

UNSTEADY-STATE DISTILLATION
ACCOMPANIED BY CHEMICAL REACTION

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Ting-Long Wu

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Chapter 1 Introduction

Most chemical processes involve two major operations, namely chemical reaction and component separation. Distillation is one of the most widely used unit operations for separating components of a mixture. Distillation can be carried out under steady-state conditions or under unsteady-state conditions. Furthermore, a chemical reaction may or may not accompany distillation. The combination of these operational modes yields the following four categories of distillation operations

- (1) Steady-State Distillation without Chemical Reaction
- (2) Unsteady-State Distillation without Chemical Reaction
- (3) Steady-State Distillation with Chemical Reaction
- (4) Unsteady-State Distillation with Chemical Reaction

The operation belonging to the first category has been almost thoroughly investigated and the chemical engineering literature is full of articles on this subject. The second category, the unsteady-state distillation without chemical reaction, has become the subject of many investigations during the last two decades. The availability of modern electronic computers as the tools for studying the unsteady-state behavior has certainly con-

tributed to the advance in this field. The most comprehensive treatment of unsteady-state distillation without chemical reaction is provided by Holland (36).

Comparing with the first and second categories, the technical papers on the subjects belonging to the third and fourth categories are so few that they can be counted on the fingers of both hands. Experimental investigation of unsteady-state distillation accompanied by chemical reaction started from a series of batch distillation experiments in a distillation column performed by Backhaus in 1921 for esterification of ethyl alcohol and acetic acid. Since the theoretical analysis of an unsteady-state distillation accompanied by chemical reaction, i. e., Category Four, is so difficult that Othmer in 1943 shifted to a series of experimental investigations on steady-state reaction-distillation systems, i. e., Category Three (3,4,17,18,28,19). However, a theoretical model for a steady-state reaction-distillation column to treat the experimental results such as obtained by Othmer was not developed until Marek (45) in 1954 presented a McCabe-Thiele graphical method to study the effect of chemical reaction on distillation.

A theoretical model for the unsteady-state distil-

lation accompanied by chemical reaction, i. e., Category Four, has not been reported in the literature. Therefore, the purpose of this study is to develop such a mathematical model and also to obtain experimental data which will then be used to demonstrate the application of the theoretical model proposed. It is hoped that this work serves as the first attempt to remove the last unknown, represented by Category Four, in the total system of distillation operations. Since the system to be treated is very complex, this first theoretical and experimental study deals with a distillation column of a single perfect tray. This approach enables a better understanding of the fundamental concepts and at the same time provides building blocks for a more complicated column of multiple distillation trays.

Mathematically, methods for solving a steady-state reaction-distillation system, Category Three, are much simpler than those for solving an unsteady-state distillation system, Category Two. However, thermodynamics, reaction kinetics and mass transfer problems involved in a system of Category Three are much more complicated. Two different types of reaction are usually associated in the reaction-distillation systems treated in the literature. One of them is the nonpolar hydrocarbon system represented by the work of Grayson and Streed in hydro-

cracking gas oil (25) and the work of Saito in alkylating meta-para xylene complex with an aluminum chloride catalyst (56). The other is the polar system typically represented by esterifications between alcohols and carboxylic acids.

It is rather astonishing that a close examination on all these known reaction-distillation systems including the most recent work of Babcock (3), reveals no fundamental concepts in describing the effects of chemical reaction on thermodynamic vapor-liquid equilibria, nor the effect of mass transfer on chemical reaction rate expressions.

According to Hougen, Watson and Ragatz (37), lack of ideal-solution behavior is attributed to chemical reaction and to differences in molecular size and polarity among the different components present. Therefore, the liquid activity coefficients with the effects of chemical reaction should be different from those without the effects of chemical reaction. However, Davies and Jeffreys (11) correlated a set of van Laar constants for liquid activity coefficient from "physical" vapor-liquid equilibrium data and then applied them into a system with chemical reaction, where the reaction can only occur at the presence of a catalyst (12). The term, "physical" is used to indicate that the equili-

brium data are measured without the effects of chemical reaction. Therefore, the term "chemical" can be used to represent the vapor-liquid equilibrium data measured with the effects of chemical reaction as well as to distinguish it from the above-mentioned "physical" vapor-liquid equilibrium data. The approach made by these researchers is then not appropriate.

A correlation of "chemical" vapor-liquid equilibrium data has been attempted by Hirata and Komatsu (32,33,34) for esterification between alcohols and carboxylic acids. However, the effects of chemical reaction on vapor-liquid equilibrium data were not mentioned. Grayson and Streed (25) correlated the vapor-liquid equilibria of the reaction products of hydrocracking gas oil, but they treated them only from the point of view of "physical" vapor-liquid equilibria. However, since their data for the correlation were obtained from "chemical" vapor-liquid equilibrium, their correlation may be properly reapplied to similar reaction systems. Their correlation may be used with care for a hydrocracking system which differs greatly from the system used by Grayson and Streed, for example, coal liquefaction systems. Different reaction systems exert different reaction effects on vapor-liquid equilibrium data.

The Grayson and Streed correlation has exactly the same framework as that used by the well known Chao and Seader (9) correlation, which is based on "physical" vapor-liquid equilibrium data. Therefore, a comparison between the two correlations may provide some useful information about the chemical effects. In order to gain a better understanding of the reaction effects on vapor-liquid equilibrium, a reaction-distillation system of esterification between acrylamide sulfate and ethyl alcohol is experimentally investigated in this work.

The major difference between this reaction system and the previously investigated esterification systems is that this has a much larger heat of reaction. It is selected in this work because it is anticipated that a large heat of reaction may promote the evaporation of immediately produced volatile compounds, and thus may provide some useful information about the reaction effects on vapor-liquid equilibrium. Correlations will also be made on the "chemical" vapor-liquid equilibrium data which are experimentally obtained in this study. The data and correlations should be new additions to chemical engineering literature.

The effects of mass transfer and reaction kinetics on the distillation with chemical reaction has been

completely ignored by previous authors. Therefore, some fundamental concepts about interface mass transfer with chemical reaction will be incorporated into the theoretical model. The application of Hatta's film theory (28,29,30,31) will be extended to the absorption of reactants as well as the evaporation of volatile products. Since the interface properties such as interface concentration, film thickness, interface area, etc., can not be measured directly, these effects will be correlated as a function of operating parameters.

It is found that Holland's recommended methods for solving Category Two problems are not suitable for solving an unsteady-state distillation problem with chemical reaction. New techniques are therefore developed in this study. Holland's techniques require three to four initially guessed values for obtaining convergent solutions for the bubble point (or the dew point) and the outlet vapor flow rate. The techniques developed by this study, however, require only one initially guessed value to obtain all the convergent solutions.

Theoretical solutions with respect to different system variables for the mathematical model of a semi-batch distillation accompanied by chemical reaction will be attempted first. Their qualitative characteristics

are analyzed. A good quantitative evaluation of the theoretical model can be made only if all the values of system parameters are accurately obtained from existing experimental data, or predicted from reliable correlation methods. Approaches for getting all the required data for a complicated reaction system such as the one used in this study, are presented and discussed. Finally, the applicability of the proposed theoretical model is tested with the experimental data obtained in this study.

Chapter 2 Literature Survey in the Related Fields

As mentioned in the previous chapter, this study is the first attempt at developing the mathematical model of unsteady-state distillation accompanied by chemical reaction (Category Four), there is no direct reference nor previous work in the literature which is related to this subject.

However, the proposed study requires knowledges in the following three major fields:

1. Vapor-liquid equilibria in presence of chemical reaction
2. Effects of mass transfer on reaction rate and vice versas
3. Mathematical methods for solving the problems of unsteady-state distillation.

Therefore, the literature survey has been made for the above three fields. Since the second item shown above will be presented in details later in Chapter 4, only literature on the other two items will be discussed in this chapter.

2.1 Vapor-Liquid Equilibria Accompanied by Chemical Reactions

The "chemical" vapor-liquid equilibria is that measured in the presence of chemical reaction. The conventional "physical" vapor-liquid equilibria does not involve any chemical reaction between components of the mixture.

There are only two types of correlations reported in the literature for "chemical" vapor-liquid equilibrium data. The first is represented by the Grayson and Streed correlation (25) which is developed for the vapor-liquid equilibrium data of hydrocracking heavy gas oil. The second type is represented by the Hirata and Komatsu correlation (32) which is based on the data of esterification between ethyl alcohol and acetic acid. The methods of correlations between the two systems are different because the Grayson-Streed correlation is for nonpolar hydrocarbon systems while the Hirata and Komatsu's correlation is for polar organic compounds. However, both methods have a similar basis in correlation of vapor-liquid equilibrium data, i.e., the correlation was made from multicomponent vapor-liquid equilibrium data experimentally obtained.

It is well known that a conventional correlation for "physical" vapor-liquid equilibrium data of a multicomponent system starts with the constituent binary systems and then applies appropriate mixing rules and

interaction parameters to combine these binary systems to a multicomponent system. For a system in the presence of chemical reaction, binary vapor-liquid equilibrium data for the two reactants can not be obtained because as soon as two reactants are mixed, the reaction products will immediately appear in the system. As reaction progresses, the molal quantity of a reactant changes from time to time if it is a batch process. For a continuous steady-state process a residence time of a reactant changes. These situations are different from "physical" vapor-liquid equilibrium, where combination of vapor and liquid molal quantities of a component is always equal to its original molal quantity.

In order to demonstrate the difference between the "physical" vapor-liquid equilibria and the "chemical" vapor-liquid equilibria, and the difference between the above two types of "chemical" vapor-liquid equilibria, the work of Grayson and Streed and that of Hirata and Komatsu are discussed briefly as follows.

2.1.1 Vapor-Liquid Equilibria Accompanied by Chemical Reaction for Nonpolar Hydrocarbon Systems

Grayson and Streed employed a steady-state continuous flow scheme to obtain vapor-liquid equilibrium data of

the heavy gas oil hydrocracking system. According to Grayson and Streed, the hydrocracking conditions must be at temperatures above 600 °F and pressure above 1000 psia (25). Although their equilibrium data are obtained in the presence of chemical reactions, they treated them as "physical" vapor-liquid equilibrium data by utilizing the framework of the well known Chao and Seader correlation (9). The Chao and Seader correlation is developed from the vapor-liquid equilibrium data of hydrogen and pure hydrocarbons. However, the hydrocarbon mixtures used by Grayson and Streed are the products obtained from hydrocracking heavy gas oil at different reaction conversions. Since the two correlations have the same framework, the difference between the two correlations may provide useful information on the effects of chemical reactions on the vapor-liquid equilibrium. Before comparing for the difference between the two correlations, it is necessary to present briefly the correlation methods employed by the above researchers.

Under the framework of Chao and Seader, or Grayson and Streed, the vapor-liquid equilibrium ratio, herein defined as equilibrium K-value for convenience, is calculated through a combination of three factors:

$$K = y/x = \frac{P_i^0 \gamma_i}{\phi_i} \quad (2-1)$$

where

ν_i^0 = fugacity coefficient of component i in the liquid phase

γ_i = activity coefficient of component i in the liquid phase

ϕ_i = vapor fugacity coefficient of component i in the vapor mixture.

The quantity ν_i^0 is a well-defined thermodynamic property under conditions where the component actually exists as a liquid. At conditions where the component cannot exist as a pure liquid but is dissolved in the liquid phase of a system, the quantity ν_i^0 becomes hypothetical. This hypothetical region exists when the system temperature is above the critical temperature of the component or when the system pressure is below the vapor pressure of the component. A liquid fugacity coefficient correlation for this hypothetical region in addition to the existing subcritical region was first developed by Chao and Seader from experimental "physical" vapor-liquid equilibrium data at moderate temperatures, i.e., the reduced temperatures of from 0.5 to 1.3 or temperatures from -100 °F to 500 °F as cited in their paper (9). Their correlations give an average error of 8.7 % for 2696 data points.

Grayson and Streed employed the same correlation

methods to correlate their high temperature "chemical" vapor-liquid equilibrium data in addition to the Chao and Seader's low temperature data. The average error of their correlation is 7.0 %.

Determination of the liquid fugacity coefficient involves solving Equation (2-1) in the form:

$$\nu_i^0 = \frac{K_i \phi_i}{\gamma_i} \quad (2-1a)$$

As mentioned previously, K_i are experimental data, so ν_i^0 can be calculated only when ϕ_i and γ_i can be determined by other methods. The above authors computed ϕ_i from the Redlich-Kwong correlation (54) and γ_i from the Hildebrand correlation (37). The Redlich-Kwong equation requires only two constants for each component. They are critical temperature, T_{c_i} and critical pressure, P_{c_i} . Any two-constant equation of state cannot be expected to yield great accuracy. Therefore, usage of the Chao and Seader correlation is limited to the following conditions:

Pressures: up to 2000 psia

Temperatures:

Hydrogen and Methane: -100 to 500 °F

All hydrocarbons
except methane } : $T_r = 0.5$ to 1.3

Hildebrand correlation for liquid activity coefficient

is derived from the regular solution theory (37). According to the regular solution theory, the activity coefficient of component i in a multicomponent mixture is given

$$\text{by} \quad \ln \gamma_i = v_i (\delta_i - \bar{\delta})^2 / RT \quad (2-4)$$

where v_i is the liquid molar volume, δ_i is the solubility parameter (the square root of the cohesive energy density), and $\bar{\delta}$ is the volume-fraction average solubility parameter for the solution.

Since regular solutions are characterized by the absence of any specific physical interactions between molecules, the theory should apply only to solutions of nonionic, nonpolar, or slightly polar molecules. According to Hougen, Watson and Ragatz(37), liquid activity coefficient is affected by molecular size and polarity as well as chemical reaction. Therefore, this theory does not apply to a system which involves any chemical interactions in producing new molecules from reactant molecules. Simply using the regular solution theory to estimate liquid activity coefficient for the reaction system of hydrocracking of heavy gas oil does not take into the account of the effects of chemical reaction on liquid activity coefficient. However, the calculated liquid fugacity coefficient, μ_i^0 using the Grayson-Streed "chemical" vapor-liquid equilibrium data and Equation (2-1a) includes the effects of chemical reaction. After the liquid fugacity coefficients μ_i^0 are calculated

from Equation (2-1a) based on the experimental data, they are then correlated within the frame work of Pitzer's modified form of the principle of corresponding states. Accordingly, ν_i^0 is given by

$$\log \nu_i^0 = \log \nu_i^{(0)} + \omega \log \nu_i^{(1)} \quad (2-5)$$

The first term on the right-hand side gives the fugacity coefficient of simple fluids characterized by a zero value of the acentric factor. The second term accounts for departure of properties of real fluids from those of the simple fluids.

The two quantities $\nu_i^{(0)}$ and $\nu_i^{(1)}$ are dependent only on reduced temperature and reduced pressure. They are fitted with approximating functions. The quantity $\nu_i^{(0)}$ is given by

$$\begin{aligned} \log \nu_i^{(0)} = & A_0 + A_1 / T_r + A_2 T_r + A_3 T_r^2 + A_4 T_r^3 + (A_5 + \\ & A_6 T_r + A_7 T_r^2) P_r + (A_8 + A_9 T_r) P_r - \log P_r \end{aligned} \quad (2-6)$$

where A_0 through A_9 are empirically fitted constants. The quantity $\nu_i^{(1)}$ is given by

$$\begin{aligned} \log \nu_i^{(1)} = & -4.23898 + 8.65808 T_r - 1.2206 / T_r - 3.15224 \\ & T_r^3 - 0.025 (P_r - 0.06) \end{aligned} \quad (2-7)$$

The coefficients in Equation (2-6) for the Chao and Seader correlation are different from those for the Grayson and Streed correlation, while Equation (2-7) is applicable to both correlations except that T_r

must be set equal to unity whenever it exceeds one for the Grayson and Streed correlation. The constants for Equation (2-6) for the two correlations are given in Appendix A.11.

The "chemical" vapor-liquid equilibrium data by Grayson and Streed were obtained at temperatures greater than the upper temperature limits of the Chao-Seader correlation, and at pressures from 1000 psia to 3000 psia. The suitable checking points to compare the two correlations are then at temperatures close to 500 °F or the reduced temperature of 1.3, and at pressures between 1000 psia and 2000 psia. As the two correlations for C_{2+} hydrocarbons are generalized functions, a properly selected compound can be used to represent the general behavior of the two correlations. It is found that isobutane is an appropriate compound because at 500 °F, it has a reduced temperature very close to 1.3.

