major reactions. The pyrolysis data indicates that three reactions are significant before the high temperature dehydrogenation occurs. This sequence of reactions was shown in Figure 1. The general sequence of reactions has the following form:



where J is acenaphthylene, K is a polymer of acenaphthylene, L is volatile acenaphthene, M is a thermally reactive zethrene species, and N are the dimers of zethrene which undergo dehydrogenation. Zethrene was used in this sequence because it was identified by Union Carbide as a constituent of the reacting mass. A typical weight-loss and temperature trace are depicted in Figure 14 for the pyrolysis of acenaphthylene. Table XXIII is a complete listing of all the pyrolysis experiments conducted on acenaphthylene. Certain experimental parameters are given in this table along with a brief description of the applicability of each run. The final temperature and corresponding yield of carbonaceous residue are also listed. The yield of carbonaceous material for acenaphthylene pyrolysis runs conducted at MSU averaged about 42%. This yield compares closely to yields reported in the literature for the pyrolysis of ace-

naphthylene. Mitchell (7) reports a yield of 40.1% while Union Carbide (1) reports 41% carbon yield in an atmospheric system under normal coking conditions. The run-to-run variation in the coke yield was quite low as can be seen from data in Table XXIII.

Reaction One of Acenaphthylene (RX-A-1):

The first reaction is the formation of a polymer of the acenaphthylene monomer. The polymerization is of the vinyl type and is thought to be a free radical reaction. This reaction did not result in weight-loss or light hydrocarbon gas evolution. However, the reaction was exothermic which then made it possible to arrive at the reaction kinetics through the use of thermal data. Thermal data obtained from three TGA pyrolysis experiments along with differential thermal analysis (DTA) data were used for this study. The analysis of thermal data to obtain kinetic correlations has been brought up to date recently by Reed (12). This has proven to be valuable in determining kinetics from DTA data. Thermal data from the TGA unit provided a continuous trace of the temperature at the center of the reacting mass. When an exothermic reaction takes place in an increasing temperature environment, the internal temperature will change at a different rate than the surroundings. From the shape of these curves information concerning the reaction kinetics can be obtained.

The heat transfer equations that were used for studying the various thermal data are given in the theoretical discussion section of this

thesis. For the study of both the TGA data and the DTA data, the analog computer was used to simulate the experimental temperature data. The analysis of the TGA thermal data was based on three pyrolysis runs conducted at different heating rates. The results from Runs EX-A-7, EX-A-8, and EX-A-10 were used for this study. The actual temperature and time data for these runs are given in Figure 15. The simulation of these runs did not provide conclusive results regarding the kinetics of this reaction. The difficulty arose in trying to decide if the first order kinetic model or the second order model provided the best correlation. Values for frequency factor and activation energy were obtained for both orders but the decision as to the best order had to be made from other correlations. Figure 16 depicts an actual analog simulated curve plotted through known experimental temperatures for Runs EX-A-7 and EX-A-8.

The DTA data proved to be valuable in deciding upon the order of the polymerization reaction. The analog block diagram for simulation of the DTA curves is shown in Figure 3. Figure 17 depicts the DTA traces used for this analysis. The first order model proved to fit the DTA curves for both the rising portion of the curve and for the decaying portion. The second order model provided a good fit only on the increasing portion of the curve. From this simulation it was determined that the reaction was first order in nature.

By combining the results from the analysis of TGA and DTA data, it was determined that a first order Arrhenius kinetic model with an activation energy of 27,500 calories per mole and a frequency factor of  $10^{7.5}$  reciprocal seconds best described the polymerization reaction.

Second Reaction of Acenaphthylene (RX-A-2):

This reaction is characterized by the weight-loss associated with the formation of acenaphthene. Thermal degradation of the polymer units results in reactive acenaphthene radicals which abstract hydrogen to form the volatile acenaphthene or form dimeric unsaturated units of acenaphthylene. Union Carbide (3) reports that the dimeric unsaturates undergo carbon-carbon bond cleavages within the strained 5-member ring to form zethrene analogs. The above sequence of events is substantiated in part by the TGA data obtained during pyrolysis. The weight-loss associated with acenaphthene begins at about 340°C and continues to a temperature of about 390°C. During the last of this weight-loss, the evolution of some hydrogen is evident. This evolution would be associated with the rearrangement of the 5-member rings to form zethrene analogs. The amount of hydrogen evolved is not sufficient to be used for kinetic analysis purposes. Weight loss for the ring cleavage reaction would be negligible and there was no evidence of an appreciable exothermic or endothermic reaction. Consequently, for kinetic evolution it can be assumed that the overall reaction in the 340 to 390°C temperature interval is the formation of volatile acenaphthene and thermally reactive zethrene analogs. The weight-loss trace for this sequence is depicted in Figure 14.

The kinetic analysis of this weight-loss reaction was similar to previous analyses except that the concentration data were not approximated with a polynomial curve to obtain rate data.

The nature of the weight-loss curve did not permit a polynomial to fit the data with sufficient accuracy to guarantee reliable rate data. Several different polynomial orders were tried but the error remained significant. To obtain rate data, a simple expression was used to approximate the slope of the concentration curve. The equation used to obtain the rate of change at each data point was:

$$y_0' = (2y_2 + y_1 - y_{-1} - 2y_{-2})/10 h$$

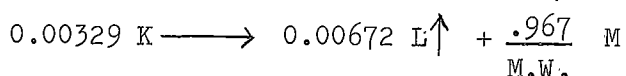
From this equation the slope at the midpoint of five consecutive concentration data points can be obtained. If  $y_0$  is the data point at which the slope is to be determined, then two data points before and two points after  $y_0$  are needed. The distance between the equally spaced data is  $h$ , and for this approximation the interval was one minute. The use of this equation made it possible to convert raw data, obtain rate data and rearrange terms for regression analysis all in one simple computer program. A simplified flow diagram for this program is given in Figure 18. The data conversion equations are also shown in this figure. The actual computer program is listed in Table XXIV.

Pyrolysis experiments EX-A-14, -15, -16, and -17 were made after the study of bifluorenyl was completed. A listing of this TGA experi-

mental data is given in Tables XXV through XXVIII. From studying bifluorenyl data it was evident that the best pyrolysis data was obtained when the rate of temperature increase was kept as constant as possible. An exact straight line for temperature could not be maintained because it was necessary to manually increase a Variac at given time intervals to increase the voltage to the reactor heating element. However, by operating in this manner, temperature fluctuations experienced with bifluorenyl were greatly minimized. The average temperature rise over the temperatures associated with this reaction are listed with the kinetic results in Table XXIX. Tables XXV through XXVIII give the tabulated pyrolysis data for Runs EX-A-14 through -17, respectively. Since these tables give the complete pyrolysis data through temperatures of 600°C, the data used for each analysis are indicated in the corresponding table.

From the results shown in Table XXIX, it is evident that the second major reaction of acenaphthylene is best described by second order kinetics. The activation energies varied from 133,851 to 163,061 calories per mole while the frequency factors varied from  $10^{45.2}$  to  $10^{55.2}$  cc/mole sec. On a percentage basis, the interval of values is about the same as reported for bifluorenyl. However, the absolute values of these kinetic parameters are more than twice as large as the values for the first reaction of bifluorenyl. The average stoichiometric equation for this analysis based on experiments EX-A-14 through -17 is:

(62)

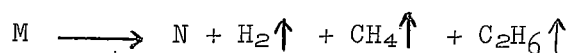


where K is the polymer with four monomer units of acenaphthylene, L is volatile acenaphthene, and M is zethrene analogs that are thermally unstable.

Third Reaction of Acenaphthylene (RX-A-3):

As in the case of the second reaction, pyrolysis data from Runs EX-A-14 through -17 were used for analysis. The data for this analysis are included in Tables XXV through XXVIII. This reaction begins when the temperature reaches about 445°C and continues until about 550°C. The evolution of hydrogen, methane, and some ethane is evident within this temperature zone. There is some weight-loss during this phase of pyrolysis but the rate of weight loss tends to be rather constant in nature. The weight loss was taken into consideration only as a term that affects the volume of material within the reactor. The shape of the hydrogen, methane, and ethane evolution curves were quite similar in nature. Sufficient evolution occurred so that the rate data for both hydrogen and methane were separately analyzed for kinetic values. Union Carbide reports that this reaction is the dimerization of zethrene.

To obtain an analysis of this step, the computer program for the gas evolution reaction of bifluorenyl was used. The only change required was to use the proper pyrolysis data and stoichiometry. The general reaction equation can be represented by:

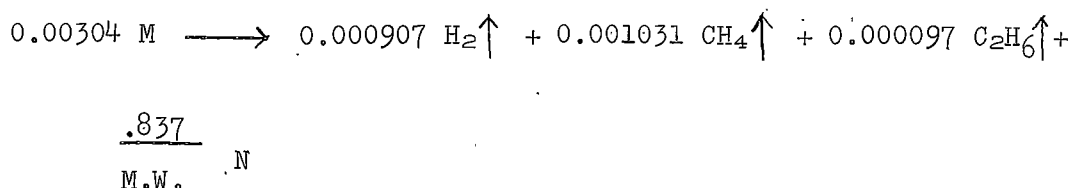


The weight loss in this step is quite small with the weight loss associated with hydrogen, methane, and ethane accounting for about half of the total loss. The remainder can be attributed to the formation of volatile trace materials. For example, if a two-gram sample of acenaphthylene is pyrolyzed, four hundredths of a gram of light hydrocarbon gases and four hundredths of a gram of volatile trace compounds would be formed.

The results of the kinetic study on hydrogen are shown in Table XXX and the results based on methane evolution are given in Table XXXI. In both cases the results indicate that the reaction is first order. It is evident that the corresponding values between hydrogen analysis and methane analysis are not exact. However, hydrogen rate data for this analysis is not as accurate as methane rate data. This is caused by the initiation of the dehydrogenation reaction prior to completion of the third acenaphthylene reaction. Methane and hydrogen evolution curves are quite similar in nature until dehydrogenation temperatures are reached. This second source of hydrogen begins to appreciably affect the rate data as the temperature enters the 535 to 550°C interval. Consequently, the values obtained from methane evolution best represent the kinetics of this reaction. A typical gas evolution curve for this phase is shown in Figure 19. This first order reaction then has activation energies between 61,440 and 68,815 calories per mole while the frequency factors vary from  $10^{13.6}$  to  $10^{16.0}$  reciprocal seconds. Also, the correlation

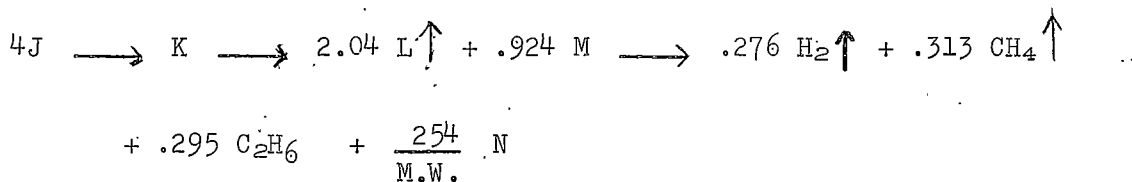
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coefficients indicate that a very good approximation was obtained on methane evolution data. Coefficients of this nature mean that the simulation is almost perfect. A general stoichiometric equation for this reaction based on Runs EX-A-14 through -17 would be:



The value for the moles of ethane was estimated from gas evolution data of pyrolysis Runs EX-A-7, EX-A-8, and EX-A-10 because no attempt was made to analyze for ethane during Runs EX-A-14 through -17. This problem relates to the inability of the chromatograph to simultaneously analyze hydrogen, methane, and ethane. This subject was discussed in the Experimental Considerations section. It was established in early runs on acenaphthylene that methane and ethane had similar evolution traces.

The stoichiometric equations for the separate reactions of acenaphthylene can be combined into one overall stoichiometric equation. Starting with four moles of acenaphthylene the general stoichiometric equation is:



The molecular weight for the coke material N was not assigned.

Kinetic Comparisons:

As a secondary objective for this pyrolysis study, it was intended that the kinetic results for acenaphthylene be compared with the results for bifluorenyl. This comparison would point out any noticeable differences in their kinetic behavior. Acenaphthylene forms a high quality coke while bifluorenyl forms a rather poor quality coke (3,7). The comparison must be qualitative at best because the study of only two compounds will not show significant trends.

From literature references (3,5,6) and from experimental data it is established that the first reaction of acenaphthylene involves a vinyl type polymerization at relatively low temperatures. This polymerization plays an important role in aiding the rearrangement of acenaphthylene to form reactive intermediates. Bifluorenyl does not show evidence of any major reaction prior to a disproportionation reaction at moderately high TGA temperatures.

Both compounds undergo a reaction in which a large percent of the original sample reacts to form a volatile product. In both cases this reaction is second order. However, the activation energies and frequency factors were quite different between compounds. Bifluorenyl had activation energies near 65 K cal/mole while acenaphthylene had values near 145 K cal/mole. Likewise, the frequency factors varied from approximately  $10^{21}$  to  $10^{50}$  cc/mole sec for bifluorenyl and acenaphthylene, respectively.

The final reaction of acenaphthylene and bifuorenyl which is just prior to dehydrogenation involves the evolution of light hydrocarbon gases. Both compounds exhibited first order kinetics for this reaction and the values for frequency factors and activation energy were also similar. Acenaphthylene pyrolysis formed hydrogen, methane, and ethane in this reaction while bifuorenyl formed only hydrogen and methane. The kinetic comparisons should be regarded as quite general since Union Carbide documents (3,5,6) indicate that many other aspects of the pyrolysis behavior must be considered. In most cases the properties of the final carbon depend to a large extent on the chemical constitution of the organic precursors.

## CONCLUSIONS

The primary objective of this study was to analyze the various pyrolysis reactions of acenaphthylene and bifuorenyl for kinetic correlations with the Arrhenius kinetic model. The pyrolysis was conducted in an inert atmospheric system to final temperatures similar to commercial coking. From the TGA experimental data it was evident that both compounds had four major reactions and that the fourth reaction in both cases was dehydrogenation. The first three reactions were correlated to a first and second order Arrhenius model and the values for the activation energy and frequency factor were determined.

The first reaction of bifuorenyl was evaluated assuming a disproportionation reaction. The analysis was simplified because the starting product was known and the weight accurately determined before pyrolysis. The weight-loss data associated with fluorene formation provided adequate data for reliable kinetic analysis. This reaction was best described by a pseudo-second order reaction. The interval for the activation energy and frequency factor was 56,675 to 67,330 cal/mole and  $10^{18.2}$  to  $10^{21.8}$  cc/mole sec, respectively.

The second reaction of bifuorenyl was analyzed using a series reaction model. The series reaction complicated the analysis since numerical approximations were employed. This analysis was also complicated because it was necessary to base the entire evaluation on a weight loss that was only 3.1% of the original sample size. The formation of fluorene by the reaction was best described by a second order reaction with an

activation energy interval of 47,007 to 66,415 cal/mole sec and a frequency factor interval of  $10^{14.4}$  to  $10^{20.6}$  cc/mole sec.

The analysis of the third bifluorenyl reaction was based on hydrogen gas evolution data. This type of data proved to be quite satisfactory for kinetic analysis and yielded correlation coefficients very close to unity. The main difficulty with this reaction was in selecting a molecular weight that would accurately represent the reacting material. The third reaction was pseudo-first order and the Arrhenius activation energy and frequency factor intervals were 62,287 to 96,874 cal/mole and  $10^{13.4}$  to  $10^{22.7}$  sec<sup>-1</sup>, respectively. Coke yield for all bifluorenyl experiments were close to 27.9 percent.

The first reaction of acenaphthylene was evaluated by simulating experimental thermal data on the analog computer. The polymerization reaction was exothermic and did not result in any weight loss. This reaction was pseudo-first order and has an activation energy of 27,500 cal/mole and a frequency factor of  $10^{7.5}$  sec<sup>-1</sup>.

The second reaction of acenaphthylene was well defined in that appreciable weight loss was associated with this reaction. The reaction was best described with a second order Arrhenius kinetic model. The activation energy varied from 133,801 to 163,061 cal/mole and the frequency factor varied from  $10^{45.2}$  to  $10^{55.2}$  cc/mole sec.

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The third reaction resulted in the formation of hydrogen, methane, and ethane. Hydrogen and methane rate data were studied to determine the reaction kinetics. Both analyses indicated that the reaction was pseudo-first order. The activation energy and frequency factor intervals associated with methane were 61,440 to 68,815 cal/mole and  $10^{13.6}$  to  $10^{16.0}$  sec<sup>-1</sup>, respectively. The average coke yield obtained from acenaphthylene experiments was 41.8 percent.

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# APPENDIX

Table I: Summary of All Pyrolysis Experiments Conducted on Bifluorenyl

| Pyrolysis Run | Sample Size Grams | Final Temp. °C | Carbon Yield Percent | Usable Data |      |      | Remarks                                |
|---------------|-------------------|----------------|----------------------|-------------|------|------|----------------------------------------|
|               |                   |                |                      | RX-1        | RX-2 | RX-3 |                                        |
| EX-B-1        | 3.337             | 610            | ---                  | No          | No   | No   | Plugged reactor                        |
| EX-B-2        | 2.213             | 620            | 27.4                 | Yes         | No   | No   | Erratic results above RX-1             |
| EX-B-3        | 2.008             | 384            | ---                  | No          | No   | No   | Plugged reactor; installed preheater   |
| EX-B-4        | 2.168             | 400            | ---                  | No          | No   | No   | Plugged reactor; Equipment modified.   |
| EX-B-5        | 2.109             | 418            | ---                  | No          | No   | No   | Gas Exit Tube Burned at 418°C          |
| EX-B-6        | 2.440             | ---            | ---                  | No          | No   | No   | Lost temperature data during pyrolysis |
| EX-B-7        | 2.500             | ---            | ---                  | No          | No   | No   | Temperature Recorder uncalibrated      |
| EX-B-8        | 2.000             | 635            | 27.6                 | No          | No   | Yes  | Temperature rise too severe for RX-1   |
| EX-B-9        | 2.000             | 632            | 27.4                 | Yes         | Yes  | Yes  |                                        |
| EX-B-10       | 2.000             | 635            | 27.8                 | Yes         | No   | No   | Weight loss trace erratic after RX-1   |
| EX-B-11       | 2.000             | 640            | 28.0                 | Yes         | Yes  | Yes  |                                        |
| EX-B-12       | 2.000             | 628            | 29.2                 | Yes         | Yes  | Yes  | Maintained constant temperature rise   |

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(71)

Table II: Analog Computer Kinetic Results for the Disproportionation  
Reaction of Bifluorenyl (RX-B-1)

| Pyrolysis<br>Run                         | EX-B-12            |                    | EX-B-2             |                    |
|------------------------------------------|--------------------|--------------------|--------------------|--------------------|
| Approximate<br>Interval                  | Lower              | Upper              | Lower              | Upper              |
| FIRST ORDER                              |                    |                    |                    |                    |
| Frequency<br>Factor<br>Sec <sup>-1</sup> | 10 <sup>8.66</sup> | 10 <sup>10.3</sup> | 10 <sup>9.56</sup> | 10 <sup>10.3</sup> |
| Energy of<br>Activation<br>cal/mole      | 42,500             | 48,200             | 46,500             | 49,000             |
| SECOND ORDER                             |                    |                    |                    |                    |
| Frequency<br>Factor<br>cc/mole sec       | 10 <sup>13.6</sup> | 10 <sup>16.0</sup> | 10 <sup>13.6</sup> | 10 <sup>17.1</sup> |
| Energy of<br>Activation<br>cal/mole      | 51,600             | 59,200             | 51,700             | 63,800             |

Table III: IBM Computer Program for Data Conversion and Rearrangement for Bifluorenyl Reaction One (RX-B-1)

ZZJOB 5  
ZZFORX5

CONVERT RAW DATA RX-B-1

```

      READ 900, N, WAO
      DO 1 I=1,N
      READ 901,WD,TM,TDC
      TS=TM*60.0
      TDK=TDG+273.0
      WDK=WD/90.5
      WDK=WAO-WDK
      RHO=0.957
      XCA=((WAO*RHO)/WDK)*(1.0/330.-1.0/166.0)+(RHO/166.0)
1     PUNCH 902, TS,XCA,TDK
900   FORMAT(I3,F10.0)
901   FORMAT(3F10.0)
902   FORMAT(10X,F10.4,10X,F10.6,10X,F10.4)
      CALL EXIT
      END

```

ZZJOB 5  
ZZFORX5

DERIVATIVE POLY RX-B-1

```

DIMENSION COE (10),DCOE (10)
READ 900,N,OD,WA0,R,IDEH,RHO
2 READ 901,IDEG,C
IF(IDEG)1,1,8
8 COE (IDEG)=C
DEG=IDEG
DCOE (IDEG)=(DEG)*COE (IDEG)
IF(IDEG)1,1,2
1 DO5I=1,N
DER=0.0
IDEG= IDEH
READ 902,TS,XCA,TDK
6 DER=DER+DCOE (IDEG )*TS** (IDEG-1)
IF(IDEG-1)3,3,4
4 IDEG=IDEG-1
GO TO 6
3 IF(DER)9,5,5
9 A1=LOGF(-DER)
A2=OD*LOGF(XCA)
Y=A1-A2
X=1.0/(R*TDK)
PUNCH 903,Y,X
5 CONTINUE

```

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Table III (continued)

```
900 FORMAT(I2,3F10.0,I2,F10.0)
901 FORMAT(3X,I2,31X,E20.8)
902 FORMAT(3F20.0)
903 FORMAT (2E14.7)
    CALL EXIT
    END
```

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Table IV: Converted Experimental Weight-Loss Data for the Formation of Fluorene, Run EX-B-2

| TIME<br>MIN. | TEMP<br>DEG. C | GRAMS<br>WDK | CONC<br>MOLES/CC |
|--------------|----------------|--------------|------------------|
| .0           | 347.000        | 2.2130       | .0029000         |
| 1.0          | 348.000        | 2.2124       | .0028992         |
| 2.0          | 349.000        | 2.2113       | .0028978         |
| 3.0          | 350.500        | 2.2102       | .0028964         |
| 4.0          | 352.000        | 2.2085       | .0028942         |
| 5.0          | 353.500        | 2.2069       | .0028921         |
| 6.0          | 349.900        | 2.2047       | .0028892         |
| 7.0          | 351.100        | 2.2036       | .0028877         |
| 8.0          | 352.300        | 2.2019       | .0028856         |
| 9.0          | 353.500        | 2.1997       | .0028827         |
| 10.0         | 354.700        | 2.1969       | .0028791         |
| 11.0         | 355.900        | 2.1936       | .0028747         |
| 12.0         | 362.100        | 2.1909       | .0028711         |
| 13.0         | 363.000        | 2.1875       | .0028667         |
| 14.0         | 364.000        | 2.1831       | .0028608         |
| 15.0         | 365.000        | 2.1787       | .0028549         |
| 16.0         | 366.000        | 2.1743       | .0028490         |
| 17.0         | 367.000        | 2.1688       | .0028416         |
| 18.0         | 368.000        | 2.1621       | .0028326         |
| 19.0         | 368.700        | 2.1555       | .0028236         |
| 20.0         | 369.400        | 2.1455       | .0028099         |
| 21.0         | 369.900        | 2.1356       | .0027962         |
| 22.0         | 370.500        | 2.1223       | .0027776         |
| 23.0         | 371.200        | 2.1080       | .0027573         |
| 24.0         | 372.000        | 2.0947       | .0027382         |
| 25.0         | 372.500        | 2.0792       | .0027157         |
| 26.0         | 373.000        | 2.0638       | .0026929         |
| 27.0         | 373.500        | 2.0472       | .0026680         |
| 28.0         | 374.000        | 2.0273       | .0026376         |
| 29.0         | 374.500        | 2.0107       | .0026118         |
| 30.0         | 375.000        | 1.9920       | .0025821         |
| 31.0         | 375.400        | 1.9743       | .0025536         |
| 32.0         | 375.900        | 1.9599       | .0025301         |
| 33.0         | 376.300        | 1.9467       | .0025080         |
| 34.0         | 376.600        | 1.9345       | .0024876         |
| 35.0         | 377.000        | 1.9223       | .0024668         |
| 36.0         | 377.400        | 1.9113       | .0024478         |
| 37.0         | 377.700        | 1.8991       | .0024265         |
| 38.0         | 378.100        | 1.8859       | .0024031         |
| 39.0         | 378.500        | 1.8726       | .0023793         |

Table IV (continued)

|      |         |        |          |
|------|---------|--------|----------|
| 40.0 | 378.800 | 1.8605 | .0023571 |
| 41.0 | 379.200 | 1.8472 | .0023327 |
| 42.0 | 379.600 | 1.8350 | .0023100 |
| 43.0 | 379.900 | 1.8240 | .0022890 |
| 44.0 | 380.300 | 1.8130 | .0022678 |
| 45.0 | 380.700 | 1.8019 | .0022464 |
| 46.0 | 381.000 | 1.7909 | .0022247 |
| 47.0 | 381.400 | 1.7809 | .0022049 |
| 48.0 | 381.800 | 1.7710 | .0021849 |
| 49.0 | 382.100 | 1.7599 | .0021624 |
| 50.0 | 382.500 | 1.7489 | .0021397 |
| 51.0 | 382.900 | 1.7389 | .0021190 |
| 52.0 | 383.200 | 1.7290 | .0020980 |
| 53.0 | 383.600 | 1.7190 | .0020768 |
| 54.0 | 384.000 | 1.7091 | .0020553 |
| 55.0 | 384.300 | 1.7002 | .0020360 |
| 56.0 | 384.700 | 1.6914 | .0020165 |
| 57.0 | 385.100 | 1.6837 | .0019993 |
| 58.0 | 385.400 | 1.6737 | .0019769 |
| 59.0 | 385.800 | 1.6638 | .0019543 |
| 60.0 | 386.200 | 1.6527 | .0019288 |
| 61.0 | 386.500 | 1.6472 | .0019160 |
| 62.0 | 386.900 | 1.6417 | .0019030 |
| 63.0 | 387.300 | 1.6339 | .0018847 |
| 64.0 | 387.600 | 1.6262 | .0018663 |
| 65.0 | 388.000 | 1.6185 | .0018476 |
| 66.0 | 388.400 | 1.6096 | .0018261 |
| 67.0 | 388.700 | 1.5997 | .0018016 |
| 68.0 | 389.100 | 1.5909 | .0017796 |
| 69.0 | 389.500 | 1.5831 | .0017601 |
| 70.0 | 389.800 | 1.5743 | .0017376 |
| 71.0 | 390.200 | 1.5654 | .0017149 |
| 72.0 | 390.400 | 1.5566 | .0016919 |
| 73.0 | 390.500 | 1.5489 | .0016716 |
| 74.0 | 390.600 | 1.5422 | .0016540 |
| 75.0 | 390.700 | 1.5334 | .0016303 |
| 76.0 | 390.800 | 1.5257 | .0016093 |
| 77.0 | 390.900 | 1.5179 | .0015881 |
| 78.0 | 391.000 | 1.5080 | .0015606 |
| 79.0 | 391.100 | 1.4991 | .0015358 |
| 80.0 | 391.200 | 1.4914 | .0015139 |
| 81.0 | 391.300 | 1.4837 | .0014917 |
| 82.0 | 391.500 | 1.4759 | .0014693 |
| 83.0 | 391.800 | 1.4682 | .0014467 |

Table IV (continued)

|              |                 |              |          |
|--------------|-----------------|--------------|----------|
| 84.0         | 392.400         | 1.4583       | .0014172 |
| 85.0         | 393.700         | 1.4450       | .0013773 |
| 86.0         | 395.200         | 1.4317       | .0013367 |
| 87.0         | 396.600         | 1.4185       | .0012953 |
| 88.0         | 398.200         | 1.4052       | .0012531 |
| 89.0         | 399.200         | 1.3886       | .0011993 |
| 90.0         | 400.200         | 1.3721       | .0011441 |
| 91.0         | 401.300         | 1.3555       | .0010876 |
| 92.0         | 402.400         | 1.3400       | .0010336 |
| 93.0         | 403.500         | 1.3234       | .0009744 |
| 94.0         | 404.600         | 1.3069       | .0009136 |
| 95.0         | 405.700         | 1.2936       | .0008639 |
| 96.0         | 406.800         | 1.2804       | .0008132 |
| 97.0         | 407.900         | 1.2682       | .0007657 |
| 98.0         | 409.000         | 1.2560       | .0007173 |
| TIME<br>MIN. | TEMP.<br>DEG. C | GRAMS<br>WDK |          |
| 99.0         | 410.100         | 1.2439       |          |
| 100.0        | 411.200         | 1.2317       |          |
| 101.0        | 412.300         | 1.2196       |          |
| 102.0        | 413.400         | 1.2074       |          |
| 103.0        | 414.500         | 1.1953       |          |
| 104.0        | 415.600         | 1.1826       |          |
| 105.0        | 416.700         | 1.1699       |          |
| 106.0        | 417.800         | 1.1571       |          |
| 107.0        | 418.900         | 1.1444       |          |
| 108.0        | 420.000         | 1.1323       |          |
| 109.0        | 421.100         | 1.1201       |          |
| 110.0        | 422.200         | 1.1091       |          |
| 111.0        | 423.300         | 1.0980       |          |
| 112.0        | 424.300         | 1.0870       |          |
| 113.0        | 425.200         | 1.0770       |          |
| 114.0        | 426.100         | 1.0671       |          |
| 115.0        | 427.000         | 1.0583       |          |
| 116.0        | 427.900         | 1.0494       |          |
| 117.0        | 428.700         | 1.0417       |          |
| 118.0        | 429.400         | 1.0339       |          |
| 119.0        | 430.000         | 1.0262       |          |
| 120.0        | 430.500         | 1.0196       |          |
| 121.0        | 431.000         | 1.0130       |          |

Table IV (continued)

|       |         |        |
|-------|---------|--------|
| 122.0 | 431.500 | 1.0063 |
| 123.0 | 432.000 | .9997  |
| 124.0 | 432.500 | .9942  |
| 125.0 | 433.000 | .9886  |
| 126.0 | 433.700 | .9842  |
| 127.0 | 434.600 | .9798  |
| 128.0 | 435.800 | .9754  |
| 129.0 | 437.400 | .9710  |
| 130.0 | 439.400 | .9676  |
| 131.0 | 441.400 | .9643  |
| 132.0 | 443.400 | .9610  |
| 133.0 | 445.400 | .9577  |
| 134.0 | 447.400 | .9544  |
| 135.0 | 449.400 | .9511  |
| 136.0 | 451.300 | .9478  |
| 137.0 | 453.100 | .9444  |
| 138.0 | 454.800 | .9422  |
| 139.0 | 456.500 | .9400  |
| 140.0 | 458.200 | .9378  |
| 141.0 | 459.900 | .9356  |
| 142.0 | 461.600 | .9334  |
| 143.0 | 463.300 | .9312  |
| 144.0 | 465.000 | .9295  |
| 145.0 | 466.700 | .9279  |
| 146.0 | 468.400 | .9262  |
| 147.0 | 466.000 | .9246  |
| 148.0 | 467.500 | .9234  |
| 149.0 | 468.900 | .9223  |
| 150.0 | 470.200 | .9212  |
| 151.0 | 471.500 | .9201  |
| 152.0 | 472.800 | .9190  |
| 153.0 | 474.000 | .9179  |
| 154.0 | 475.200 | .9174  |
| 155.0 | 476.400 | .9168  |
| 156.0 | 477.600 | .9163  |
| 157.0 | 478.700 | .9157  |
| 158.0 | 479.800 | .9152  |