For hydrogen and methane, both correlations are obtained on the basis that the acentric factors for the two components are equal to zero. Each of the two components has its individual constants for Equation (2-6). Thus, the comparisons are made for the three compounds, namely hydrogen, methane and isobutane.

Table 2.1 lists the comparison between the two

correlations for the liquid fugacity coefficients, γ_i^0 , of hydrogen, methane and isobutane at 500 °F.

Table 2.1 Comparison of Liquid Fugacities determined by (C-S) Correlation and the Grayson Streed Correlation for γ_i^0 at 500 °F for Hydrogen, Methane and Isobutane

	<u>at 1000 psia</u>			<u>at 2000 psia</u>		
	C-S	G-S	% Dev.	C-S	G-S	% Dev.
Hydrogen	4.3	5.0	16	2.5	2.8	12
Methane	3.05	5.0	64	1.51	2.75	80
Isobutane	0.626	1.02	63	0.265	0.68	157

Small deviation between the two correlations is observed for hydrogen. However, for methane and isobutane, the Grayson-Streed correlation gives much higher liquid fugacity coefficients than those by the Chao-Seader correlation. For an even clearer illustration of these discrepancies, the liquid fugacity coefficients for methane at 1000 psia and 2000 psia are plotted as a function of temperature and shown in Fig. 2.1.

As mentioned previously, the Grayson-Streed correlation is obtained on the basis of both their own high temperature data and the Chao and Seader low temperature data. Therefore, it is natural that the two correlations

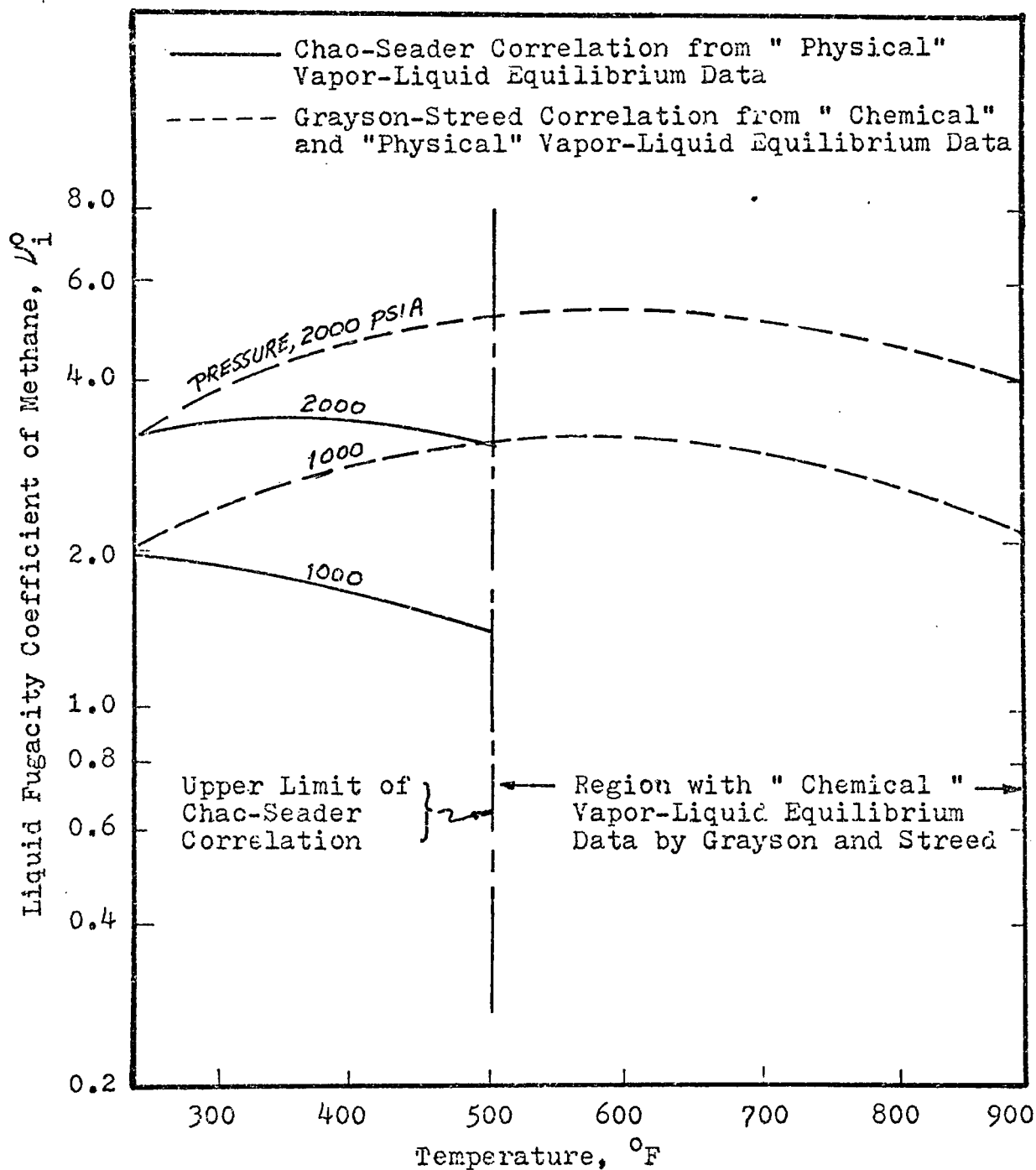
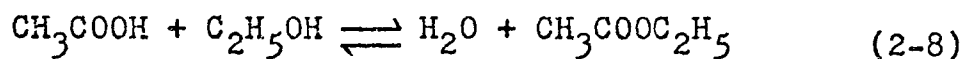


Fig. 2.1 Comparison of ν_i^o for Methane between Chao-Seader Correlation and Grayson-Streed Correlation

have good agreements at low temperature. However, at higher temperatures near the upper limit of the Chao-Seader correlation, γ_i^0 calculated by Grayson and Streed correlation is appreciably higher than that obtained by the Chao-Seader correlation, implying a positive effect of chemical reaction on the vapor-liquid equilibrium K-values for methane. Further discussion on this positive effect of chemical reaction on the vapor-liquid equilibrium K-values will be presented later in Chapter 6 along with the experimental results obtained by this work.

2.1.2 Vapor-Liquid Equilibria Accompanied by Chemical Reaction for Polar System

The other available correlation for "chemical" vapor-liquid equilibria was reported by Hirata and Komatsu (32) in 1966 for the following esterification reaction between ethyl alcohol and acetic acid:



Their experiments were performed in an Othmer Still at atmospheric pressure. Thus, their system is a batch process. Like the conventional measurement for "physical" vapor-liquid equilibrium data, a vapor sample is obtained as condensate by using a small overhead condenser while the liquid sample is directly obtained from the liquid

holdup. When a vapor sample is not taken, the vapor condensate is returned to the liquid holdup as a reflux stream.

This technique is good for measurement of "physical" vapor-liquid equilibrium data because of the continuous refluxing which enables both the liquid and vapor compositions to reach at their steady-state values as well as to be in equilibrium. However, for obtaining "chemical" vapor-liquid equilibrium data, this technique requires a special attention because the liquid composition changes continuously until chemical equilibrium is reached. The vapor sample in the condensate trap is actually in equilibrium with the liquid mixture of sometime ago when the condensed vapor just left the liquid surface. In other words, there is a time lag between vapor sampling and liquid sampling. If the heat flux of the Othmer Still is small, the vapor flow rate will be small which induces a large time lag between the vapor sample and the liquid sample obtained. This time-inconsistent-vapor and liquid samples will, of course, give erroneous results. In general, the faster the reaction or the smaller the vapor flow rate, the greater the effects of the time lag. Since the heat flux to their Othmer Still was not given, and since consideration of reaction kinetics was not made in their paper, it is impossible to check the effect of time lag on their vapor-liquid equilibrium data.

In a batch "chemical" vapor-liquid equilibrium system, the liquid composition changes continuously as the reaction proceeds. Thus, the bubble point of the liquid mixture also varies as a function of time at isobaric operation. The instantaneous reaction rate of the system depends not only on the concentrations of reactants but also on the temperature. A conventional batch measurement of reaction rate in the liquid phase can be made isothermally at a subcooled temperature. At a subcooled temperature, an isothermal condition may be mechanically controlled by adding heat into or removing heat from the system. However, in a "chemical" vapor-liquid equilibrium system, temperature varies as the composition is changed by chemical reaction. Thermal control over a boiling reaction system can change the vapor flow rate but can not adjust the liquid composition to reach the exactly desired bubble point of a batch mixture.

In correlating their "chemical" vapor-liquid equilibrium data, Hirata and Komatsu did not use standard thermodynamic procedures such as the van Laar Equation, the Margules equation, etc., for liquid activity coefficient for polar organic compounds. Instead, for the least volatile component, acetic acid, they correlate its K-value as a linear function of the bubble point:

$$K_1 = 0.0225 t - 1.666, \quad t > 74 \text{ } ^\circ\text{C}$$

$$K_1 = 0.001, \quad t \leq 74 \text{ } ^\circ\text{C} \quad (2-9)$$

where t is the bubble point in $^\circ\text{C}$. The above equation implies that the K -value of acetic acid is not sensitive to the variation in the liquid composition.

For the other three volatile components, ethyl alcohol, water and ethyl acetate, their K -values are experimentally proven to be dependent on both temperature and liquid composition in a peculiar way.

The measured instantaneous "chemical" vapor-liquid equilibrium K -values for the three volatile components are all linearly proportional to the reciprocal of the absolute temperature of the instantaneously measured liquid bubble point. The initial composition of a mixture must satisfy the hypothetical zero conversion which means that at least one product, water or ethyl acetate, should not be present initially. Moreover, their results show that slopes for the these linear equations are same not only for all zero hypothetical conversions but also for all three volatile components. The correlating equation for the K -values of ethyl alcohol, water and ethyl acetate can then be given as follows:

$$\log K_i = - \frac{2300}{T} + B_i \quad (2-10)$$

where B_i is only a function of the initial composition of a

volatile component. For example, for a mixture of which the initial liquid composition is:

$$\begin{aligned}x_1 \text{ (acetic acid)} &= 0.49 \\x_2 \text{ (ethyl alcohol)} &= 0.44 \\x_3 \text{ (water)} &= 0.07 \\x_4 \text{ (ethyl acetate)} &= 0. ,\end{aligned}$$

the corresponding B_i 's are

$$\begin{aligned}B_2 &= 6.492 \\B_3 &= 6.438 \\B_4 &= 6.704 .\end{aligned}$$

Each calculated B_i is then plotted as a function of liquid mole fraction. For example, B_2 is plotted as a function of x_2 for each constant x_4 for all the experimental runs with $x_3=0$. Such plots can be seen very arbitrary because B_2 can also be plotted as a function of any combinations of x_1 , x_2 , x_3 and x_4 . Furthermore, to convert such a graphical representation into a computer program, requires tedious curve fittings and interpolations between any two constant x_i 's. Therefore, the correlation used by these authours for K_2 , K_3 and K_4 are impractical for computer application.

In this study, the reaction system is also composed of polar compounds. However, a different method based on the standard thermodynamic procedures will be used to

correlate the vapor-liquid equilibrium data. The details are discussed in Chapter 6.

2.2 Unsteady-State Distillation

The beginning of the quantitative analysis of the unsteady-state operation of a distillation column was marked by the work of Marshall and Pigford in 1947 (47), who formulated the differential equations that describe the transient behavior of a plate of a distillation column. These authors demonstrated the use of Laplace transforms for solving various types of distillation problems. The following simplifying assumptions were made in order to obtain analytical solutions.

- (1) linear vapor-liquid equilibrium relationship of the form $y=mx+b$, where m and b depend only upon the identity of a component
- (2) total liquid and vapor flow rates are independent of time
- (3) liquid holdup on a tray is independent of time
- (4) vapor holdup is negligible
- (5) a complete liquid mixing on a tray
- (6) a binary system

In 1950, Lapidus and Amundson (40) extended the method of Marshall and Pigford to obtain transient response of an absorber. A single volatile component was

transferred between two inert phases. The carrier liquid phase was taken to be nonvolatile and the carrier gas was taken to be insoluble in the liquid phase. Also, a linear equilibrium relationship that was independent of temperature was employed. Later in 1953, Acrivos and Amundson (1) obtained solutions to this same problem by use of an analog computer. In addition to linear equilibrium relationships, they also employed nonlinear equilibrium relationship for their analog computer simulation.

Since then many workers had proposed different methods for solving various types of distillation problems, but the number of assumptions made above were not reduced until 1964 when Waggoner applied a combined scheme of the Thiele and Geddes method with Holland's θ method of convergence (59).

In Waggoner's method, any type of vapor-liquid equilibrium relationship can be used and the total molal vapor or the total liquid flow rate is not necessary to be constant. The variation of total flow rates reflects the effect of the energy balance on each tray representing a more realistic situation. However, the following simplified assumptions are still required:

- (1) Constant liquid holdup
- (2) Negligible vapor holdup

(3) $Y_i = K_i x_i$ for an ideal tray

$Y_i = E_i^0 K_i x_i$ for a non-ideal tray

where E_i^0 = vapor tray efficiency as defined by Holland.

In 1966, Holland compiled major unsteady-state distillation problems in his textbook (36) and recommended the uses of an implicit method for integration and his θ method for convergence. Since his method is the most general approach for solving an unsteady-state distillation problem, it is briefly reviewed here. It is noted, however, that the problems treated by him are the distillation in absence of chemical reaction.

A system of unsteady-state distillation with the above three assumptions can be illustrated by Fig. 2.2.

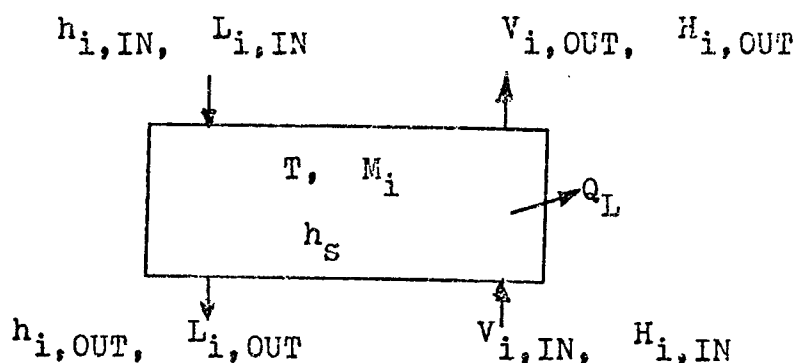


Fig. 2.2. Holland's Model for Unsteady-State Distillation

The unsteady-state component material balance equation can be represented by Equation (2-11)

$$\frac{dM_i}{dt} = L_{i,IN} + V_{i,IN} - L_{i,OUT} - V_{i,OUT},$$

$$\left[\begin{array}{c} \text{Rate of} \\ \text{Accumulation} \\ \text{of Mass in} \\ \text{Liquid Holdup} \end{array} \right] = \left[\begin{array}{c} \text{Inlet} \\ \text{Liquid} \\ \text{Flow} \\ \text{Rate} \end{array} \right] + \left[\begin{array}{c} \text{Inlet} \\ \text{vapor} \\ \text{Flow} \\ \text{Rate} \end{array} \right] - \left[\begin{array}{c} \text{Outlet} \\ \text{Liquid} \\ \text{Flow} \\ \text{Rate} \end{array} \right] + \left[\begin{array}{c} \text{Outlet} \\ \text{Vapor} \\ \text{Flow} \\ \text{Rate} \end{array} \right]$$

$$i=1, \dots, n \quad (2-11)$$

where

n = number of components

L_i = molal liquid flow rate for component i

V_i = molal vapor flow rate for component i

M_i = molal quantity of component i in the liquid holdup

The overall material balance is written as

$$\frac{dM}{dt} = L_{IN} + V_{IN} - L_{OUT} - V_{OUT}$$

$$\left[\begin{array}{c} \text{Rate of} \\ \text{Accumulation} \\ \text{of total} \\ \text{Mass In the} \\ \text{Liquid Holdup} \end{array} \right] = \left[\begin{array}{c} \text{Total} \\ \text{Inlet} \\ \text{Liquid} \\ \text{Flow} \\ \text{Rate} \end{array} \right] + \left[\begin{array}{c} \text{Total} \\ \text{Inlet} \\ \text{Vapor} \\ \text{Flow} \\ \text{Rate} \end{array} \right] - \left[\begin{array}{c} \text{Total} \\ \text{Outlet} \\ \text{Liquid} \\ \text{Flow} \\ \text{Rate} \end{array} \right] - \left[\begin{array}{c} \text{Total} \\ \text{Outlet} \\ \text{Vapor} \\ \text{Flow} \\ \text{Rate} \end{array} \right]$$

$$(2-12)$$

where

L_{IN} = Total liquid inlet molal flow rate

V_{IN} = Total vapor inlet molal flow rate

L_{OUT} = Total liquid outlet molal flow rate

V_{OUT} = Total vapor outlet molal flow rate

$M = \sum_{i=1}^n M_i$ = Total molal liquid holdup on the tray

In his applications, Holland assumed that the liquid holdup (either molal or volumetric) is constant.

If taking constant molal holdup case as example, the term, dM/dt , is equal to zero, and Equation (2-12) is reduced to

$$L_{IN} + V_{IN} - L_{OUT} - V_{OUT} = 0 \quad (2-13)$$

The unsteady-state overall energy balance can be expressed by

$$\begin{aligned} \frac{d}{dt} [Mh_s] &= L_{IN}h_{IN} + V_{IN}h_{IN} - L_{OUT}h_{OUT} \\ \left[\begin{array}{l} \text{Rate of} \\ \text{Accumulation} \\ \text{of Energy} \\ \text{in the} \\ \text{System} \end{array} \right] &= \left[\begin{array}{l} \text{Rate of Inlet} \\ \text{Energy} \\ \text{with} \\ \text{Inlet Liquid} \\ \text{Flow} \end{array} \right] + \left[\begin{array}{l} \text{Rate of} \\ \text{Inlet} \\ \text{Energy} \\ \text{with} \\ \text{Inlet} \\ \text{Vapor} \\ \text{Flow} \end{array} \right] - \left[\begin{array}{l} \text{Rate of} \\ \text{Outlet} \\ \text{Energy} \\ \text{with} \\ \text{Outlet} \\ \text{Liquid} \\ \text{Flow} \end{array} \right] \\ &\quad - V_{OUT}h_{OUT} - Q_L \quad (2-14) \end{aligned}$$

$$- \begin{bmatrix} \text{Rate of Out-} \\ \text{let Energy} \\ \text{with Outlet} \\ \text{Vapor Flow} \end{bmatrix} - \begin{bmatrix} \text{Rate of} \\ \text{Heat Loss} \\ \text{to the} \\ \text{Surrounding} \end{bmatrix}$$

where:

h_{IN} = Inlet liquid enthalpy per mole

h_{OUT} = Outlet liquid enthalpy per mole

H_{IN} = Inlet vapor enthalpy per mole

h_S = Enthalpy of holdup on the tray (assuming negligible vapor holdup) per mole

Q_L = Net heat transfer rate from the system to the surrounding

It is noted that no heat of solution is considered in Holland's model. No analytical methods have been available for solving an unsteady-state distillation, with variable total flow rates and exact vapor-liquid relationships. Thus, they have been solved by numerical methods.

According to Holland, the following numerical methods can be applied to solve an unsteady-state distillation problem. They may be divided into three general classes:

(1) Predictor methods

(a) Euler's method

(b) Runge-Kutta method

(2) Predictor-Corrector Method

(a) Two-points Formulas

(b) Milne's Methods

b.1. Milne's Method I (Three-point Formulas)

b.2. Milne's Method II (Five-point Formulas)

(3) Implicit and Corrector Methods

(a) Implicit Methods

(b) Corrector Methods

Detailed discussions on the above methods are given in Holland's book (36). Since this study deals with an unsteady-state distillation accompanied by chemical reaction for a single distillation tray, the following discussion will be limited to Holland's method for a single distillation tray without chemical reaction. His method will be compared later to the methods developed by this work.

Since there are no differential equations which can represent the outlet vapor rate, V_{OUT} , and the system temperature, T , these two quantities are solved by trial-and-error for each integration step. Holland's method employs two θ 's for such an unsteady-state distillation system. They are defined as follows.

$$\left(\frac{L_{i,OUT}}{V_{i,OUT}} \right)_{co} = \theta_{-1} \left(\frac{L_{i,OUT}}{V_{i,OUT}} \right)_{ca} \quad (2-15)$$

$$\left(\frac{M_i}{V_{i,OUT}} \right)_{co} = \theta_o \left(\frac{M_i}{V_{i,OUT}} \right)_{ca} \quad (2-16)$$

where

()_{ca} : calculated value

()_{co} : corrected value after multiplication
of θ 's

θ_{-1} and θ_o are two assumed values. Methods of selecting these two θ 's for convergent solutions will be discussed later in this section. The formulation for the two calculated quantities, $(L_{i,OUT}/V_{i,OUT})_{ca}$ and $(M_i/V_{i,OUT})_{ca}$, shown in the above two equations is discussed first as follows.

The integrated form of Equation (2-11) can be expressed by

$$\begin{aligned} \int_{t_n}^{t_n + \Delta t} (L_{i,IN} + V_{i,IN} - L_{i,OUT} - V_{i,OUT}) dt \\ = M_i \Big|_{t_n + \Delta t} - M_i \Big|_{t_n} \end{aligned} \quad (2-17)$$

If the integration is approximated by the implicit method, as recommended by Holland, Equation (2-17) is reduced to

$$\begin{aligned} L_{i,IN} + V_{i,IN} - L_{i,OUT} - V_{i,OUT} + \sigma (L_{i,IN}^o + V_{i,IN}^o - L_{i,OUT}^o \\ - V_{i,OUT}^o) = \frac{1}{\mu \Delta t} (M_i - M_i^o) \end{aligned}$$

which may be solved for $V_{i,OUT}$ to give

$$V_{i,OUT} = \left\{ L_{i,IN} + V_{i,IN} + \sigma(L_{i,IN}^0 + V_{i,IN}^0 - L_{i,OUT}^0 - V_{i,OUT}^0) + (M_i^0/V_{i,OUT}) \right\} / \left\{ 1 + (L_{i,OUT}/V_{i,OUT}) + (1/\mu \Delta t) (M_i/V_{i,OUT}) \right\} \quad (2-18)$$

where

μ = multiplier for the implicit method ($0 \leq \mu \leq 1$)

Δt = size of an integration step

$\sigma = (1-\mu)/\mu$

t_n = time at the end of nth integration step

By the definitions, the following relationships can be established.

$$\frac{L_{i,OUT}}{V_{i,OUT}} = \frac{x_i L_{OUT}}{y_i V_{OUT}} = \frac{L_{OUT}}{K_i V_{OUT}} \quad (2-19)$$

and

$$\frac{M_i}{V_{i,OUT}} = \frac{x_i M}{y_i V_{OUT}} = \frac{M}{K_i V_{OUT}} \quad (2-20)$$

where

x_i = liquid mole fraction of component i

y_i = vapor mole fraction of component i

$K_i = y_i/x_i$ = vapor-liquid equilibrium ratio of component i

It is noted that only an ideal tray will be discussed here, therefore the vaporization efficiency E_i^0 is set to unity. For an assumed outlet vapor flow rate, $(V_{OUT})_a$,

the corresponding assumed outlet liquid flow rate,

$(L_{OUT})_a$, can be calculated from Equation (2-13).

Substituting Equations (2-19) and (2-20), and the above two assumed values into Equation (2-18) gives the calculated outlet vapor flow rate of component i as follows:

$$\begin{aligned} (V_{i,OUT})_{ca} = & \left\{ L_{i,IN} + V_{i,IN} + \sigma(L_{i,IN}^O + V_{i,IN}^O \right. \\ & \left. - L_{i,OUT}^O - V_{i,OUT}^O) + (M_i^O/\mu \Delta t) \right\} \\ & / \left\{ 1 + (L_{OUT}/V_{OUT})_a (1/K_i) + \right. \\ & \left. (1/\mu \Delta t) (M/V_{OUT})_a (1/K_i) \right\} \end{aligned} \quad (2-21)$$

The corresponding values of $L_{i,OUT}$ and M_i can be calculated by use of the following relationships, after $(V_{i,OUT})_{ca}$ has been determined.

$$L_{i,OUT} = V_{i,OUT} A_i \quad (2-22)$$

$$M_i = (M/L_{OUT}) L_{i,OUT} \quad (2-23)$$

where

$$A_i = L_{OUT}/K_i = \text{absorption factor} \quad (2-24)$$

The above calculated values can now be used to determine the two corrected molal ratios, $(L_{i,OUT}/V_{i,OUT})_{co}$ and $(M_i/V_{i,OUT})_{co}$, by Equations (2-15) and (2-16). If these two molal ratios are substituted into Equation (2-18), a corresponding corrected outlet vapor flow rate,

$(V_{i,OUT})_{co}$ can be calculated. If Equations (2-15) and

(2-16) are substituted into Equation (2-18), the corrected value, $(V_{i,OUT})_{co}$, can then be directly expressed as a function of all the calculated values determined from Equations (2-21) through (2-24) as follows.

$$(V_{i,OUT})_{co} = \left\{ L_{i,IN} + V_{i,IN} + \sigma(L_{i,IN}^o + V_{i,IN}^o - L_{i,OUT}^o - V_{i,OUT}^o) + (M_i^o/\mu\Delta t) \right\} / \left\{ 1 + \theta_{-1}(L_{i,OUT}/V_{i,OUT})_{ca} + \theta_o(1/\mu\Delta t)(M_i/V_{i,OUT}) \right\} \quad (2-25)$$

Again, the corrected $L_{i,OUT}$ and M_i can be determined from Equations (2-22) and (2-23). These corrected values, $(V_{i,OUT})_{co}$, $(L_{i,OUT})_{co}$ and $(M_i)_{co}$ can be considered as convergent solutions if and only if they can satisfy the criteria for a specified set of operating conditions. If the operating pressure is assumed to be constant throughout an unsteady-state operation, the criterion for a convergent solution is established on the basis of temperature requirement. The criterion can be an isothermal or a nonisothermal operation.

a. Isothermal Distillation Tray

There are two θ 's to be determined. Therefore, two criteria are required for testing convergent solutions. For an isothermal distillation tray, the first

criterion is that the vapor leaves at its dew point, which is constant throughout an unsteady-state operation. Mathematically, this criterion can be represented by

$$\frac{\sum_{i=1}^n (V_{i,OUT})_{co} / K_i}{\sum_{i=1}^n (V_{i,OUT})_{co}} = 1 \quad (2-26)$$

The second criterion is that the summation of all the corrected molal quantities of individual component in the liquid hold-up must be equal to the specified constant total holdup:

$$\sum_{i=1}^n (M_i)_{co} = M \quad (2-27)$$

Define the difference between both sides of Equation (2-26) as

$$g_{-1}(\theta_{-1}, \theta_o) = \sum_{i=1}^n (V_{i,OUT})_{co} \left[1 - \frac{1}{K_i} \right] \quad (2-28)$$

and that of Equation (2-27) as

$$g_o(\theta_{-1}, \theta_o) = \sum_{i=1}^n (M_i)_{co} - M. \quad (2-29)$$

The two θ 's having convergent solutions are then the values which can satisfy $g_{-1} = g_o = 0$, simultaneously. The values of θ_{-1} and θ_o are found by use of the Newton-Raphson Method. In this method, the following equations are solved repeatedly for θ_{-1} and θ_o until a set of values for θ_{-1} and θ_o of the desired accuracy is obtained.

$$g_{-1} + \frac{\partial g_{-1}}{\partial \theta_{-1}} \Delta \theta_{-1} + \frac{\partial g_{-1}}{\partial \theta_o} \Delta \theta_o = 0 \quad (2-30)$$

$$g_o + \frac{\partial g_o}{\partial \theta_{-1}} \Delta \theta_{-1} + \frac{\partial g_o}{\partial \theta_o} \Delta \theta_o = 0 \quad (2-31)$$

where

$\Delta \theta_{-1} = \theta_{-1,z+1} - \theta_{-1,z}$ and z denotes the trial number, and

$$\Delta \theta_o = \theta_{o,z+1} - \theta_{o,z}$$

To initiate the calculational procedure, three values must be assumed by utilizing Holland's method. They are V_{OUT} , θ_{-1} and θ_o . For every assumed value of V_{OUT} , there is a corresponding value of L_{OUT} found by Equation (2-13) to give $(L_{OUT}/V_{OUT})_a$. Then, the corresponding values of $(L_{i,OUT}/V_{i,OUT})_{ca}$ and $(M_i/V_{i,OUT})_{ca}$ are found by use of Equations (2-15) and (2-17). These quantities are held fixed at these values throughout the succession of trials required to find the θ 's for the given time period. Let $\theta_{-1,z}$ and $\theta_{o,z}$ be the two θ 's at the iteration number equal to z . The functions g_{-1} and g_o and their derivatives are then evaluated at this iteration step. The partial derivatives may be evaluated at the assumed set $(\theta_{-1,z}, \theta_{o,z})$ by use of analytical expressions for these quantities. For example,

$$\frac{\partial g_{-1}}{\partial \theta_{-1}} = - \sum_{i=1}^n \left\{ (L_{i,OUT}/V_{i,OUT})_{ca} \left[L_{i,IN} + V_{i,IN} + \sigma(L_{i,IN}^o + V_{i,IN}^o - V_{i,OUT}^o - L_{i,OUT}^o) + (M_i^o/u \Delta t) \right] \right\} /$$

$$\left\{ 1 + \theta_{-1} (L_{i,OUT}/V_{i,OUT})_{ca} + \theta_0 \left[(1/\mu \Delta t) (M_i/V_{i,OUT})_{ca} \right] \right\}$$

(2-32)

After θ_{-1} and θ_0 have been determined, the θ 's to be assumed for the next trial are given by

$$\theta_{-1,z+1} = \theta_{-1,z} + \Delta \theta_{-1} \quad (2-33)$$

$$\theta_{0,z+1} = \theta_{0,z} + \Delta \theta_0 \quad (2-34)$$

The above procedures are repeated until $|g_{-1}|$ and $|g_0|$ are both less than allowable error limits. The finally corrected values of $V_{i,OUT}$, $L_{i,OUT}$ and M_i are then the convergent solutions for this integration step. These convergent solutions become the initial conditions of the next integration step. Solutions for the next integration step can be obtained by following exactly the same trial-and-error procedures stated above.

The solution for an unsteady-state isothermal distillation has been discussed as above. Now, let's discuss the case for a nonisothermal distillation tray.

b. Nonisothermal Distillation Tray

For a nonisothermal distillation tray two criteria are also required for convergent solution because the same two θ 's are unknowns. One of the two criteria is the same as Equation (2-23) and repeated as follows:

$$g_o (\theta_{-1}, \theta_o) = \sum_{i=1}^n (M_i)_{co} - M \quad (2-23)$$

The other must be setup from the energy balance, Equation (2-14), because temperature is an unknown. In an integrated form, Equation (2-14) can be expressed as

$$\int_{t_n}^{t_n + \Delta t} (L_{IN} h_{IN} + V_{IN} H_{IN} - L_{OUT} h_{OUT} - V_{OUT} H_{OUT} - Q_L) dt \\ = M h_s \Big|_{t_n + \Delta t} - M h_s \Big|_{t_n}$$

When the integral appearing on the left-hand side of this equation is approximated by use of the implicit method, the following result is obtained.

$$(L_{IN} h_{IN} + V_{IN} H_{IN} - L_{OUT} h_{OUT} - V_{OUT} H_{OUT} - Q_L) + \sigma [L_{IN}^o h_{IN}^o \\ + V_{IN}^o H_{IN}^o - L_{OUT}^o h_{OUT}^o - V_{OUT}^o H_{OUT}^o - Q_L^o] \\ = \frac{1}{\mu \Delta t} [M h_s - M^o h_s^o] \quad (2-35)$$

The instantaneous temperature of the system is then the temperature that can satisfy the above energy balance equation. Let $g_{-1} (\theta_{-1}, \theta_o)$ be the difference between both sides of Equation (2-35) with outlet vapor and liquid rates expressed as corrected values of $(V_{OUT})_{co}$ and $(L_{OUT})_{co}$.