Table V: Converted Experimental Weight-Loss Data for the Formation of Fluorene, Run EX-B-9

| TIME<br>MIN. | TEMP<br>DEG. C | GRAMS<br>WDK | CONC<br>MOLES/CC |
|--------------|----------------|--------------|------------------|
| .0           | 347.000        | 2.0000       | .0029000         |
| 1.0          | 349.000        | 1.9994       | .0028992         |
| 2.0          | 351.000        | 1.9983       | .0028976         |
| 3.0          | 353.000        | 1.9966       | .0028952         |
| 4.0          | 354.800        | 1.9939       | .0028912         |
| 5.0          | 356.300        | 1.9900       | .0028856         |
| 6.0          | 357.500        | 1.9856       | .0028792         |
| 7.0          | 358.700        | 1.9801       | .0028712         |
| 8.0          | 359.600        | 1.9734       | .0028614         |
| 9.0          | 360.400        | 1.9668       | .0028517         |
| 10.0         | 361.000        | 1.9602       | .0028418         |
| 11.0         | 361.500        | 1.9535       | .0028319         |
| 12.0         | 362.000        | 1.9458       | .0028202         |
| 13.0         | 362.500        | 1.9370       | .0028068         |
| 14.0         | 363.200        | 1.9270       | .0027915         |
| 15.0         | 364.000        | 1.9149       | .0027727         |
| 16.0         | 364.900        | 1.9005       | .0027500         |
| 17.0         | 365.800        | 1.8839       | .0027235         |
| 18.0         | 366.800        | 1.8640       | .0026911         |
| 19.0         | 367.700        | 1.8397       | .0026504         |
| 20.0         | 368.700        | 1.8154       | .0026087         |
| 21.0         | 369.600        | 1.7900       | .0025639         |
| 22.0         | 370.600        | 1.7646       | .0025178         |
| 23.0         | 371.500        | 1.7392       | .0024704         |
| 24.0         | 372.500        | 1.7138       | .0024215         |
| 25.0         | 373.400        | 1.7005       | .0023954         |
| 26.0         | 374.400        | 1.6762       | .0023466         |
| 27.0         | 375.300        | 1.6519       | .0022963         |
| 28.0         | 376.300        | 1.6287       | .0022469         |
| 29.0         | 377.200        | 1.6055       | .0021960         |
| 30.0         | 378.200        | 1.5834       | .0021462         |
| 31.0         | 379.100        | 1.5613       | .0020950         |
| 32.0         | 380.100        | 1.5403       | .0020450         |
| 33.0         | 381.000        | 1.5182       | .0019908         |
| 34.0         | 382.000        | 1.5005       | .0019463         |
| 35.0         | 382.900        | 1.4817       | .0018979         |
| 36.0         | 383.900        | 1.4629       | .0018483         |
| 37.0         | 384.800        | 1.4441       | .0017973         |
| 38.0         | 385.800        | 1.4265       | .0017482         |
| 39.0         | 386.700        | 1.4088       | .0016977         |

Table V (continued)

|      |         |        |          |
|------|---------|--------|----------|
| 40.0 | 387.700 | 1.3922 | .0016493 |
| 41.0 | 388.600 | 1.3756 | .0015997 |
| 42.0 | 389.600 | 1.3591 | .0015489 |
| 43.0 | 390.500 | 1.3425 | .0014969 |
| 44.0 | 391.500 | 1.3259 | .0014435 |
| 45.0 | 392.400 | 1.3104 | .0013925 |
| 46.0 | 393.400 | 1.2950 | .0013403 |
| 47.0 | 394.300 | 1.2795 | .0012868 |
| 48.0 | 395.200 | 1.2651 | .0012360 |
| 49.0 | 396.000 | 1.2508 | .0011840 |
| 50.0 | 396.800 | 1.2364 | .0011307 |
| 51.0 | 397.600 | 1.2232 | .0010805 |
| 52.0 | 398.400 | 1.2099 | .0010292 |
| 53.0 | 399.200 | 1.1966 | .0009767 |
| 54.0 | 400.000 | 1.1834 | .0009230 |
| 55.0 | 400.800 | 1.1712 | .0008728 |
| 56.0 | 401.700 | 1.1591 | .0008215 |
| 57.0 | 402.600 | 1.1469 | .0007691 |
| 58.0 | 403.500 | 1.1348 | .0007156 |
| 59.0 | 404.400 | 1.1237 | .0006659 |
| 60.0 | 405.300 | 1.1127 | .0006153 |

| TIME<br>MIN. | TEMP.<br>DEG. C | GRAMS<br>WDK |
|--------------|-----------------|--------------|
| 61.0         | 406.100         | 1.1016       |
| 62.0         | 406.900         | 1.0906       |
| 63.0         | 407.700         | 1.0795       |
| 64.0         | 408.500         | 1.0685       |
| 65.0         | 409.300         | 1.0574       |
| 66.0         | 410.100         | 1.0475       |
| 67.0         | 410.900         | 1.0375       |
| 68.0         | 411.700         | 1.0276       |
| 69.0         | 412.500         | 1.0176       |
| 70.0         | 413.300         | 1.0088       |
| 71.0         | 414.100         | 1.0000       |
| 72.0         | 414.900         | .9911        |
| 73.0         | 415.700         | .9834        |
| 74.0         | 416.500         | .9756        |
| 75.0         | 417.300         | .9690        |
| 76.0         | 418.100         | .9624        |
| 77.0         | 418.700         | .9558        |
| 78.0         | 419.700         | .9502        |

Table V (continued)

|       |         |       |
|-------|---------|-------|
| 79.0  | 420.500 | .9447 |
| 80.0  | 421.300 | .9403 |
| 81.0  | 422.100 | .9359 |
| 82.0  | 422.900 | .9314 |
| 83.0  | 423.700 | .9270 |
| 84.0  | 424.500 | .9237 |
| 85.0  | 425.400 | .9204 |
| 86.0  | 426.300 | .9171 |
| 87.0  | 427.200 | .9138 |
| 88.0  | 428.100 | .9104 |
| 89.0  | 429.000 | .9071 |
| 90.0  | 429.900 | .9044 |
| 91.0  | 431.000 | .9016 |
| 92.0  | 432.200 | .8994 |
| 93.0  | 433.600 | .8972 |
| 94.0  | 435.100 | .8950 |
| 95.0  | 436.600 | .8928 |
| 96.0  | 438.100 | .8906 |
| 97.0  | 439.600 | .8883 |
| 98.0  | 441.100 | .8861 |
| 99.0  | 442.600 | .8839 |
| 100.0 | 444.100 | .8823 |
| 101.0 | 445.600 | .8806 |
| 102.0 | 447.100 | .8790 |
| 103.0 | 448.400 | .8773 |
| 104.0 | 449.700 | .8756 |
| 105.0 | 451.000 | .8740 |
| 106.0 | 452.300 | .8723 |
| 107.0 | 453.600 | .8707 |
| 108.0 | 454.900 | .8690 |
| 109.0 | 456.200 | .8674 |
| 110.0 | 457.500 | .8662 |
| 111.0 | 458.800 | .8651 |
| 112.0 | 460.100 | .8640 |
| 113.0 | 461.400 | .8629 |
| 114.0 | 462.900 | .8618 |
| 115.0 | 464.500 | .8613 |
| 116.0 | 466.200 | .8607 |
| 117.0 | 467.900 | .8602 |
| 118.0 | 469.600 | .8596 |
| 119.0 | 471.300 | .8591 |
| 120.0 | 473.000 | .8585 |

Table VI: Converted Experimental Weight-Loss Data for the Formation of Fluorene, Run EX-B-10

| TIME<br>MIN. | TEMP<br>DEG. C | GRAMS<br>WDK | CONC<br>MOLES/CC |
|--------------|----------------|--------------|------------------|
| 0.0          | 351.500        | 2.0000       | .0029000         |
| 1.0          | 353.500        | 1.9994       | .0028992         |
| 2.0          | 355.500        | 1.9988       | .0028984         |
| 3.0          | 357.000        | 1.9977       | .0028968         |
| 4.0          | 358.500        | 1.9955       | .0028936         |
| 5.0          | 360.000        | 1.9928       | .0028896         |
| 6.0          | 361.000        | 1.9889       | .0028840         |
| 7.0          | 362.000        | 1.9845       | .0028776         |
| 8.0          | 363.000        | 1.9779       | .0028679         |
| 9.0          | 364.000        | 1.9701       | .0028566         |
| 10.0         | 365.000        | 1.9613       | .0028435         |
| 11.0         | 366.000        | 1.9502       | .0028269         |
| 12.0         | 367.000        | 1.9381       | .0028085         |
| 13.0         | 368.000        | 1.9237       | .0027864         |
| 14.0         | 369.000        | 1.9071       | .0027605         |
| 15.0         | 370.000        | 1.8883       | .0027306         |
| 16.0         | 371.000        | 1.8685       | .0026983         |
| 17.0         | 372.000        | 1.8486       | .0026653         |
| 18.0         | 373.000        | 1.8287       | .0026316         |
| 19.0         | 374.000        | 1.8088       | .0025972         |
| 20.0         | 375.000        | 1.7878       | .0025600         |
| 21.0         | 376.000        | 1.7668       | .0025219         |
| 22.0         | 377.000        | 1.7458       | .0024829         |
| 23.0         | 378.000        | 1.7248       | .0024429         |
| 24.0         | 379.000        | 1.7038       | .0024020         |
| 25.0         | 380.000        | 1.6828       | .0023600         |
| 26.0         | 381.000        | 1.6629       | .0023193         |
| 27.0         | 382.000        | 1.6453       | .0022823         |
| 28.0         | 383.000        | 1.6298       | .0022492         |
| 29.0         | 384.000        | 1.6154       | .0022180         |
| 30.0         | 384.500        | 1.6011       | .0021862         |
| 31.0         | 385.000        | 1.5878       | .0021563         |
| 32.0         | 385.500        | 1.5745       | .0021259         |
| 33.0         | 386.000        | 1.5613       | .0020950         |
| 34.0         | 386.500        | 1.5480       | .0020635         |
| 35.0         | 387.000        | 1.5348       | .0020316         |
| 36.0         | 387.500        | 1.5215       | .0019990         |
| 37.0         | 388.000        | 1.5071       | .0019631         |
| 38.0         | 388.500        | 1.4939       | .0019294         |
| 39.0         | 389.100        | 1.4806       | .0018950         |

Table VI (continued)

|      |         |        |          |
|------|---------|--------|----------|
| 40.0 | 398.800 | 1.4674 | .0018601 |
| 41.0 | 390.600 | 1.4541 | .0018245 |
| 42.0 | 391.500 | 1.4397 | .0017851 |
| 43.0 | 392.400 | 1.4265 | .0017482 |
| 44.0 | 393.300 | 1.4132 | .0017105 |
| 45.0 | 394.200 | 1.4000 | .0016721 |
| 46.0 | 395.100 | 1.3856 | .0016296 |
| 47.0 | 396.000 | 1.3723 | .0015897 |
| 48.0 | 397.000 | 1.3591 | .0015489 |
| 49.0 | 398.000 | 1.3458 | .0015074 |
| 50.0 | 399.000 | 1.3325 | .0014650 |
| 51.0 | 400.000 | 1.3182 | .0014182 |
| 52.0 | 401.000 | 1.3027 | .0013666 |
| 53.0 | 402.000 | 1.2872 | .0013137 |
| 54.0 | 403.000 | 1.2718 | .0012596 |
| 55.0 | 404.000 | 1.2563 | .0012041 |
| 56.0 | 405.000 | 1.2408 | .0011472 |
| 57.0 | 406.000 | 1.2265 | .0010932 |
| 58.0 | 407.000 | 1.2121 | .0010378 |
| 59.0 | 408.000 | 1.1977 | .0009811 |
| 60.0 | 409.000 | 1.1845 | .0009275 |
| 61.0 | 410.000 | 1.1712 | .0008728 |
| 62.0 | 411.000 | 1.1580 | .0008168 |
| 63.0 | 412.000 | 1.1447 | .0007595 |
| 64.0 | 413.000 | 1.1325 | .0007057 |
| 65.0 | 414.000 | 1.1204 | .0006508 |
| 66.0 | 415.000 | 1.1082 | .0005948 |
| 67.0 | 416.000 | 1.0972 | .0005427 |

Table VII: Converted Experimental Weight-Loss Data for the Formation of Fluorene, Run EX-B-11

| TIME<br>MIN. | TEMP<br>DEG. C | GRAMS<br>WDK | CONC<br>MOLES/CC |
|--------------|----------------|--------------|------------------|
| .0           | 343.300        | 2.0000       | .0029000         |
| 1.0          | 346.000        | 1.9994       | .0028992         |
| 2.0          | 348.700        | 1.9983       | .0028976         |
| 3.0          | 351.400        | 1.9966       | .0028952         |
| 4.0          | 354.000        | 1.9944       | .0028920         |
| 5.0          | 356.400        | 1.9917       | .0028880         |
| 6.0          | 358.500        | 1.9889       | .0028840         |
| 7.0          | 360.400        | 1.9861       | .0028800         |
| 8.0          | 362.100        | 1.9834       | .0028760         |
| 9.0          | 363.600        | 1.9801       | .0028712         |
| 10.0         | 365.000        | 1.9762       | .0028655         |
| 11.0         | 366.200        | 1.9712       | .0028582         |
| 12.0         | 367.400        | 1.9646       | .0028484         |
| 13.0         | 368.600        | 1.9558       | .0028352         |
| 14.0         | 369.800        | 1.9436       | .0028169         |
| 15.0         | 371.100        | 1.9303       | .0027966         |
| 16.0         | 372.300        | 1.9149       | .0027727         |
| 17.0         | 373.500        | 1.8961       | .0027430         |
| 18.0         | 374.700        | 1.8751       | .0027092         |
| 19.0         | 375.900        | 1.8519       | .0026709         |
| 20.0         | 377.200        | 1.8276       | .0026297         |
| 21.0         | 378.400        | 1.8022       | .0025855         |
| 22.0         | 379.600        | 1.7767       | .0025400         |
| 23.0         | 380.800        | 1.7502       | .0024912         |
| 24.0         | 382.100        | 1.7237       | .0024408         |
| 25.0         | 383.300        | 1.6972       | .0023889         |
| 26.0         | 384.500        | 1.6707       | .0023353         |
| 27.0         | 385.700        | 1.6453       | .0022823         |
| 28.0         | 386.900        | 1.6198       | .0022277         |
| 29.0         | 388.200        | 1.5944       | .0021713         |
| 30.0         | 389.400        | 1.5701       | .0021156         |
| 31.0         | 390.600        | 1.5458       | .0020582         |
| 32.0         | 391.800        | 1.5215       | .0019990         |
| 33.0         | 393.100        | 1.4983       | .0019407         |
| 34.0         | 394.300        | 1.4751       | .0018805         |
| 35.0         | 395.500        | 1.4530       | .0018215         |
| 36.0         | 396.700        | 1.4309       | .0017606         |
| 37.0         | 397.900        | 1.4099       | .0017009         |
| 38.0         | 399.200        | 1.3889       | .0016395         |
| 39.0         | 400.400        | 1.3690       | .0015796         |

Table VII (continued)

|      |         |        |          |
|------|---------|--------|----------|
| 40.0 | 401.600 | 1.3491 | .0015179 |
| 41.0 | 402.800 | 1.3303 | .0014579 |
| 42.0 | 404.100 | 1.3116 | .0013962 |
| 43.0 | 405.300 | 1.2939 | .0013365 |
| 44.0 | 406.500 | 1.2762 | .0012752 |
| 45.0 | 407.700 | 1.2596 | .0012161 |
| 46.0 | 408.900 | 1.2430 | .0011554 |
| 47.0 | 410.200 | 1.2276 | .0010974 |
| 48.0 | 411.400 | 1.2121 | .0010378 |
| 49.0 | 412.300 | 1.1977 | .0009811 |
| 50.0 | 413.400 | 1.1834 | .0009230 |
| 51.0 | 414.400 | 1.1701 | .0008682 |
| 52.0 | 415.300 | 1.1569 | .0008120 |
| 53.0 | 416.100 | 1.1447 | .0007595 |
| 54.0 | 416.900 | 1.1348 | .0007156 |
| 55.0 | 417.700 | 1.1237 | .0006659 |
| 56.0 | 418.500 | 1.1127 | .0006153 |

|      |        |       |
|------|--------|-------|
| TIME | TEMP   | GRAMS |
| MIN. | DEG. C | WDK   |

|      |         |        |
|------|---------|--------|
| 57.0 | 419.200 | 1.1016 |
| 58.0 | 419.800 | 1.0906 |
| 59.0 | 420.400 | 1.0795 |
| 60.0 | 421.000 | 1.0696 |
| 61.0 | 421.600 | 1.0596 |
| 62.0 | 422.200 | 1.0497 |
| 63.0 | 422.800 | 1.0397 |
| 64.0 | 423.400 | 1.0298 |
| 65.0 | 424.000 | 1.0209 |
| 66.0 | 424.600 | 1.0132 |
| 67.0 | 425.200 | 1.0066 |
| 68.0 | 425.800 | 1.0011 |
| 69.0 | 426.400 | .9966  |
| 70.0 | 427.100 | .9922  |
| 71.0 | 427.800 | .9889  |
| 72.0 | 428.500 | .9856  |
| 73.0 | 429.200 | .9823  |
| 74.0 | 429.900 | .9790  |
| 75.0 | 430.600 | .9756  |
| 76.0 | 431.300 | .9723  |
| 77.0 | 432.000 | .9690  |

Table VII (continued)

|       |         |       |
|-------|---------|-------|
| 78.0  | 432.700 | .9668 |
| 79.0  | 433.400 | .9646 |
| 80.0  | 434.100 | .9624 |
| 81.0  | 434.800 | .9602 |
| 82.0  | 435.600 | .9580 |
| 83.0  | 436.400 | .9563 |
| 84.0  | 437.200 | .9546 |
| 85.0  | 438.000 | .9530 |
| 86.0  | 438.800 | .9513 |
| 87.0  | 439.600 | .9497 |
| 88.0  | 440.400 | .9480 |
| 89.0  | 441.200 | .9469 |
| 90.0  | 442.000 | .9458 |
| 91.0  | 442.800 | .9447 |
| 92.0  | 443.800 | .9436 |
| 93.0  | 444.800 | .9430 |
| 94.0  | 445.800 | .9425 |
| 95.0  | 446.800 | .9419 |
| 96.0  | 447.800 | .9414 |
| 97.0  | 448.800 | .9403 |
| 98.0  | 449.800 | .9392 |
| 99.0  | 450.800 | .9381 |
| 100.0 | 451.800 | .9370 |
| 101.0 | 452.800 | .9353 |
| 102.0 | 454.000 | .9337 |
| 103.0 | 455.400 | .9320 |
| 104.0 | 457.000 | .9303 |
| 105.0 | 459.600 | .9292 |
| 106.0 | 461.200 | .9281 |
| 107.0 | 462.800 | .9276 |
| 108.0 | 464.400 | .9270 |
| 109.0 | 466.000 | .9265 |
| 110.0 | 467.600 | .9259 |
| 111.0 | 469.200 | .9254 |
| 112.0 | 470.800 | .9248 |
| 113.0 | 472.400 | .9243 |
| 114.0 | 474.000 | .9237 |
| 115.0 | 475.600 | .9232 |

Table VIII: Converted Experimental Weight-Loss Data for the Formation of Fluorene, Run EX-B-12

| TIME<br>MIN. | TEMP<br>DEG. C | GRAMS<br>WDK | CONC<br>MOLES/CC |
|--------------|----------------|--------------|------------------|
| 0.0          | 351.000        | 2.0000       | .0029000         |
| 1.0          | 353.000        | 1.9988       | .0028984         |
| 2.0          | 355.000        | 1.9966       | .0028952         |
| 3.0          | 357.000        | 1.9944       | .0028920         |
| 4.0          | 359.000        | 1.9911       | .0028872         |
| 5.0          | 360.500        | 1.9867       | .0028808         |
| 6.0          | 362.000        | 1.9812       | .0028728         |
| 7.0          | 363.500        | 1.9745       | .0028631         |
| 8.0          | 365.000        | 1.9668       | .0028517         |
| 9.0          | 366.000        | 1.9591       | .0028402         |
| 10.0         | 367.000        | 1.9491       | .0028252         |
| 11.0         | 368.000        | 1.9359       | .0028051         |
| 12.0         | 368.700        | 1.9226       | .0027847         |
| 13.0         | 369.400        | 1.9093       | .0027640         |
| 14.0         | 370.000        | 1.8939       | .0027395         |
| 15.0         | 370.800        | 1.8784       | .0027146         |
| 16.0         | 371.600        | 1.8629       | .0026892         |
| 17.0         | 372.400        | 1.8453       | .0026598         |
| 18.0         | 373.200        | 1.8232       | .0026221         |
| 19.0         | 374.000        | 1.8011       | .0025836         |
| 20.0         | 374.800        | 1.7790       | .0025440         |
| 21.0         | 375.600        | 1.7569       | .0025035         |
| 22.0         | 376.400        | 1.7348       | .0024620         |
| 23.0         | 377.200        | 1.7138       | .0024215         |
| 24.0         | 378.000        | 1.6928       | .0023801         |
| 25.0         | 379.000        | 1.6718       | .0023375         |
| 26.0         | 380.000        | 1.6541       | .0023009         |
| 27.0         | 381.000        | 1.6342       | .0022588         |
| 28.0         | 382.000        | 1.6132       | .0022131         |
| 29.0         | 383.000        | 1.5911       | .0021638         |
| 30.0         | 384.000        | 1.5690       | .0021131         |
| 31.0         | 385.000        | 1.5491       | .0020662         |
| 32.0         | 386.000        | 1.5292       | .0020181         |
| 33.0         | 387.000        | 1.5127       | .0019770         |
| 34.0         | 388.000        | 1.4939       | .0019294         |
| 35.0         | 389.000        | 1.4773       | .0018864         |
| 36.0         | 390.000        | 1.4596       | .0018394         |
| 37.0         | 391.000        | 1.4419       | .0017912         |
| 38.0         | 392.000        | 1.4232       | .0017388         |
| 39.0         | 393.000        | 1.4077       | .0016946         |

Table VIII (continued)

|      |         |        |          |
|------|---------|--------|----------|
| 40.0 | 394.000 | 1.3911 | .0016461 |
| 41.0 | 395.000 | 1.3756 | .0015997 |
| 42.0 | 395.900 | 1.3613 | .0015558 |
| 43.0 | 396.700 | 1.3469 | .0015109 |
| 44.0 | 397.600 | 1.3325 | .0014650 |
| 45.0 | 398.400 | 1.3182 | .0014182 |
| 46.0 | 399.300 | 1.3027 | .0013666 |
| 47.0 | 400.100 | 1.2883 | .0013175 |
| 48.0 | 401.000 | 1.2729 | .0012635 |
| 49.0 | 401.800 | 1.2574 | .0012081 |
| 50.0 | 402.700 | 1.2441 | .0011595 |
| 51.0 | 403.500 | 1.2309 | .0011099 |
| 52.0 | 404.400 | 1.2154 | .0010507 |
| 53.0 | 405.200 | 1.2022 | .0009987 |
| 54.0 | 405.900 | 1.1889 | .0009455 |
| 55.0 | 407.000 | 1.1756 | .0008912 |
| 56.0 | 408.100 | 1.1624 | .0008356 |
| 57.0 | 409.200 | 1.1480 | .0007739 |
| 58.0 | 410.300 | 1.1359 | .0007205 |
| 59.0 | 411.400 | 1.1237 | .0006659 |
| 60.0 | 412.500 | 1.1116 | .0006102 |

|      |        |       |
|------|--------|-------|
| TIME | TEMP   | GRAMS |
| MIN. | DEG. C | WDK   |

|      |         |        |
|------|---------|--------|
| 61.0 | 413.600 | 1.0994 |
| 62.0 | 414.700 | 1.0883 |
| 63.0 | 415.800 | 1.0773 |
| 64.0 | 416.900 | 1.0662 |
| 65.0 | 418.000 | 1.0563 |
| 66.0 | 419.100 | 1.0464 |
| 67.0 | 420.200 | 1.0375 |
| 68.0 | 421.200 | 1.0287 |
| 69.0 | 422.200 | 1.0209 |
| 70.0 | 423.200 | 1.0132 |
| 71.0 | 424.200 | 1.0066 |
| 72.0 | 425.200 | 1.0000 |
| 73.0 | 426.200 | .9944  |
| 74.0 | 427.100 | .9889  |
| 75.0 | 428.000 | .9834  |
| 76.0 | 428.800 | .9790  |
| 77.0 | 429.600 | .9745  |

Table VIII (continued)

|       |         |       |
|-------|---------|-------|
| 78.0  | 430.400 | .9712 |
| 79.0  | 431.200 | .9679 |
| 80.0  | 431.800 | .9646 |
| 81.0  | 432.400 | .9613 |
| 82.0  | 433.000 | .9580 |
| 83.0  | 433.600 | .9546 |
| 84.0  | 434.100 | .9524 |
| 85.0  | 434.600 | .9502 |
| 86.0  | 435.100 | .9480 |
| 87.0  | 435.600 | .9458 |
| 88.0  | 436.100 | .9436 |
| 89.0  | 436.600 | .9414 |
| 90.0  | 437.000 | .9392 |
| 91.0  | 437.400 | .9370 |
| 92.0  | 437.800 | .9359 |
| 93.0  | 438.200 | .9337 |
| 94.0  | 438.600 | .9325 |
| 95.0  | 439.000 | .9314 |
| 96.0  | 440.500 | .9303 |
| 97.0  | 442.000 | .9292 |
| 98.0  | 443.500 | .9281 |
| 99.0  | 445.000 | .9270 |
| 100.0 | 446.500 | .9259 |
| 101.0 | 448.000 | .9248 |
| 102.0 | 449.500 | .9237 |
| 103.0 | 451.000 | .9226 |
| 104.0 | 452.500 | .9215 |
| 105.0 | 454.000 | .9204 |
| 106.0 | 455.500 | .9193 |
| 107.0 | 457.000 | .9182 |
| 108.0 | 458.500 | .9171 |
| 109.0 | 460.000 | .9160 |
| 110.0 | 461.000 | .9149 |
| 111.0 | 462.000 | .9138 |
| 112.0 | 463.000 | .9138 |
| 113.0 | 464.000 | .9127 |
| 114.0 | 465.000 | .9127 |
| 115.0 | 466.000 | .9116 |
| 116.0 | 467.000 | .9116 |
| 117.0 | 468.000 | .9104 |
| 118.0 | 470.000 | .9104 |
| 119.0 | 472.000 | .9093 |
| 120.0 | 474.000 | .9093 |

Table IX: IBM Computer Kinetic Results for the Analysis of Bifluorenyl Reaction One (RX-B-1)

| Pyrolysis Run                         | EX-B-2            | EX-B-9            | EX-B-10           | EX-B-11           | EX-B-12           |
|---------------------------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| Initial Temp.,<br>°C                  | 347               | 347               | 351               | 343               | 351               |
| Final Temp.,<br>°C                    | 409               | 405               | 416               | 418               | 412               |
| FIRST ORDER                           |                   |                   |                   |                   |                   |
| Frequency Factor<br>sec <sup>-1</sup> | e <sup>25.3</sup> | e <sup>24.6</sup> | e <sup>18.3</sup> | e <sup>28.6</sup> | e <sup>26.3</sup> |
| Activation Energy<br>cal/mole         | 43,449            | 41,768            | 34,054            | 47,679            | 44,418            |
| Correlation<br>Coefficient            | .885              | .902              | .862              | .886              | .872              |
| SECOND ORDER                          |                   |                   |                   |                   |                   |
| Frequency Factor<br>cc/sec mole       | e <sup>48.3</sup> | e <sup>49.9</sup> | e <sup>41.9</sup> | e <sup>49.4</sup> | e <sup>50.2</sup> |
| Activation Energy<br>cal/mole         | 65,336            | 66,394            | 56,675            | 66,741            | 67,330            |
| Correlation<br>Coefficient            | .921              | .962              | .950              | .957              | .948              |

Table X: Effect of Temperature on the Reaction Rate Constant when the Arrhenius Kinetic Model is Employed

| Temp.<br>°K                 | E = 67,330<br>$k_o = e^{50.17}$ | E = 56,675<br>$k_o = e^{41.87}$ | Percent Error<br>(approx.) |
|-----------------------------|---------------------------------|---------------------------------|----------------------------|
| 622.0                       | .01310                          | .01814                          | 33                         |
| 624.0                       | .01560                          | .02101                          | 30                         |
| 626.0                       | .01855                          | .02431                          | 27                         |
| 628.0                       | .02005                          | .02811                          | 24                         |
| 630.0                       | .02617                          | .03248                          | 22                         |
| 632.0                       | .03103                          | .03748                          | 19                         |
| 634.0                       | .03675                          | .04322                          | 16                         |
| 636.0                       | .04348                          | .04979                          | 14                         |
| 638.0                       | .05138                          | .05731                          | 11                         |
| 640.0                       | .06067                          | .06591                          | 8                          |
| 642.0                       | .07155                          | .07573                          | 6                          |
| 644.0                       | .08430                          | .08694                          | 3                          |
| 646.0                       | .09923                          | .09973                          | 1                          |
| 648.0                       | .11667                          | .11429                          | 2                          |
| 650.0                       | .13705                          | .13088                          | 5                          |
| 652.0                       | .16083                          | .14975                          | 7                          |
| 654.0                       | .18855                          | .17120                          | 10                         |
| 656.0                       | .22083                          | .19555                          | 12                         |
| 658.0                       | .25839                          | .22320                          | 15                         |
| 660.0                       | .30206                          | .25455                          | 17                         |
| 662.0                       | .35276                          | .29007                          | 20                         |
| 664.0                       | .41160                          | .33028                          | 22                         |
| 666.0                       | .47980                          | .37578                          | 25                         |
| 668.0                       | .55880                          | .52722                          | 27                         |
| 670.0                       | .65020                          | .48533                          | 29                         |
| 672.0                       | .75588                          | .55092                          | 31                         |
| 674.0                       | .87794                          | .62491                          | 34                         |
| Average Error Approximately |                                 |                                 | 17%                        |

Table XI: IBM Computer Program for Data Conversion for Bifluorenyl  
Reaction Two (RX-B-2)

```

ZZJOB 5
ZZFORX5
*LIST PRINTER
  FY(TN,CA)=-XKO*EXPF(-E/(R*TN))*CA**2
  READ 900, N, WAO
  READ 1,XKO,E,R,DX
  XKO=EXPF(XKO)
  READ 2,CANO,TNO
2  FORMAT(30X,F10.6,10X,F10.6)
  READ 2,CAN1,TN1
  READ 2,CAN2,TN2
  READ 2, CAN3,TN3
  READ 2,CAN4,TN4
  PRINT 905
73 DO 10 I=1,N
  READ 901,WD,TM,TDC
  TDK=TDC+273.0
  WDK=WD/90.5
  WDK=WAO-WDK
  TS=TM*60.0
  RHO=0.957
  TN5=TDK
  Y4=FY(TN4,CAN4)
  Y3=FY(TN3,CAN3)
  Y2=FY(TN2,CAN2)
  Y1=FY(TN1,CAN1)
  CAN5=CAN4+DX*(Y4+0.5*(Y4-Y3)+(5./12.)*(Y4-2.*Y3+Y2)+(3
1./8.)*(Y4-3.*Y3+3.*Y2-Y1)+(251./720.)*(Y4-4.*Y3+6.*Y2-
24.*Y1+FY(TNO,CANO)))
  DO 17 IX=1,4
  Y5=FY(TN5,CAN5)
  CAN5=CAN4+DX*(Y5-0.5*(Y5-Y4)-(1./12.)*(Y5-2.*Y4+Y3)-(Y
15-3.*Y4+3.*Y3-Y2)/24.-19.*(Y5-4.*Y4+6.*Y3-4.*Y2+Y1)/72
20.)
17 CONTINUE
  Y5=FY(TN5,CAN5)
9  FORMAT(1H ,F10.4,E13.6,F10.4,19HTHEORETICAL A VALUE)
  PRINT 9, TM,CAN5,TN5
1  FORMAT(E14.7,6X,3F10.6)
  TN1=TN2
  TN2=TN3
  TN3=TN4
  TN4=TN5
  CANO=CAN1

```

Table XI (continued)

```

CAN1=CAN2
CAN2=CAN3
CAN3=CAN4
CAN4=CAN5
CAO=.957/330.
CC=.5*(CAO*WAO/WDK-CAN5)-( .00303/.00055)*((RHO/WDK)*(W
1AO-WDK)/166.-CAO*WAO/WDK+CAN5)
PRINT903, TM, CC, TDK, Y5
10 PUNCH902, TS, CC, TDK, Y5
900 FORMAT( I2, F10.0)
901 FORMAT (3F10.0)
902 FORMAT (10X, F10.4, 10X, F10.6, 10X, F10.4, E13.6)
903 FORMAT(1H , F10.4, E13.6, F10.4, 20X, E13.6)
905 FORMAT(1H , 6X, 4HTIME, 13HCONCENTRATION, 4X, 4HTEMP, 30X, 17
1HRATE OF FORMATION)
CALL EXIT
END

```

Table XII: IBM Computer Program for the Derivative of a Polynomial  
for Bifluorenyl Reaction Two (RX-B-2)

```

ZZJOB 5                                DER OF POLY RX-B-2.
ZZFORX5
  DIMENSION COE (10),DCOE (10)
  READ 900,N,OD,WAO,R,IDEH,RHO
  2 READ 901,IDEG,C
    IF(IDEG)1,1,8
  8 COE (IDEG)=C
    DEG=IDEG
    DCOE (IDEG)=(DEG)*COE (IDEG)
    IF(IDEG)1,1,2
  1 DO5I=1,N
    DER=0.0
    IDEG= IDEH
    READ 902,TS,XNA,TDK,RATECA
  6 DER=DER+DCOE (IDEG )*TS**( IDEG-1)
    IF(IDEG-1)3,3,4
  4 IDEG=IDEG-1
    GO TO 6
  3 RATECC=-DER-RATECA
    IF(RATECC) 7,7,9
  9 Z=LOGF(RATECC)
    X1=-LOGF(XNA)
    Y=Z-OD*X1
    X=1./(R*TDK)
    PUNCH 903,Y,X
    GO TO 5
  7 PRINT 904,TS,XNA,TDK,RATECA,RATECC
  5 CONTINUE
900 FORMAT(I2,3F10.0,I2,F10.0)
901 FORMAT(3X,I2,3I1X,E20.8)
902 FORMAT(3F20.0,E13.6)
903 FORMAT(2E14.7)
904 FORMAT(1H ,5E13.6,8HBAD CARD)
  CALL EXIT
  END

```

Table XIII: Kinetic Results for the Analysis of Bifluorenyl Reaction Two (RX-B-2)

| Run                               | EX-B-9  | EX-B-9  | EX-B-9   | EX-B-9*  | EX-B-9*  | EX-B-9*  |
|-----------------------------------|---------|---------|----------|----------|----------|----------|
| Stoich (n)                        | .00086  | .00088  | .00090   | .00088   | .00090   | .00092   |
| 1 <sup>st</sup> ln k <sub>o</sub> | 5.14    | 11.11   | -1.88    |          |          |          |
| E                                 | 16,954  | 11,499  | 7,445    |          |          |          |
| First Correlation                 | .838    | .776    | .664     |          |          |          |
| 2 <sup>nd</sup> ln k <sub>o</sub> | 43.4    | 35.4    | 29.6     | 33.9     | 27.9     | 21.0     |
| E                                 | 60,543  | 49,750  | 41,800   | 47,530   | 39,354   | 30,108   |
| Second Correlation                | .975    | .978    | .977     | .984     | .984     | .980     |
| Run                               | EX-B-11 | EX-B-11 | EX-B-11* | EX-B-11* | EX-B-11* | EX-B-11* |
| Stoich (n)                        | .00043  | .00044  | .00044   | .00046   | .00047   | .00048   |
| 1 <sup>st</sup> ln k <sub>o</sub> |         | -16.54  |          |          |          |          |
| E                                 |         | 43,493  |          |          |          |          |
| First Correlation                 |         | .719    |          |          |          |          |
| 2 <sup>nd</sup> ln k <sub>o</sub> | 47.5    | 45.86   | 99.6     | 51.2     | 42.1     | 35.37    |
| E                                 | 66,415  | 64,212  | 139,547  | 72,055   | 59,431   | 50,141   |
| Second Correlation                | .943    | .939    | .868     | .902     | .889     | .869     |

\* Note: The starting point for the numerical solution was altered.