Then,

$$g_{-1} (\theta_{-1}, \theta_o) = L_{IN} h_{IN} + V_{IN} H_{IN} - (L_{OUT})_{co} h_{OUT} - (V_{OUT})_{co}$$

$$H_{OUT} - Q_L + \sigma [L_{IN}^o h_{IN}^o + V_{IN}^o H_{IN}^o - L_{OUT}^o h_{OUT}^o - V_{OUT}^o H_{OUT}^o$$

$$- Q_L^o] - \frac{1}{\Delta t} [Mh_s - M^o h_s^o] \quad (2-36)$$

The two corrected values, $(V_{OUT})_{co}$ and $(L_{OUT})_{co}$ can be calculated by following exactly the same procedures as those used for the isothermal case as described previously. The system temperature at the elapsed time of an integration step is then obtained by trial-and-error until the following criterion is satisfied.

$$g_{-1}(\theta_{-1}, \theta_o) = 0. \quad (2-37)$$

The trial-and-error procedures are described below.

For an assumed set of $\theta_{-1}, \theta_o, V_{OUT}$ and T , there are the corresponding set of $(M_i)_{co}$ and $(V_{i,OUT})_{co}$.

The corrected vapor and liquid mole fractions can then be determined by the following definitions:

$$(x_i)_{co} = \frac{(M_i)_{co}}{M} \quad (2-38)$$

and

$$(y_i)_{co} = \frac{(V_{i,OUT})_{co}}{\sum (V_{i,OUT})_{co}} \quad (2-39)$$

From these corrected vapor-liquid relationships, a corresponding temperature can then be determined from the vapor-liquid equilibrium relationship of the system. This newly determined temperature becomes the assumed temperature for the next trial-and-error calculations. As soon as two convergent θ 's are found, the latest $(V_{OUT})_{co}$,

$(M_i)_{co}$ and assumed temperature become the convergent solutions for this integration step for a nonisothermal operation. If the heat loss term, Q_L is zero, the nonisothermal distillation tray is reduced to an adiabatic distillation tray. For an unsteady-state adiabatic distillation tray, its criteria of convergence and the method of solution are exactly the same as those for an unsteady-state nonisothermal distillation tray as presented here.

Although Holland's θ method is applicable for solving an unsteady-state distillation without chemical reaction, it can not be used to solve a general problem of unsteady-state distillation accompanied by chemical reactions. According to Equation (2-18), the basic concept of Holland's method is to obtain vapor-liquid molal ratio for each component so that the θ method can be used according to the definitions of Equations (2-15) and (2-16). In order to obtain such a molal ratio, all the molal quantities which are dependent variables must be linear. Otherwise, a form of $\frac{M_i M_j}{V_{i,OUT}}$, $\frac{(L_{i,OUT})^n}{V_{i,OUT}}$, or $\frac{(M_i)^m}{V_{i,OUT}}$ will be obtained, where n and m are integers unequal to unity, and i and j are different component identity numbers. The above nonlinear forms are some of the possible reaction rate terms. Therefore, only unsteady-state distillation system with first-order reaction can be solved

by the θ method. However, all the known practical distillation accompanied by chemical reaction systems have reaction orders equal to two or higher and Holland's θ method is then not applicable. In Chapter 4 a new method is developed to solve a general problem of unsteady-state distillation accompanied by chemical reaction. Furthermore, Holland's θ method requires four initially guessed values. They are outlet vapor flow rate, V_{OUT} , temperature, T , θ_0 and θ_{-1} . The new method developed here will require only one initially guessed value, which is the outlet vapor flow rate, V_{OUT} .

Chapter 3 Mathematic Model for Unsteady-State Distillation with Chemical Reaction

3.1 General Mathematic Model for Unsteady-State Distillation with Chemical Reaction

As discussed earlier Holland (36) has made an intensive investigation on unsteady-state distillation. However, his study has limited to those systems where no chemical reaction takes place. Therefore, it is believed that this study is the first attempt to develop a general mathematic model for unsteady-state distillation accompanied by chemical reaction.

A system of unsteady-state distillation accompanied by chemical reaction is best illustrated by Fig. 3.1.

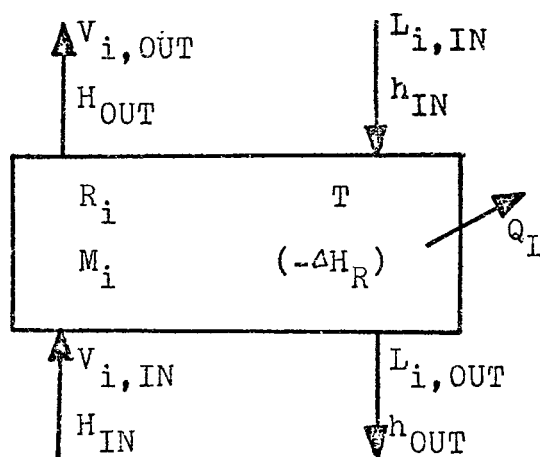


Fig. 3.1 Material and Energy Balance Around a
Distillation Tray with Chemical Reactions

The following assumptions are made for developing the mathematic model.

- (1) The liquid phase is completely mixed.
- (2) The vapor holdup on the tray is negligibly small.
- (3) The reactions occur only in the liquid film or the bulkphase liquid.

The unsteady-state material balance for component i can be expressed as

$$\frac{dM_i}{dt} = L_{i,IN} + V_{i,IN} - L_{i,OUT}$$

$$\left[\begin{array}{l} \text{Rate of} \\ \text{Accumulation} \\ \text{of Mass in} \\ \text{Liquid Holdup} \end{array} \right] = \left[\begin{array}{l} \text{Inlet} \\ \text{Liquid} \\ \text{Flow} \\ \text{Rate} \end{array} \right] + \left[\begin{array}{l} \text{Inlet} \\ \text{Vapor} \\ \text{Flow} \\ \text{Rate} \end{array} \right] - \left[\begin{array}{l} \text{Outlet} \\ \text{Liquid} \\ \text{Flow} \\ \text{Rate} \end{array} \right]$$

$$\begin{aligned} & - V_{i,OUT} + vR_i \\ & - \left[\begin{array}{l} \text{Outlet} \\ \text{Vapor} \\ \text{Flow} \\ \text{Rate} \end{array} \right] + \left[\begin{array}{l} \text{Net Rate of Mass} \\ \text{Generated by} \\ \text{Chemical Reactions} \end{array} \right] \end{aligned}$$

$$i=1, \dots, n \quad (3-1)$$

where

n = number of components

L_i = molal liquid flow rate for component i

V_i = molal vapor flow rate for component i

R_i = net rate of component i produced
and/or consumed by reaction

M_i = Molal quantity of component i in the liquid
holdup

v = Total volume of liquid holdup.

The overall material balance can be written as

$$\frac{dM}{dt} = L_{IN} + V_{IN} - L_{OUT}$$

$$\begin{aligned} \left[\begin{array}{l} \text{Rate of} \\ \text{Accumulation} \\ \text{of Total Mass} \\ \text{in the Liquid} \\ \text{Holdup} \end{array} \right] &= \left[\begin{array}{l} \text{Total} \\ \text{Inlet} \\ \text{Liquid} \\ \text{Flow} \\ \text{Rate} \end{array} \right] + \left[\begin{array}{l} \text{Total} \\ \text{Inlet} \\ \text{Vapor} \\ \text{Flow} \\ \text{Rate} \end{array} \right] - \left[\begin{array}{l} \text{Total} \\ \text{Outlet} \\ \text{Liquid} \\ \text{Flow} \\ \text{Rate} \end{array} \right] \\ &- V_{OUT} + v \sum_{i=1}^n R_i \quad (3-2) \\ &- \left[\begin{array}{l} \text{Total} \\ \text{Outlet} \\ \text{Vapor} \\ \text{Flow} \\ \text{Rate} \end{array} \right] + \left[\begin{array}{l} \text{Total Net} \\ \text{Rate of Mass} \\ \text{Generated} \\ \text{by Chemical} \\ \text{Reactions} \end{array} \right] \end{aligned}$$

where

L_{IN} = Total liquid inlet rate, molal quantity

L_{OUT} = Total liquid outlet rate, molal quantity

V_{IN} = Total vapor inlet rate, molal quantity

V_{OUT} = Total vapor outlet rate, molal quantity

$M = \sum_{i=1}^n M_i$, Total molal holdup on the tray

$\sum_{i=1}^n R_i$ = Total net rate of mass produced and/or consumed by chemical reactions

Holland (36) assumed that all the trays have constant holdup, implying that dM/dt is equal to zero for a constant molal holdup, or $\sum M_i / \bar{\rho}_i$ is a fixed value, where $\bar{\rho}_i$ is molal liquid density, for a constant volumetric holdup. However, the Holland assumption is not necessarily valid for the problem in hands where chemical reactions occur. Thus, for the present development a more realistic postulation of the liquid holdup being a time-dependent function is adopted.

The unsteady-state overall energy balance can be expressed as follows:

$$\frac{d}{dt} Mh_s = L_{IN} h_{IN} + V_{IN} H_{IN}$$

Rate of Accumulation of Energy in the System	=	Rate of Inlet Energy with Inlet Liquid Flow	+	Rate of Inlet Energy with Vapor Flow
--	---	---	---	--

$$\begin{aligned}
 & - L_{OUT} h_{OUT} & - V_{OUT} H_{OUT} \\
 & \left[\begin{array}{c} \text{Rate of} \\ \text{Outlet} \\ \text{Energy} \\ \text{with Liquid} \\ \text{Flow} \end{array} \right] & \left[\begin{array}{c} \text{Rate of} \\ \text{Outlet} \\ \text{Energy} \\ \text{with Vapor} \\ \text{Flow} \end{array} \right] \\
 & - Q_L & + \sum_{j=1}^{n_r} R_j (-\Delta H_{R,j}) \\
 & \left[\begin{array}{c} \text{Rate of} \\ \text{Heat Loss} \\ \text{to the} \\ \text{Surrounding} \end{array} \right] & + \left[\begin{array}{c} \text{Rate of} \\ \text{Heat} \\ \text{Generated} \\ \text{by Reaction} \end{array} \right]
 \end{aligned} \tag{3-3}$$

where:

h_{IN} = Inlet liquid enthalpy

h_{OUT} = Out liquid enthalpy

H_{IN} = Inlet vapor enthalpy

H_{OUT} = Outlet vapor enthalpy

h_S = Enthalpy of holdup on the tray
(assuming negligible vapor holdup)

Q_L = Net heat transfer rate form the system to
the surrounding

R_j = Rate of reaction for reaction j

$-\Delta H_{R,j}$ = heat of reaction of Reaction j

N_r = Number of reactions

It is noted that heat of solution is assumed negligible

and thus not shown in the above equation. All the enthalpy terms shown above represent the molal enthalpies for the mixture.

The rate of accumulation of energy, i.e., the left-hand side of Equation (4-3), can be rewritten in terms of temperature change as follows.

$$\frac{d}{dt}(Mh_s) = h_s \frac{dM}{dt} + M \frac{dh_s}{dT} \frac{dT}{dt} \quad (3-4)$$

Since the term dh_s/dT is equivalent to heat capacity C_p at temperature T , Equation (3-4) can now be rewritten as

$$\frac{d(Mh_s)}{dt} = h_s \frac{dM}{dt} + C_p \frac{dT}{dt} \quad (3-5)$$

where:

T is the temperature of liquid holdup. Equation (3-5) is substituted into Equation (3-3), and the term $h_s \frac{dM}{dt}$ shifted to the right-hand side of the equation. The temperature change with time can then be expressed as

$$MC_p \frac{dT}{dt} = L_{IN}h_{IN} + V_{IN}H_{IN} - L_{OUT}h_{OUT} - V_{OUT}H_{OUT} - Q_L + \sum_{j=1}^{n_r} R_j(-\Delta H_{R,j}) - h_s \frac{dM}{dt} \quad (3-6)$$

Equation (3-2) is introduced to Equation (3-6) and a proper algebraic rearrangement will yield the following equation where the $\frac{dM}{dt}$ disappears.

$$\begin{aligned}
 \frac{dT}{dt} = \frac{1}{MC_p} & \left[L_{IN}h_{IN} + V_{IN}H_{IN} - L_{OUT}h_{OUT} - V_{OUT}H_{OUT} \right. \\
 & - Q_L + \sum_{j=1}^n R_j(-\Delta H_{R,j}) - h_s(L_{IN} + V_{IN} - L_{OUT} - \\
 & \left. V_{OUT} + v \sum_{i=1}^n R_i) \right] \quad (3-7)
 \end{aligned}$$

Thus, the unsteady-state distillation accompanied by chemical reaction can be mathematically formulated into Equations (3-1), (3-2), and (3-7). It should be noted that since the liquid on the tray is assumed to be completely mixed, the variation of local temperatures and concentrations within the liquid bulk is considered to be negligible. The proposed general model, i. e., Equations (3-1), (3-2), and (3-7) are the basic working equations from which analytical or numerical solutions can be obtained for a given specific reaction-distillation system.

3.2 Unsteady-State Distillation without Chemical Reaction (Category Two Problems).

In the case, the distillation is not accompanied by chemical reaction, the reaction terms in Equation (3-1), (3-2), and (3-3) can be equated zero.

Then, the following equations are obtained.

$$\frac{dM_i}{dt} = L_{i,IN} + V_{i,IN} - L_{i,OUT} - V_{i,OUT} \quad (3-8)$$

$$\frac{dM}{dt} = L_{IN} + V_{IN} - L_{OUT} - V_{OUT} \quad (3-9)$$

$$\frac{d}{dt}(Mh_s) = L_{IN}h_{IN} + V_{IN}H_{IN} - L_{OUT}h_{OUT} - V_{OUT}H_{OUT} - Q_L \quad (3-10)$$

The above equations are identical to those developed by Holland (36) for unsteady-state distillation without chemical reaction. Since no temperature term is shown in Equation (3-10), temperature should be obtained by trial-and-error. The iteration procedure is proposed by Holland (36). If the rate of accumulation of energy in Equation (3-10) is changed into the rate of temperature change, the resulting equation is Equation (3-7) without the reaction term. It can be written as follows:

$$\frac{dT}{dt} = \frac{1}{MC_p} \left[L_{IN}h_{IN} + V_{IN}H_{IN} - L_{OUT}h_{OUT} - V_{OUT}H_{OUT} - h_s (L_{IN} + V_{IN} - L_{OUT} - V_{OUT}) \right] \quad (3-11)$$

The above equation can give the instantaneous temperature without trial-and-error on the temperature term. Also if Holland's method is used to solve the above rate equations, as stated before the tray must have constant liquid holdup implying the steady inlet and outlet streams.

Equation (3-10) is then reduced to

$$0 = L_{IN} + V_{IN} - L_{OUT} - V_{OUT}$$

$$\text{or } L_{IN} + V_{IN} = L_{OUT} + V_{OUT} \quad (3-12)$$

3.3 Steady-State Distillation with Chemical Reaction (Category Three Problems).

On the other hand, if the distillation is accompanied by chemical reaction but it is operated at steady-state conditions, the derivative terms in Equation (3-1), (3-2), (3-7) can be set to zero:

$$\frac{dM_i}{dt} = 0$$

$$\frac{dM}{dt} = 0$$

$$\frac{dT}{dt} = 0$$

Substituting the above to Equations (3-1), (3-2), and (3-7) yields the following sets of equations.

$$L_{i,IN} + V_{i,IN} - L_{i,OUT} - V_{i,OUT} + vR_i = 0 \quad (3-13)$$

$$L_{IN} + V_{IN} - L_{OUT} - V_{OUT} + v \sum_{i=1}^n R_i = 0 \quad (3-14)$$

$$L_{IN}h_{IN} + V_{IN}H_{IN} - L_{OUT}h_{OUT} - V_{OUT}H_{OUT} - Q_L + \sum_{i=1}^{n_r} R_j(-\Delta H_{R,j}) = 0 \quad (3-15)$$

The above equations are identical to those proposed by Marek (45) and Belck (5) and utilized by Davies and Jeffreys (12) for analysis of their steady-state

experimental data.

The methods of solution for above algebraic equations can be obtained by graphical procedures or analytical solutions for distillation with a single and simple chemical reaction.