Table XIII (continued)

| Run                   | EX-B-12 | EX-B-12 | EX-B-12 | EX-B-12 | EX-B-12 | EX-B-12 |
|-----------------------|---------|---------|---------|---------|---------|---------|
| Stoich (n)            | .00054  | .00055  | .00056  | .00057  | .00058  | .00059  |
| 1st $\ln k_o$         |         |         |         |         |         |         |
| E                     |         |         |         |         |         |         |
| First<br>Correlation  |         |         |         |         |         |         |
| 2nd $\ln k_o$         | 46.6    | 39.1    | 33.2    | 28.4    | 24.3    | 20.9    |
| E                     | 65,465  | 55,104  | 47,007  | 40,399  | 34,840  | 30,152  |
| Second<br>Correlation | .978    | .982    | .983    | .982    | .981    | .977    |

(96)

Table XIV: Summary of Kinetic Results for the Analysis of Bifluorenyl  
Reaction Two (RX-B-2) Second Order

| Run                        | EX-B-9     | EX-B-11    | EX-B-12    |
|----------------------------|------------|------------|------------|
| Steich                     | .00088     | .00043     | .00056     |
| Frequency<br>Factor        | $e^{33.9}$ | $e^{47.5}$ | $e^{33.2}$ |
| Energy of<br>Activation    | 47,530     | 66,415     | 47,007     |
| Correlation<br>Coefficient | .984       | .943       | .983       |

Table XV: IBM Computer Program for Analysis of Reactions Involving Gas Evolution

```

ZZJOB 5
ZZFORX5
C  CONVERT RAW DATA AND X-Y CALCULATION FOR RX 3
    DIMENSION XNH2(200), DNH2(200), WD(200), TM(200), TDC(200)
    READ 2, N, RHO, WRO, OD, XNEO, DT
    2 FORMAT(I3,5F10.0)
C  N IS NO. OF EXPTL POINTS DT IS TIME INCREMENT IN MINUTES
    CARDS = 0.
    HTO = 0.
    SUMT = 0.
    DO 50 I=1, N
        READ 3, WD(I), TM(I), TDC(I), DNH2(I)
        3 FORMAT(4F10.0)
        DNH2(I) = DNH2(I) / .1E6
        XNH2(I) = SUMT + (HTO + DNH2(I)) * DT / 2.
        SUMT = XNH2(I)
    50 HTO = DNH2(I)
        PRINT 4, SUMT
        4 FORMAT(1H, E13.6, 28HTOTAL MOLES HYDROGEN EVOLVED)
        DO 60 I=1, N
C  WD= UNITS FROM TGA, HTO=DNH2 AT BEGINNING OF AREA INTERVAL
        TDK = TDC(I) + 273.
        WDK = WD(I) / 90.5
        WDK = WRO - WDK
C  WRO IS SAMPLE WEIGHT FROM START OF EXPERIMENT
C  CHANGE DERIVATIVE TO SECOND UNITS
        DCE = RHO * XNEO * DNH2(I) / (WDK * SUMT * 60.)
        V = WDK / RHO
        IF (DCE) 51, 51, 55
    51 PRINT 500, DCE, TM(I)
    500 FORMAT(1H, E14.6, F8.1, 19HBAD DERIVATIVE CARD)
        GO TO 60
    55 CE = XNEO * (1. - XNH2(I) / SUMT) / V
        IF (CE) 56, 56, 57
    56 PRINT 501, CE, TM(I)
    501 FORMAT(1H, E14.6, F8.1, 22HBAD CONCENTRATION CARD)
        GO TO 60
    57 PRINT 502, DCE, CE
    502 FORMAT(11H RATE OF E=, E14.6, 10HCONC OF E=, E14.6)
        Y1 = LOGF(DCE)
        Y2 = LOGF(CE)
        Y = Y1 - OD * Y2
        X = 1. / (1.9864 * TDK)
        PUNCH 903, Y, X

```

Table XV (continued)

```
903 FORMAT (2E14.7)
    CARDS = CARDS +1.
60  CONTINUE
    PRINT 904, CARDS
904 FORMAT (//10H THERE ARE,F5.0,20HCARDS FOR REGRESSION)
    CALL EXIT
    END
```

Table XVI: Converted Experimental Data for Analysis of Bifluorenyl  
Reaction Three, Pyrolysis Run EX-B-8

| TIME<br>MIN. | TEMP<br>DEG. C | GRAMS<br>WDK | CONC<br>MOLES/CC | RATE<br>HYDROGEN |
|--------------|----------------|--------------|------------------|------------------|
| 103.0        | 459.600        | .8629        | .0015852         | .00000100        |
| 104.0        | 461.000        | .8618        | .0015862         | .00000110        |
| 105.0        | 462.400        | .8602        | .0015881         | .00000120        |
| 106.0        | 463.800        | .8585        | .0015899         | .00000130        |
| 107.0        | 465.200        | .8563        | .0015927         | .00000140        |
| 108.0        | 466.600        | .8541        | .0015953         | .00000150        |
| 109.0        | 468.000        | .8519        | .0015979         | .00000160        |
| 110.0        | 469.400        | .8497        | .0016004         | .00000170        |
| 111.0        | 470.800        | .8475        | .0016028         | .00000181        |
| 112.0        | 472.200        | .8453        | .0016051         | .00000191        |
| 113.0        | 473.600        | .8436        | .0016062         | .00000202        |
| 114.0        | 475.000        | .8419        | .0016073         | .00000212        |
| 115.0        | 476.800        | .8403        | .0016082         | .00000223        |
| 116.0        | 478.700        | .8384        | .0016095         | .00000233        |
| 117.0        | 480.600        | .8375        | .0016087         | .00000244        |
| 118.0        | 482.200        | .8364        | .0016083         | .00000254        |
| 119.0        | 483.800        | .8353        | .0016077         | .00000265        |
| 120.0        | 485.400        | .8342        | .0016070         | .00000276        |
| 121.0        | 487.000        | .8329        | .0016067         | .00000287        |
| 122.0        | 488.600        | .8313        | .0016066         | .00000298        |
| 123.0        | 490.200        | .8298        | .0016065         | .00000309        |
| 124.0        | 491.800        | .8281        | .0016064         | .00000321        |
| 125.0        | 493.400        | .8262        | .0016067         | .00000333        |
| 126.0        | 495.000        | .8241        | .0016072         | .00000346        |
| 127.0        | 496.600        | .8217        | .0016083         | .00000360        |
| 128.0        | 497.400        | .8192        | .0016094         | .00000376        |
| 129.0        | 498.200        | .8165        | .0016105         | .00000393        |
| 130.0        | 499.000        | .8138        | .0016117         | .00000411        |
| 131.0        | 499.900        | .8109        | .0016130         | .00000430        |
| 132.0        | 500.800        | .8080        | .0016140         | .00000450        |
| 133.0        | 501.700        | .8051        | .0016149         | .00000471        |
| 134.0        | 502.600        | .8023        | .0016155         | .00000493        |
| 135.0        | 503.500        | .7994        | .0016158         | .00000518        |
| 136.0        | 504.400        | .7964        | .0016161         | .00000543        |
| 137.0        | 505.300        | .7934        | .0016162         | .00000569        |
| 138.0        | 506.200        | .7904        | .0016159         | .00000595        |
| 139.0        | 507.100        | .7875        | .0016154         | .00000620        |
| 140.0        | 508.000        | .7845        | .0016146         | .00000645        |
| 141.0        | 508.900        | .7814        | .0016137         | .00000670        |
| 142.0        | 509.800        | .7783        | .0016126         | .00000695        |

Table XVI (continued)

|       |         |       |          |           |
|-------|---------|-------|----------|-----------|
| 143.0 | 510.700 | .7752 | .0016111 | .00000720 |
| 144.0 | 511.600 | .7720 | .0016096 | .00000745 |
| 145.0 | 512.500 | .7688 | .0016078 | .00000770 |
| 146.0 | 513.400 | .7655 | .0016060 | .00000796 |
| 147.0 | 514.500 | .7622 | .0016038 | .00000824 |
| 148.0 | 515.400 | .7587 | .0016015 | .00000852 |
| 149.0 | 516.300 | .7553 | .0015989 | .00000881 |
| 150.0 | 517.200 | .7518 | .0015961 | .00000912 |
| 151.0 | 517.800 | .7482 | .0015930 | .00000942 |
| 152.0 | 518.400 | .7446 | .0015897 | .00000976 |
| 153.0 | 519.000 | .7409 | .0015860 | .00001007 |
| 154.0 | 519.600 | .7372 | .0015821 | .00001038 |
| 155.0 | 520.200 | .7332 | .0015783 | .00001070 |
| 156.0 | 520.900 | .7290 | .0015746 | .00001100 |
| 157.0 | 521.600 | .7247 | .0015707 | .00001132 |
| 158.0 | 522.300 | .7204 | .0015663 | .00001165 |
| 159.0 | 523.000 | .7159 | .0015620 | .00001198 |
| 160.0 | 523.700 | .7112 | .0015575 | .00001230 |
| 161.0 | 524.400 | .7068 | .0015520 | .00001262 |
| 162.0 | 525.000 | .7027 | .0015454 | .00001294 |
| 163.0 | 525.600 | .6990 | .0015375 | .00001326 |
| 164.0 | 526.200 | .6955 | .0015284 | .00001358 |
| 165.0 | 526.800 | .6924 | .0015182 | .00001390 |
| 166.0 | 527.400 | .6896 | .0015069 | .00001422 |
| 167.0 | 528.000 | .6868 | .0014949 | .00001454 |
| 168.0 | 528.600 | .6841 | .0014822 | .00001486 |
| 169.0 | 529.200 | .6816 | .0014687 | .00001519 |
| 170.0 | 529.800 | .6791 | .0014548 | .00001542 |
| 171.0 | 530.400 | .6763 | .0014408 | .00001583 |
| 172.0 | 531.000 | .6733 | .0014267 | .00001619 |
| 173.0 | 531.600 | .6702 | .0014122 | .00001654 |
| 174.0 | 532.600 | .6671 | .0013972 | .00001690 |
| 175.0 | 533.600 | .6640 | .0013815 | .00001725 |
| 176.0 | 534.600 | .6608 | .0013655 | .00001763 |
| 177.0 | 535.600 | .6576 | .0013487 | .00001800 |
| 178.0 | 536.600 | .6543 | .0013316 | .00001840 |
| 179.0 | 537.600 | .6510 | .0013137 | .00001882 |
| 180.0 | 538.600 | .6476 | .0012953 | .00001928 |
| 181.0 | 539.600 | .6441 | .0012760 | .00001988 |
| 182.0 | 540.600 | .6407 | .0012556 | .00002054 |
| 183.0 | 541.600 | .6373 | .0012342 | .00002120 |
| 184.0 | 542.600 | .6339 | .0012114 | .00002200 |
| 185.0 | 543.700 | .6304 | .0011873 | .00002290 |
| 186.0 | 544.800 | .6271 | .0011615 | .00002380 |

Table XVI (continued)

|       |         |       |          |           |
|-------|---------|-------|----------|-----------|
| 187.0 | 545.900 | .6239 | .0011341 | .00002457 |
| 188.0 | 547.000 | .6208 | .0011051 | .00002522 |
| 189.0 | 547.700 | .6179 | .0010749 | .00002582 |
| 190.0 | 548.400 | .6151 | .0010432 | .00002630 |
| 191.0 | 549.100 | .6125 | .0010103 | .00002654 |
| 192.0 | 549.800 | .6102 | .0009766 | .00002659 |
| 193.0 | 550.600 | .6081 | .0009423 | .00002659 |
| 194.0 | 551.400 | .6061 | .0009076 | .00002655 |
| 195.0 | 552.200 | .6043 | .0008727 | .00002632 |
| 196.0 | 553.000 | .6025 | .0008378 | .00002600 |
| 197.0 | 553.800 | .6007 | .0008032 | .00002568 |
| 198.0 | 554.600 | .5991 | .0007687 | .00002538 |
| 199.0 | 555.400 | .5974 | .0007344 | .00002510 |
| 200.0 | 556.200 | .5959 | .0007002 | .00002484 |
| 201.0 | 557.000 | .5944 | .0006660 | .00002459 |
| 202.0 | 557.800 | .5931 | .0006320 | .00002433 |
| 203.0 | 558.600 | .5919 | .0005980 | .00002408 |
| 204.0 | 559.400 | .5908 | .0005642 | .00002383 |
| 205.0 | 560.200 | .5898 | .0005305 | .00002360 |
| 206.0 | 561.000 | .5888 | .0004970 | .00002331 |
| 207.0 | 561.800 | .5878 | .0004638 | .00002306 |
| 208.0 | 562.600 | .5868 | .0004309 | .00002280 |
| 209.0 | 563.400 | .5858 | .0003983 | .00002252 |
| 210.0 | 564.200 | .5848 | .0003660 | .00002226 |
| 211.0 | 565.000 | .5838 | .0003339 | .00002200 |
| 212.0 | 565.800 | .5828 | .0003022 | .00002174 |
| 213.0 | 566.600 | .5819 | .0002706 | .00002147 |
| 214.0 | 567.400 | .5811 | .0002394 | .00002121 |
| 215.0 | 568.200 | .5802 | .0002084 | .00002095 |
| 216.0 | 569.000 | .5793 | .0001777 | .00002070 |
| 217.0 | 569.800 | .5785 | .0001473 | .00002044 |
| 218.0 | 570.600 | .5777 | .0001172 | .00002018 |
| 219.0 | 571.400 | .5771 | .0000874 | .00001991 |
| 220.0 | 572.200 | .5764 | .0000579 | .00001964 |
| 221.0 | 573.000 | .5759 | .0000288 | .00001938 |

Table XVII: Converted Experimental Data for Analysis of Bifluorenyl  
Reaction Three, Pyrolysis Run EX-B-9

| TIME<br>MIN. | TEMP<br>DEG. C | GRAMS<br>WDK | CONC<br>MOLES/CC | RATE<br>HYDROGEN |
|--------------|----------------|--------------|------------------|------------------|
| 117.0        | 467.700        | .8585        | .0015844         | .00000110        |
| 118.0        | 469.200        | .8569        | .0015863         | .00000120        |
| 119.0        | 470.700        | .8552        | .0015880         | .00000130        |
| 120.0        | 472.200        | .8535        | .0015897         | .00000142        |
| 121.0        | 473.600        | .8519        | .0015912         | .00000155        |
| 122.0        | 475.000        | .8502        | .0015926         | .00000159        |
| 123.0        | 476.200        | .8483        | .0015944         | .00000174        |
| 124.0        | 477.400        | .8465        | .0015960         | .00000201        |
| 125.0        | 478.600        | .8446        | .0015972         | .00000222        |
| 126.0        | 479.800        | .8427        | .0015983         | .00000245        |
| 127.0        | 481.000        | .8407        | .0015994         | .00000268        |
| 128.0        | 482.200        | .8386        | .0016004         | .00000288        |
| 129.0        | 483.400        | .8364        | .0016014         | .00000307        |
| 130.0        | 484.600        | .8342        | .0016023         | .00000323        |
| 131.0        | 485.800        | .8320        | .0016029         | .00000337        |
| 132.0        | 487.000        | .8298        | .0016035         | .00000350        |
| 133.0        | 487.800        | .8274        | .0016043         | .00000361        |
| 134.0        | 488.600        | .8249        | .0016051         | .00000370        |
| 135.0        | 489.400        | .8225        | .0016057         | .00000377        |
| 136.0        | 490.200        | .8201        | .0016063         | .00000383        |
| 137.0        | 491.000        | .8176        | .0016069         | .00000388        |
| 138.0        | 491.800        | .8152        | .0016073         | .00000393        |
| 139.0        | 492.600        | .8130        | .0016074         | .00000396        |
| 140.0        | 493.400        | .8108        | .0016073         | .00000400        |
| 141.0        | 494.200        | .8088        | .0016068         | .00000403        |
| 142.0        | 495.000        | .8068        | .0016063         | .00000405        |
| 143.0        | 495.800        | .8048        | .0016057         | .00000408        |
| 144.0        | 496.600        | .8030        | .0016046         | .00000413        |
| 145.0        | 497.400        | .8013        | .0016035         | .00000419        |
| 146.0        | 498.200        | .7995        | .0016023         | .00000426        |
| 147.0        | 499.000        | .7977        | .0016010         | .00000434        |
| 148.0        | 499.800        | .7960        | .0015996         | .00000442        |
| 149.0        | 500.600        | .7940        | .0015985         | .00000452        |
| 150.0        | 501.400        | .7920        | .0015974         | .00000464        |
| 151.0        | 502.200        | .7900        | .0015960         | .00000477        |
| 152.0        | 503.000        | .7878        | .0015950         | .00000491        |
| 153.0        | 504.100        | .7856        | .0015938         | .00000506        |
| 154.0        | 505.200        | .7830        | .0015930         | .00000524        |
| 155.0        | 506.300        | .7805        | .0015921         | .00000543        |
| 156.0        | 507.400        | .7777        | .0015913         | .00000565        |

Table XVII (continued)

|       |         |       |          |           |
|-------|---------|-------|----------|-----------|
| 157.0 | 508.500 | .7750 | .0015903 | .00000587 |
| 158.0 | 509.600 | .7722 | .0015890 | .00000613 |
| 159.0 | 510.700 | .7695 | .0015873 | .00000647 |
| 160.0 | 511.800 | .7667 | .0015852 | .00000685 |
| 161.0 | 512.900 | .7637 | .0015831 | .00000726 |
| 162.0 | 514.000 | .7606 | .0015807 | .00000770 |
| 163.0 | 515.100 | .7573 | .0015782 | .00000815 |
| 164.0 | 516.200 | .7540 | .0015752 | .00000863 |
| 165.0 | 517.300 | .7507 | .0015715 | .00000915 |
| 166.0 | 518.400 | .7474 | .0015671 | .00000968 |
| 167.0 | 519.500 | .7438 | .0015625 | .00001025 |
| 168.0 | 520.600 | .7403 | .0015572 | .00001075 |
| 169.0 | 521.700 | .7365 | .0015517 | .00001128 |
| 170.0 | 522.800 | .7328 | .0015455 | .00001185 |
| 171.0 | 523.900 | .7288 | .0015389 | .00001245 |
| 172.0 | 525.000 | .7248 | .0015316 | .00001300 |
| 173.0 | 526.000 | .7208 | .0015234 | .00001360 |
| 174.0 | 527.000 | .7169 | .0015144 | .00001420 |
| 175.0 | 528.000 | .7138 | .0015027 | .00001480 |
| 176.0 | 529.000 | .7093 | .0014929 | .00001540 |
| 177.0 | 530.000 | .7047 | .0014827 | .00001600 |
| 178.0 | 531.000 | .6998 | .0014721 | .00001663 |
| 179.0 | 532.000 | .6948 | .0014609 | .00001725 |
| 180.0 | 533.000 | .6895 | .0014493 | .00001785 |
| 181.0 | 534.000 | .6839 | .0014371 | .00001843 |
| 182.0 | 535.000 | .6782 | .0014245 | .00001898 |
| 183.0 | 536.000 | .6724 | .0014109 | .00001954 |
| 184.0 | 537.000 | .6669 | .0013959 | .00002008 |
| 185.0 | 538.000 | .6616 | .0013794 | .00002055 |
| 186.0 | 539.000 | .6565 | .0013616 | .00002103 |
| 187.0 | 540.000 | .6517 | .0013425 | .00002143 |
| 188.0 | 541.000 | .6470 | .0013220 | .00002184 |
| 189.0 | 542.000 | .6426 | .0013003 | .00002225 |
| 190.0 | 542.850 | .6384 | .0012772 | .00002270 |
| 191.0 | 543.700 | .6344 | .0012527 | .00002313 |
| 192.0 | 544.550 | .6306 | .0012271 | .00002353 |
| 193.0 | 545.400 | .6268 | .0012003 | .00002410 |
| 194.0 | 546.250 | .6232 | .0011718 | .00002515 |
| 195.0 | 547.100 | .6196 | .0011413 | .00002610 |
| 196.0 | 547.950 | .6162 | .0011088 | .00002710 |
| 197.0 | 548.800 | .6129 | .0010743 | .00002810 |
| 198.0 | 549.650 | .6096 | .0010382 | .00002868 |
| 199.0 | 550.500 | .6064 | .0010010 | .00002898 |
| 200.0 | 551.350 | .6033 | .0009627 | .00002920 |

Table XVII (continued)

|       |         |       |          |           |
|-------|---------|-------|----------|-----------|
| 201.0 | 552.200 | .6003 | .0009237 | .00002930 |
| 202.0 | 553.050 | .5974 | .0008840 | .00002933 |
| 203.0 | 553.800 | .5945 | .0008439 | .00002930 |
| 204.0 | 554.500 | .5918 | .0008034 | .00002920 |
| 205.0 | 555.200 | .5892 | .0007625 | .00002890 |
| 206.0 | 555.900 | .5868 | .0007217 | .00002848 |
| 207.0 | 556.600 | .5846 | .0006812 | .00002780 |
| 208.0 | 557.300 | .5825 | .0006413 | .00002700 |
| 209.0 | 558.000 | .5806 | .0006021 | .00002630 |
| 210.0 | 558.700 | .5788 | .0005636 | .00002560 |
| 211.0 | 559.500 | .5773 | .0005258 | .00002490 |
| 212.0 | 560.300 | .5760 | .0004887 | .00002420 |
| 213.0 | 561.200 | .5749 | .0004522 | .00002360 |
| 214.0 | 562.100 | .5739 | .0004164 | .00002310 |
| 215.0 | 563.000 | .5730 | .0003812 | .00002262 |
| 216.0 | 563.900 | .5722 | .0003465 | .00002212 |
| 217.0 | 564.800 | .5716 | .0003125 | .00002160 |
| 218.0 | 565.700 | .5710 | .0002794 | .00002090 |
| 219.0 | 566.600 | .5706 | .0002473 | .00002010 |
| 220.0 | 567.500 | .5702 | .0002164 | .00001930 |
| 221.0 | 568.400 | .5701 | .0001866 | .00001850 |
| 222.0 | 569.300 | .5701 | .0001580 | .00001775 |
| 223.0 | 570.200 | .5701 | .0001303 | .00001734 |
| 224.0 | 571.100 | .5701 | .0001033 | .00001697 |
| 225.0 | 572.000 | .5701 | .0000767 | .00001666 |
| 226.0 | 572.200 | .5701 | .0000507 | .00001638 |
| 227.0 | 572.400 | .5701 | .0000251 | .00001609 |

Table XVIII: Converted Experimental Data for Analysis of Bifluorenyl  
Reaction Three, Pyrolysis Run EX-B-11

| TIME<br>MIN. | TEMP<br>DEG. C | GRAMS<br>WDK | CONC<br>MOLES/CC | RATE<br>HYDROGEN |
|--------------|----------------|--------------|------------------|------------------|
| 121.0        | 485.200        | .9049        | .0015850         | .00000024        |
| 122.0        | 486.800        | .9027        | .0015885         | .00000026        |
| 123.0        | 488.400        | .9005        | .0015921         | .00000028        |
| 124.0        | 490.000        | .8982        | .0015958         | .00000031        |
| 125.0        | 491.600        | .8959        | .0015996         | .00000035        |
| 126.0        | 493.200        | .8934        | .0016034         | .00000040        |
| 127.0        | 494.800        | .8910        | .0016073         | .00000044        |
| 128.0        | 496.400        | .8886        | .0016111         | .00000049        |
| 129.0        | 498.000        | .8860        | .0016150         | .00000055        |
| 130.0        | 499.600        | .8835        | .0016189         | .00000062        |
| 131.0        | 501.000        | .8809        | .0016227         | .00000070        |
| 132.0        | 502.200        | .8784        | .0016265         | .00000077        |
| 133.0        | 503.300        | .8759        | .0016301         | .00000085        |
| 134.0        | 504.400        | .8733        | .0016337         | .00000095        |
| 135.0        | 505.500        | .8818        | .0016167         | .00000106        |
| 136.0        | 506.500        | .8682        | .0016405         | .00000117        |
| 137.0        | 507.600        | .8657        | .0016437         | .00000128        |
| 138.0        | 508.600        | .8632        | .0016468         | .00000140        |
| 139.0        | 509.600        | .8606        | .0016497         | .00000152        |
| 140.0        | 510.700        | .8580        | .0016527         | .00000165        |
| 141.0        | 511.700        | .8563        | .0016536         | .00000180        |
| 142.0        | 512.700        | .8522        | .0016591         | .00000195        |
| 143.0        | 513.800        | .8490        | .0016626         | .00000210        |
| 144.0        | 514.800        | .8456        | .0016664         | .00000227        |
| 145.0        | 515.800        | .8419        | .0016704         | .00000244        |
| 146.0        | 516.090        | .8381        | .0016747         | .00000260        |
| 147.0        | 517.900        | .8340        | .0016793         | .00000278        |
| 148.0        | 518.900        | .8297        | .0016840         | .00000298        |
| 149.0        | 520.000        | .8251        | .0016890         | .00000319        |
| 150.0        | 521.000        | .8204        | .0016942         | .00000342        |
| 151.0        | 522.000        | .8155        | .0016994         | .00000368        |
| 152.0        | 523.000        | .8107        | .0017042         | .00000396        |
| 153.0        | 524.000        | .8058        | .0017087         | .00000418        |
| 154.0        | 525.000        | .8009        | .0017129         | .00000461        |
| 155.0        | 526.000        | .7961        | .0017165         | .00000495        |
| 156.0        | 527.000        | .7911        | .0017199         | .00000530        |
| 157.0        | 528.000        | .7861        | .0017228         | .00000570        |
| 158.0        | 529.000        | .7812        | .0017252         | .00000610        |
| 159.0        | 530.000        | .7762        | .0017270         | .00000650        |
| 160.0        | 530.900        | .7712        | .0017283         | .00000690        |

Table XVIII (continued)

|       |         |       |          |           |
|-------|---------|-------|----------|-----------|
| 161.0 | 531.700 | .7661 | .0017292 | .00000728 |
| 162.0 | 532.400 | .7611 | .0017296 | .00000764 |
| 163.0 | 533.000 | .7560 | .0017295 | .00000798 |
| 164.0 | 533.600 | .7508 | .0017291 | .00000831 |
| 165.0 | 534.200 | .7455 | .0017285 | .00000867 |
| 166.0 | 534.800 | .7401 | .0017275 | .00000904 |
| 167.0 | 535.400 | .7346 | .0017260 | .00000939 |
| 168.0 | 536.000 | .7292 | .0017239 | .00000975 |
| 169.0 | 536.600 | .7237 | .0017214 | .00001011 |
| 170.0 | 537.200 | .7182 | .0017184 | .00001047 |
| 171.0 | 537.800 | .7125 | .0017150 | .00001082 |
| 172.0 | 538.400 | .7069 | .0017109 | .00001125 |
| 173.0 | 539.000 | .7014 | .0017058 | .00001164 |
| 174.0 | 540.000 | .6959 | .0017000 | .00001206 |
| 175.0 | 541.000 | .6904 | .0016931 | .00001250 |
| 176.0 | 542.000 | .6850 | .0016853 | .00001300 |
| 177.0 | 543.000 | .6797 | .0016760 | .00001380 |
| 178.0 | 544.000 | .6745 | .0016648 | .00001480 |
| 179.0 | 545.000 | .6693 | .0016516 | .00001590 |
| 180.0 | 546.000 | .6643 | .0016359 | .00001730 |
| 181.0 | 547.000 | .6593 | .0016170 | .00001890 |
| 182.0 | 548.000 | .6543 | .0015950 | .00002055 |
| 183.0 | 549.000 | .6495 | .0015695 | .00002220 |
| 184.0 | 550.000 | .6447 | .0015404 | .00002390 |
| 185.0 | 551.000 | .6401 | .0015077 | .00002550 |
| 186.0 | 552.000 | .6355 | .0014714 | .00002700 |
| 187.0 | 552.900 | .6312 | .0014314 | .00002854 |
| 188.0 | 553.800 | .6272 | .0013885 | .00002886 |
| 189.0 | 554.700 | .6236 | .0013438 | .00002905 |
| 190.0 | 555.600 | .6203 | .0012976 | .00002915 |
| 191.0 | 556.500 | .6173 | .0012501 | .00002918 |
| 192.0 | 557.400 | .6146 | .0012016 | .00002915 |
| 193.0 | 558.300 | .6122 | .0011523 | .00002905 |
| 194.0 | 559.200 | .6099 | .0011028 | .00002875 |
| 195.0 | 560.100 | .6077 | .0010537 | .00002790 |
| 196.0 | 561.000 | .6056 | .0010079 | .00002480 |
| 197.0 | 561.900 | .6036 | .0009652 | .00002410 |
| 198.0 | 562.800 | .6017 | .0009231 | .00002360 |
| 199.0 | 563.700 | .6000 | .0008814 | .00002323 |
| 200.0 | 564.600 | .5983 | .0008400 | .00002287 |
| 201.0 | 565.500 | .5967 | .0007989 | .00002254 |
| 202.0 | 566.400 | .5953 | .0007583 | .00002203 |
| 203.0 | 567.300 | .5940 | .0007185 | .00002135 |
| 204.0 | 567.900 | .5928 | .0006801 | .00002020 |

Table XVIII (continued)

|       |         |       |          |           |
|-------|---------|-------|----------|-----------|
| 205.0 | 568.500 | .5917 | .0006440 | .00001870 |
| 206.0 | 569.100 | .5907 | .0006103 | .00001740 |
| 207.0 | 569.700 | .5898 | .0005787 | .00001625 |
| 208.0 | 570.300 | .5889 | .0005489 | .00001555 |
| 209.0 | 570.900 | .5881 | .0005200 | .00001507 |
| 210.0 | 571.500 | .5875 | .0004918 | .00001470 |
| 211.0 | 572.100 | .5867 | .0004642 | .00001440 |
| 212.0 | 572.600 | .5859 | .0004372 | .00001412 |
| 213.0 | 573.100 | .5851 | .0004106 | .00001384 |
| 214.0 | 573.600 | .5845 | .0003844 | .00001355 |
| 215.0 | 574.100 | .5838 | .0003587 | .00001328 |
| 216.0 | 574.600 | .5832 | .0003335 | .00001300 |
| 217.0 | 575.100 | .5825 | .0003087 | .00001273 |
| 218.0 | 575.600 | .5818 | .0002844 | .00001248 |
| 219.0 | 576.100 | .5812 | .0002606 | .00001222 |
| 220.0 | 576.600 | .5806 | .0002371 | .00001200 |
| 221.0 | 577.100 | .5800 | .0002140 | .00001180 |
| 222.0 | 577.600 | .5794 | .0001913 | .00001157 |
| 223.0 | 578.500 | .5788 | .0001690 | .00001138 |
| 224.0 | 579.400 | .5783 | .0001469 | .00001120 |
| 225.0 | 580.300 | .5777 | .0001252 | .00001102 |
| 226.0 | 581.200 | .5772 | .0001037 | .00001088 |
| 227.0 | 582.100 | .5766 | .0000825 | .00001073 |
| 228.0 | 583.000 | .5761 | .0000615 | .00001058 |
| 229.0 | 583.900 | .5756 | .0000408 | .00001046 |
| 230.0 | 584.800 | .5751 | .0000203 | .00001034 |

Table XIX: Converted Experimental Data for Analysis of Bifluorenyl  
Reaction Three, Pyrolysis Run EX-B-12

| TIME<br>MIN. | TEMP<br>DEG. C | GRAMS<br>WDK | CONC<br>MOLES/CC | RATE<br>HYDROGEN |
|--------------|----------------|--------------|------------------|------------------|
| 129.0        | 483.000        | .8972        | .0015858         | .00000030        |
| 130.0        | 484.000        | .8955        | .0015883         | .00000037        |
| 131.0        | 485.000        | .8937        | .0015911         | .00000044        |
| 132.0        | 486.000        | .8918        | .0015938         | .00000051        |
| 133.0        | 487.000        | .8899        | .0015964         | .00000058        |
| 134.0        | 488.000        | .8880        | .0015990         | .00000065        |
| 135.0        | 489.000        | .8861        | .0016015         | .00000072        |
| 136.0        | 490.000        | .8839        | .0016045         | .00000079        |
| 137.0        | 491.000        | .8817        | .0016074         | .00000086        |
| 138.0        | 492.000        | .8795        | .0016102         | .00000093        |
| 139.0        | 493.000        | .8773        | .0016130         | .00000100        |
| 140.0        | 494.000        | .8751        | .0016156         | .00000107        |
| 141.0        | 495.000        | .8729        | .0016182         | .00000114        |
| 142.0        | 496.000        | .8707        | .0016207         | .00000121        |
| 143.0        | 497.000        | .8685        | .0016231         | .00000128        |
| 144.0        | 498.000        | .8662        | .0016255         | .00000136        |
| 145.0        | 499.000        | .8640        | .0016277         | .00000144        |
| 146.0        | 500.000        | .8618        | .0016298         | .00000152        |
| 147.0        | 501.000        | .8596        | .0016319         | .00000160        |
| 148.0        | 502.000        | .8574        | .0016338         | .00000169        |
| 149.0        | 503.000        | .8550        | .0016360         | .00000178        |
| 150.0        | 504.000        | .8525        | .0016382         | .00000188        |
| 151.0        | 505.000        | .8500        | .0016404         | .00000198        |
| 152.0        | 505.900        | .8474        | .0016427         | .00000208        |
| 153.0        | 506.800        | .8447        | .0016448         | .00000218        |
| 154.0        | 507.600        | .8419        | .0016471         | .00000229        |
| 155.0        | 508.400        | .8391        | .0016494         | .00000240        |
| 156.0        | 509.100        | .8362        | .0016516         | .00000251        |
| 157.0        | 509.800        | .8333        | .0016536         | .00000262        |
| 158.0        | 510.500        | .8304        | .0016555         | .00000274        |
| 159.0        | 511.200        | .8276        | .0016572         | .00000286        |
| 160.0        | 511.900        | .8245        | .0016592         | .00000299        |
| 161.0        | 512.600        | .8214        | .0016611         | .00000313        |
| 162.0        | 513.300        | .8183        | .0016627         | .00000328        |
| 163.0        | 514.000        | .8152        | .0016641         | .00000344        |
| 164.0        | 514.700        | .8121        | .0016653         | .00000361        |
| 165.0        | 515.400        | .8088        | .0016667         | .00000379        |
| 166.0        | 516.100        | .8055        | .0016678         | .00000398        |
| 167.0        | 516.800        | .8022        | .0016687         | .00000418        |
| 168.0        | 517.500        | .7988        | .0016692         | .00000439        |

Table XIX (continued)

|       |         |       |          |           |
|-------|---------|-------|----------|-----------|
| 169.0 | 518.200 | .7950 | .0016707 | .00000460 |
| 170.0 | 518.800 | .7911 | .0016718 | .00000482 |
| 171.0 | 519.400 | .7872 | .0016725 | .00000504 |
| 172.0 | 520.000 | .7834 | .0016730 | .00000527 |
| 173.0 | 520.600 | .7790 | .0016743 | .00000550 |
| 174.0 | 521.200 | .7745 | .0016752 | .00000574 |
| 175.0 | 521.800 | .7701 | .0016758 | .00000598 |
| 176.0 | 522.400 | .7657 | .0016760 | .00000624 |
| 177.0 | 523.000 | .7613 | .0016758 | .00000651 |
| 178.0 | 523.600 | .7569 | .0016751 | .00000679 |
| 179.0 | 524.200 | .7524 | .0016740 | .00000708 |
| 180.0 | 524.800 | .7480 | .0016725 | .00000738 |
| 181.0 | 525.400 | .7436 | .0016704 | .00000768 |
| 182.0 | 526.000 | .7392 | .0016678 | .00000798 |
| 183.0 | 526.600 | .7353 | .0016634 | .00000829 |
| 184.0 | 527.200 | .7314 | .0016585 | .00000860 |
| 185.0 | 528.800 | .7281 | .0016518 | .00000891 |
| 186.0 | 529.400 | .7248 | .0016445 | .00000923 |
| 187.0 | 530.000 | .7215 | .0016366 | .00000955 |
| 188.0 | 530.600 | .7182 | .0016281 | .00000987 |
| 189.0 | 531.200 | .7149 | .0016190 | .00001019 |
| 190.0 | 531.800 | .7116 | .0016093 | .00001051 |
| 191.0 | 532.400 | .7082 | .0015990 | .00001083 |
| 192.0 | 533.000 | .7049 | .0015880 | .00001115 |
| 193.0 | 533.500 | .7016 | .0015763 | .00001147 |
| 194.0 | 534.000 | .6983 | .0015641 | .00001179 |
| 195.0 | 534.500 | .6950 | .0015511 | .00001211 |
| 196.0 | 535.000 | .6917 | .0015375 | .00001243 |
| 197.0 | 535.500 | .6883 | .0015232 | .00001275 |
| 198.0 | 536.000 | .6850 | .0015082 | .00001308 |
| 199.0 | 536.500 | .6817 | .0014924 | .00001343 |
| 200.0 | 537.200 | .6784 | .0014759 | .00001381 |
| 201.0 | 538.000 | .6751 | .0014585 | .00001425 |
| 202.0 | 539.000 | .6718 | .0014400 | .00001480 |
| 203.0 | 540.000 | .6685 | .0014203 | .00001550 |
| 204.0 | 541.000 | .6649 | .0013993 | .00001640 |
| 205.0 | 542.000 | .6612 | .0013768 | .00001760 |
| 206.0 | 543.000 | .6572 | .0013520 | .00001910 |
| 207.0 | 544.000 | .6532 | .0013239 | .00002090 |
| 208.0 | 545.000 | .6492 | .0012921 | .00002270 |
| 209.0 | 546.000 | .6454 | .0012567 | .00002430 |
| 210.0 | 547.000 | .6417 | .0012176 | .00002570 |
| 211.0 | 548.000 | .6384 | .0011750 | .00002690 |
| 212.0 | 549.000 | .6355 | .0011291 | .00002790 |

Table XIX (continued)

|       |         |       |          |           |
|-------|---------|-------|----------|-----------|
| 213.0 | 550.000 | .6329 | .0010808 | .00002870 |
| 214.0 | 551.000 | .6304 | .0010304 | .00002930 |
| 215.0 | 552.000 | .6282 | .0009782 | .00002975 |
| 216.0 | 553.000 | .6262 | .0009247 | .00003000 |
| 217.0 | 554.000 | .6245 | .0008703 | .00003000 |
| 218.0 | 555.000 | .6228 | .0008157 | .00002975 |
| 219.0 | 556.000 | .6213 | .0007613 | .00002930 |
| 220.0 | 556.900 | .6198 | .0007076 | .00002860 |
| 221.0 | 557.700 | .6185 | .0006551 | .00002770 |
| 222.0 | 558.400 | .6173 | .0006041 | .00002670 |
| 223.0 | 559.000 | .6162 | .0005549 | .00002560 |
| 224.0 | 559.600 | .6151 | .0005075 | .00002450 |
| 225.0 | 560.200 | .6141 | .0004621 | .00002340 |
| 226.0 | 560.800 | .6131 | .0004185 | .00002240 |
| 227.0 | 561.400 | .6122 | .0003766 | .00002140 |
| 228.0 | 562.000 | .6113 | .0003366 | .00002040 |
| 229.0 | 562.600 | .6106 | .0002983 | .00001940 |
| 230.0 | 563.200 | .6098 | .0002618 | .00001850 |
| 231.0 | 563.800 | .6090 | .0002270 | .00001760 |
| 232.0 | 564.400 | .6083 | .0001937 | .00001680 |
| 233.0 | 565.000 | .6077 | .0001619 | .00001600 |
| 234.0 | 565.600 | .6071 | .0001314 | .00001530 |
| 235.0 | 566.200 | .6066 | .0001023 | .00001460 |
| 236.0 | 566.800 | .6066 | .0000747 | .00001360 |
| 237.0 | 567.400 | .6066 | .0000488 | .00001290 |
| 238.0 | 568.000 | .6066 | .0000240 | .00001240 |

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Table XX: Kinetic Results for the Analysis of Gas Evolution Data of Bifluorenyl Reaction Three (RX-B-3)

|                          |                   |                   |                   |                   |
|--------------------------|-------------------|-------------------|-------------------|-------------------|
| Pyrolysis Run            | EX-B-8            | EX-B-9            | EX-B-11           | EX-B-12           |
| Stoich                   | .001430           | .001422           | .001499           | .001487           |
| Initial Temp., °C        | 460               | 467               | 485               | 483               |
| Final Temp., °C          | 573               | 572               | 584               | 568               |
| FIRST ORDER              |                   |                   |                   |                   |
| $k_0$ -sec <sup>-1</sup> | e <sup>30.8</sup> | e <sup>32.7</sup> | e <sup>48.2</sup> | e <sup>52.2</sup> |
| E - cal/mole             | 62,287            | 65,105            | 91,811            | 96,874            |
| Correlation Coefficient  | .973              | .977              | .991              | .989              |
| SECOND ORDER             |                   |                   |                   |                   |
| $k_0$ cc/mole sec        | e <sup>50.7</sup> | e <sup>54.1</sup> | e <sup>74.1</sup> | e <sup>77.2</sup> |
| E - cal/mole             | 82,751            | 88,026            | 122,431           | 125,769           |
| Correlation Coefficient  | .915              | .921              | .961              | .942              |

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Table XXI: IBM Computer Program for Analysis of Weight Losses Data of Bifluorenyl Reaction Three (RX-B-3)

ZZJOB 5 DATA CONVERT RX-B-3(WL)  
ZZFORX5

```
READ 900, N, WAO, XNEO, XNDO, WEO
DO 1 I=1, N
READ 901, WD, TM, TDC
TDK=TDC+273.0
WDK=WD/90.5
WDK=WAO-WDK
TS=TM*60.0
XCD=(.957*XNEO/WDK)*(1.0-(WEO-WDK)/(328.*XNDO))
1 PUNCH 902, TS, XCD, TDK
900 FORMAT(I3,4F10.6)
901 FORMAT(3F10.0)
902 FORMAT(10X,F10.3,10X,F10.8,10X,F10.4)
CALL EXIT
END
```

ZZJOB 5 DER OF POLY RX-B-3(WL)  
ZZFORX5

```
DIMENSION COE (10), DCOE (10)
READ 900, N, OD, R, IDEH
2 READ 901, IDEG, C
IF(IDEG)1,1,8
8 COE(IDEG)=C
DEG=IDEG
DCOE(IDEG)=(DEG)*COE(IDEG)
IF(IDEG)1,1,2
1 DO5 I=1, N
DER=0.0
IDEG= IDEH
READ 902, TS, XNA, TDK
6 DER=DER+DCOE(IDEG)*TS** (IDEG-1)
IF(IDEG-1)3,3,4
4 IDEG=IDEG-1
GO TO 6
3 IF(DER)9,5,5
9 A1=LOGF(-DER)
A2=OD*LOGF(XNA)
Y=A1-A2
X=1.0/(R*TDK)
PUNCH 903, Y, X
5 CONTINUE
900 FORMAT(I3,2F10.0,I2)
```

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Table XXI (continued)

```
901 FORMAT(3X,I2,31X,E20.8)
902 FORMAT(3F20.0)
903 FORMAT (2E14.7)
    CALL EXIT
    END
```

Table XXII: Kinetic Results for the Analysis of Weight-Loss Data of Bifluorenyl Reaction Three (RX-B-3)

| Pyrolysis Run            | EX-B-8            | EX-B-9            | EX-B-11           | EX-B-12           |
|--------------------------|-------------------|-------------------|-------------------|-------------------|
| Weight of E Initially    | .863              | .858              | .905              | .898              |
| Moles of E Initially     | .001430           | .001422           | .001499           | .001487           |
| Moles of D Formed        | .000878           | .000880           | .001008           | .000886           |
| FIRST ORDER              |                   |                   |                   |                   |
| $k_0$ -sec <sup>-1</sup> | e <sup>23.6</sup> | e <sup>39.6</sup> | e <sup>33.8</sup> | e <sup>33.4</sup> |
| E - cal/mole             | 49,810            | 75,069            | 66,702            | 65,352            |
| Correlation Coefficient  | .996              | .970              | .969              | .995              |
| SECOND ORDER             |                   |                   |                   |                   |
| $k_0$ -cc/mole sec       | e <sup>52.8</sup> | e <sup>76.7</sup> | e <sup>67.7</sup> | e <sup>76.1</sup> |
| E - cal/mole             | 84,235            | 121,965           | 109,834           | 121,167           |
| Correlation Coefficient  | .971              | .948              | .988              | .960              |

Table XXIII: Summary of All Pyrolysis Experiments Conducted on Acenaphthylene

| Pyrolysis<br>Run | Sample<br>Size<br>Grams | Final<br>Temp.,<br>°C | Carbon<br>Yield<br>Percent | Usable Data |             |             | Remarks                                                                |
|------------------|-------------------------|-----------------------|----------------------------|-------------|-------------|-------------|------------------------------------------------------------------------|
|                  |                         |                       |                            | <u>RX-1</u> | <u>RX-2</u> | <u>RX-3</u> |                                                                        |
| EX-A-1           | ≈8.0                    | ---                   | ---                        | ---         | ---         | ---         | Equipment modifica-<br>tions & changing op-<br>erating procedures<br>↓ |
| EX-A-2           | 4.478                   | ---                   | ---                        | ---         | ---         | ---         |                                                                        |
| EX-A-3           | 4.081                   | 535                   | 41.2                       | ---         | ---         | ---         |                                                                        |
| EX-A-4           | 3.222                   | 535                   | 40.1                       | ---         | ---         | ---         |                                                                        |
| EX-A-5           | 3.044                   | 573                   | 40.7                       | ---         | ---         | ---         |                                                                        |
| EX-A-6           | 3.029                   | 575                   | 40.6                       | ---         | ---         | ---         | Installed chromato-<br>graph sampling valve                            |
| EX-A-7           | 3.335                   | 613                   | 40.0                       | Yes         | No          | No          | Temperature erratic<br>above RX-1                                      |
| EX-A-8           | 3.361                   | 612                   | 40.4                       | Yes         | No          | No          | Temperature erratic<br>above RX-1                                      |
| EX-A-9           | 3.317                   | ---                   | ----                       | ---         | ---         | ---         | Reactor plugged                                                        |
| EX-A-10          | 3.295                   | 620                   | 40.3                       | Yes         | No          | No          | Temperature erratic<br>above RX-1                                      |
| EX-A-11          | 3.415                   | 350                   | ----                       | No          | No          | No          | Tried isothermal<br>operation at<br>350°C                              |

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Table XXIII (continued)

| Pyrolysis<br>Run | Sample<br>Size<br>Grams | Final<br>Temp.,<br>°C | Carbon<br>Yield<br>Percent | Usable Data |      |      | Remarks                                  |
|------------------|-------------------------|-----------------------|----------------------------|-------------|------|------|------------------------------------------|
|                  |                         |                       |                            | RX-1        | RX-2 | RX-3 |                                          |
| EX-A-12          | 3.225                   | 605                   | 43.2                       | No          | No   | No   | Tried isothermal op-<br>erating plateaus |
| EX-A-13          | 3.273                   | 605                   | 42.6                       | No          | No   | No   | Tried isothermal op-<br>ating plateaus   |
| EX-A-14          | 2.500                   | 608                   | 42.2                       | Yes         | Yes  | Yes  | Contant temperature<br>rise              |
| EX-A-15          | 2.500                   | 610                   | 41.2                       | Yes         | Yes  | Yes  | ↓                                        |
| EX-A-16          | 2.000                   | 607                   | 42.4                       | Yes         | Yes  | Yes  |                                          |
| EX-A-17          | 2.000                   | 606                   | 41.6                       | Yes         | Yes  | Yes  |                                          |

Table XXIV: IBM Computer Program for Analysis of Acenaphthylene  
Reaction Two (RX-A-2)

```

ZZJOB 5
ZZFORX5
  DIMENSION XCA(200),XDCA(200),TDK(200)
  READ 2, N,RHO, WAO, OD, XNBO
  2 FORMAT (I3,4F10.0)
  DO 50 I=1,N
    READ 3, WD, TM, TDC
    3 FORMAT (3F10.0)
    TDK(I)=TDC +273.0
    WDK=WD/90.5
    WDK=WAO-WDK
  50 XCA(I)=(WAO*RHO/(608.*WDK))*(1.0-(WAO-WDK)/(154.*XNBO))
    CARDS=0.0
    N=N-2
    DO 51 I=3,N
      IA=I-2
      IB=I-1
      IC=I+1
      ID=I+2
      XDCA(I)=(2.*XCA(ID)+XCA(IC)-XCA(IB)-2.*XCA(IA))/600.
      PRINT 501, XCA(I),XDCA(I),TDK(I)
      XDCA(I)=-XDCA(I)
      IF (XDCA(I)) 51,51,53
  501 FORMAT (F10.8,5X,F10.8,5X,F10.3)
  53 Y1=LOGF(XDCA(I))
      Y2=LOGF(XCA(I))
      Y=Y1-OD*Y2
      X=1./ (1.986*TDK(I))
      PUNCH 903,Y,X
  903 FORMAT (2E14.7)
      CARDS=CARDS+1.0
  51 CONTINUE
      PRINT 940,CARDS
  940 FORMAT (//10H THERE ARE,F5.0,20HCARDS FOR REGRESSION)
      CALL EXIT
      END

```

Table XXV: Converted Experimental Data for Analysis of Acenaphthylene  
Reactions Two and Three, Pyrolysis Run EX-A-14

| TIME<br>MIN. | TEMP<br>DEG. C | GRAMS<br>WDK | CONC<br>MOLES/CC |
|--------------|----------------|--------------|------------------|
| 0.0          | 336.300        | 2.4889       | .0016380         |
| 1.0          | 337.400        | 2.4886       | .0016378         |
| 2.0          | 338.500        | 2.4880       | .0016374         |
| 3.0          | 339.600        | 2.4872       | .0016369         |
| 4.0          | 340.700        | 2.4862       | .0016363         |
| 5.0          | 341.800        | 2.4850       | .0016356         |
| 6.0          | 342.900        | 2.4836       | .0016347         |
| 7.0          | 344.000        | 2.4819       | .0016337         |
| 8.0          | 345.100        | 2.4802       | .0016326         |
| 9.0          | 346.200        | 2.4783       | .0016314         |
| 10.0         | 347.300        | 2.4762       | .0016302         |
| 11.0         | 348.400        | 2.4740       | .0016288         |
| 12.0         | 349.500        | 2.4717       | .0016273         |
| 13.0         | 350.600        | 2.4691       | .0016258         |
| 14.0         | 351.700        | 2.4665       | .0016241         |
| 15.0         | 352.800        | 2.4636       | .0016223         |
| 16.0         | 353.900        | 2.4591       | .0016195         |
| 17.0         | 355.000        | 2.4524       | .0016153         |
| 18.0         | 356.100        | 2.4436       | .0016097         |
| 19.0         | 357.200        | 2.4303       | .0016013         |
| 20.0         | 358.300        | 2.4116       | .0015892         |
| 21.0         | 359.100        | 2.3895       | .0015746         |
| 22.0         | 359.900        | 2.3629       | .0015568         |
| 23.0         | 360.700        | 2.3320       | .0015356         |
| 24.0         | 361.500        | 2.2933       | .0015082         |
| 25.0         | 362.300        | 2.2348       | .0014649         |
| 26.0         | 363.100        | 2.1696       | .0014140         |
| 27.0         | 363.900        | 2.1044       | .0013599         |
| 28.0         | 364.700        | 2.0392       | .0013024         |
| 29.0         | 365.500        | 1.9740       | .0012410         |
| 30.0         | 366.300        | 1.9088       | .0011755         |
| 31.0         | 367.300        | 1.8436       | .0011053         |
| 32.0         | 368.300        | 1.7784       | .0010300         |
| 33.0         | 369.400        | 1.7132       | .0009490         |
| 34.0         | 370.500        | 1.6480       | .0008615         |
| 35.0         | 371.600        | 1.5828       | .0007669         |
| 36.0         | 372.700        | 1.5331       | .0006892         |
| 37.0         | 373.800        | 1.4944       | .0006253         |
| 38.0         | 374.900        | 1.4613       | .0005678         |
| 39.0         | 376.000        | 1.4325       | .0005158         |

Table XXV (continued)

|      |         |        |          |
|------|---------|--------|----------|
| 40.0 | 377.000 | 1.4060 | .0004660 |
| 41.0 | 378.000 | 1.3828 | .0004208 |
| 42.0 | 379.000 | 1.3629 | .0003808 |
| 43.0 | 380.000 | 1.3441 | .0003420 |
| 44.0 | 381.000 | 1.3265 | .0003044 |
| 45.0 | 382.000 | 1.3110 | .0002707 |
| 46.0 | 383.000 | 1.2966 | .0002387 |
| 47.0 | 384.000 | 1.2845 | .0002111 |
| 48.0 | 385.000 | 1.2734 | .0001855 |
| 49.0 | 386.000 | 1.2646 | .0001647 |
| 50.0 | 387.000 | 1.2569 | .0001463 |
| 51.0 | 388.000 | 1.2502 | .0001303 |
| 52.0 | 389.000 | 1.2447 | .0001169 |
| 53.0 | 390.000 | 1.2414 | .0001087 |
| 54.0 | 390.900 | 1.2370 | .0000978 |
| 55.0 | 391.800 | 1.2337 | .0000896 |
| 56.0 | 392.700 | 1.2303 | .0000813 |
| 57.0 | 393.600 | 1.2281 | .0000758 |
| 58.0 | 394.400 | 1.2259 | .0000702 |
| 59.0 | 395.200 | 1.2235 | .0000641 |
| 60.0 | 396.000 | 1.2213 | .0000585 |
| 61.0 | 396.800 | 1.2192 | .0000531 |
| 62.0 | 397.600 | 1.2172 | .0000481 |
| 63.0 | 398.400 | 1.2153 | .0000433 |
| 64.0 | 399.200 | 1.2135 | .0000387 |
| 65.0 | 400.000 | 1.2129 | .0000370 |

| TIME<br>MIN. | TEMP.<br>DEG. C | GRAMS<br>WDK |
|--------------|-----------------|--------------|
|--------------|-----------------|--------------|

|      |         |        |
|------|---------|--------|
| 66.0 | 400.800 | 1.2112 |
| 67.0 | 401.600 | 1.2096 |
| 68.0 | 402.400 | 1.2080 |
| 69.0 | 403.200 | 1.2065 |
| 70.0 | 404.000 | 1.2049 |
| 71.0 | 404.700 | 1.2035 |
| 72.0 | 405.400 | 1.2020 |
| 73.0 | 406.100 | 1.2006 |
| 74.0 | 406.800 | 1.1992 |
| 75.0 | 407.500 | 1.1979 |
| 76.0 | 408.200 | 1.1965 |
| 77.0 | 408.900 | 1.1952 |

Table XXV (continued)

|       |         |        |
|-------|---------|--------|
| 78.0  | 409.600 | 1.1939 |
| 79.0  | 410.300 | 1.1927 |
| 80.0  | 411.000 | 1.1914 |
| 81.0  | 411.700 | 1.1902 |
| 82.0  | 412.400 | 1.1891 |
| 83.0  | 413.100 | 1.1880 |
| 84.0  | 413.800 | 1.1869 |
| 85.0  | 414.500 | 1.1858 |
| 86.0  | 415.200 | 1.1847 |
| 87.0  | 415.900 | 1.1836 |
| 88.0  | 416.600 | 1.1825 |
| 89.0  | 417.300 | 1.1814 |
| 90.0  | 418.000 | 1.1803 |
| 91.0  | 418.700 | 1.1791 |
| 92.0  | 419.400 | 1.1780 |
| 93.0  | 420.100 | 1.1769 |
| 94.0  | 420.800 | 1.1758 |
| 95.0  | 421.500 | 1.1746 |
| 96.0  | 422.200 | 1.1734 |
| 97.0  | 422.900 | 1.1723 |
| 98.0  | 423.600 | 1.1712 |
| 99.0  | 424.300 | 1.1701 |
| 100.0 | 425.000 | 1.1690 |
| 101.0 | 425.700 | 1.1678 |
| 102.0 | 426.400 | 1.1667 |
| 103.0 | 427.100 | 1.1656 |
| 104.0 | 427.800 | 1.1645 |
| 105.0 | 428.500 | 1.1634 |
| 106.0 | 429.200 | 1.1622 |
| 107.0 | 429.900 | 1.1611 |
| 108.0 | 430.600 | 1.1600 |
| 109.0 | 431.300 | 1.1588 |
| 110.0 | 432.000 | 1.1577 |
| 111.0 | 432.500 | 1.1565 |
| 112.0 | 433.000 | 1.1554 |
| 113.0 | 433.500 | 1.1543 |
| 114.0 | 434.000 | 1.1532 |
| 115.0 | 434.500 | 1.1521 |
| 116.0 | 435.000 | 1.1509 |
| 117.0 | 435.500 | 1.1498 |
| 118.0 | 436.000 | 1.1487 |
| 119.0 | 436.500 | 1.1476 |
| 120.0 | 437.000 | 1.1469 |
| 121.0 | 437.500 | 1.1453 |

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Table XXV (continued)

|       |         |        |
|-------|---------|--------|
| 122.0 | 438.000 | 1.1441 |
| 123.0 | 438.500 | 1.1430 |
| 124.0 | 439.000 | 1.1419 |

| TIME<br>MIN. | TEMP<br>DEG. °C | GRAMS<br>WDK | CONC<br>MOLES/CC | RATE<br>METHANE |
|--------------|-----------------|--------------|------------------|-----------------|
| 125.0        | 440.300         | 1.1408       | .0033036         | .00000057       |
| 126.0        | 441.600         | 1.1397       | .0033052         | .00000060       |
| 127.0        | 442.900         | 1.1386       | .0033066         | .00000063       |
| 128.0        | 444.200         | 1.1375       | .0033080         | .00000067       |
| 129.0        | 445.500         | 1.1364       | .0033093         | .00000071       |
| 130.0        | 446.800         | 1.1353       | .0033105         | .00000075       |
| 131.0        | 448.100         | 1.1342       | .0033115         | .00000080       |
| 132.0        | 449.400         | 1.1331       | .0033124         | .00000085       |
| 133.0        | 450.800         | 1.1320       | .0033131         | .00000090       |
| 134.0        | 452.200         | 1.1309       | .0033138         | .00000095       |
| 135.0        | 453.600         | 1.1298       | .0033142         | .00000100       |
| 136.0        | 455.000         | 1.1287       | .0033146         | .00000106       |
| 137.0        | 456.400         | 1.1276       | .0033147         | .00000112       |
| 138.0        | 457.800         | 1.1265       | .0033147         | .00000118       |
| 139.0        | 459.200         | 1.1254       | .0033145         | .00000124       |
| 140.0        | 460.600         | 1.1243       | .0033141         | .00000131       |
| 141.0        | 461.900         | 1.1232       | .0033135         | .00000138       |
| 142.0        | 463.200         | 1.1220       | .0033128         | .00000146       |
| 143.0        | 464.600         | 1.1209       | .0033117         | .00000154       |
| 144.0        | 466.000         | 1.1198       | .0033105         | .00000163       |
| 145.0        | 467.400         | 1.1187       | .0033089         | .00000173       |
| 146.0        | 468.800         | 1.1176       | .0033071         | .00000183       |
| 147.0        | 470.200         | 1.1165       | .0033050         | .00000194       |
| 148.0        | 471.600         | 1.1154       | .0033025         | .00000205       |
| 149.0        | 473.000         | 1.1143       | .0032997         | .00000217       |
| 150.0        | 474.400         | 1.1132       | .0032966         | .00000230       |
| 151.0        | 475.900         | 1.1121       | .0032930         | .00000244       |
| 152.0        | 477.400         | 1.1110       | .0032890         | .00000260       |
| 153.0        | 478.900         | 1.1099       | .0032845         | .00000278       |
| 154.0        | 480.400         | 1.1088       | .0032795         | .00000298       |
| 155.0        | 481.900         | 1.1077       | .0032738         | .00000320       |
| 156.0        | 483.400         | 1.1066       | .0032675         | .00000345       |
| 157.0        | 484.900         | 1.1055       | .0032604         | .00000370       |
| 158.0        | 486.400         | 1.1044       | .0032525         | .00000400       |
| 159.0        | 487.900         | 1.1033       | .0032436         | .00000433       |

Table XXV (continued)

|       |         |        |          |           |
|-------|---------|--------|----------|-----------|
| 160.0 | 489.400 | 1.1022 | .0032338 | .00000468 |
| 161.0 | 490.900 | 1.1011 | .0032226 | .00000520 |
| 162.0 | 492.400 | 1.1000 | .0032099 | .00000579 |
| 163.0 | 493.900 | 1.0988 | .0031954 | .00000638 |
| 164.0 | 495.400 | 1.0977 | .0031791 | .00000697 |
| 165.0 | 496.900 | 1.0966 | .0031611 | .00000756 |
| 166.0 | 498.400 | 1.0955 | .0031413 | .00000815 |
| 167.0 | 499.900 | 1.0944 | .0031198 | .00000874 |
| 168.0 | 501.400 | 1.0933 | .0030964 | .00000933 |
| 169.0 | 502.900 | 1.0922 | .0030713 | .00000992 |
| 170.0 | 504.400 | 1.0911 | .0030445 | .00001050 |
| 171.0 | 505.800 | 1.0900 | .0030156 | .00001127 |
| 172.0 | 507.200 | 1.0889 | .0029844 | .00001200 |
| 173.0 | 508.600 | 1.0878 | .0029509 | .00001278 |
| 174.0 | 510.000 | 1.0867 | .0029152 | .00001353 |
| 175.0 | 511.400 | 1.0856 | .0028771 | .00001425 |
| 176.0 | 512.800 | 1.0845 | .0028365 | .00001523 |
| 177.0 | 514.200 | 1.0834 | .0027929 | .00001621 |
| 178.0 | 515.600 | 1.0823 | .0027463 | .00001719 |
| 179.0 | 517.000 | 1.0812 | .0026968 | .00001817 |
| 180.0 | 518.400 | 1.0801 | .0026442 | .00001915 |
| 181.0 | 519.800 | 1.0790 | .0025878 | .00002063 |
| 182.0 | 521.200 | 1.0779 | .0025268 | .00002220 |
| 183.0 | 522.600 | 1.0767 | .0024611 | .00002375 |
| 184.0 | 524.000 | 1.0756 | .0023906 | .00002525 |
| 185.0 | 525.400 | 1.0745 | .0023158 | .00002660 |
| 186.0 | 526.800 | 1.0734 | .0022369 | .00002790 |
| 187.0 | 528.200 | 1.0723 | .0021542 | .00002895 |
| 188.0 | 529.600 | 1.0712 | .0020684 | .00002992 |
| 189.0 | 531.000 | 1.0701 | .0019800 | .00003057 |
| 190.0 | 532.400 | 1.0690 | .0018894 | .00003128 |
| 191.0 | 533.800 | 1.0679 | .0017967 | .00003180 |
| 192.0 | 535.200 | 1.0668 | .0017024 | .00003228 |
| 193.0 | 536.600 | 1.0657 | .0016067 | .00003253 |
| 194.0 | 538.000 | 1.0646 | .0015104 | .00003258 |
| 195.0 | 539.400 | 1.0635 | .0014140 | .00003247 |
| 196.0 | 540.600 | 1.0624 | .0013195 | .00003120 |
| 197.0 | 541.800 | 1.0613 | .0012285 | .00003000 |
| 198.0 | 543.000 | 1.0602 | .0011409 | .00002885 |
| 199.0 | 544.200 | 1.0591 | .0010565 | .00002770 |
| 200.0 | 545.400 | 1.0580 | .0009755 | .00002655 |
| 201.0 | 546.600 | 1.0577 | .0008970 | .00002540 |
| 202.0 | 547.800 | 1.0575 | .0008220 | .00002425 |
| 203.0 | 549.000 | 1.0573 | .0007505 | .00002310 |