3.4 Steady-State Distillation without Chemical Reaction (Category One Problems).

Equations (3-13), (3-14), and (3-15) can be reduced to the mathematical model for the steady-state distillation without chemical reaction. This can be accomplished by substituting $R_i=0$ into Equation (3-13), (3-14), and (3-15). The following equations are then obtained.

$$L_{i,IN} + V_{i,IN} - L_{i,OUT} - V_{i,OUT} = 0 \quad (3-16)$$

$$L_{IN} + V_{IN} - L_{OUT} - V_{OUT} = 0 \quad (3-17)$$

$$L_{IN}h_{IN} + V_{IN}H_{IN} - L_{OUT}h_{OUT} - V_{OUT}H_{OUT} - Q_L = 0 \quad (3-18)$$

The above are the familiar model to represent the steady-state distillation without chemical reaction. Many articles have been published about the solutions for those equations.

3.5 Semi-Batch Distillation with Chemical Reaction

When the outlet liquid flow is not present, the gen-

eral system shown in Figure 3.1 is reduced to a semi-batch distillation accompanied by chemical reaction.

For this case,

$$L_{i,OUT} = L_{OUT} = 0 \quad (3-19)$$

and the general model is reduced to the following set of equation:

$$\frac{dM_i}{dt} = L_{i,IN} + V_{i,IN} - V_{i,OUT} + vR_i \quad (3-20)$$

$$\frac{dM}{dt} = L_{IN} + V_{IN} - V_{OUT} + v \sum_{i=1}^n R_i \quad (3-21)$$

$$\begin{aligned} \frac{dT}{dt} = \frac{1}{MC_p} & \left[L_{IN} h_{IN} + V_{IN} H_{IN} - V_{OUT} H_{OUT} - Q_L \right. \\ & + \sum_{j=1}^{n_r} R_j (-\Delta H_{R,j}) - h_s (L_{IN} + V_{IN} - V_{OUT} \\ & \left. + v \sum_{i=1}^n R_i) \right] \quad (3-22) \end{aligned}$$

The simultaneous solution of the above equations for a complex system including several simultaneous reactions will be given in the next chapter.

Summarizing, generality of the proposed model can be best illustrated in Fig. 3.2

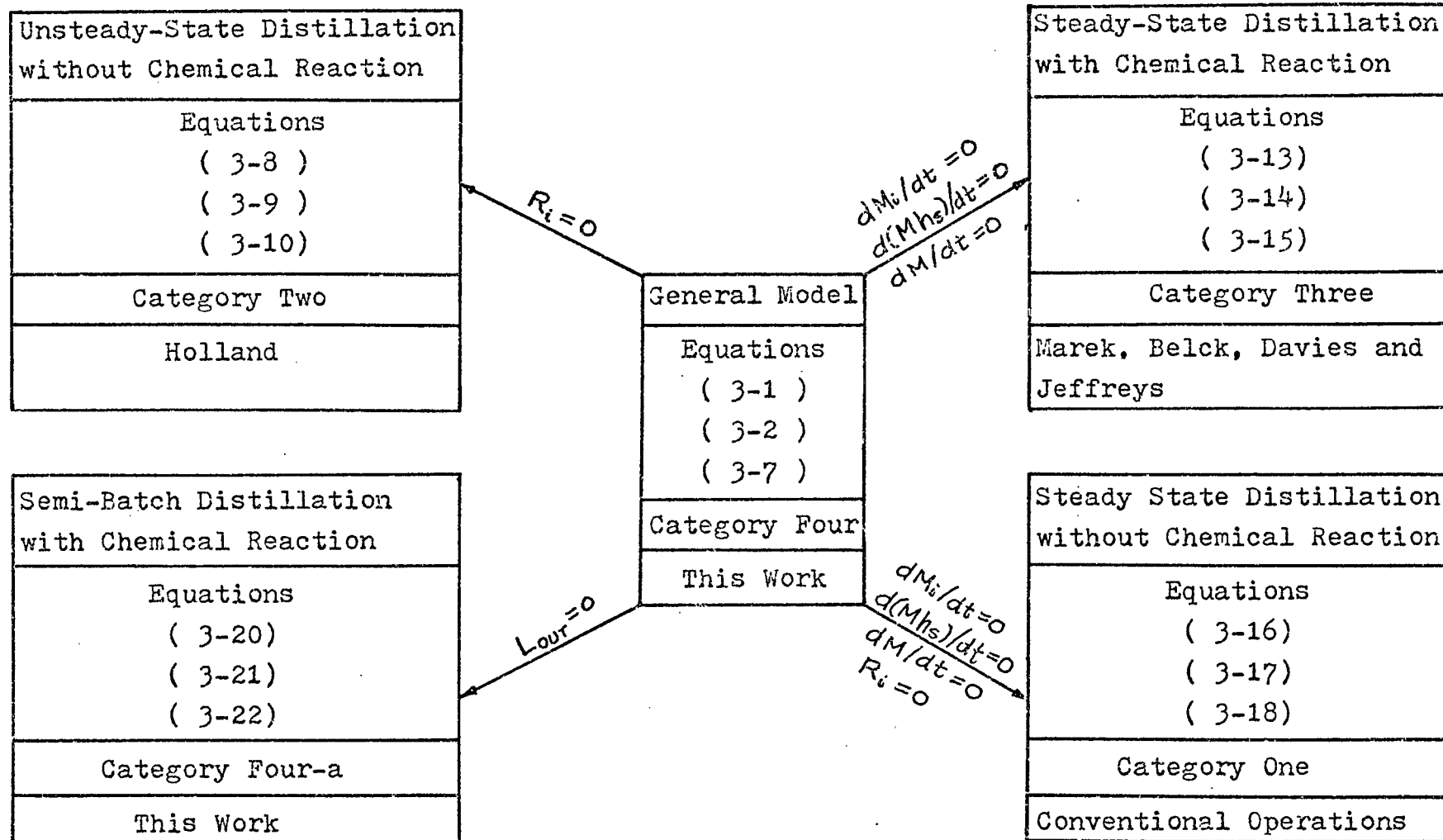


Fig. 3.2. Inter-Relations Among Theories of Distillation

Chapter 4 Theoretical Model for Semi-Batch Distillation Accompanied by Chemical Reaction

4.1 Basic Mathematical Model and Reactions

The mathematical model for a semi-batch distillation accompanied by chemical reaction can be obtained by reducing the general model as shown in the previous chapter. These are repeated below.

$$\frac{dM_i}{dt} = L_{i,IN} + V_{i,IN} - V_{i,OUT} + R_i \quad (3-20)$$

$$\frac{dM}{dt} = L_{IN} + V_{IN} - V_{OUT} + \sum_{i=1}^n R_i \quad (3-21)$$

$$\begin{aligned} \frac{dT}{dt} = \frac{1}{MC_p} & \left[L_{IN} h_{IN} + V_{IN} H_{IN} - V_{OUT} H_{OUT} \right. \\ & - Q_L + \sum_{j=1}^{n_r} R_j (-\Delta H_{R,j}) - h_s (L_{IN} + \\ & \left. V_{IN} - V_{OUT} + \sum_{i=1}^n R_i) \right] \quad (3-22) \end{aligned}$$

The simultaneous solution for the above model now will be given in this chapter. The system for which the solutions are developed is the esterification of acrylamide sulfate and ethyl alcohol. The product, namely ethyl acrylate, is distilled into the vapor phase. The proposed system is best illustrated in Figure 4.1.

Initially, a known volume of the equilibrium

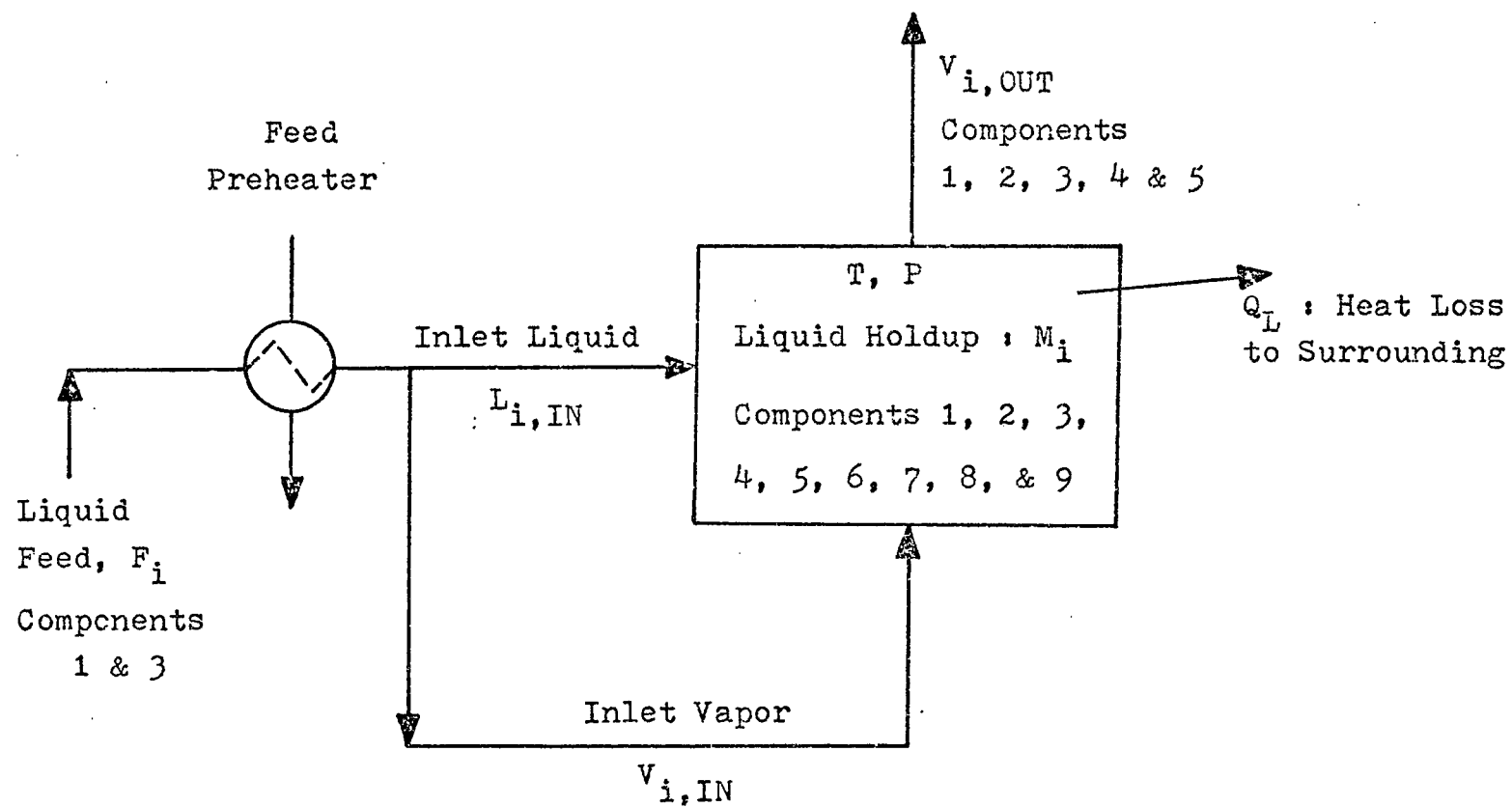
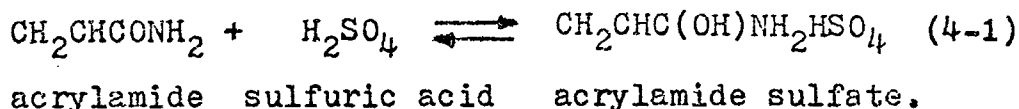


Fig. 4.1 Semi-Batch Distillation
With Chemical Reaction

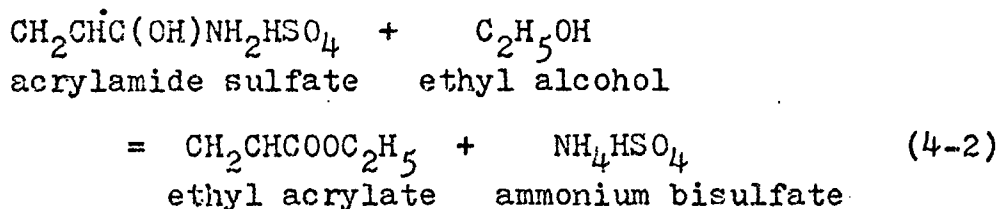
solution containing acrylamide, sulfuric acid, acrylamide sulfate is prepared and charged to the reaction-distillation tray. The equilibrium relationship can be represented as

Equilibrium Reaction

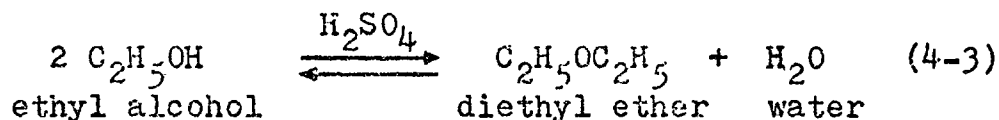


The method of preparing the above solution and other experimental set-ups and procedures for this study are described in more details in the following chapter. The continuous feed, liquid and vapor, of ethyl alcohol and water, are charged to the reaction-distillation tray. The tray is a micro-sieve tray, with perforations of 60 - 75 μ . As soon as ethyl alcohol comes into contact with acrylamide sulfate, the following three chemical reactions occur.

a. Major Reaction - Esterification



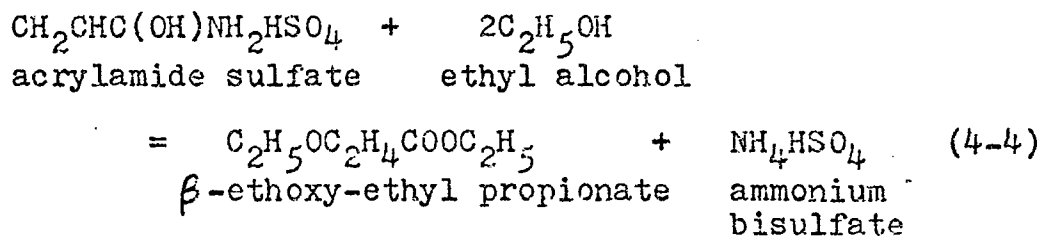
b. Minor Side Reaction - Dehydration



The catalyst for the reaction is H_2SO_4 which is present in the solution.

c. Minor Successive Reaction

Another by-product, β -ethoxy-ethyl propionate is produced from two successive reaction routes. One of them is the addition of ethyl alcohol into the main product, ethyl acrylate. The other is the reaction between ethyl alcohol and the intermediate complex, $C_2H_5OC_2H_4C(OH)NH_2HSO_4$, whose formation will be discussed later in this chapter. The combined reaction may be represented by the following third-order reaction with respect to acrylamide sulfate and ethyl alcohol:



From the above three equations, it is obvious that the system is a complex mixture including the following nine separate chemical species.

<u>Identifying Subscripts</u>	<u>Compound Names</u>	<u>Chemical Formulas</u>
1	Ethyl Alcohol	C_2H_5OH
2	Ethyl Acrylate	$CH_2CHCOOC_2H_5$
3	Water	H_2O
4	Diethyl Ether	$C_2H_5OC_2H_5$

5	β -Ethoxy-ethyl Propionate	$C_2H_5CC_2H_4COOC_2H_5$
6	Acrylamide Sulfate	$CH_2CHC(OH)NH_2HSO_4$
7	Sulfuric Acid	H_2SO_4
8	Ammonium Bisulfate	NH_4HSO_4
9	Acrylamide	$CH_2CHCONH_2$

It is noted that at the time of the initial introduction of the ethyl alcohol-water mixture to the system, the reaction moves slowly and a negligible amount of vapor containing ethyl acrylate is produced. The heat of reaction and the heat of condensation of the feed vapor provide the energy to raise the system temperature rapidly until it reaches the bubble point of the liquid mixture. With the continuous feed of the volatile ethyl alcohol-water mixture, the reactions proceed, yielding the vapor products which include ethyl acrylate. In addition to ethyl acrylate, the outlet vapor contains four other components, namely ethyl alcohol, water, diethyl ether and β -ethoxy-ethyl propionate. The semi-batch distillation system to be dealt in this investigation does not have an outgoing liquid stream. The liquid holdup on the tray contains all the nine components which are listed earlier.

The fundamental equations, i. e., Equations (3-20), (3-21), (3-22), derived in the previous chapter are readily applicable where the component subscript i (from 1 to 9) represents for each compound respectively. There are basically four reactions occurring in the system and the reaction subscript j (from 1 to 4) represents the four reactions, i. e., Equations (4-1), (4-2), (4-3), (4-4), as follows.

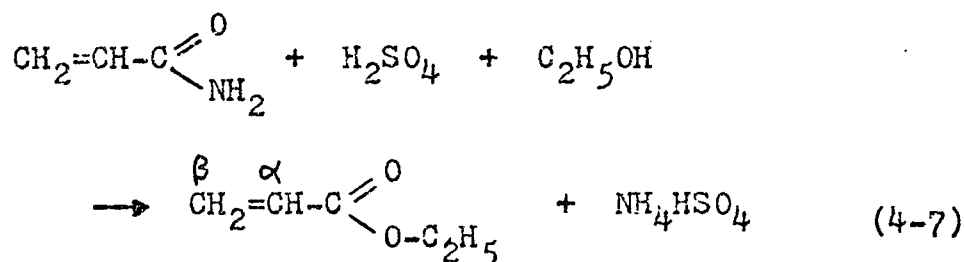
<u>Reaction Identifi-</u> <u>cation Subscript j</u>	<u>Reaction</u>	<u>Reaction</u> <u>Equation</u>
1	Esterification	(4-2)
2	Dehydration	(4-3)
3	Successive Reaction	(4-4)
4	Equilibrium Reaction	(4-1)

4.2 Reaction Mechanisms

4.2.1 Structural Formula of Molecular Complex, Acrylamide Sulfate

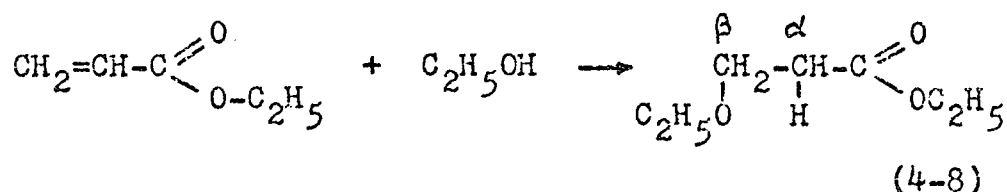
Before discussing the kinetics and mechanisms of the reaction system, a complex reactant, acrylamide sulfate, should be understood first. Three formulas (38,57,60) have been proposed to represent acrylamide sulfate. They are:

acrylamide, sulfuric acid and ethyl alcohol can be shown as



The reaction shows the addition of high electronegative oxygen of ethyl alcohol onto the carboxyl carbon of acrylamide. Therefore, this carbon is an electron acceptor.

A further reaction of ethyl acrylate with ethyl alcohol gives the by-product, β -ethoxy-ethyl propionate:



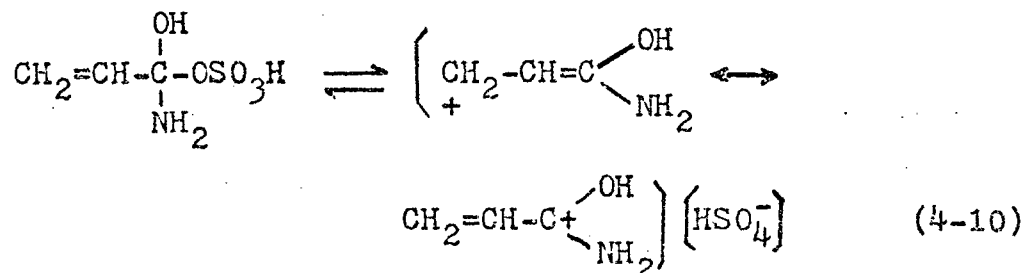
The addition of ethoxyl oxygen onto the β -carbon of ethyl acrylate also indicates the β -carbon is an electron acceptor.

The above discussion justifies the ionic resonance form (4-6). Except a strong acid, a strong base or their salts, a compound seldom dissociates completely to its ionic forms. Acrylamide sulfate is no exception and, therefore, there exists a structural formula with

covalent bond for acrylamide sulfate:



Of course, the covalent bond should be in equilibrium with the ionic bond, which can be expressed as follows:

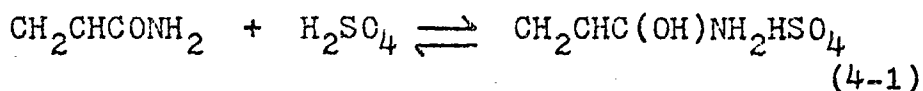


During the alcoholysis, electrophilic ethoxyl oxygen should first attack the ionic molecules, then the covalent bond dissociates instantaneously into ionic bond to supply the ionic reactant for further alcoholysis.

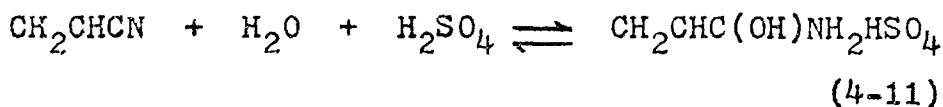
4.2.2 Preparation of Acrylamide Sulfate

Three methods have been reported in literature for preparing acrylamide sulfate. A different reactant is used to react with sulfuric acid in an aqueous solution.

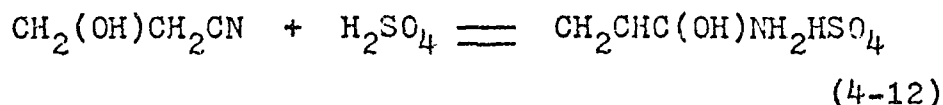
1. Starting with acrylamide (57):



2. Starting with acrylonitrile (27):



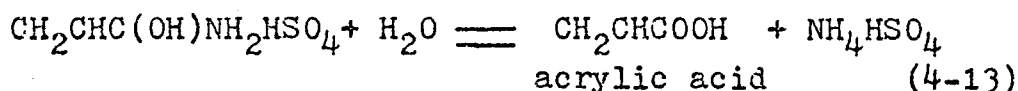
3. Starting with ethylene cyanohydrin (57):



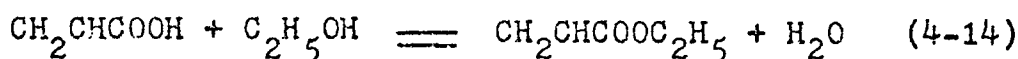
It was reported that the reactions starting with acrylonitrile or ethylene cyanohydrin are accompanied by side reactions and consequently not all the reactants are converted to the sulfate. On the other hand, the reaction starting with acrylamide is not accompanied by a competitive side reaction. Therefore, for this study, acrylamide sulfate is prepared by reacting acrylamide with sulfuric acid in an aqueous solution as represented in Equation (4-1).

4.2.3 Esterification of Acrylamide Sulfate and Ethyl Alcohol

Two different reaction mechanisms can be postulated depending on the concentration of water in the mixture. If a large amount of water is presented in the acrylamide sulfate solution (57,2), most of acrylamide sulfate will be hydrolysed to produce acrylic acid first:



Then acrylic acid reacts with ethyl alcohol to yield the desired product, ethyl acrylate:



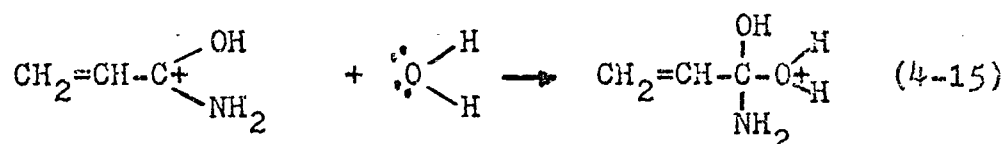
The mechanisms of the above reactions are best explained from the structural point of view as presented in Section

4.2.1. In the ionic resonance form $\left[\overset{+}{\text{CH}_2-\text{CH}=\text{C}} \begin{matrix} \text{OH} \\ \text{NH}_2 \end{matrix} \right]$

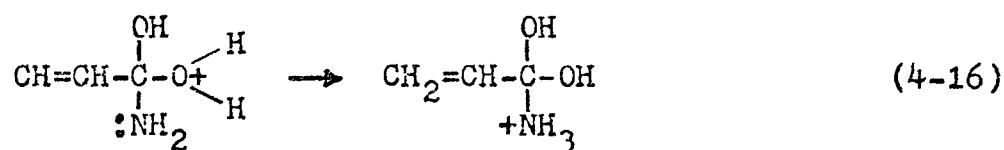
$\longleftrightarrow \text{CH}_2=\text{CH}-\text{C}^+ \begin{matrix} \text{OH} \\ \text{NH}_2 \end{matrix} \right]$, the structure $\left[\text{CH}_2=\text{CH}-\text{C}^+ \begin{matrix} \text{OH} \\ \text{NH}_2 \end{matrix} \right]$

is much more stable than $\left[\overset{+}{\text{CH}_2-\text{CH}=\text{C}} \begin{matrix} \text{OH} \\ \text{NH}_2 \end{matrix} \right]$ because

hydroxyl group -OH and amine group -NH₂ have very high electron-negativity, which will suppress the electron of unsaturated carbon from moving to the positive carboxyl carbon. Therefore, the hydrolysis is proceeded mostly with the stable ion $\left[\text{CH}_2=\text{CH}-\text{C}^+ \begin{matrix} \text{OH} \\ \text{NH}_2 \end{matrix} \right]$:

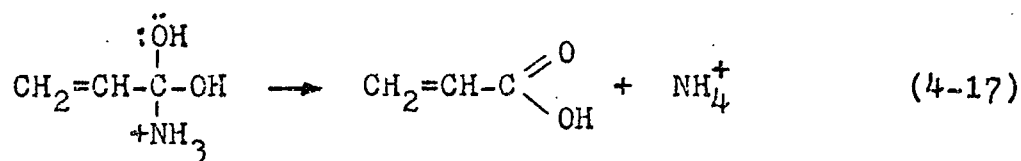


Then, the proton is released from the hydroxyl oxygen and shifted to amine group:

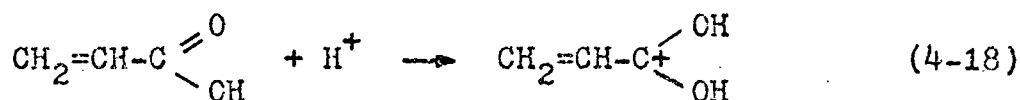


Since +NH_3 is an electron acceptor, the electrons on hydroxyl oxygen will shift to the adjacent carbon and the proton is then released from it. The shift of

electrons to the carboxyl carbon expels the electrons in C-N bond. Free ammonia is then released and combined together with proton to form ammonium ion:

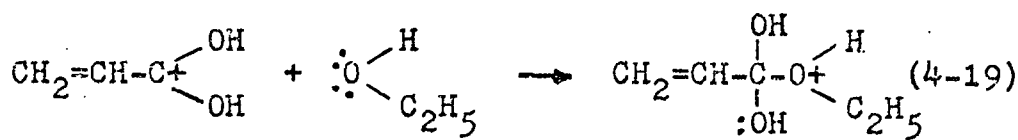


The mechanism for the consecutive alcoholysis of acrylic acid is initiated also by the proton which is abundant in the dilute sulfuric acid solution:

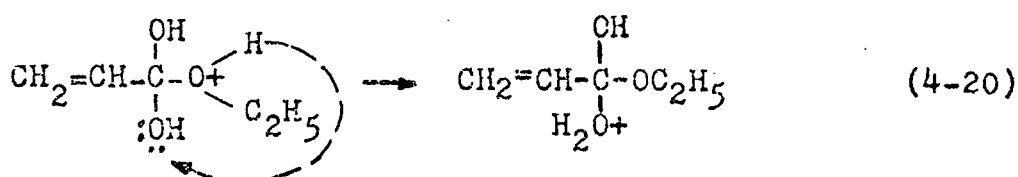


Both the hydroxyl oxygens with high electronegativity suppress the electron of unsaturated carbon from coming to the positive carboxyl carbon and give the stable structure of the ionic resonance form $\left[\text{CH}_2-\text{CH}=\underset{\text{OH}}{\overset{\text{OH}}{\text{C}}}^+ \longleftrightarrow \text{CH}_2=\text{CH}-\underset{\text{OH}}{\overset{\text{OH}}{\text{C}}}^+ \right]$.

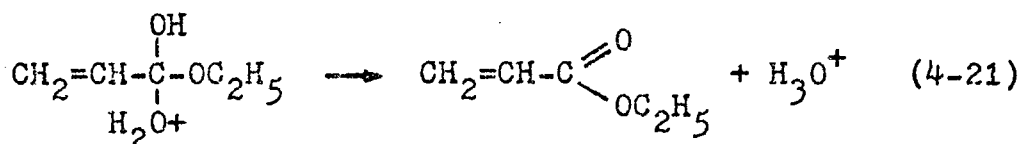
Then the carbonyl ion reacts with ethyl alcohol



The proton is then released and attached onto the hydroxyl oxygen

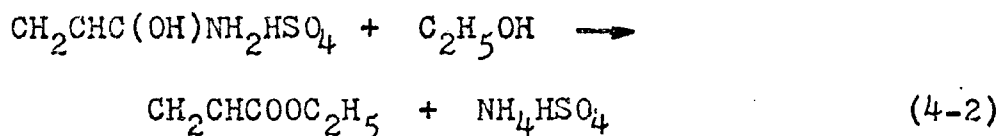


The group $-\text{OH}_2^+$ will attract the electron from another hydroxyl oxygen. The proton is then released from the oxygen. Also the addition of electrons on the carboxyl carbon will expel the water molecule. The water molecule is then combined with proton to form hydronium ion H_3O^+ :



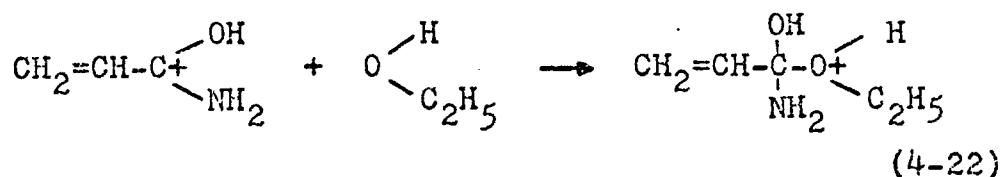
The above reaction in a dilute sulfate solution yields acrylic acid as intermediate by-product, and hence substantially reduce the yield of the desired product, ethyl acrylate.

Thus, the other reaction in the solution having small amount of water should be investigated to determine the preferable reaction conditions. With a small amount of water, the water is used mostly to dissociate protons from the sulfuric acid which in turn initiates the formation of acrylamide sulfate. The esterification of acrylamide sulfate and ethyl alcohol can be represented by

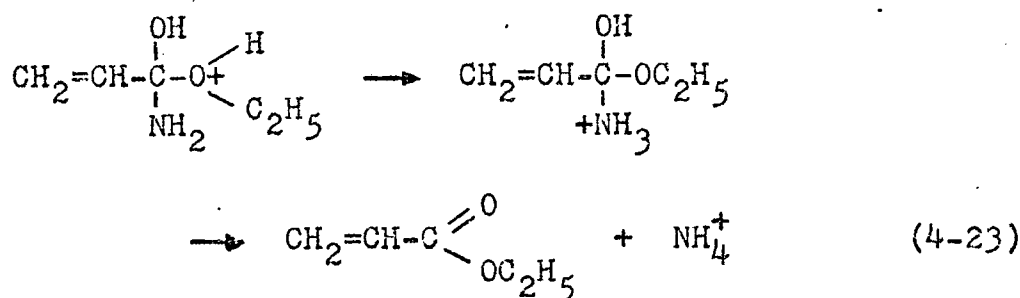


Its reaction mechanism can be explained starting with

the stable ionic structure $\text{CH}_2=\text{CH}-\text{C}^+\begin{smallmatrix} \text{OH} \\ \text{NH}_2 \end{smallmatrix}$ of acrylamide sulfate. It reacts with ethyl alcohol in the following manner.