Table XXV (continued)

|       |         |        |          |           |
|-------|---------|--------|----------|-----------|
| 204.0 | 550.200 | 1.0571 | .0006823 | .00002195 |
| 205.0 | 551.400 | 1.0569 | .0006177 | .00002080 |
| 206.0 | 552.600 | 1.0566 | .0005565 | .00001965 |
| 207.0 | 553.800 | 1.0564 | .0004988 | .00001850 |
| 208.0 | 555.000 | 1.0562 | .0004445 | .00001735 |
| 209.0 | 556.200 | 1.0560 | .0003937 | .00001620 |
| 210.0 | 557.400 | 1.0558 | .0003464 | .00001505 |
| 211.0 | 558.800 | 1.0555 | .0003022 | .00001412 |
| 212.0 | 560.200 | 1.0553 | .0002606 | .00001332 |
| 213.0 | 561.600 | 1.0551 | .0002213 | .00001258 |
| 214.0 | 563.000 | 1.0549 | .0001842 | .00001188 |
| 215.0 | 564.300 | 1.0546 | .0001492 | .00001120 |
| 216.0 | 565.600 | 1.0544 | .0001161 | .00001060 |
| 217.0 | 566.900 | 1.0542 | .0000848 | .00001005 |
| 218.0 | 568.200 | 1.0540 | .0000551 | .00000953 |
| 219.0 | 569.500 | 1.0538 | .0000269 | .00000903 |

|      |        |       |
|------|--------|-------|
| TIME | TEMP   | GRAMS |
| MIN. | DEG. C | WDK   |

|       |         |        |
|-------|---------|--------|
| 221.0 | 572.200 | 1.0533 |
| 222.0 | 573.600 | 1.0531 |
| 223.0 | 575.000 | 1.0529 |
| 224.0 | 576.400 | 1.0527 |
| 225.0 | 577.800 | 1.0524 |
| 226.0 | 579.200 | 1.0522 |
| 227.0 | 580.600 | 1.0520 |
| 228.0 | 582.000 | 1.0518 |
| 229.0 | 583.400 | 1.0516 |
| 230.0 | 584.800 | 1.0513 |
| 231.0 | 586.300 | 1.0511 |
| 232.0 | 587.800 | 1.0509 |
| 233.0 | 589.300 | 1.0507 |
| 234.0 | 590.800 | 1.0504 |
| 235.0 | 592.300 | 1.0502 |
| 236.0 | 593.800 | 1.0500 |
| 237.0 | 595.300 | 1.0498 |
| 238.0 | 596.800 | 1.0496 |
| 239.0 | 598.300 | 1.0493 |
| 240.0 | 599.800 | 1.0491 |

Table XXVI: Converted Experimental Data for Analysis of Acenaphthylene  
Reactions Two and Three, Pyrolysis Run EX-A-15

| TIME<br>MIN. | TEMP.<br>DEG. C | GRAMS<br>WDK | CONC<br>MOLES/CC |
|--------------|-----------------|--------------|------------------|
| 5.0          | 335.000         | 2.4917       | .0016395         |
| 6.0          | 335.900         | 2.4913       | .0016393         |
| 7.0          | 336.800         | 2.4909       | .0016390         |
| 8.0          | 337.700         | 2.4903       | .0016386         |
| 9.0          | 338.600         | 2.4897       | .0016382         |
| 10.0         | 339.500         | 2.4889       | .0016377         |
| 11.0         | 340.200         | 2.4880       | .0016372         |
| 12.0         | 340.900         | 2.4871       | .0016366         |
| 13.0         | 341.600         | 2.4861       | .0016360         |
| 14.0         | 342.300         | 2.4851       | .0016354         |
| 15.0         | 343.000         | 2.4840       | .0016347         |
| 16.0         | 343.700         | 2.4828       | .0016339         |
| 17.0         | 344.400         | 2.4815       | .0016331         |
| 18.0         | 345.100         | 2.4801       | .0016321         |
| 19.0         | 345.800         | 2.4784       | .0016311         |
| 20.0         | 346.500         | 2.4765       | .0016299         |
| 21.0         | 347.500         | 2.4744       | .0016285         |
| 22.0         | 348.600         | 2.4720       | .0016270         |
| 23.0         | 349.700         | 2.4690       | .0016251         |
| 24.0         | 350.800         | 2.4657       | .0016230         |
| 25.0         | 351.800         | 2.4613       | .0016201         |
| 26.0         | 352.800         | 2.4546       | .0016158         |
| 27.0         | 353.800         | 2.4469       | .0016108         |
| 28.0         | 354.800         | 2.4375       | .0016046         |
| 29.0         | 355.300         | 2.4259       | .0015969         |
| 30.0         | 355.800         | 2.4116       | .0015873         |
| 31.0         | 356.300         | 2.3928       | .0015746         |
| 32.0         | 356.800         | 2.3696       | .0015586         |
| 33.0         | 357.300         | 2.3342       | .0015336         |
| 34.0         | 357.800         | 2.2790       | .0014930         |
| 35.0         | 358.300         | 2.2177       | .0014456         |
| 36.0         | 358.800         | 2.1565       | .0013956         |
| 37.0         | 359.400         | 2.0953       | .0013426         |
| 38.0         | 360.000         | 2.0341       | .0012864         |
| 39.0         | 360.600         | 1.9740       | .0012279         |
| 40.0         | 361.200         | 1.9128       | .0011644         |
| 41.0         | 361.800         | 1.8538       | .0010994         |
| 42.0         | 362.400         | 1.7972       | .0010330         |
| 43.0         | 363.000         | 1.7497       | .0009739         |
| 44.0         | 364.000         | 1.7033       | .0009130         |

Table XXVI (continued)

|      |         |        |          |
|------|---------|--------|----------|
| 45.0 | 365.000 | 1.6602 | .0008534 |
| 46.0 | 366.000 | 1.6193 | .0007939 |
| 47.0 | 367.000 | 1.5806 | .0007348 |
| 48.0 | 368.000 | 1.5441 | .0006764 |
| 49.0 | 369.000 | 1.5121 | .0006227 |
| 50.0 | 370.000 | 1.4834 | .0005726 |
| 51.0 | 371.000 | 1.4591 | .0005287 |
| 52.0 | 371.900 | 1.4381 | .0004895 |
| 53.0 | 372.800 | 1.4193 | .0004536 |
| 54.0 | 373.700 | 1.4016 | .0004188 |
| 55.0 | 374.600 | 1.3850 | .0003854 |
| 56.0 | 375.500 | 1.3707 | .0003558 |
| 57.0 | 376.400 | 1.3618 | .0003373 |
| 58.0 | 377.300 | 1.3497 | .0003114 |
| 59.0 | 378.200 | 1.3386 | .0002875 |
| 60.0 | 379.100 | 1.3287 | .0002656 |
| 61.0 | 380.000 | 1.3187 | .0002435 |
| 62.0 | 380.600 | 1.3099 | .0002234 |
| 63.0 | 381.200 | 1.3011 | .0002032 |
| 64.0 | 381.800 | 1.2933 | .0001852 |
| 65.0 | 382.400 | 1.2867 | .0001696 |
| 66.0 | 383.000 | 1.2801 | .0001539 |
| 67.0 | 383.500 | 1.2745 | .0001406 |
| 68.0 | 384.000 | 1.2690 | .0001273 |
| 69.0 | 384.600 | 1.2657 | .0001192 |
| 70.0 | 385.200 | 1.2624 | .0001111 |
| 71.0 | 385.800 | 1.2591 | .0001029 |
| 72.0 | 386.400 | 1.2558 | .0000947 |
| 73.0 | 387.000 | 1.2530 | .0000878 |
| 74.0 | 387.600 | 1.2502 | .0000809 |
| 75.0 | 388.200 | 1.2475 | .0000740 |
| 76.0 | 388.800 | 1.2447 | .0000671 |
| 77.0 | 389.400 | 1.2425 | .0000615 |
| 78.0 | 390.000 | 1.2403 | .0000559 |
| 79.0 | 390.400 | 1.2381 | .0000502 |
| 80.0 | 390.800 | 1.2359 | .0000446 |
| 81.0 | 391.200 | 1.2337 | .0000389 |
| 82.0 | 391.600 | 1.2320 | .0000347 |
| 83.0 | 392.000 | 1.2303 | .0000304 |
| 84.0 | 392.400 | 1.2287 | .0000261 |
| 85.0 | 392.900 | 1.2270 | .0000218 |

TIME

TEMP

GRAMS

Table XXVI (continued)

| MIN.  | DEG. C  | WDK    |
|-------|---------|--------|
| 86.0  | 393.400 | 1.2255 |
| 87.0  | 393.900 | 1.2239 |
| 88.0  | 394.400 | 1.2224 |
| 89.0  | 394.900 | 1.2208 |
| 90.0  | 395.400 | 1.2193 |
| 91.0  | 395.900 | 1.2177 |
| 92.0  | 396.400 | 1.2162 |
| 93.0  | 396.900 | 1.2146 |
| 94.0  | 397.500 | 1.2131 |
| 95.0  | 398.300 | 1.2116 |
| 96.0  | 399.100 | 1.2100 |
| 97.0  | 399.900 | 1.2085 |
| 98.0  | 400.700 | 1.2069 |
| 99.0  | 401.500 | 1.2054 |
| 100.0 | 402.300 | 1.2038 |
| 101.0 | 403.100 | 1.2023 |
| 102.0 | 403.900 | 1.2007 |
| 103.0 | 404.700 | 1.1992 |
| 104.0 | 405.600 | 1.1976 |
| 105.0 | 406.500 | 1.1961 |
| 106.0 | 407.400 | 1.1945 |
| 107.0 | 408.300 | 1.1930 |
| 108.0 | 409.200 | 1.1914 |
| 109.0 | 410.100 | 1.1899 |
| 110.0 | 411.000 | 1.1883 |
| 111.0 | 411.900 | 1.1868 |
| 112.0 | 412.800 | 1.1853 |
| 113.0 | 413.700 | 1.1837 |
| 114.0 | 414.600 | 1.1822 |
| 115.0 | 415.500 | 1.1806 |
| 116.0 | 416.400 | 1.1791 |
| 117.0 | 417.300 | 1.1775 |
| 118.0 | 418.600 | 1.1760 |
| 119.0 | 420.000 | 1.1744 |
| 120.0 | 421.300 | 1.1729 |
| 121.0 | 422.700 | 1.1713 |
| 122.0 | 424.000 | 1.1698 |
| 123.0 | 425.400 | 1.1682 |
| 124.0 | 426.700 | 1.1667 |
| 125.0 | 428.100 | 1.1651 |
| 126.0 | 429.400 | 1.1636 |

Table XXVI (continued)

|       |         |        |
|-------|---------|--------|
| 127.0 | 430.800 | 1.1620 |
| 128.0 | 432.100 | 1.1605 |
| 129.0 | 433.500 | 1.1590 |
| 130.0 | 434.800 | 1.1574 |
| 131.0 | 436.200 | 1.1558 |
| 132.0 | 437.500 | 1.1541 |
| 133.0 | 438.900 | 1.1524 |
| 134.0 | 440.200 | 1.1508 |

| TIME<br>MIN. | TEMP<br>DEG. C | GRAMS<br>WDK | CONC<br>MOLES/CC | RATE<br>METHANE |
|--------------|----------------|--------------|------------------|-----------------|
| 135.0        | 441.600        | 1.1491       | .0033059         | .00000060       |
| 136.0        | 442.900        | 1.1475       | .0033091         | .00000064       |
| 137.0        | 444.300        | 1.1458       | .0033122         | .00000068       |
| 138.0        | 445.600        | 1.1441       | .0033152         | .00000073       |
| 139.0        | 447.000        | 1.1425       | .0033180         | .00000079       |
| 140.0        | 448.300        | 1.1408       | .0033207         | .00000086       |
| 141.0        | 449.600        | 1.1392       | .0033232         | .00000094       |
| 142.0        | 450.900        | 1.1375       | .0033255         | .00000103       |
| 143.0        | 452.200        | 1.1359       | .0033275         | .00000112       |
| 144.0        | 453.500        | 1.1342       | .0033293         | .00000121       |
| 145.0        | 454.800        | 1.1325       | .0033309         | .00000130       |
| 146.0        | 456.100        | 1.1309       | .0033323         | .00000139       |
| 147.0        | 457.400        | 1.1292       | .0033334         | .00000148       |
| 148.0        | 458.700        | 1.1276       | .0033343         | .00000158       |
| 149.0        | 460.000        | 1.1259       | .0033350         | .00000168       |
| 150.0        | 461.300        | 1.1243       | .0033353         | .00000179       |
| 151.0        | 462.600        | 1.1228       | .0033347         | .00000191       |
| 152.0        | 463.900        | 1.1214       | .0033338         | .00000204       |
| 153.0        | 465.200        | 1.1200       | .0033325         | .00000219       |
| 154.0        | 466.500        | 1.1185       | .0033308         | .00000235       |
| 155.0        | 467.800        | 1.1171       | .0033286         | .00000252       |
| 156.0        | 469.400        | 1.1156       | .0033260         | .00000269       |
| 157.0        | 471.000        | 1.1142       | .0033229         | .00000290       |
| 158.0        | 472.600        | 1.1128       | .0033192         | .00000310       |
| 159.0        | 474.200        | 1.1113       | .0033150         | .00000331       |
| 160.0        | 475.800        | 1.1099       | .0033101         | .00000356       |
| 161.0        | 477.400        | 1.1086       | .0033042         | .00000388       |
| 162.0        | 479.000        | 1.1072       | .0032973         | .00000422       |
| 163.0        | 480.600        | 1.1059       | .0032895         | .00000459       |
| 164.0        | 482.200        | 1.1046       | .0032806         | .00000500       |

Table XXVI (continued)

|       |         |        |          |           |
|-------|---------|--------|----------|-----------|
| 165.0 | 483.800 | 1.1033 | .0032706 | .00000547 |
| 166.0 | 485.400 | 1.1019 | .0032592 | .00000594 |
| 167.0 | 487.000 | 1.1006 | .0032465 | .00000643 |
| 168.0 | 488.600 | 1.0993 | .0032325 | .00000694 |
| 169.0 | 490.200 | 1.0980 | .0032169 | .00000753 |
| 170.0 | 491.800 | 1.0966 | .0031997 | .00000813 |
| 171.0 | 493.400 | 1.0955 | .0031800 | .00000890 |
| 172.0 | 495.000 | 1.0944 | .0031581 | .00000970 |
| 173.0 | 496.600 | 1.0933 | .0031340 | .00001050 |
| 174.0 | 498.200 | 1.0922 | .0031077 | .00001128 |
| 175.0 | 499.800 | 1.0911 | .0030792 | .00001206 |
| 176.0 | 501.400 | 1.1232 | .0029584 | .00001300 |
| 177.0 | 503.000 | 1.0889 | .0030149 | .00001400 |
| 178.0 | 504.600 | 1.0878 | .0029786 | .00001500 |
| 179.0 | 506.200 | 1.0867 | .0029394 | .00001600 |
| 180.0 | 507.800 | 1.0856 | .0028975 | .00001700 |
| 181.0 | 509.100 | 1.0845 | .0028528 | .00001800 |
| 182.0 | 510.400 | 1.0834 | .0028053 | .00001900 |
| 183.0 | 511.700 | 1.0823 | .0027549 | .00002000 |
| 184.0 | 513.000 | 1.0812 | .0027017 | .00002100 |
| 185.0 | 514.300 | 1.0801 | .0026455 | .00002210 |
| 186.0 | 515.600 | 1.0790 | .0025861 | .00002330 |
| 187.0 | 516.900 | 1.0779 | .0025234 | .00002440 |
| 188.0 | 518.200 | 1.0767 | .0024576 | .00002545 |
| 189.0 | 519.500 | 1.0756 | .0023887 | .00002650 |
| 190.0 | 520.800 | 1.0745 | .0023169 | .00002758 |
| 191.0 | 522.100 | 1.0734 | .0022419 | .00002863 |
| 192.0 | 523.400 | 1.0723 | .0021640 | .00002960 |
| 193.0 | 524.700 | 1.0712 | .0020832 | .00003060 |
| 194.0 | 526.000 | 1.0701 | .0019995 | .00003160 |
| 195.0 | 527.300 | 1.0690 | .0019129 | .00003260 |
| 196.0 | 528.600 | 1.0679 | .0018238 | .00003323 |
| 197.0 | 529.900 | 1.0668 | .0017333 | .00003350 |
| 198.0 | 531.200 | 1.0657 | .0016419 | .00003370 |
| 199.0 | 532.500 | 1.0646 | .0015499 | .00003384 |
| 200.0 | 533.800 | 1.0635 | .0014574 | .00003390 |
| 201.0 | 535.100 | 1.0628 | .0013646 | .00003355 |
| 202.0 | 536.400 | 1.0622 | .0012740 | .00003225 |
| 203.0 | 537.700 | 1.0615 | .0011874 | .00003050 |
| 204.0 | 539.000 | 1.0608 | .0011056 | .00002880 |
| 205.0 | 540.300 | 1.0602 | .0010283 | .00002720 |
| 206.0 | 541.600 | 1.0595 | .0009544 | .00002623 |
| 207.0 | 543.000 | 1.0588 | .0008829 | .00002548 |
| 208.0 | 544.300 | 1.0582 | .0008130 | .00002500 |

Table XXVI(continued)

|       |         |        |          |           |
|-------|---------|--------|----------|-----------|
| 209.0 | 545.700 | 1.0575 | .0007441 | .00002464 |
| 210.0 | 547.000 | 1.0569 | .0006763 | .00002427 |
| 211.0 | 548.400 | 1.0563 | .0006095 | .00002373 |
| 212.0 | 549.700 | 1.0558 | .0005444 | .00002300 |
| 213.0 | 551.100 | 1.0552 | .0004817 | .00002200 |
| 214.0 | 552.400 | 1.0546 | .0004225 | .00002045 |
| 215.0 | 553.800 | 1.0541 | .0003690 | .00001790 |
| 216.0 | 555.100 | 1.0535 | .0003213 | .00001623 |
| 217.0 | 556.500 | 1.0530 | .0002774 | .00001520 |
| 218.0 | 557.800 | 1.0524 | .0002359 | .00001445 |
| 219.0 | 559.200 | 1.0519 | .0001965 | .00001375 |
| 220.0 | 560.500 | 1.0513 | .0001588 | .00001310 |
| 221.0 | 561.900 | 1.0508 | .0001231 | .00001237 |
| 222.0 | 563.200 | 1.0502 | .0000894 | .00001165 |
| 223.0 | 564.600 | 1.0497 | .0000576 | .00001097 |
| 224.0 | 565.900 | 1.0486 | .0000278 | .00001023 |

| TIME<br>MIN. | TEMP<br>DEG. C | GRAMS<br>WDK |
|--------------|----------------|--------------|
| 226.0        | 568.600        | 1.0475       |
| 227.0        | 570.000        | 1.0469       |
| 228.0        | 571.300        | 1.0464       |
| 229.0        | 572.700        | 1.0458       |
| 230.0        | 574.100        | 1.0453       |
| 231.0        | 575.400        | 1.0447       |
| 232.0        | 576.800        | 1.0441       |
| 233.0        | 578.100        | 1.0436       |
| 234.0        | 579.500        | 1.0430       |
| 235.0        | 580.800        | 1.0425       |
| 236.0        | 582.200        | 1.0419       |
| 237.0        | 583.500        | 1.0414       |
| 238.0        | 584.900        | 1.0408       |
| 239.0        | 586.200        | 1.0403       |
| 240.0        | 587.600        | 1.0397       |
| 241.0        | 588.900        | 1.0392       |
| 242.0        | 590.300        | 1.0386       |
| 243.0        | 591.600        | 1.0381       |
| 244.0        | 593.000        | 1.0375       |
| 245.0        | 594.300        | 1.0370       |
| 246.0        | 595.700        | 1.0364       |
| 247.0        | 597.000        | 1.0359       |

Table XXVI (continued)

|       |         |        |
|-------|---------|--------|
| 248.0 | 598.400 | 1.0353 |
| 249.0 | 599.700 | 1.0348 |
| 250.0 | 601.100 | 1.0342 |
| 251.0 | 602.400 | 1.0337 |

Table XXVII: Converted Experimental Data for Analysis of Acenaphthylene  
Reactions Two and Three, Pyrolysis Run EX-A-16

| TIME<br>MIN. | TEMP<br>DEG. C | GRAMS<br>WDK | CONC<br>MOLES/CC |
|--------------|----------------|--------------|------------------|
| .0           | 340.000        | 1.9889       | .0016361         |
| 1.0          | 341.000        | 1.9883       | .0016357         |
| 2.0          | 342.000        | 1.9877       | .0016352         |
| 3.0          | 343.000        | 1.9869       | .0016346         |
| 4.0          | 344.000        | 1.9859       | .0016338         |
| 5.0          | 345.000        | 1.9847       | .0016328         |
| 6.0          | 346.000        | 1.9832       | .0016316         |
| 7.0          | 346.400        | 1.9814       | .0016302         |
| 8.0          | 346.800        | 1.9794       | .0016287         |
| 9.0          | 347.200        | 1.9772       | .0016269         |
| 10.0         | 347.600        | 1.9746       | .0016249         |
| 11.0         | 348.000        | 1.9718       | .0016226         |
| 12.0         | 348.400        | 1.9682       | .0016198         |
| 13.0         | 348.800        | 1.9636       | .0016161         |
| 14.0         | 349.100        | 1.9569       | .0016107         |
| 15.0         | 349.400        | 1.9497       | .0016049         |
| 16.0         | 349.700        | 1.9403       | .0015972         |
| 17.0         | 350.000        | 1.9303       | .0015890         |
| 18.0         | 350.300        | 1.9187       | .0015794         |
| 19.0         | 350.600        | 1.9044       | .0015672         |
| 20.0         | 350.900        | 1.8895       | .0015544         |
| 21.0         | 351.200        | 1.8723       | .0015395         |
| 22.0         | 351.500        | 1.8530       | .0015223         |
| 23.0         | 351.800        | 1.8265       | .0014981         |
| 24.0         | 352.700        | 1.8000       | .0014732         |
| 25.0         | 353.600        | 1.7690       | .0014432         |
| 26.0         | 354.500        | 1.7348       | .0014088         |
| 27.0         | 355.400        | 1.6972       | .0013694         |
| 28.0         | 356.300        | 1.6596       | .0013282         |
| 29.0         | 357.200        | 1.6220       | .0012851         |
| 30.0         | 358.100        | 1.5845       | .0012400         |
| 31.0         | 359.000        | 1.5469       | .0011927         |
| 32.0         | 359.900        | 1.5093       | .0011430         |
| 33.0         | 360.800        | 1.4718       | .0010908         |
| 34.0         | 361.700        | 1.4342       | .0010359         |
| 35.0         | 362.600        | 1.3966       | .0009780         |
| 36.0         | 363.400        | 1.3591       | .0009169         |
| 37.0         | 364.200        | 1.3215       | .0008524         |
| 38.0         | 365.000        | 1.2872       | .0007902         |
| 39.0         | 365.800        | 1.2585       | .0007355         |

Table XXVII (continued)

|      |         |        |          |
|------|---------|--------|----------|
| 40.0 | 366.600 | 1.2309 | .0006804 |
| 41.0 | 367.400 | 1.2044 | .0006252 |
| 42.0 | 368.200 | 1.1801 | .0005724 |
| 43.0 | 368.600 | 1.1591 | .0005251 |
| 44.0 | 369.000 | 1.1403 | .0004812 |
| 45.0 | 369.400 | 1.1232 | .0004399 |
| 46.0 | 369.800 | 1.1077 | .0004015 |
| 47.0 | 370.200 | 1.0939 | .0003664 |
| 48.0 | 370.600 | 1.0817 | .0003346 |
| 49.0 | 371.000 | 1.0712 | .0003067 |
| 50.0 | 371.400 | 1.0574 | .0002691 |
| 51.0 | 371.800 | 1.0530 | .0002568 |
| 52.0 | 372.200 | 1.0458 | .0002367 |
| 53.0 | 372.600 | 1.0397 | .0002194 |
| 54.0 | 373.100 | 1.0348 | .0002052 |
| 55.0 | 373.600 | 1.0300 | .0001914 |
| 56.0 | 374.100 | 1.0259 | .0001795 |
| 57.0 | 374.600 | 1.0220 | .0001681 |
| 58.0 | 375.100 | 1.0184 | .0001573 |
| 59.0 | 375.600 | 1.0149 | .0001467 |
| 60.0 | 376.000 | 1.0116 | .0001367 |
| 61.0 | 376.400 | 1.0085 | .0001274 |
| 62.0 | 376.800 | 1.0056 | .0001186 |
| 63.0 | 377.200 | 1.0029 | .0001105 |
| 64.0 | 377.600 | 1.0005 | .0001030 |
| 65.0 | 378.000 | .9983  | .0000962 |
| 66.0 | 378.400 | .9963  | .0000900 |
| 67.0 | 378.800 | .9944  | .0000842 |
| 68.0 | 379.200 | .9927  | .0000787 |
| 69.0 | 379.600 | .9910  | .0000735 |
| 70.0 | 380.000 | .9895  | .0000686 |
| 71.0 | 380.400 | .9880  | .0000641 |
| 72.0 | 380.800 | .9867  | .0000599 |
| 73.0 | 381.200 | .9855  | .0000560 |
| 74.0 | 381.600 | .9844  | .0000525 |
| 75.0 | 382.000 | .9834  | .0000493 |
| 76.0 | 382.400 | .9825  | .0000465 |
| 77.0 | 382.800 | .9817  | .0000440 |
| 78.0 | 383.200 | .9809  | .0000415 |
| 79.0 | 383.600 | .9803  | .0000394 |
| 80.0 | 384.000 | .9796  | .0000373 |

TIME

TEMP

GRAMS

Table XXVII (continued)

| MIN.  | DEG. C  | WDK   |
|-------|---------|-------|
| 81.0  | 384.400 | .9785 |
| 82.0  | 384.800 | .9774 |
| 83.0  | 385.200 | .9763 |
| 84.0  | 385.600 | .9752 |
| 85.0  | 386.000 | .9741 |
| 86.0  | 386.400 | .9730 |
| 87.0  | 386.800 | .9719 |
| 88.0  | 387.200 | .9708 |
| 89.0  | 387.600 | .9697 |
| 90.0  | 388.400 | .9686 |
| 91.0  | 389.200 | .9675 |
| 92.0  | 390.000 | .9664 |
| 93.0  | 390.800 | .9653 |
| 94.0  | 391.600 | .9641 |
| 95.0  | 392.400 | .9630 |
| 96.0  | 393.200 | .9620 |
| 97.0  | 394.000 | .9611 |
| 98.0  | 394.800 | .9601 |
| 99.0  | 395.600 | .9591 |
| 100.0 | 396.400 | .9581 |
| 101.0 | 397.200 | .9571 |
| 102.0 | 398.000 | .9561 |
| 103.0 | 398.800 | .9551 |
| 104.0 | 399.600 | .9541 |
| 105.0 | 400.400 | .9531 |
| 106.0 | 401.200 | .9521 |
| 107.0 | 402.000 | .9511 |
| 108.0 | 402.800 | .9501 |
| 109.0 | 403.200 | .9491 |
| 110.0 | 403.600 | .9481 |
| 111.0 | 404.000 | .9475 |
| 112.0 | 404.900 | .9468 |
| 113.0 | 405.800 | .9461 |
| 114.0 | 406.700 | .9455 |
| 115.0 | 407.600 | .9448 |
| 116.0 | 408.500 | .9441 |
| 117.0 | 409.400 | .9435 |
| 118.0 | 410.300 | .9428 |
| 119.0 | 411.200 | .9422 |
| 120.0 | 412.100 | .9415 |
| 121.0 | 413.000 | .9408 |

Table XXVII (continued)

|       |         |       |
|-------|---------|-------|
| 122.0 | 413.900 | .9402 |
| 123.0 | 414.800 | .9395 |
| 124.0 | 415.700 | .9388 |
| 125.0 | 416.500 | .9382 |
| 126.0 | 417.500 | .9375 |
| 127.0 | 418.400 | .9369 |
| 128.0 | 419.300 | .9362 |
| 129.0 | 420.200 | .9355 |
| 130.0 | 420.600 | .9349 |
| 131.0 | 421.000 | .9342 |
| 132.0 | 421.400 | .9335 |
| 133.0 | 422.300 | .9328 |
| 134.0 | 423.200 | .9320 |
| 135.0 | 424.100 | .9312 |
| 136.0 | 425.000 | .9304 |
| 137.0 | 426.000 | .9297 |
| 138.0 | 426.900 | .9289 |
| 139.0 | 427.800 | .9281 |
| 140.0 | 428.700 | .9274 |
| 141.0 | 429.600 | .9266 |
| 142.0 | 430.500 | .9258 |
| 143.0 | 431.500 | .9250 |
| 144.0 | 432.400 | .9243 |
| 145.0 | 433.300 | .9235 |
| 146.0 | 434.200 | .9227 |
| 147.0 | 435.100 | .9219 |
| 148.0 | 436.000 | .9212 |
| 149.0 | 437.000 | .9204 |
| 150.0 | 437.900 | .9196 |
| 151.0 | 438.800 | .9188 |
| 152.0 | 439.700 | .9181 |
| 153.0 | 440.600 | .9173 |
| 154.0 | 441.500 | .9165 |
| 155.0 | 442.500 | .9158 |
| 156.0 | 443.400 | .9150 |
| 157.0 | 444.300 | .9142 |
| 158.0 | 445.200 | .9134 |
| 159.0 | 446.100 | .9127 |

TIME  
MIN.TEMP  
DEG. CGRAMS  
WDKCONC  
MOLES/CCRATE  
METHANE

Table XXVII (continued)

|       |         |       |          |           |
|-------|---------|-------|----------|-----------|
| 160.0 | 447.000 | .9119 | .0033100 | .00000075 |
| 161.0 | 448.000 | .9111 | .0033094 | .00000077 |
| 162.0 | 448.900 | .9103 | .0033088 | .00000080 |
| 163.0 | 449.800 | .9096 | .0033080 | .00000084 |
| 164.0 | 450.700 | .9088 | .0033070 | .00000089 |
| 165.0 | 451.600 | .9080 | .0033058 | .00000094 |
| 166.0 | 452.500 | .9071 | .0033048 | .00000099 |
| 167.0 | 453.500 | .9064 | .0033031 | .00000104 |
| 168.0 | 454.400 | .9055 | .0033017 | .00000109 |
| 169.0 | 455.300 | .9046 | .0032999 | .00000115 |
| 170.0 | 456.200 | .9038 | .0032975 | .00000121 |
| 171.0 | 457.100 | .9029 | .0032953 | .00000127 |
| 172.0 | 458.000 | .9022 | .0032924 | .00000133 |
| 173.0 | 459.000 | .9013 | .0032895 | .00000140 |
| 174.0 | 459.900 | .9005 | .0032860 | .00000147 |
| 175.0 | 460.800 | .8996 | .0032825 | .00000154 |
| 176.0 | 461.700 | .8988 | .0032784 | .00000161 |
| 177.0 | 462.600 | .8980 | .0032742 | .00000169 |
| 178.0 | 463.500 | .8972 | .0032693 | .00000178 |
| 179.0 | 464.500 | .8963 | .0032644 | .00000187 |
| 180.0 | 465.400 | .8955 | .0032587 | .00000196 |
| 181.0 | 466.300 | .8946 | .0032530 | .00000205 |
| 182.0 | 467.200 | .8939 | .0032464 | .00000214 |
| 183.0 | 468.100 | .8930 | .0032399 | .00000223 |
| 184.0 | 469.000 | .8922 | .0032325 | .00000232 |
| 185.0 | 470.000 | .8913 | .0032251 | .00000241 |
| 186.0 | 471.600 | .8906 | .0032169 | .00000250 |
| 187.0 | 473.200 | .8897 | .0032086 | .00000259 |
| 188.0 | 474.800 | .8889 | .0031996 | .00000268 |
| 189.0 | 476.400 | .8880 | .0031905 | .00000277 |
| 190.0 | 478.000 | .8872 | .0031806 | .00000286 |
| 191.0 | 479.600 | .8864 | .0031707 | .00000297 |
| 192.0 | 481.200 | .8856 | .0031596 | .00000314 |
| 193.0 | 482.800 | .8847 | .0031482 | .00000333 |
| 194.0 | 484.400 | .8839 | .0031355 | .00000352 |
| 195.0 | 486.000 | .8830 | .0031221 | .00000378 |
| 196.0 | 487.600 | .8823 | .0031071 | .00000405 |
| 197.0 | 488.900 | .8814 | .0030911 | .00000440 |
| 198.0 | 490.200 | .8806 | .0030729 | .00000482 |
| 199.0 | 491.500 | .8797 | .0030527 | .00000540 |
| 200.0 | 492.800 | .8790 | .0030291 | .00000618 |
| 201.0 | 494.100 | .8781 | .0030031 | .00000660 |
| 202.0 | 495.400 | .8773 | .0029750 | .00000688 |
| 203.0 | 496.700 | .8764 | .0029462 | .00000710 |

Table XXVII (continued)

|       |         |       |          |           |
|-------|---------|-------|----------|-----------|
| 204.0 | 498.000 | .8756 | .0029159 | .00000732 |
| 205.0 | 499.300 | .8748 | .0028848 | .00000758 |
| 206.0 | 500.600 | .8740 | .0028520 | .00000790 |
| 207.0 | 501.800 | .8734 | .0028167 | .00000830 |
| 208.0 | 503.000 | .8729 | .0027792 | .00000890 |
| 209.0 | 504.200 | .8723 | .0027379 | .00000990 |
| 210.0 | 505.400 | .8718 | .0026894 | .00001200 |
| 211.0 | 506.600 | .8712 | .0026340 | .00001290 |
| 212.0 | 507.800 | .8707 | .0025754 | .00001337 |
| 213.0 | 509.000 | .8701 | .0025148 | .00001374 |
| 214.0 | 510.200 | .8696 | .0024525 | .00001410 |
| 215.0 | 511.400 | .8690 | .0023882 | .00001455 |
| 216.0 | 512.600 | .8685 | .0023217 | .00001503 |
| 217.0 | 513.800 | .8679 | .0022525 | .00001567 |
| 218.0 | 515.000 | .8674 | .0021800 | .00001642 |
| 219.0 | 516.200 | .8668 | .0021038 | .00001727 |
| 220.0 | 517.400 | .8662 | .0020233 | .00001820 |
| 221.0 | 518.300 | .8657 | .0019383 | .00001920 |
| 222.0 | 519.200 | .8651 | .0018497 | .00001973 |
| 223.0 | 520.100 | .8646 | .0017589 | .00002005 |
| 224.0 | 521.000 | .8640 | .0016669 | .00002023 |
| 225.0 | 521.900 | .8635 | .0015743 | .00002026 |
| 226.0 | 522.800 | .8629 | .0014817 | .00002018 |
| 227.0 | 523.700 | .8624 | .0013897 | .00001995 |
| 228.0 | 524.600 | .8618 | .0012988 | .00001965 |
| 229.0 | 525.400 | .8613 | .0012093 | .00001930 |
| 230.0 | 526.200 | .8607 | .0011212 | .00001900 |
| 231.0 | 527.000 | .8602 | .0010344 | .00001870 |
| 232.0 | 527.800 | .8596 | .0009488 | .00001842 |
| 233.0 | 528.600 | .8591 | .0008645 | .00001810 |
| 234.0 | 529.400 | .8585 | .0007816 | .00001777 |
| 235.0 | 530.200 | .8580 | .0007002 | .00001740 |
| 236.0 | 531.000 | .8577 | .0006204 | .00001695 |
| 237.0 | 531.800 | .8575 | .0005426 | .00001650 |
| 238.0 | 532.600 | .8573 | .0004670 | .00001600 |
| 239.0 | 533.400 | .8571 | .0003937 | .00001553 |
| 240.0 | 534.200 | .8569 | .0003225 | .00001505 |
| 241.0 | 535.000 | .8566 | .0002535 | .00001457 |
| 242.0 | 535.800 | .8564 | .0001867 | .00001408 |
| 243.0 | 536.600 | .8562 | .0001222 | .00001360 |
| 244.0 | 537.400 | .8560 | .0000599 | .00001310 |

TIME

TEMP

GRAMS

Table XXVII (continued)

| MIN.  | DEG. C  | WDK   |
|-------|---------|-------|
| 246.0 | 539.000 | .8555 |
| 247.0 | 539.800 | .8553 |
| 248.0 | 540.600 | .8551 |
| 249.0 | 541.400 | .8549 |
| 250.0 | 542.200 | .8546 |
| 251.0 | 543.000 | .8544 |
| 252.0 | 543.800 | .8542 |
| 253.0 | 544.600 | .8540 |
| 254.0 | 545.400 | .8538 |
| 255.0 | 546.200 | .8535 |
| 256.0 | 547.000 | .8533 |
| 257.0 | 547.800 | .8531 |
| 258.0 | 548.600 | .8529 |
| 259.0 | 549.400 | .8527 |
| 260.0 | 550.200 | .8524 |
| 261.0 | 552.000 | .8522 |
| 262.0 | 554.000 | .8520 |
| 263.0 | 556.000 | .8518 |
| 264.0 | 558.000 | .8516 |
| 265.0 | 560.000 | .8513 |
| 266.0 | 561.300 | .8511 |
| 267.0 | 562.600 | .8509 |
| 268.0 | 563.900 | .8507 |
| 269.0 | 565.200 | .8504 |
| 270.0 | 566.500 | .8502 |
| 271.0 | 567.800 | .8500 |
| 272.0 | 569.100 | .8498 |
| 273.0 | 570.400 | .8496 |
| 274.0 | 571.700 | .8493 |
| 275.0 | 573.000 | .8491 |
| 276.0 | 574.100 | .8489 |
| 277.0 | 575.200 | .8487 |
| 278.0 | 576.300 | .8485 |
| 279.0 | 577.400 | .8482 |
| 280.0 | 578.500 | .8480 |
| 281.0 | 579.600 | .8478 |
| 282.0 | 580.700 | .8476 |
| 283.0 | 581.800 | .8474 |
| 284.0 | 582.900 | .8471 |
| 285.0 | 584.000 | .8469 |
| 286.0 | 585.100 | .8467 |

Table XXVII (continued)

|       |         |       |
|-------|---------|-------|
| 287.0 | 586.200 | .8465 |
| 288.0 | 587.300 | .8462 |
| 289.0 | 588.400 | .8460 |
| 290.0 | 589.500 | .8458 |
| 291.0 | 590.600 | .8456 |
| 292.0 | 591.700 | .8454 |
| 293.0 | 592.800 | .8451 |
| 294.0 | 593.900 | .8449 |
| 295.0 | 595.000 | .8447 |
| 296.0 | 596.100 | .8445 |
| 297.0 | 597.200 | .8443 |
| 298.0 | 598.300 | .8440 |
| 299.0 | 599.400 | .8438 |
| 300.0 | 600.500 | .8436 |
| 301.0 | 601.600 | .8434 |
| 302.0 | 602.700 | .8432 |
| 303.0 | 603.800 | .8429 |
| 304.0 | 604.900 | .8427 |

Table XXVIII: Converted Experimental Data for Analysis of Acenaphthylene Reactions Two and Three, Pyrolysis Run EX-A-17

| TIME<br>MIN. | TEMP<br>DEG. C | GRAMS<br>WDK | CONC<br>MOLES/CC |
|--------------|----------------|--------------|------------------|
| 0.0          | 340.800        | 1.9889       | .0016362         |
| 1.0          | 341.600        | 1.9883       | .0016358         |
| 2.0          | 342.400        | 1.9876       | .0016352         |
| 3.0          | 343.200        | 1.9866       | .0016344         |
| 4.0          | 344.000        | 1.9853       | .0016334         |
| 5.0          | 344.800        | 1.9838       | .0016323         |
| 6.0          | 345.500        | 1.9823       | .0016311         |
| 7.0          | 346.200        | 1.9806       | .0016298         |
| 8.0          | 346.900        | 1.9787       | .0016283         |
| 9.0          | 347.600        | 1.9878       | .0016354         |
| 10.0         | 348.300        | 1.9745       | .0016251         |
| 11.0         | 349.000        | 1.9718       | .0016229         |
| 12.0         | 349.700        | 1.9685       | .0016203         |
| 13.0         | 350.400        | 1.9646       | .0016173         |
| 14.0         | 351.200        | 1.9602       | .0016138         |
| 15.0         | 352.000        | 1.9546       | .0016094         |
| 16.0         | 352.800        | 1.9464       | .0016027         |
| 17.0         | 353.600        | 1.9348       | .0015933         |
| 18.0         | 354.400        | 1.9160       | .0015779         |
| 19.0         | 355.200        | 1.8939       | .0015593         |
| 20.0         | 356.000        | 1.8696       | .0015384         |
| 21.0         | 356.800        | 1.8397       | .0015119         |
| 22.0         | 357.600        | 1.8055       | .0014805         |
| 23.0         | 358.400        | 1.7635       | .0014403         |
| 24.0         | 359.100        | 1.7171       | .0013936         |
| 25.0         | 359.800        | 1.6685       | .0013418         |
| 26.0         | 360.500        | 1.6198       | .0012870         |
| 27.0         | 361.200        | 1.5712       | .0012287         |
| 28.0         | 361.900        | 1.5226       | .0011668         |
| 29.0         | 362.600        | 1.4740       | .0011007         |
| 30.0         | 363.300        | 1.4276       | .0010335         |
| 31.0         | 364.200        | 1.3845       | .0009670         |
| 32.0         | 365.100        | 1.3447       | .0009019         |
| 33.0         | 366.000        | 1.3071       | .0008367         |
| 34.0         | 366.900        | 1.2718       | .0007719         |
| 35.0         | 367.800        | 1.2397       | .0007099         |
| 36.0         | 368.700        | 1.2099       | .0006493         |
| 37.0         | 369.600        | 1.1856       | .0005976         |
| 38.0         | 370.500        | 1.1646       | .0005513         |
| 39.0         | 371.400        | 1.1447       | .0005058         |

Table XXVIII (continued)

|      |         |        |          |
|------|---------|--------|----------|
| 40.0 | 372.300 | 1.1270 | .0004640 |
| 41.0 | 373.200 | 1.1082 | .0004181 |
| 42.0 | 374.100 | 1.0939 | .0003820 |
| 43.0 | 375.000 | 1.0795 | .0003449 |
| 44.0 | 375.800 | 1.0674 | .0003128 |
| 45.0 | 376.700 | 1.0574 | .0002859 |
| 46.0 | 377.500 | 1.0480 | .0002601 |
| 47.0 | 378.400 | 1.0397 | .0002369 |
| 48.0 | 379.200 | 1.0331 | .0002181 |
| 49.0 | 380.000 | 1.0270 | .0002006 |
| 50.0 | 380.800 | 1.0215 | .0001846 |
| 51.0 | 381.300 | 1.0165 | .0001700 |
| 52.0 | 381.800 | 1.0121 | .0001569 |
| 53.0 | 382.300 | 1.0088 | .0001470 |
| 54.0 | 382.800 | 1.0060 | .0001387 |
| 55.0 | 383.300 | 1.0038 | .0001320 |
| 56.0 | 383.800 | 1.0016 | .0001253 |
| 57.0 | 384.300 | .9995  | .0001189 |
| 58.0 | 384.800 | .9975  | .0001128 |
| 59.0 | 385.200 | .9956  | .0001071 |
| 60.0 | 385.600 | .9939  | .0001016 |
| 61.0 | 386.000 | .9921  | .0000961 |
| 62.0 | 386.400 | .9904  | .0000910 |
| 63.0 | 386.800 | .9889  | .0000862 |
| 64.0 | 387.200 | .9874  | .0000814 |
| 65.0 | 387.600 | .9859  | .0000769 |
| 66.0 | 388.000 | .9846  | .0000727 |
| 67.0 | 388.400 | .9834  | .0000689 |
| 68.0 | 388.800 | .9823  | .0000654 |
| 69.0 | 389.200 | .9812  | .0000619 |
| 70.0 | 389.600 | .9802  | .0000587 |
| 71.0 | 390.000 | .9792  | .0000556 |
| 72.0 | 390.400 | .9783  | .0000528 |
| 73.0 | 390.800 | .9774  | .0000499 |
| 74.0 | 391.200 | .9766  | .0000475 |
| 75.0 | 391.600 | .9759  | .0000450 |

TIME  
MIN.TEMP  
DEG. CGRAMS  
WDK

|      |         |       |
|------|---------|-------|
| 76.0 | 393.000 | .9750 |
| 77.0 | 394.500 | .9741 |

Table XXVIII (continued)

|       |         |       |          |           |
|-------|---------|-------|----------|-----------|
| 78.0  | 396.000 | .9732 |          |           |
| 79.0  | 397.500 | .9723 |          |           |
| 80.0  | 399.000 | .9712 |          |           |
| 81.0  | 400.500 | .9700 |          |           |
| 82.0  | 402.000 | .9687 |          |           |
| 83.0  | 403.500 | .9674 |          |           |
| 84.0  | 405.000 | .9660 |          |           |
| 85.0  | 406.500 | .9647 |          |           |
| 86.0  | 407.600 | .9633 |          |           |
| 87.0  | 408.700 | .9617 |          |           |
| 88.0  | 409.800 | .9601 |          |           |
| 89.0  | 410.900 | .9584 |          |           |
| 90.0  | 412.000 | .9569 |          |           |
| 91.0  | 413.100 | .9555 |          |           |
| 92.0  | 414.200 | .9543 |          |           |
| 93.0  | 415.300 | .9530 |          |           |
| 94.0  | 416.400 | .9518 |          |           |
| 95.0  | 417.500 | .9504 |          |           |
| 96.0  | 418.600 | .9492 |          |           |
| 97.0  | 419.600 | .9479 |          |           |
| 98.0  | 420.600 | .9467 |          |           |
| 99.0  | 421.600 | .9454 |          |           |
| 100.0 | 422.600 | .9441 |          |           |
| 101.0 | 423.600 | .9428 |          |           |
| 102.0 | 424.600 | .9416 |          |           |
| 103.0 | 425.600 | .9403 |          |           |
| 104.0 | 426.600 | .9391 |          |           |
| 105.0 | 427.600 | .9377 |          |           |
| 106.0 | 429.000 | .9365 |          |           |
| 107.0 | 430.400 | .9352 |          |           |
| 108.0 | 431.800 | .9340 |          |           |
| 109.0 | 433.200 | .9327 |          |           |
| 110.0 | 434.600 | .9314 |          |           |
| 111.0 | 436.000 | .9301 |          |           |
| 112.0 | 437.200 | .9289 |          |           |
| 113.0 | 438.400 | .9276 |          |           |
| 114.0 | 439.800 | .9264 |          |           |
| TIME  | TEMP    | GRAMS | CONC     | RATE      |
| MIN.  | DEG. C  | WDK   | MOLES/CC | METHANE   |
| 115.0 | 441.200 | .9250 | .0033067 | .00000060 |

Table XXVIII (continued)

|       |         |       |          |           |
|-------|---------|-------|----------|-----------|
| 116.0 | 442.600 | .9238 | .0033088 | .00000061 |
| 117.0 | 444.000 | .9225 | .0033113 | .00000062 |
| 118.0 | 445.400 | .9213 | .0033133 | .00000064 |
| 119.0 | 446.800 | .9200 | .0033157 | .00000067 |
| 120.0 | 448.200 | .9187 | .0033175 | .00000071 |
| 121.0 | 449.600 | .9174 | .0033196 | .00000076 |
| 122.0 | 451.000 | .9162 | .0033211 | .00000081 |
| 123.0 | 452.400 | .9149 | .0033228 | .00000087 |
| 124.0 | 453.800 | .9137 | .0033239 | .00000093 |
| 125.0 | 455.200 | .9123 | .0033251 | .00000100 |
| 126.0 | 456.600 | .9111 | .0033257 | .00000107 |
| 127.0 | 458.000 | .9098 | .0033265 | .00000114 |
| 128.0 | 459.100 | .9086 | .0033265 | .00000121 |
| 129.0 | 460.200 | .9072 | .0033267 | .00000128 |
| 130.0 | 461.300 | .9060 | .0033263 | .00000135 |
| 131.0 | 462.400 | .9047 | .0033259 | .00000142 |
| 132.0 | 463.500 | .9035 | .0033249 | .00000151 |
| 133.0 | 464.600 | .9023 | .0033236 | .00000160 |
| 134.0 | 465.700 | .9009 | .0033223 | .00000169 |
| 135.0 | 466.800 | .9000 | .0033194 | .00000178 |
| 136.0 | 467.900 | .8991 | .0033158 | .00000188 |
| 137.0 | 469.000 | .8982 | .0033117 | .00000200 |
| 138.0 | 470.100 | .8973 | .0033072 | .00000213 |
| 139.0 | 471.200 | .8964 | .0033023 | .00000217 |
| 140.0 | 472.200 | .8955 | .0032969 | .00000241 |
| 141.0 | 473.200 | .8946 | .0032907 | .00000255 |
| 142.0 | 474.200 | .8938 | .0032840 | .00000270 |
| 143.0 | 475.200 | .8929 | .0032767 | .00000285 |
| 144.0 | 476.200 | .8920 | .0032689 | .00000300 |
| 145.0 | 477.200 | .8911 | .0032604 | .00000315 |
| 146.0 | 478.600 | .8903 | .0032509 | .00000331 |
| 147.0 | 480.000 | .8896 | .0032408 | .00000348 |
| 148.0 | 481.400 | .8877 | .0032340 | .00000366 |
| 149.0 | 482.800 | .8869 | .0032225 | .00000385 |
| 150.0 | 484.200 | .8861 | .0032102 | .00000406 |
| 151.0 | 485.600 | .8854 | .0031970 | .00000430 |
| 152.0 | 487.100 | .8846 | .0031827 | .00000463 |
| 153.0 | 488.600 | .8838 | .0031669 | .00000506 |
| 154.0 | 490.000 | .8830 | .0031494 | .00000548 |
| 155.0 | 491.400 | .8823 | .0031303 | .00000590 |
| 156.0 | 492.800 | .8815 | .0031095 | .00000632 |
| 157.0 | 494.200 | .8807 | .0030871 | .00000674 |
| 158.0 | 495.600 | .8800 | .0030631 | .00000715 |
| 159.0 | 497.000 | .8792 | .0030374 | .00000758 |

Table XXVIII (continued)

|       |         |       |          |           |
|-------|---------|-------|----------|-----------|
| 160.0 | 498.400 | .8784 | .0030099 | .00000802 |
| 161.0 | 499.800 | .8776 | .0029807 | .00000848 |
| 162.0 | 501.200 | .8769 | .0029497 | .00000890 |
| 163.0 | 502.600 | .8761 | .0029170 | .00000934 |
| 164.0 | 504.000 | .8753 | .0028826 | .00000977 |
| 165.0 | 505.400 | .8745 | .0028464 | .00001020 |
| 166.0 | 506.800 | .8738 | .0028086 | .00001062 |
| 167.0 | 508.200 | .8730 | .0027689 | .00001107 |
| 168.0 | 509.600 | .8722 | .0027275 | .00001152 |
| 169.0 | 510.100 | .8713 | .0026846 | .00001193 |
| 170.0 | 510.600 | .8704 | .0026399 | .00001244 |
| 171.0 | 511.700 | .8696 | .0025930 | .00001300 |
| 172.0 | 512.800 | .8687 | .0025437 | .00001358 |
| 173.0 | 513.900 | .8678 | .0024921 | .00001418 |
| 174.0 | 515.000 | .8669 | .0024381 | .00001472 |
| 175.0 | 516.100 | .8660 | .0023819 | .00001524 |
| 176.0 | 517.200 | .8651 | .0023236 | .00001578 |
| 177.0 | 518.300 | .8643 | .0022629 | .00001635 |
| 178.0 | 519.400 | .8634 | .0021999 | .00001690 |
| 179.0 | 520.500 | .8625 | .0021347 | .00001745 |
| 180.0 | 521.600 | .8616 | .0020671 | .00001800 |
| 181.0 | 522.700 | .8607 | .0019973 | .00001850 |
| 182.0 | 523.800 | .8598 | .0019255 | .00001898 |
| 183.0 | 524.900 | .8590 | .0018516 | .00001945 |
| 184.0 | 526.000 | .8581 | .0017758 | .00001990 |
| 185.0 | 527.100 | .8572 | .0016979 | .00002038 |
| 186.0 | 528.200 | .8567 | .0016176 | .00002067 |
| 187.0 | 529.300 | .8564 | .0015362 | .00002074 |
| 188.0 | 530.400 | .8560 | .0014550 | .00002070 |
| 189.0 | 531.500 | .8556 | .0013738 | .00002052 |
| 190.0 | 532.600 | .8552 | .0012939 | .00002016 |
| 191.0 | 533.700 | .8549 | .0012153 | .00001974 |
| 192.0 | 534.800 | .8544 | .0011384 | .00001934 |
| 193.0 | 535.900 | .8541 | .0010628 | .00001895 |
| 194.0 | 537.000 | .8537 | .0009889 | .00001853 |
| 195.0 | 538.000 | .8533 | .0009165 | .00001813 |
| 196.0 | 539.800 | .8529 | .0008456 | .00001773 |
| 197.0 | 541.600 | .8525 | .0007763 | .00001733 |
| 198.0 | 543.400 | .8521 | .0007085 | .00001692 |
| 199.0 | 545.200 | .8518 | .0006423 | .00001650 |
| 200.0 | 547.000 | .8513 | .0005780 | .00001592 |
| 201.0 | 548.700 | .8510 | .0005160 | .00001532 |
| 202.0 | 550.400 | .8506 | .0004563 | .00001478 |
| 203.0 | 552.100 | .8502 | .0003985 | .00001428 |

Table XXVIII (continued)

|       |         |       |          |           |
|-------|---------|-------|----------|-----------|
| 204.0 | 553.800 | .8498 | .0003427 | .00001380 |
| 205.0 | 555.500 | .8495 | .0002885 | .00001343 |
| 206.0 | 556.700 | .8490 | .0002359 | .00001296 |
| 207.0 | 557.900 | .8487 | .0001852 | .00001248 |
| 208.0 | 559.100 | .8482 | .0001364 | .00001200 |
| 209.0 | 560.300 | .8479 | .0000893 | .00001158 |
| 210.0 | 561.500 | .8475 | .0000438 | .00001118 |

| TIME<br>MIN. | TEMP<br>DEG. C | GRAMS<br>WDK |
|--------------|----------------|--------------|
| 212.0        | 563.400        | .8467        |
| 213.0        | 564.100        | .8464        |
| 214.0        | 564.800        | .8459        |
| 215.0        | 565.500        | .8456        |
| 216.0        | 566.200        | .8451        |
| 217.0        | 566.900        | .8448        |
| 218.0        | 567.700        | .8444        |
| 219.0        | 568.500        | .8440        |
| 220.0        | 569.300        | .8436        |
| 221.0        | 570.100        | .8433        |
| 222.0        | 570.800        | .8428        |
| 223.0        | 571.500        | .8425        |
| 224.0        | 572.200        | .8420        |
| 225.0        | 573.000        | .8417        |
| 226.0        | 574.200        | .8413        |
| 227.0        | 575.400        | .8409        |
| 228.0        | 576.600        | .8405        |
| 229.0        | 577.800        | .8402        |
| 230.0        | 579.000        | .8397        |
| 231.0        | 580.200        | .8394        |
| 232.0        | 581.400        | .8390        |
| 233.0        | 582.600        | .8386        |
| 234.0        | 583.800        | .8382        |
| 235.0        | 585.000        | .8379        |
| 236.0        | 586.200        | .8374        |
| 237.0        | 587.400        | .8371        |
| 238.0        | 588.600        | .8366        |
| 239.0        | 589.800        | .8363        |
| 240.0        | 591.000        | .8359        |
| 241.0        | 592.200        | .8355        |
| 242.0        | 593.400        | .8351        |

Table XXVIII (continued)

|       |         |       |
|-------|---------|-------|
| 243.0 | 594.600 | .8348 |
| 244.0 | 595.800 | .8343 |
| 245.0 | 597.000 | .8340 |
| 246.0 | 598.200 | .8369 |
| 247.0 | 599.400 | .8332 |
| 248.0 | 600.600 | .8328 |
| 249.0 | 601.800 | .8324 |
| 250.0 | 603.000 | .8320 |
| 251.0 | 604.200 | .8317 |

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Table XXIX: Kinetic Results for the Analysis of Weight Data for  
Acenaphthylene Reaction Two (RX-A-2)

| Run                                   | EX-B-14            | EX-B-15            | EX-B-16            | EX-B-17            |
|---------------------------------------|--------------------|--------------------|--------------------|--------------------|
| Sample Size, grams                    | 2.500              | 2.500              | 2.000              | 2.000              |
| Moles formed<br>Acenaphthene          | .00845             | .00832             | .00670             | .00674             |
| FIRST ORDER                           |                    |                    |                    |                    |
| Frequency Factor<br>Sec <sup>-1</sup> | e <sup>59.9</sup>  | e <sup>65.6</sup>  | e <sup>61.3</sup>  | e <sup>47.0</sup>  |
| Activation Energy<br>cal/mole         | 86,525             | 93,548             | 87,441             | 69,742             |
| Correlation<br>Coefficient            | .897               | .900               | .848               | .794               |
| SECOND ORDER                          |                    |                    |                    |                    |
| Frequency Factor<br>cc/mole-sec       | e <sup>107.2</sup> | e <sup>116.3</sup> | e <sup>127.4</sup> | e <sup>103.6</sup> |
| Activation Energy<br>cal/mole         | 139,059            | 149,971            | 163,061            | 133,851            |
| Correlation<br>Coefficient            | .984               | .982               | .981               | .967               |
| Temp.. Start °C                       | 336                | 335                | 340                | 341                |
| Temp.. Final °C                       | 400                | 393                | 384                | 392                |

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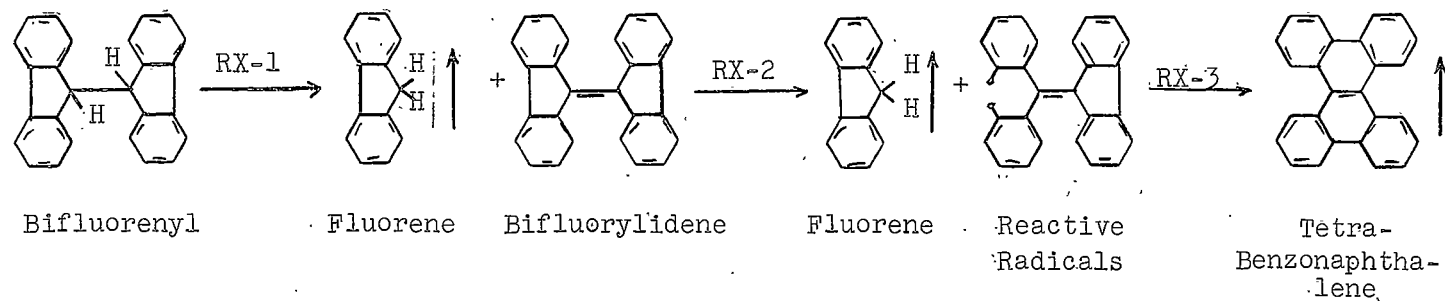
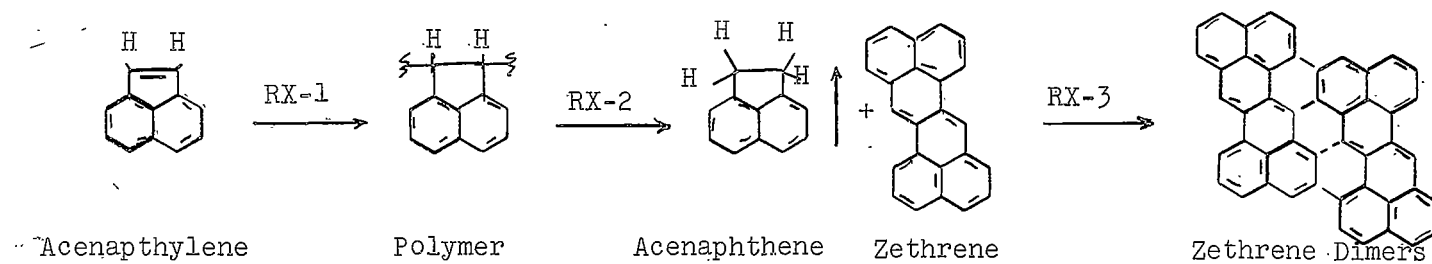
Table XXX: Kinetic Results for the Analysis of Hydrogen Evolution Data  
for Acenaphthylene Reaction Three (RX-A-3)

|                            |            |            |            |            |
|----------------------------|------------|------------|------------|------------|
| Pyrolysis Run              | EX-A-14    | EX-A-15    | EX-A-16    | EX-A-17    |
| Moles of<br>Hydrogen       | .001462    | .001302    | .000834    | .001077    |
| Initial<br>Temp., °C       | 440        | 442        | 447        | 441        |
| Final Temp., °C            | 570        | 574        | 546        | 569        |
| FIRST ORDER                |            |            |            |            |
| Frequency Factor           | $e^{23.5}$ | $e^{25.6}$ | $e^{27.6}$ | $e^{23.0}$ |
| Activation Energy          | 49,401     | 52,268     | 55,137     | 48,660     |
| Correlation<br>Coefficient | .965       | .963       | .949       | .966       |
| SECOND ORDER               |            |            |            |            |
| Frequency Factor           | $e^{41.8}$ | $e^{43.9}$ | $e^{47.9}$ | $e^{42.1}$ |
| Activation Energy          | 68,019     | 70,894     | 76,707     | 68,511     |
| Correlation<br>Coefficient | .914       | .912       | .892       | .915       |

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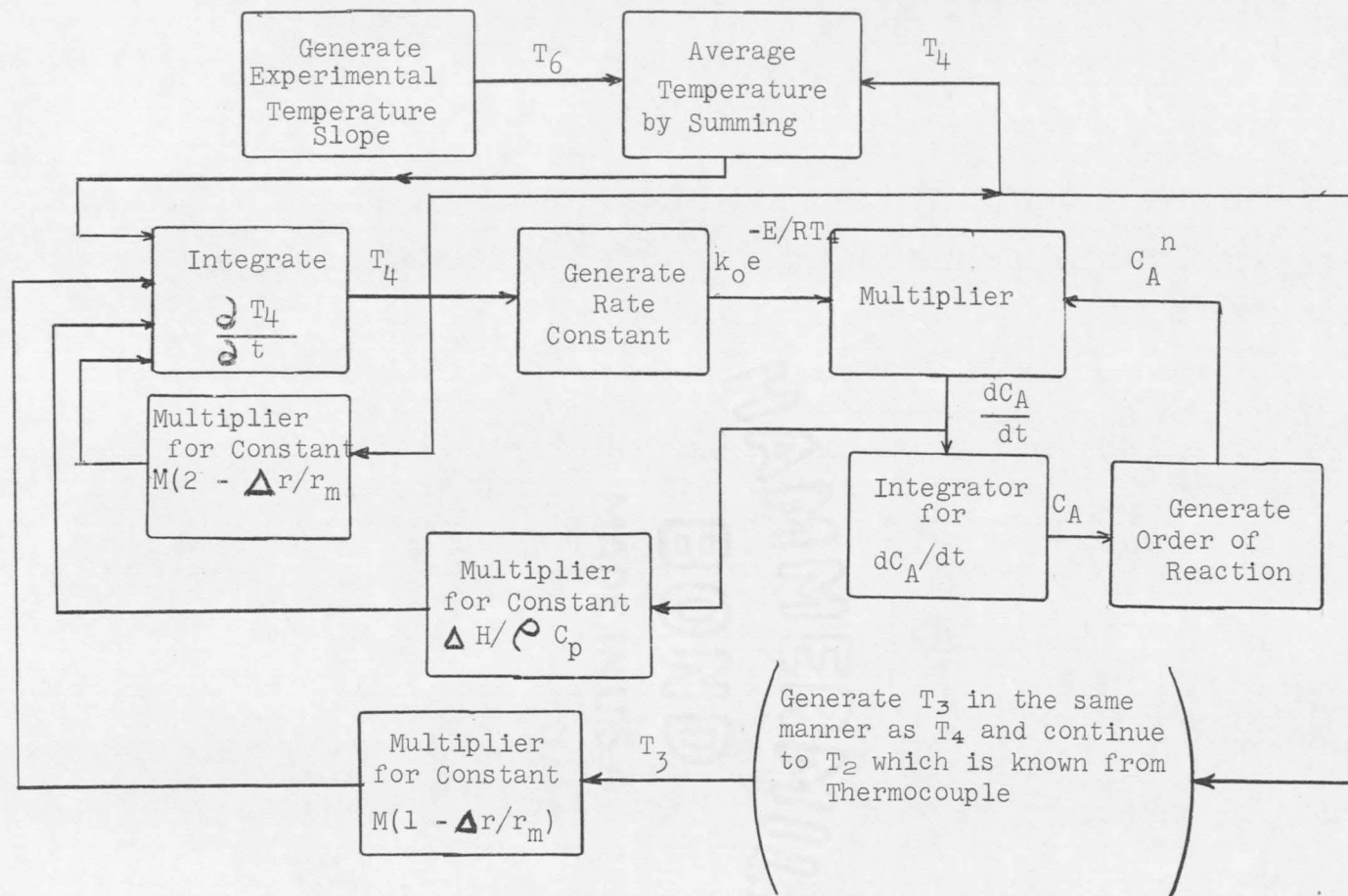
Table XXXI: Kinetic Results for the Analysis of Methane Evolution Data for Acenaphthylene Reaction Three (RX-A-3)

|                         |            |            |            |            |
|-------------------------|------------|------------|------------|------------|
| Pyrolysis Run           | EX-A-14    | EX-B-15    | EX-A-16    | EX-A-17    |
| Moles of Methane        | .001177    | .001286    | .000756    | .000902    |
| Initial Temp., °C       | 440        | 442        | 447        | 441        |
| Final Temp., °C         | 569        | 566        | 537        | 561        |
| FIRST ORDER             |            |            |            |            |
| Frequency Factor        | $e^{31.2}$ | $e^{32.0}$ | $e^{36.8}$ | $e^{31.7}$ |
| Activation Energy       | 61,440     | 62,287     | 68,815     | 61,666     |
| Correlation Coefficient | .993       | .995       | .976       | .993       |
| SECOND ORDER            |            |            |            |            |
| Frequency Factor        | $e^{53.5}$ | $e^{55.1}$ | $e^{58.8}$ | $e^{53.4}$ |
| Activation Energy       | 86,007     | 88,050     | 92,921     | 85,431     |
| Correlation Coefficient | .954       | .959       | .925       | .957       |