The rest of steps leading to the product, ethyl acrylate, are similar to those of hydrolysis leading to the acrylic acid:



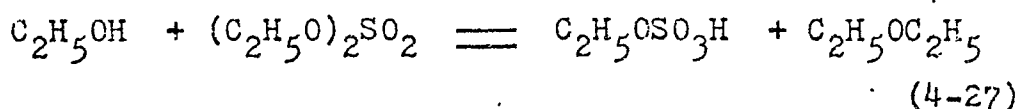
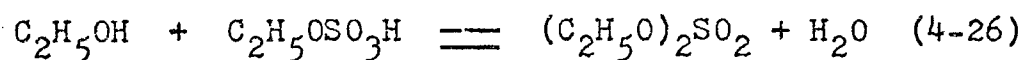
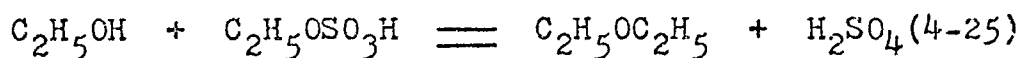
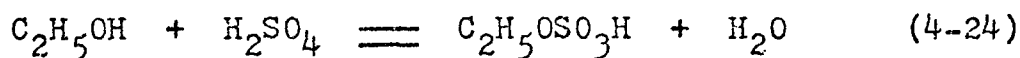
From the above analysis, appropriate amount of water is then selected here according to the previous worker(27) so that the yield of acrylic acid becomes negligible while enough protons can be produced to initiate the esterification.

4.2.4 Side Reactions

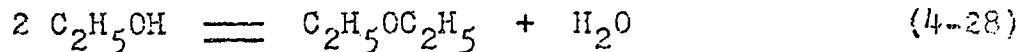
As mentioned in Section 4.1, there are two important side reactions which produce volatile by-products, namely diethyl ether and β -ethoxy-ethyl propionate.

a. Production of Diethyl Ether:

The mechanism of forming diethyl ether from ethyl alcohol in the presence of H_2SO_4 as catalyst can be thought of a series of the following successive reactions:

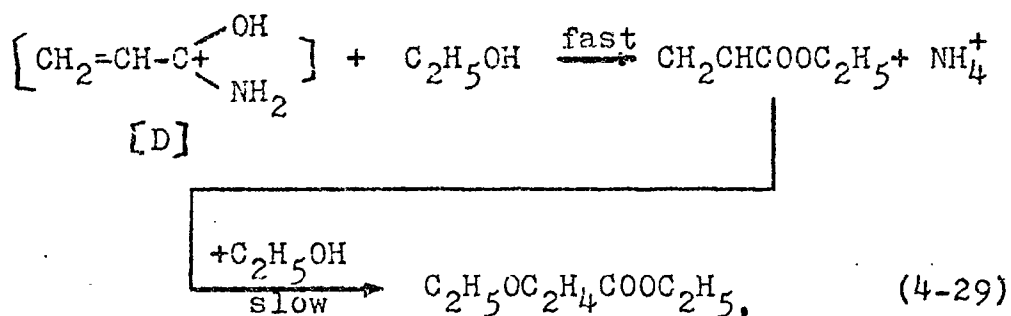


The overall results of the above reactions can be given by the following equation:

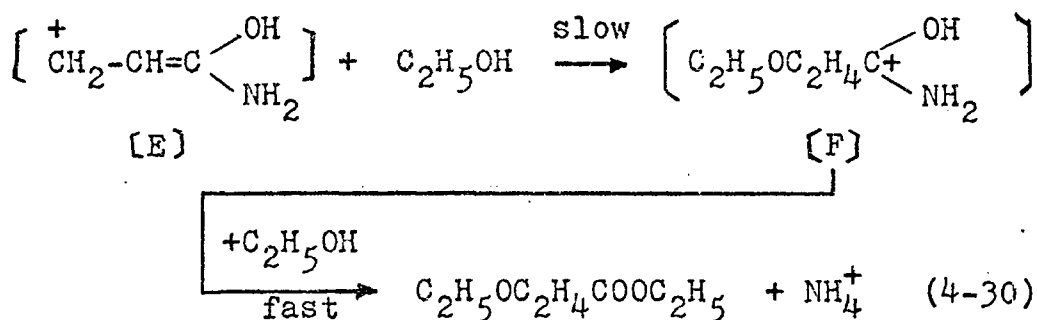


b. Production of β -Ethoxy-Ethyl Propionate:

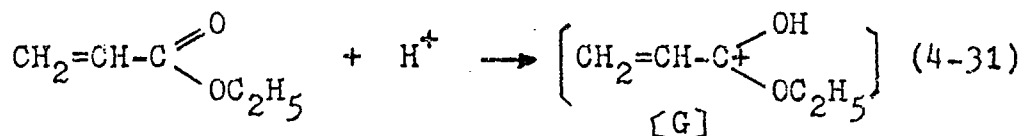
The formation of β -ethoxy-ethyl propionate is obtained from two successive reaction routes. They are:



and

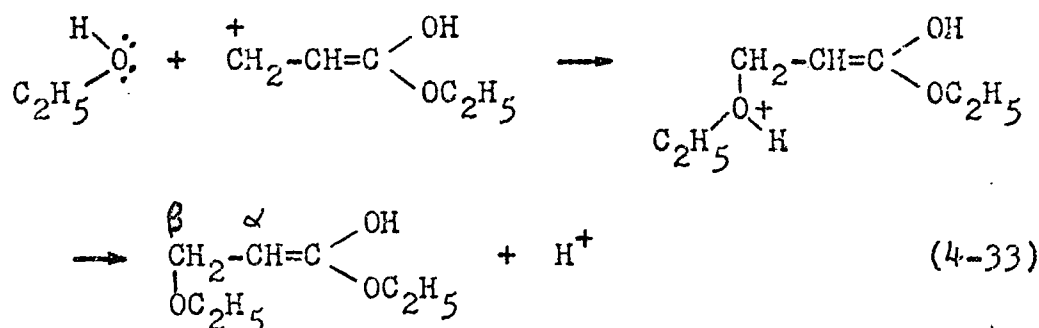
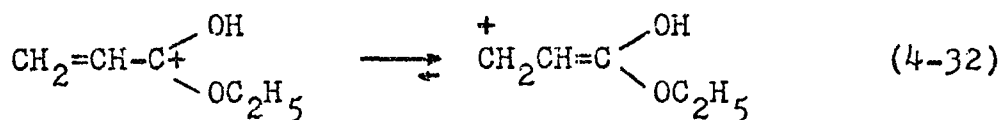


The first step of Equation (4-29) is formation of the desired product, ethyl acrylate. It is a fast reaction. Its mechanism has been discussed in Section 4.2.3. The last step of this successive reaction is formation of the by-product, β -ethoxy-ethyl propionate. Its mechanism begins from the formation of carbonyl ion by the addition of proton into ethyl acrylate.

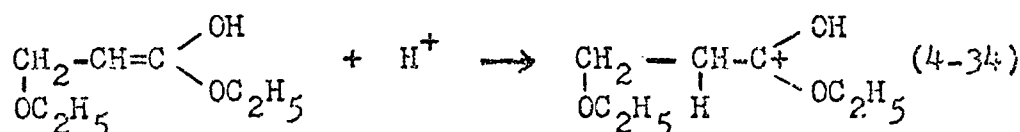


Since the ethoxyl group, $-\text{OC}_2\text{H}_5$, is much less electronegative than amine group, $-\text{NH}_2$, as in the previous case, the other resonance form $\left[\overset{+}{\text{CH}_2} - \text{CH} = \text{C} \begin{array}{l} \text{OH} \\ \text{OC}_2\text{H}_5 \end{array} \right]$ will be comparably more stable than $\left[\overset{+}{\text{CH}_2} - \text{CH} = \text{C} \begin{array}{l} \text{OH} \\ \text{NH}_2 \end{array} \right]$. Also,

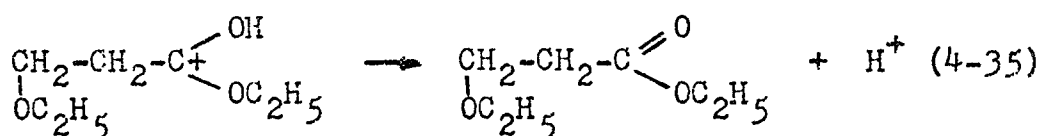
the steric effect of larger molecular groups OH and OC_2H_5 prevent alcohol from adding to the carboxyl carbon of formula [G]. Therefore, the mechanism for this side reaction can be represented as follows:



The proton released in the above equation then attaches on the unsaturated α -carbon because it has much less steric hinderance than carboxyl carbon:

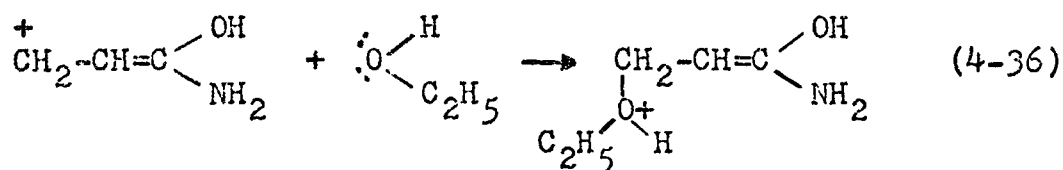


The positive carbonyl ion then attracts the electron from hydroxyl oxygen and then proton is released again to give the by-product, β -ethoxy-ethyl propionate:

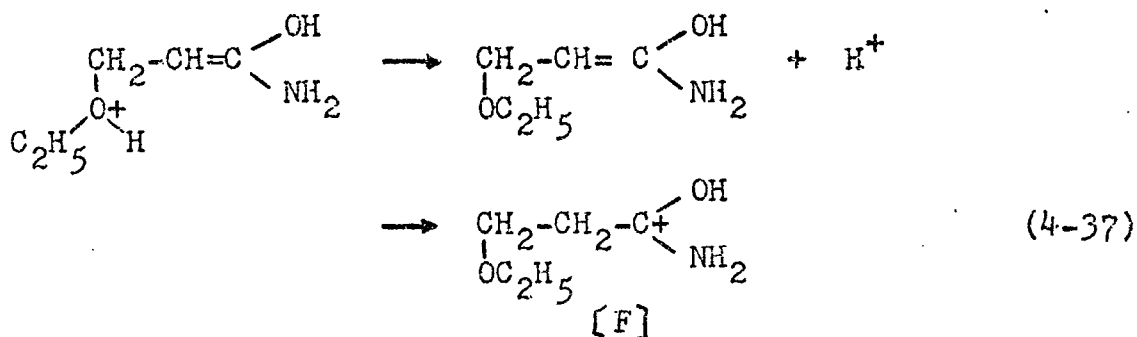


The proton is then a catalyst for the above addition reaction.

Equation (4-30) is an alternate reaction route leading to the by-product, β -ethoxy-ethyl propionate. Since formula [E] is much less stable than formula [D] as mentioned in Section 4.2.1, the following addition reaction is then a very slow reaction:

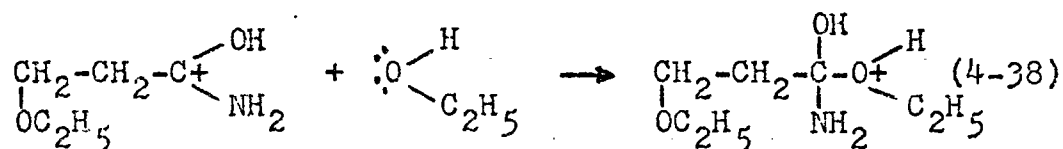


Following the same mechanisms given in Equations (4-33), and (4-34), the product of the above reaction proceeds to the intermediate complex ion, $\left[\begin{array}{c} \text{CH}_2-\text{CH}_2-\text{C}^+ \begin{array}{l} \text{OH} \\ \text{NH}_2 \end{array} \\ | \\ \text{OC}_2\text{H}_5 \end{array} \right]$.

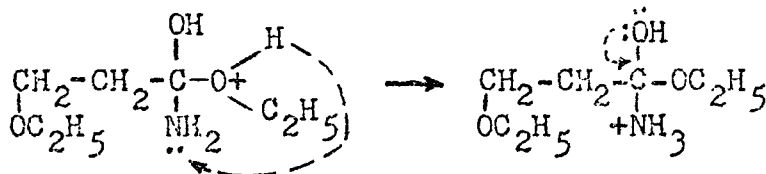


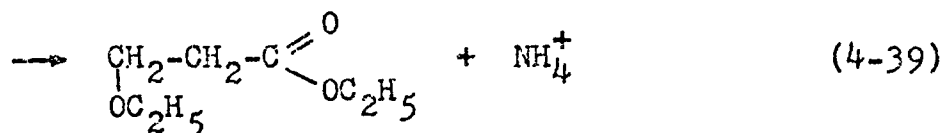
Formula [F] with bisulfate ion, HSO_4^- gives the intermediate complex, $\text{C}_2\text{H}_5\text{OC}_2\text{H}_4\text{C}(\text{OH})\text{NH}_2\text{HSO}_4$ as mentioned in Section 4.1.

As soon as the above positive carbonyl ion is formed and more ethyl alcohol is added, the hydroxyl oxygen in ethyl alcohol will attach onto the carboxyl carbon.

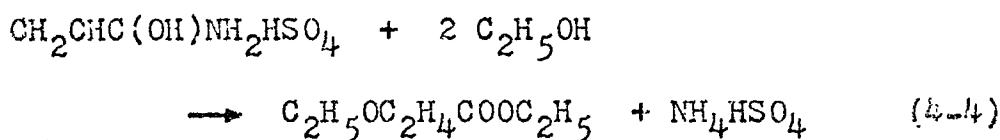


Shifts of proton and formation of ammonium ion are similar to those shown in Equation (4-23).





Since the reaction rate for this stage is much faster than the previous stage, the yield of the intermediate complex, $\text{C}_2\text{H}_5\text{OC}_2\text{H}_4\text{C}(\text{OH})\text{NH}_2\text{HSO}_4$ is then essentially negligible. Summarizing the mechanisms described above, the formation of β -ethoxy-ethyl propionate can then be represented by the following overall reaction.

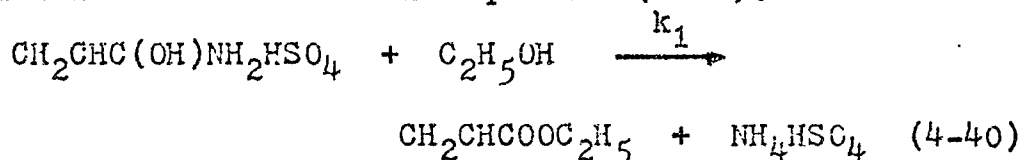


4.3 Reaction Rate Expressions

4.3.1 Esterification of Acrylamide Sulfate

Since the amount of water presented in the system is small, the reaction mechanism of esterification is best expressed by Equations (4-22) and (4-23). Since the transient electron shifts can be considered to be instantaneous and since the ionic structure of

$\left[\text{CH}_2=\text{CH}-\text{C}^+ \begin{array}{l} \nearrow \text{OH} \\ \searrow \text{NH}_2 \end{array} \right]$ dominates the reaction, the overall reaction may be represented by its equivalent molecular formula as shown in Equation (4-40).