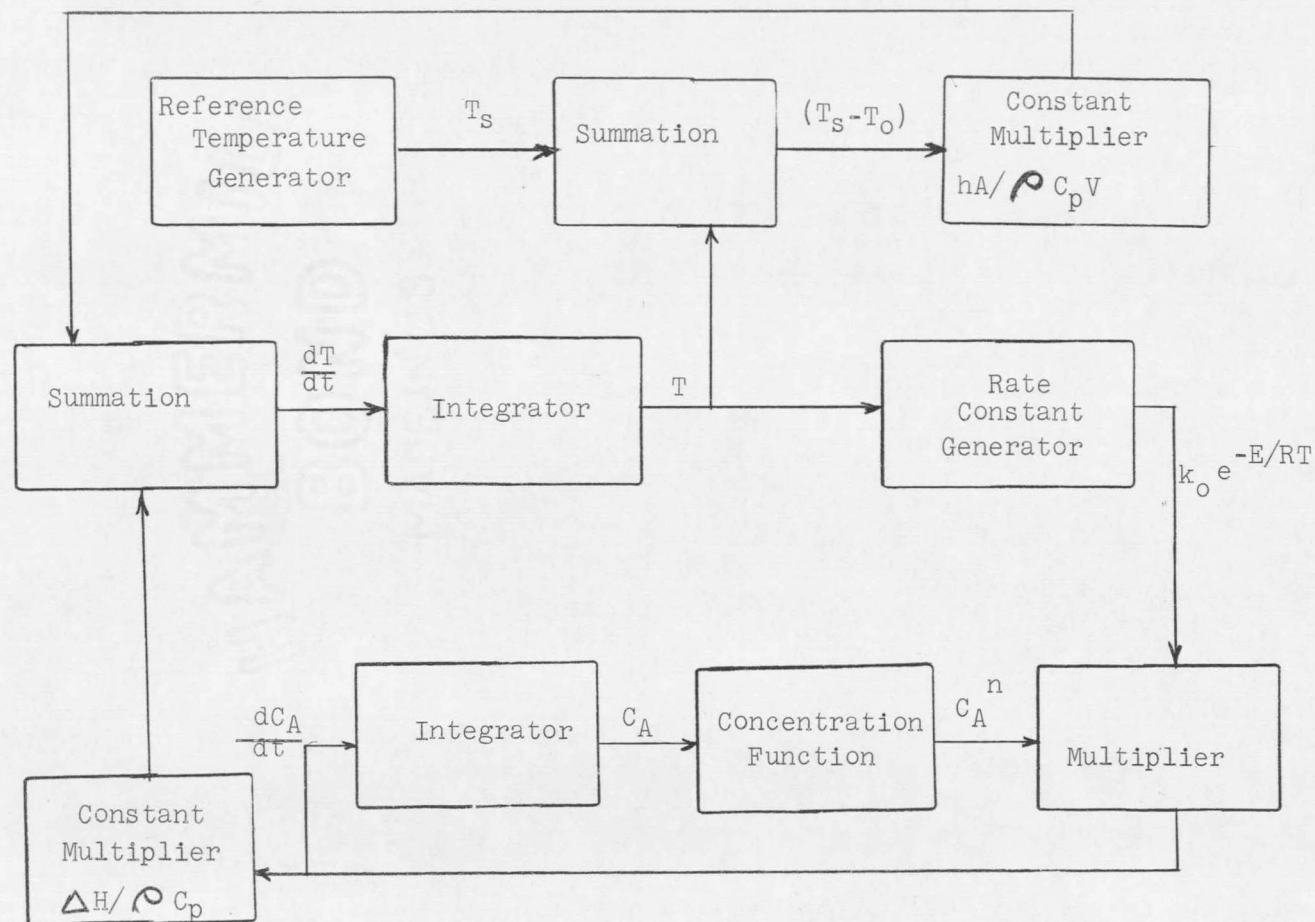
+ Analogous Non-Planar Radicals

Figure 1. Major Reactions of Acenaphthylene and Bifluorenyl for Kinetic Analysis.



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Figure 2. Analog Computer Block Diagram for Simulating TGA Thermal Data.



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$$\frac{dT}{dt} = \frac{hA}{\rho C_p V} (T_s - T) + \frac{k_o}{\rho C_p} e^{-E/RT} C_A^n \Delta H$$

Figure 3. Analog Computer Block Diagram for Simulating DTA Thermal Data.

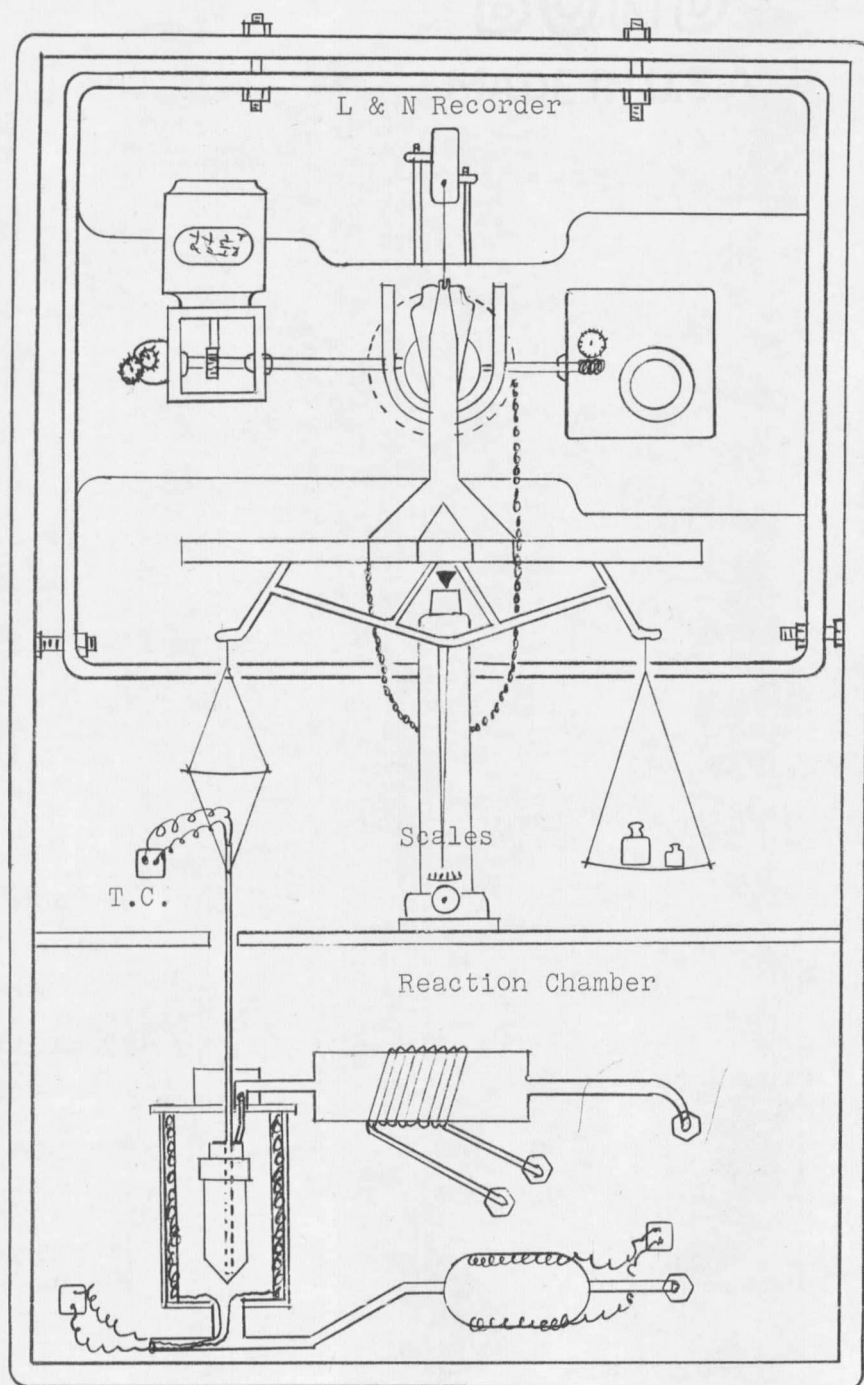


Figure 4. Modifications to a Leeds and Northrup Recorder for use as an Automatic Recording Balance.

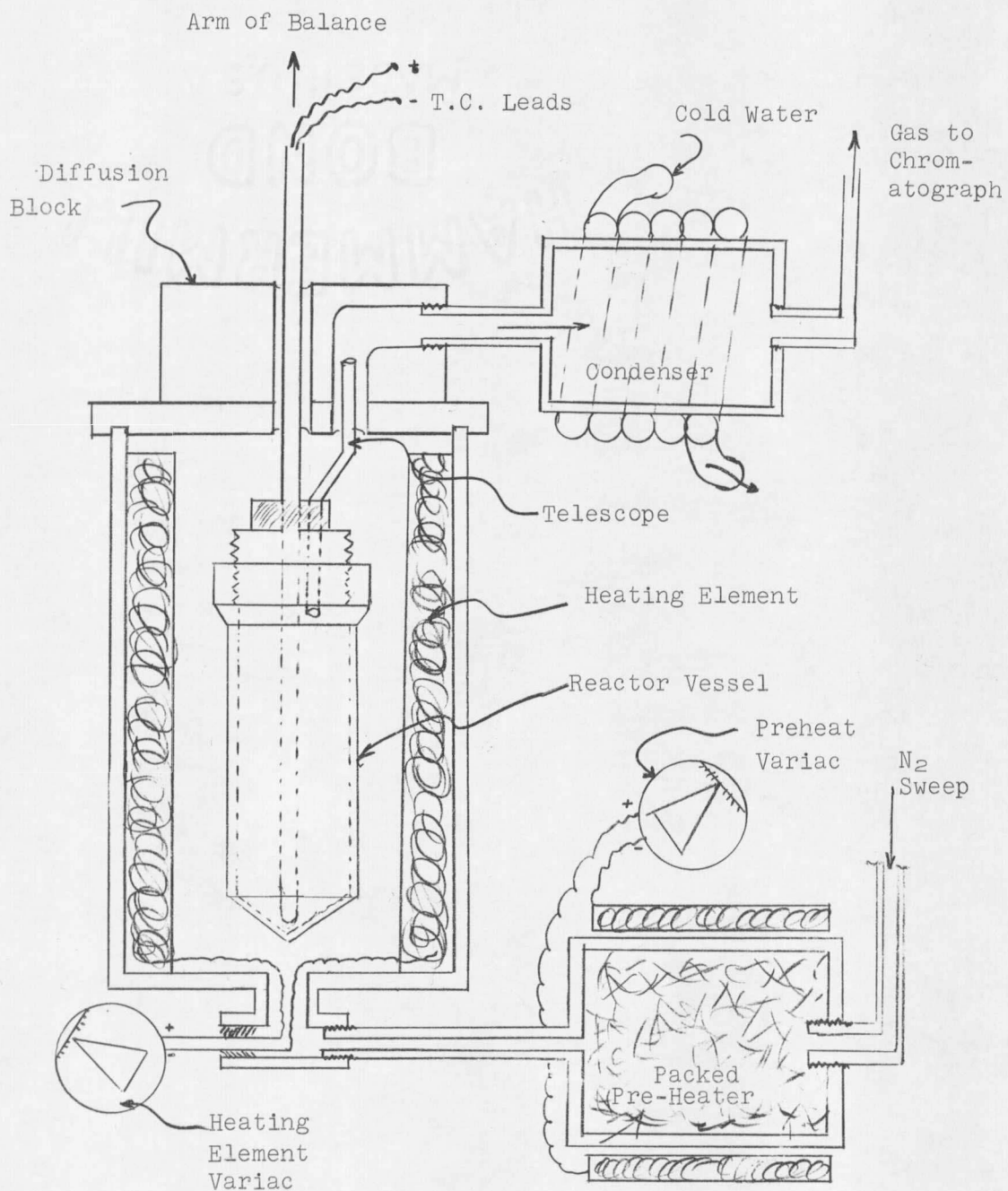
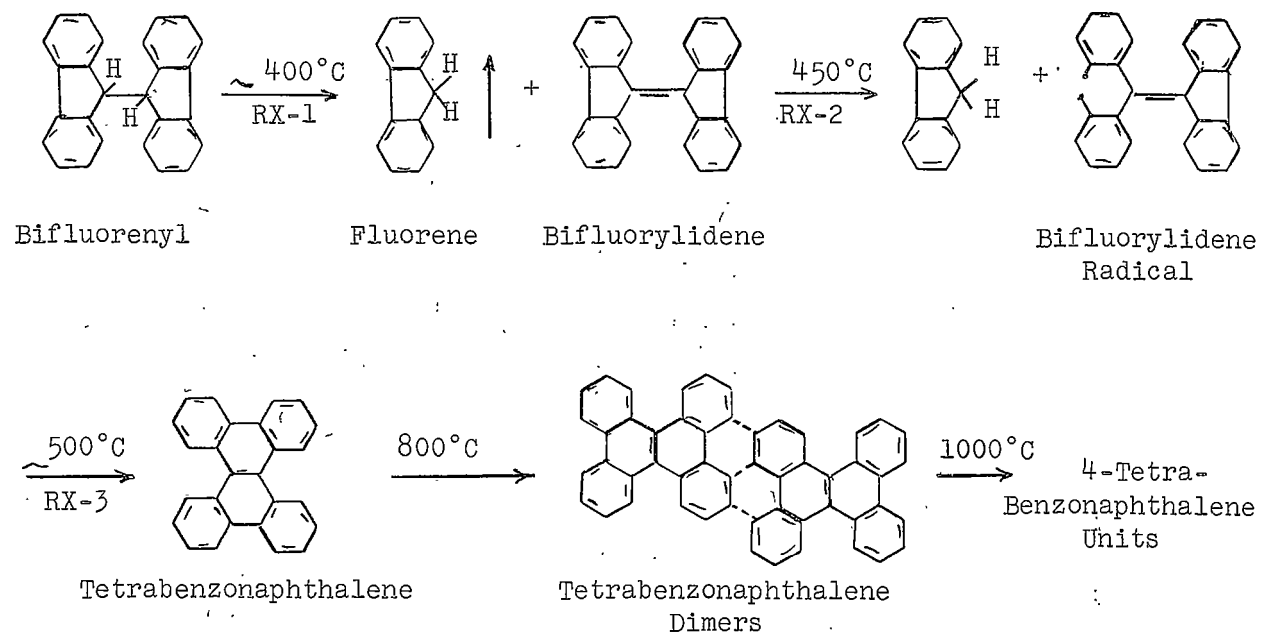


Figure 5. Design and Assembly of the TGA Pyrolysis Reaction Chamber.



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Figure 6. Formation of Coke by the Pyrolysis Reactions of Bifluorenyl.

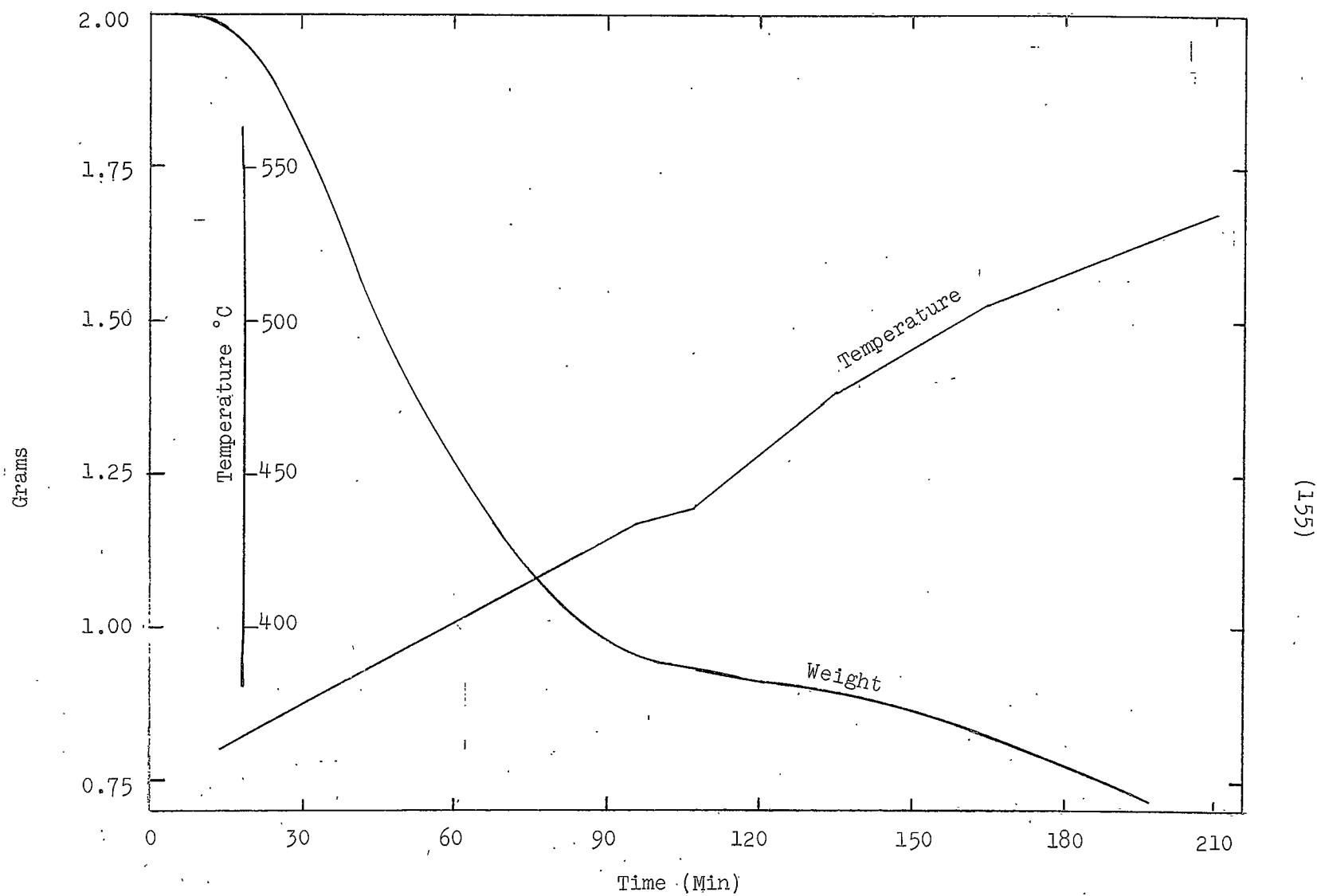


Figure 7. Typical Weight Loss and Temperature Trace for Pyrolysis of Bifluorenyl.

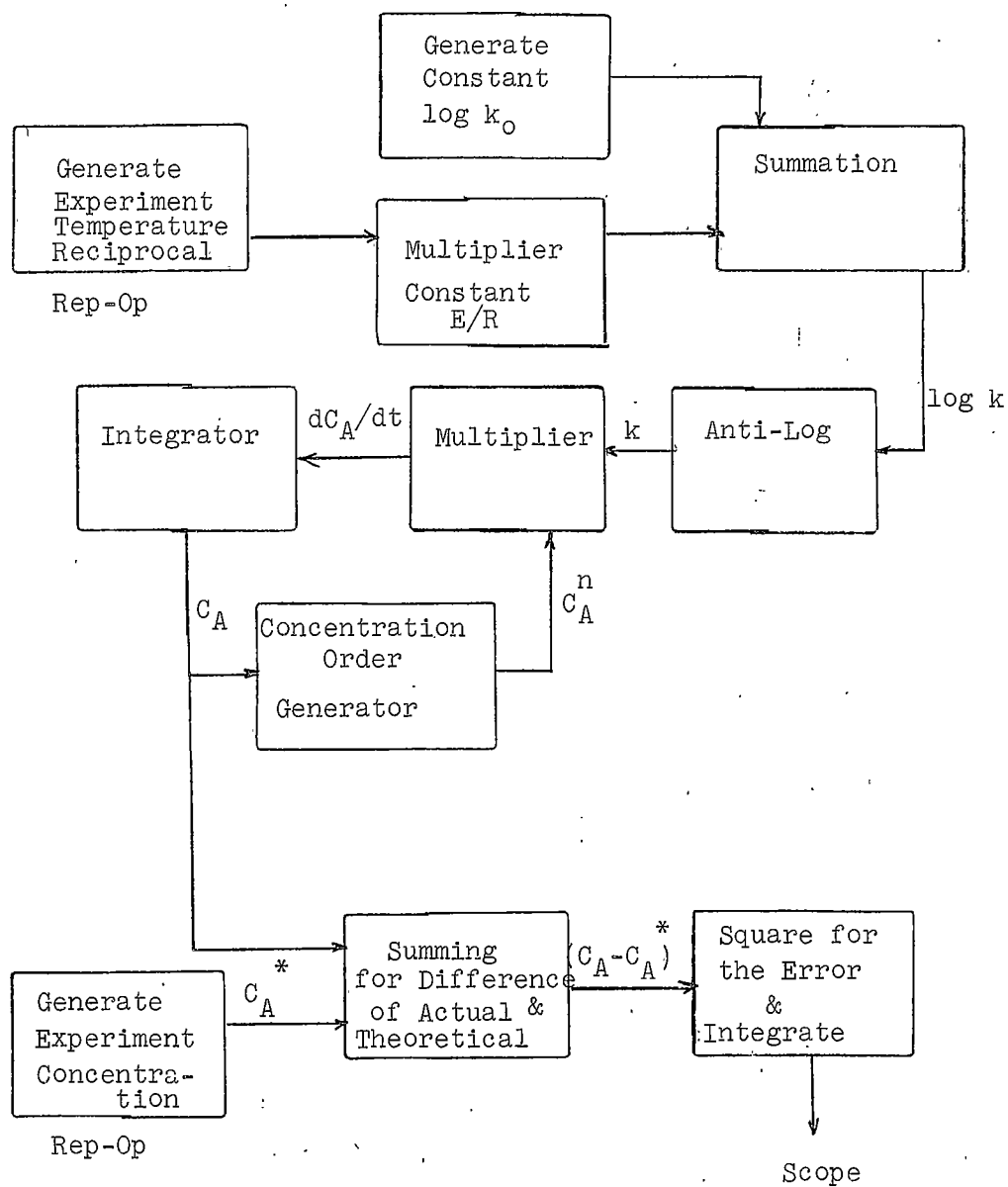


Figure 8. Analog Computer Block Diagram for Simulating Weight Loss Data with the Arrhenius Kinetic Model.

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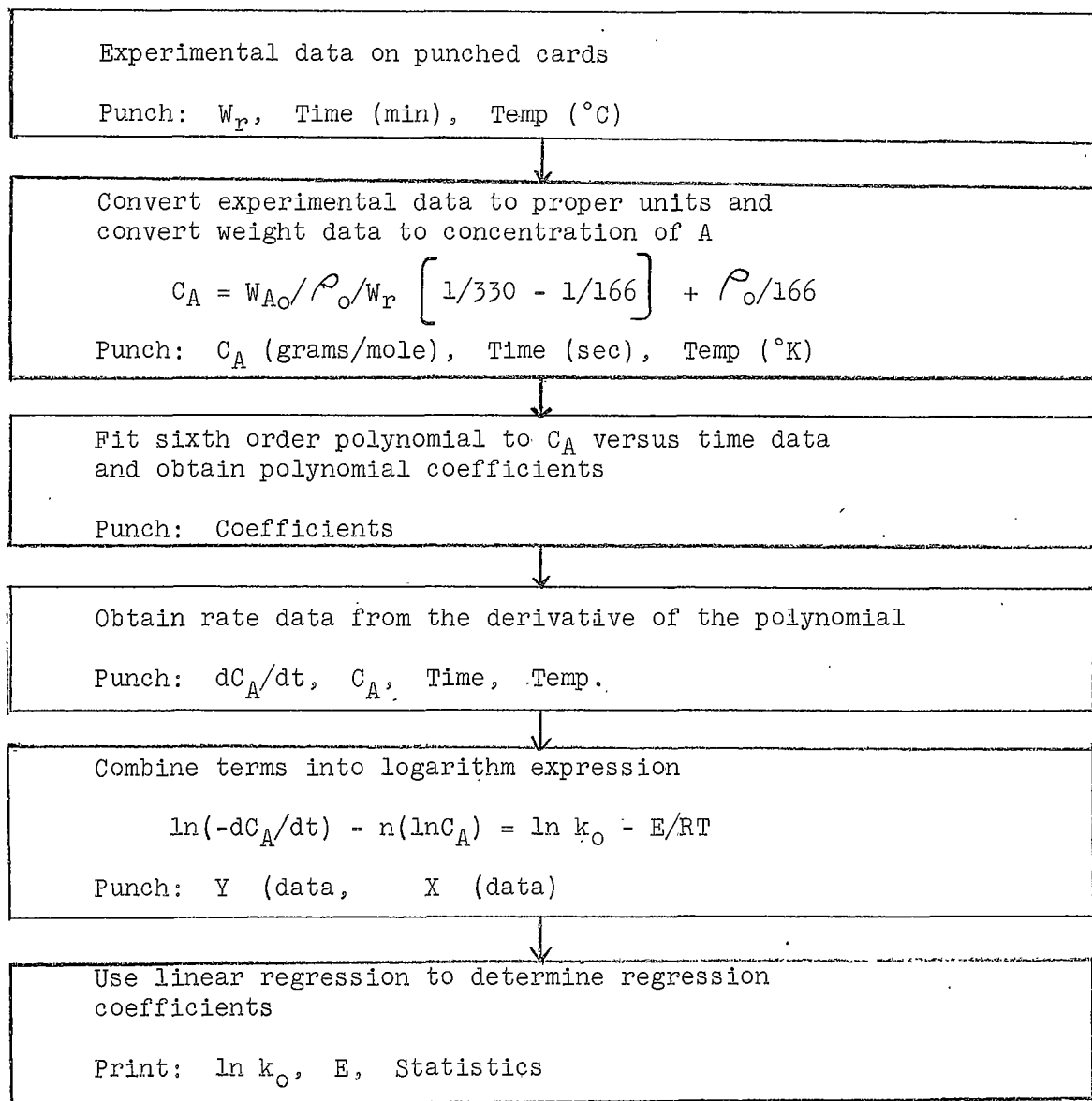


Figure 9. IBM Computer Flow Diagram for Analysis of  
Bifluorenyl Reaction One

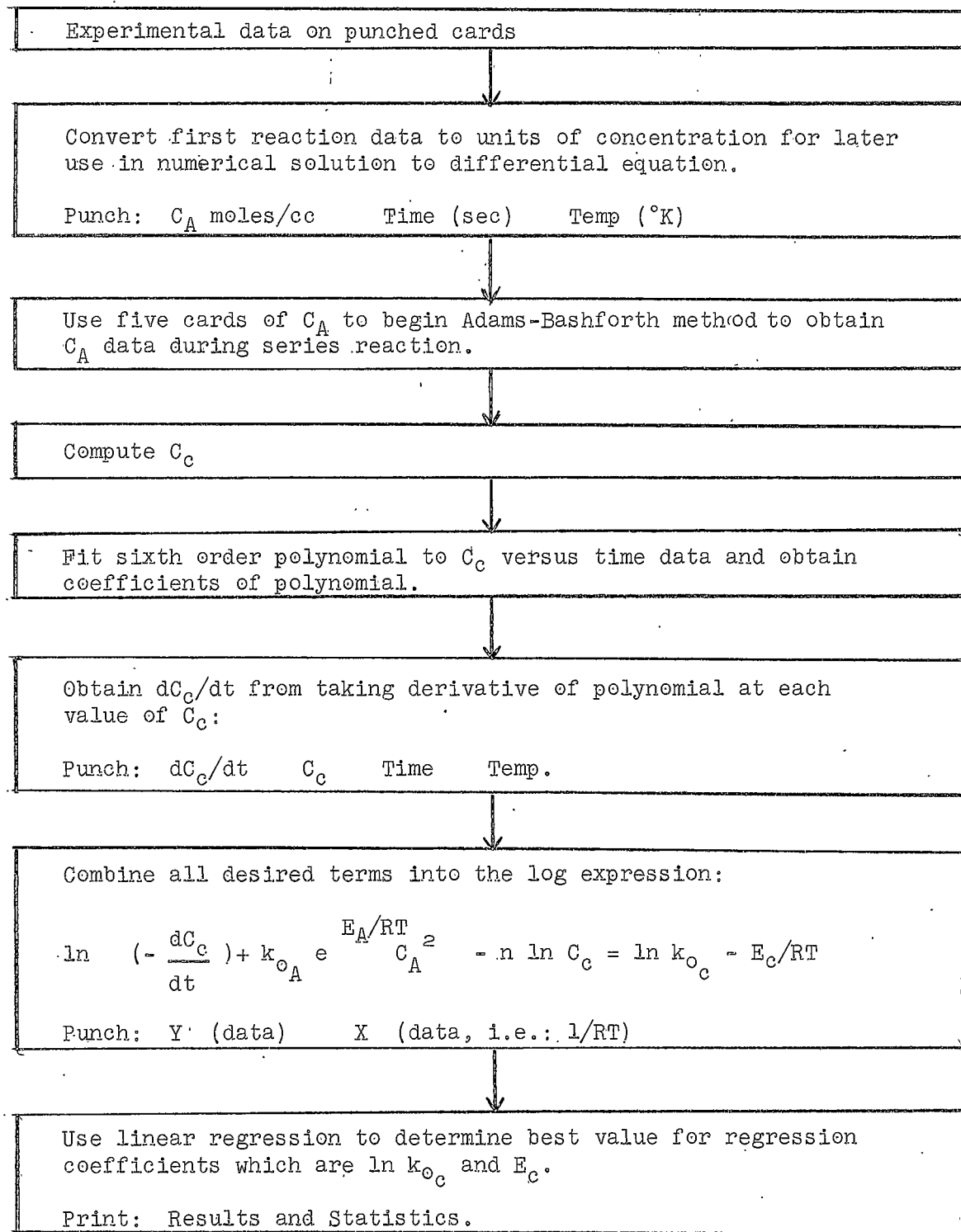


Figure 10. IBM Computer Flow Diagram for Analysis of Bifluorenyl Reaction Two.

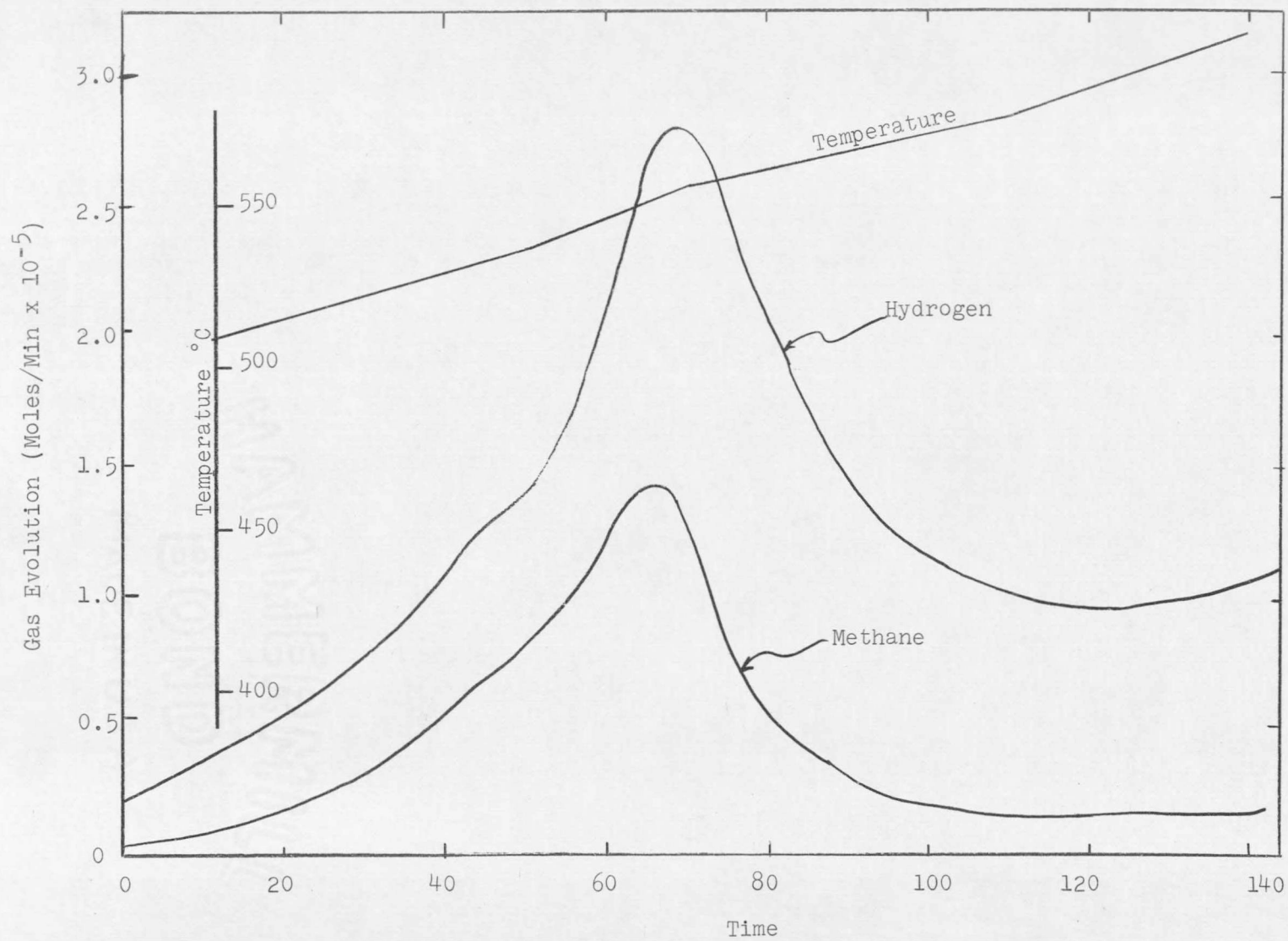


Figure 11. Typical Gas Evolution and Temperature Trace for the Pyrolysis of Bifluorenyl.

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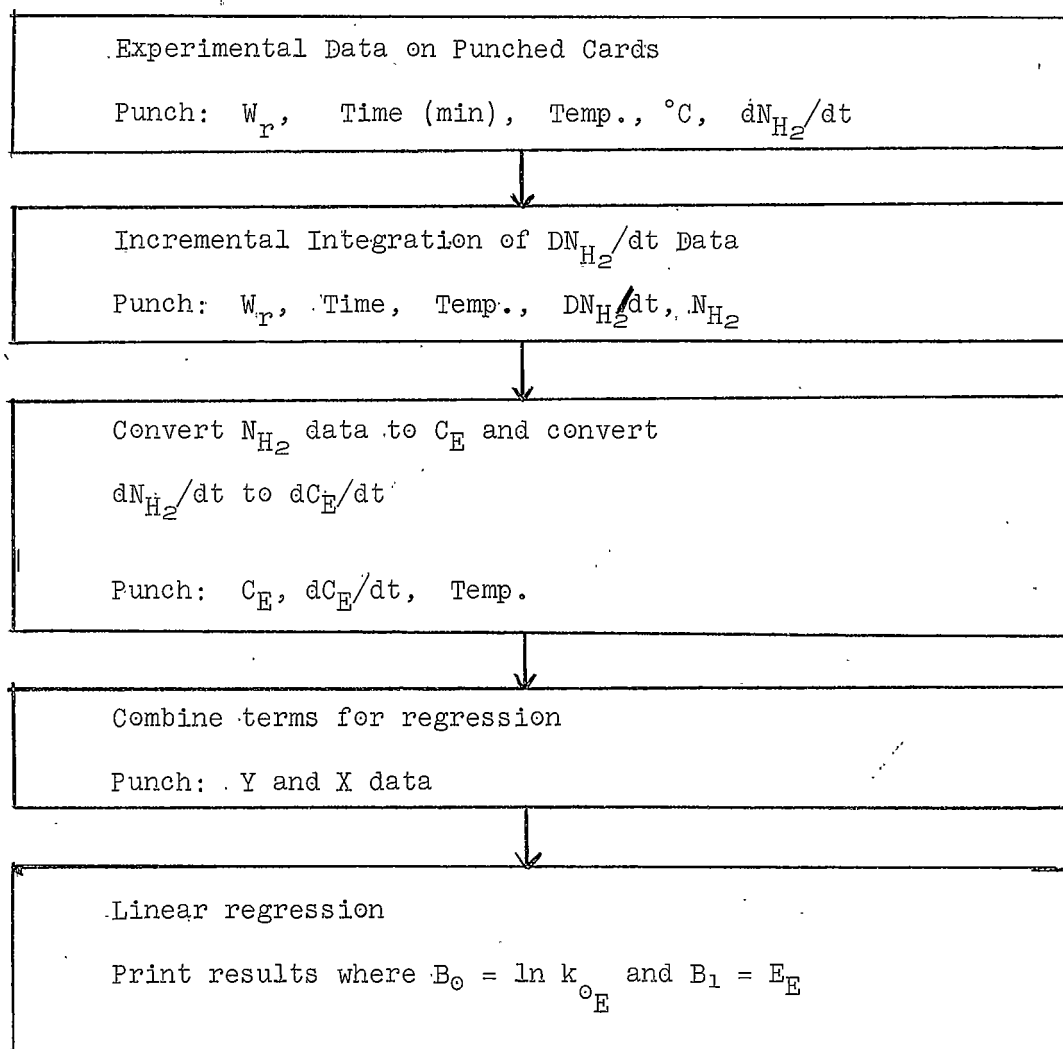


Figure 12. IBM Computer Flow Diagram for Analysis of Gas Evolution Data

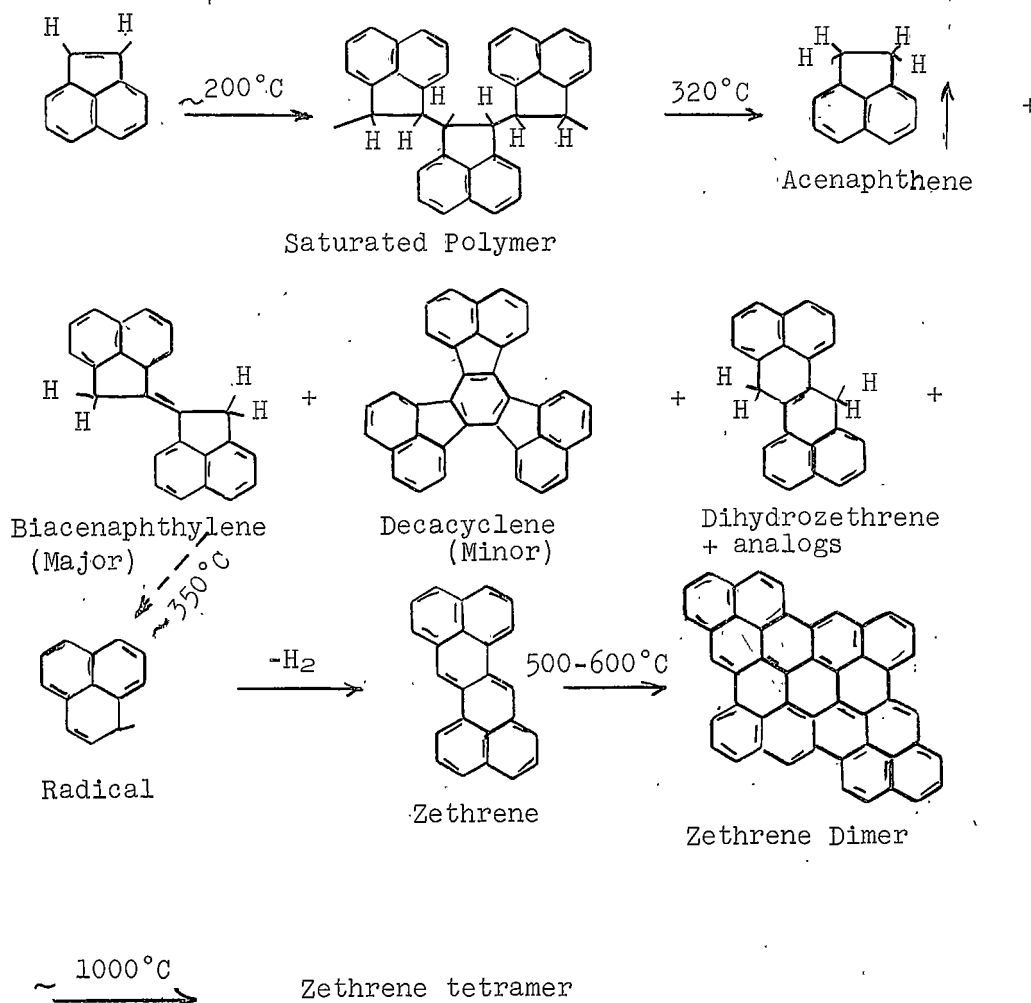


Figure 13. Formation of Coke by the Pyrolysis Reactions of Acenaphthylene.

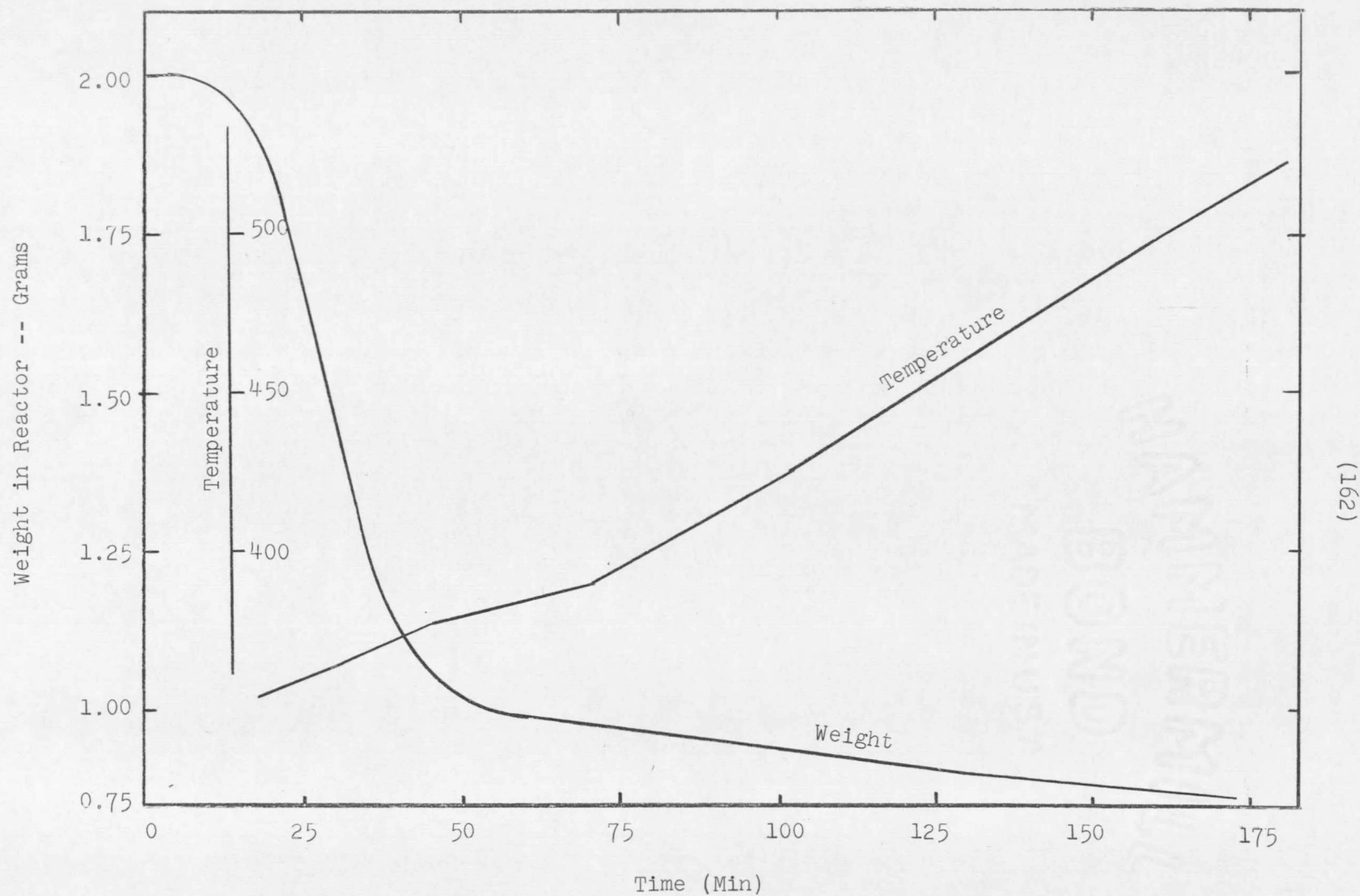


Figure 14. Typical Weight Loss and Temperature Trace for the Pyrolysis of Acenaphthylene.

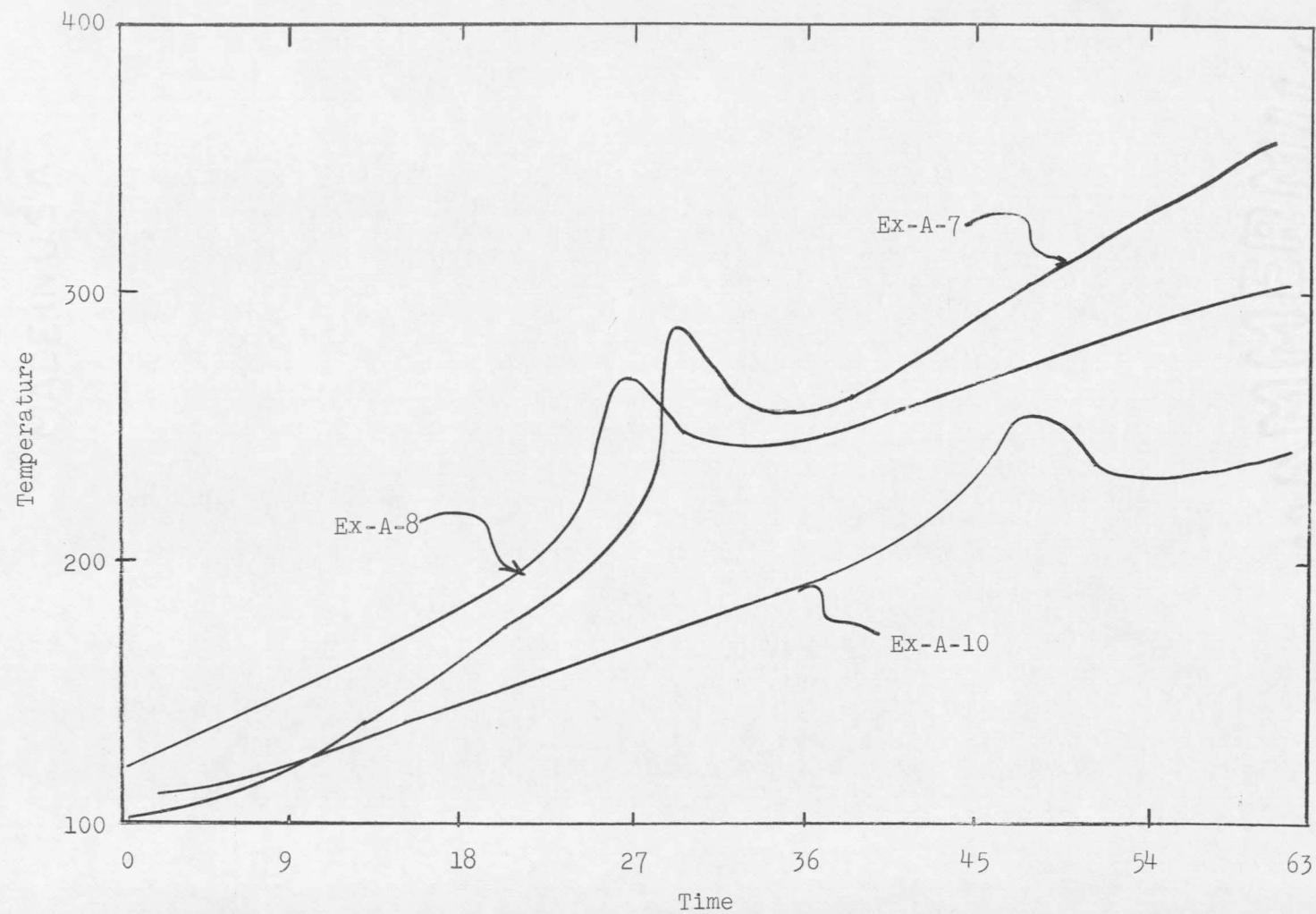


Figure 15. TGA Thermal Data for Pyrolysis Runs Ex-A-7, Ex-A-8, and Ex-A-10.

Results:  $E = 27,500 \text{ cal/mole}$   
 $K^\circ = 10^{7.5} \text{ sec}^{-1}$

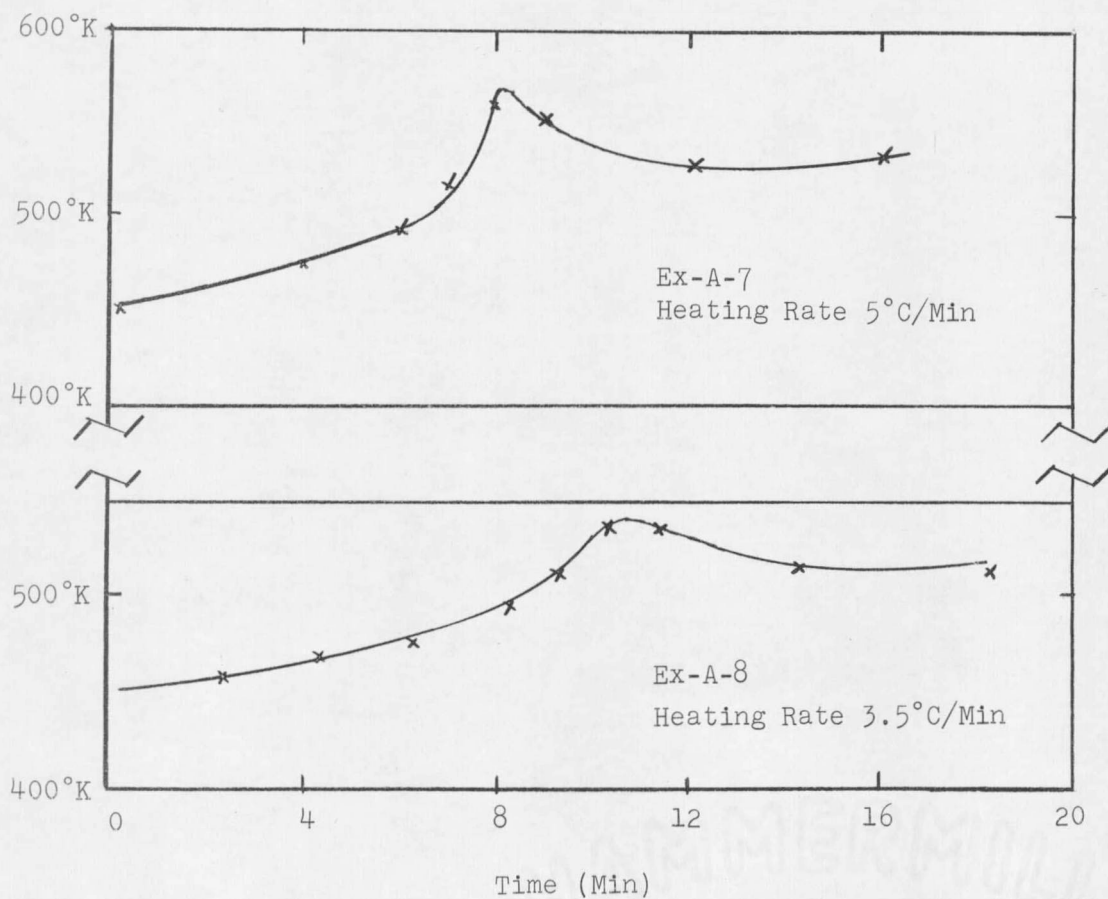


Figure 16. Simulation of TGA Thermal Data by using the Analog Computer. (RX-A-1).

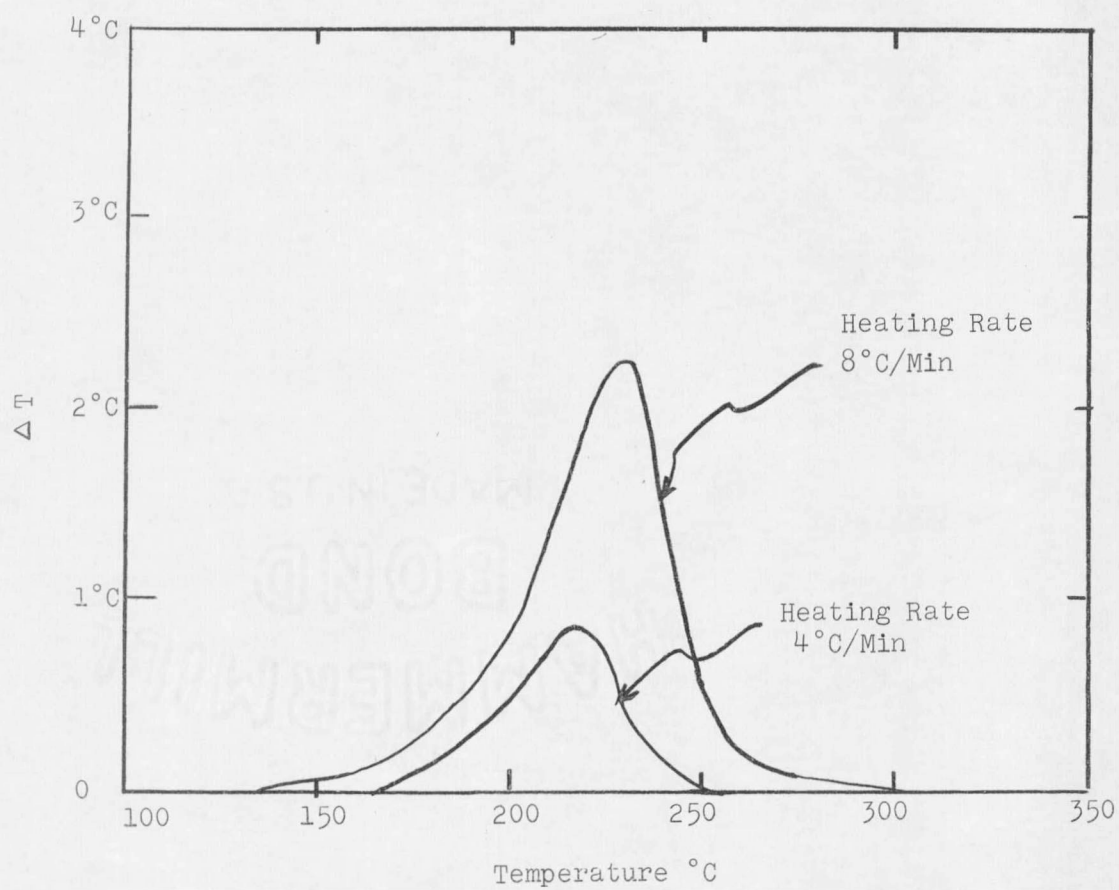


Figure 17. Thermal Data for Acenaphthylene as Obtained From Conoco's DTA Unit.

(166)

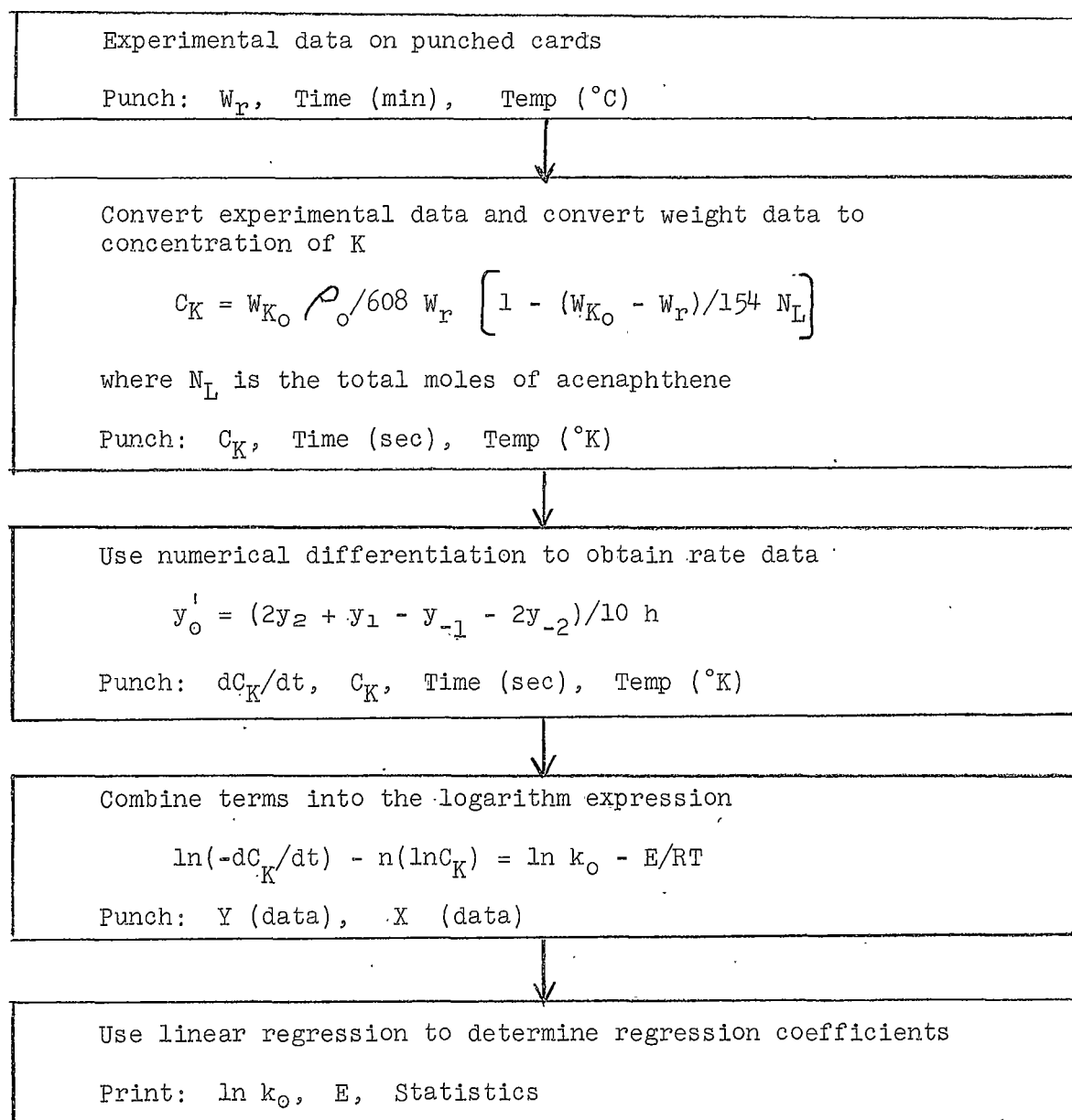


Figure 18. IBM Computer Flow Diagram for Analysis of Acenaphthylene Reaction Two

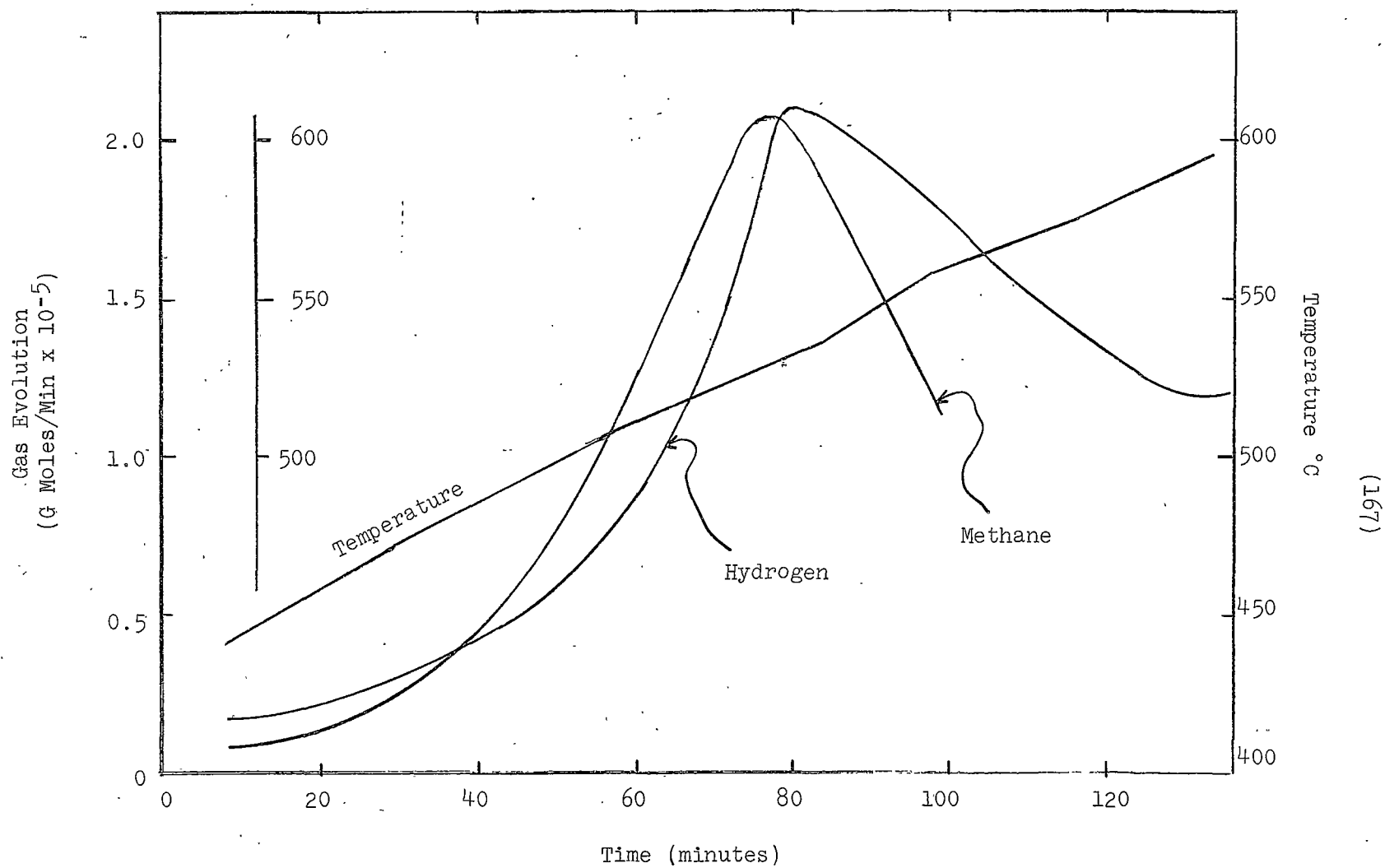


Figure 19. Typical Gas Evolution and Temperature Trace for the Pyrolysis of Acenaphthylene.

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