As most of product, $\text{CH}_2\text{CHCOOC}_2\text{H}_5$ is distilled and leaves the system, the above reaction can be considered as a second-order irreversible reaction. Then, the rate expression of producing ethyl acrylate by the above overall reaction can be expressed as

$$R'_1 = k_1 C_1 C_6 \quad (4-41)$$

where

R'_1 = reaction rate yielding ethyl acrylate,
g-mole/l-min

k_1 = reaction rate constant, l/g-mole-min

C_i = concentration for component i, g-mole/l

The Arrhenius equation states that

$$k = k_o e^{-E_o / 1.987T} \quad (4-42)$$

where

k_o = frequency factor

E_o = activation energy, cal/g-mole

T = absolute temperature, $^{\circ}\text{K}$

Substituting Equation (4-42) into Equation (4-41) with the corresponding subscript gives

$$R'_1 = k_{o1} e^{-E_{o1} / 1.987T} C_1 C_6 \quad (4-43)$$

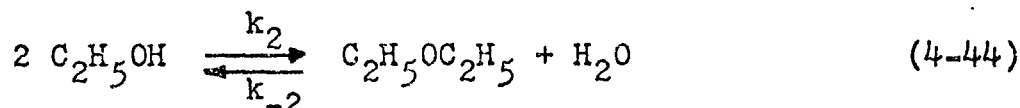
where

E_{o1} = activation energy for the rate constant k_1

k_{o1} = frequency factor for the rate constant k_1

4.3.2 Production of Diethyl Ether

The reaction forming diethyl ether as represented by Equation (4-3) can be written as a second-order reversible reaction:



However, the product, diethyl ether, is very volatile and thus the concentration of diethyl ether in the liquid phase is negligibly small. Under this condition, the backward reaction may be neglected and the reaction treated as a second-order irreversible reaction. The rate of producing diethyl ether is then expressed by

$$R'_2 = k_2 C_1^2 \quad (4-45)$$

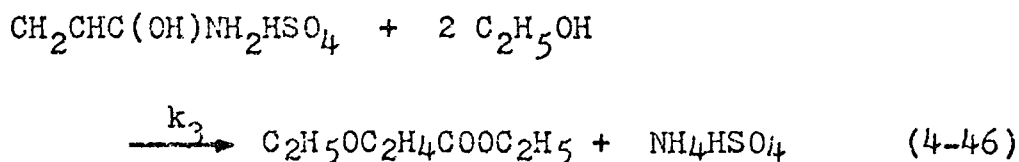
where

R'_2 = production rate of diethyl ether

k_2 = forward reaction rate constant

4.3.3 Formation of β -Ethoxy-ethyl propionate

The overall reaction expressed by Equation (4-4) has been shown in Section 4.2.5 as a combination of two consecutive reactions. It is repeated below



Since the reactant, ethyl alcohol, is supplied continuously and the product, β -ethoxy-ethyl propionate is partly vaporized and removed from the reacting mixture, the reaction can be considered as an irreversible third-order reaction. The rate equation is, then, written

$$R_3' = k_3 C_1^2 C_6 \quad (4-47)$$

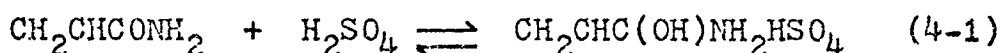
where

R_3' = production rate of β -ethoxy-ethyl propionate

k_3 = rate constant for Reaction 3.

4.3.4 Equilibrium Reaction Forming Acrylamide Sulfate Complex

The acrylamide sulfate is not continuously charged to the reaction mixture, but is formed instead in the reaction mixture by the following reaction:

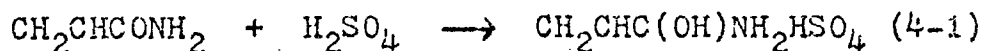


When acrylamide is dissolved in the aqueous sulfuric acid at a ratio of about 1:1.2, as used in this work, acrylamide crystal can be seen in equilibrium with the brown product, acrylamide sulfate in the mixture at the temperature below the melting point of acrylamide, 84.5 °C. However, when the temperature is increased to the range of 90 - 130 °C as used in this study, acrylamide sulfate is formed almost instantaneously. Accord-

ing to American Cynamid Company (2), molten acrylamide polymerizes vigorously with evolution of heat. Since no polymerization (viscous material) has been found in any of the acrylamide sulfate solutions prepared in this experimental system, it is evident that acrylamide is stabilized in the form of molecular complex, acrylamide sulfate. Amount of free acrylamide in the sulfate solution is then negligible. Thus, it may be assumed that all the added acrylamide is converted into acrylamide sulfate for the experiments being investigated. When the temperature exceeds 135°C , acrylamide sulfate may be decomposed because strong odors can be detected from the liquid. To avoid such a decomposition at high temperatures, and to avoid the equilibrium reaction at low temperatures, the moderate temperature of $90-130^{\circ}\text{C}$ is chosen as an appropriate range for this study.

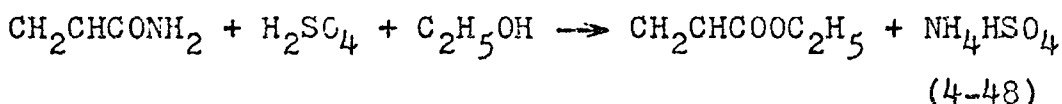
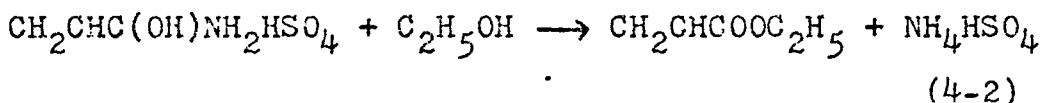
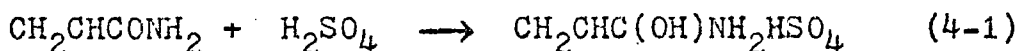
The molal quantity of the acrylamide sulfate complex can be represented in terms of initial molal quantity of acrylamide and its consumptions by the reactions. All the added acrylamide is consumed to produce acrylamide sulfate while acrylamide sulfate is consumed to produce two components, namely ethyl acrylate and β -ethoxy-ethyl propionate as follows.

(i) For producing acrylamide sulfate

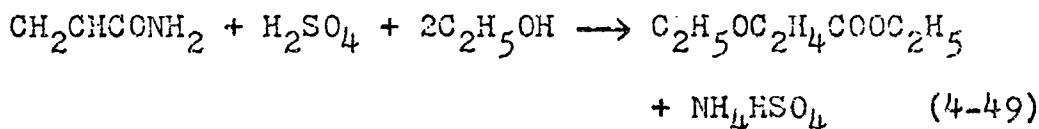
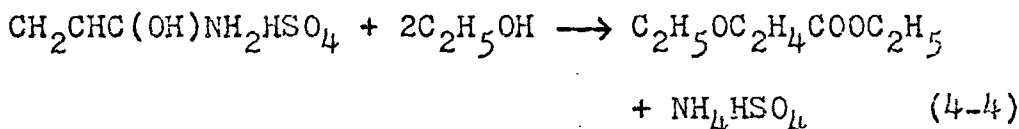
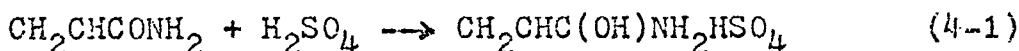


(ii) For producing ethyl acrylate

Equations (4-1) and (4-2) can be combined together stoichiometrically:



(iii) For producting β -ethoxy-ethyl propionate



Now, let A_i represent the total molal quantities of component i in both liquid and vapor phases. Stoichiometric consideration of Equations (4-1), (4-48) and (4-49) then lead to the following expressions:

$$\left. \begin{aligned} \text{Moles of initial acrylamide sulfate} &= A_{6,0} \\ &= \text{Moles of total added acrylamide} = A_{9,0} \\ \text{Moles of acrylamide sulfate consumed} &= A_2 + A_5 \end{aligned} \right\} (4-50)$$

Thus, the amounts of acrylamide and sulfuric acid remained in the reaction mixture at any time can be represented by

$$M_7 = M_{7,0} - M_{9,0} \quad (4-51)$$

$$M_9 = 0 \quad (4-52)$$

where $M_{7,0}$ is the molal quantity of sulfuric acid presented in the initial mixture. Since acrylamide sulfate is very nonvolatile.

$$A_6 \cong M_6 \quad (4-53)$$

Equation (4-53) can be incorporated with the relationships given in Equation (4-50) to give

$$M_6 = M_{9,0} - (A_2 + A_5) \quad (4-54)$$

4.4 Individual Rates of Mass Appearance and/or Disappearance

4.4.1 Ethyl Alcohol

Ethyl alcohol is involved in three chemical reactions, i.e., Reactions (1), (2) and (3). The molal rate of ethyl alcohol consumptions by the reactions is

$$v(R_1 + 2R_2 + 2R_3).$$

Substituting the above into Equation (3-20) for ethyl alcohol yields

$$\frac{dM_1}{dt} = L_{1,IN} + V_{1,IN} - V_{1,OUT} - v(R_1 + 2R_2 + 2R_3) \quad (4-55)$$

4.4.2 Ethyl Acrylate

Both liquid and vapor feeds to the system contain no ethyl acrylate. Therefore,

$$L_{2,IN} = V_{2,IN} = 0$$

It is the main product of the esterification and leaves the system as a part of the exit vapor. It may be consumed by addition of ethyl alcohol to give β -ethoxy-ethyl propionate. However, the formation of β -ethoxy-ethyl propionate is a very slow reaction and has been proved to be more dependent on the concentrations of ethyl alcohol and acrylamide sulfate. Thus, the molal reaction rate of ethyl acrylate is mostly attributed to Reaction (1), vR_1 . Substituting this quantity into Equation (3-20) gives the equation for rate of appearance of ethyl acrylate in the system.

$$\frac{dM_2}{dt} = -V_{2,OUT} + vR_1 \quad (4-56)$$

4.4.3 Water

All the streams entering and leaving the system contain water. It is also formed as a by-product by Reaction (2) of which main product is diethyl ether. Its rate of formation is vR_2 and Equation (3-20) can be written in the following form for water.

$$\frac{dM_3}{dt} = L_{3,IN} + V_{3,IN} - V_{3,OUT} + vR_2 \quad (4-57)$$

4.4.4 Diethyl Ether

The feeds contain no ether and it is produced by Reaction (2). Thus, the rate of mass change of diethyl ether is expressed as

$$\frac{dM_4}{dt} = -V_{4,OUT} + vR_2 \quad (4-58)$$

4.4.5 β -Ethoxy-Ethyl Propionate

The source of β -ethoxy ethyl propionate is Reaction (3). It is volatile and leaves the system in the exit vapor. Thus,

$$\frac{dM_5}{dt} = -V_{5,OUT} + vR_3 \quad (4-59)$$

4.4.6 Acrylamide Sulfate

Acrylamide sulfate does not enter and leave the system. It is only consumed by chemical reactions within the system. Differentiation of Equation (4-54) gives the rate of consumption of acrylamide sulfate as a function of production rates of ethyl acrylate and β -ethoxy-ethyl propionate as follows:

$$\frac{dM_6}{dt} = -\left(\frac{dA_2}{dt} + \frac{dA_5}{dt} \right) \quad (4-60)$$

Now, the rate of production of ethyl acrylate can be expressed as

$$\frac{dA_2}{dt} = vR_1 \quad (4-61)$$

where v is the volume of total liquid in the system.

The production rate of β -ethoxy ethyl propionate can be expressed by Equation (4-47) which can be rewritten as follows:

$$\frac{dA_5}{dt} = vR_3 \quad (4-62)$$

Equations (4-61) and (4-62) can be introduced into Equation (4-60) to yield

$$\frac{dM_6}{dt} = -v(R_1 + R_3) \quad (4-63)$$

4.4.7 Sulfuric Acid

Sulfuric acid is charged to the system only once before the system operation. It is very nonvolatile. Its presence in vapor condensate can not be detected by titration with barium chloride solution. Since sulfuric acid is also not generated or consumed by chemical reactions, it has a zero molal rate of change obtained from differentiation of Equation (4-52) with respect to

time.

$$\frac{dM_7}{dt} = 0 \quad (4-64)$$

4.4.8 Ammonium Bisulfate

The sources for ammonium bisulfate are Reactions (1) and (3). Thus,

$$\frac{dM_8}{dt} = v(R_1 + R_3) \quad (4-65)$$

Ammonium bisulfate is a very nonvolatile solid. The outlet vapor contains no trace of it.

4.4.9 Acrylamide

Similar to sulfuric acid, the expression for $\frac{dM_9}{dt}$ can be obtained by differentiating Equation (4-53).

$$\frac{dM_9}{dt} = 0 \quad (4-66)$$

4.4.10 Overall Rates of Mass and Energy Changes

Summation of Equations (4-55) to (4-59) and (4-63) to (4-66) gives the overall mass change rate as follows:

$$\frac{dM}{dt} = V_{IN} + L_{IN} - V_{OUT} - vR_3 \quad (4-67)$$

where

$$L_{IN} = L_{1,IN} + L_{3,IN}$$

$$V_{IN} = V_{1,IN} + V_{3,IN}$$

$$V_{OUT} = \sum_{i=1}^5 V_{i,OUT}$$

The heat loss from the system to the surrounding can be represented by the heat transfer rate equation.

$$Q_L = U_i a_i (T - T_o) \quad (4-68)$$

where

a_i = inside heat transfer area

U_i = overall heat transfer coefficient in terms
of inside heat transfer area

Substituting this equation into Equation (3-14a) yields the following expression for temperature change in the system

$$\frac{dT}{dt} = \frac{1}{MC_p} \left[L_{IN} h_{IN} + V_{IN} H_{IN} - V_{OUT} H_{OUT} + v \sum_{j=1}^3 R_j (- \Delta H_{R,j}) - U_i a_i (T - T_o) - h_s \frac{dM}{dt} \right] \quad (4-69)$$

4.5 Mass Transfer Effects on Reaction Rates

4.5.1 Hatta's Film Theory

The reaction rates as discussed in the previous sections are affected by mass transfer of molecular

species at the interface. The mass transfer effects are very complex, but its characteristics can be analyzed and discussed by the use of Hatta's film theory (28,29,30,31). Though actual reactions involved in the present study are the pseudo-high-order reactions, the film theory will be initially considered for a first-order irreversible chemical reaction. A basic mathematical model developed will then be modified and extended to the present system. Let the reaction be



where

A= reactant

P= product

k= reaction rate constant

In this study, the reactant enters the system through both gas and liquid feed streams. The case with only gas feed stream will be discussed first. Its liquid-gas interface can best be postulated by Fig. 4.2.

According to Hatta's film theory, for any given moment, the rate of change of mass flux by diffusion was set equal to the chemical reaction rate, assuming the rate of accumulation in the thin film is comparable very small and negligible. The relationship can be expressed as

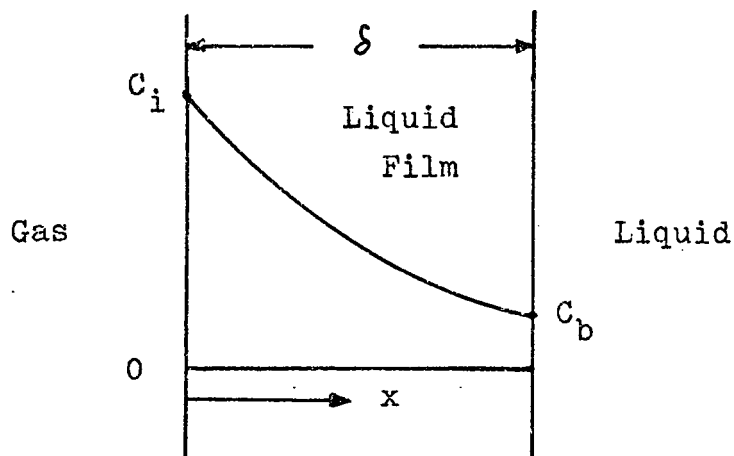


Fig. 4.2 Gas Absorption Accompanied by Chemical Reaction

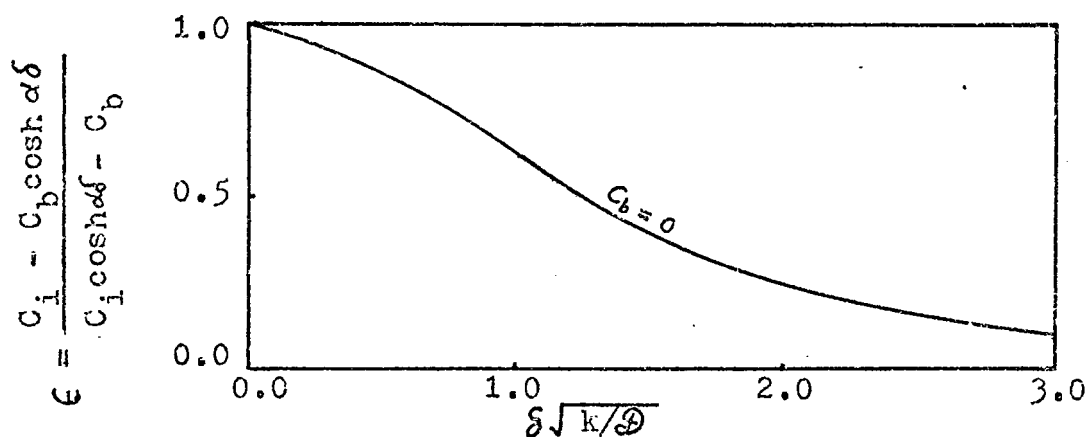


Fig. 4.3 Fraction of Unreacted Reactant Entering the Liquid Bulk

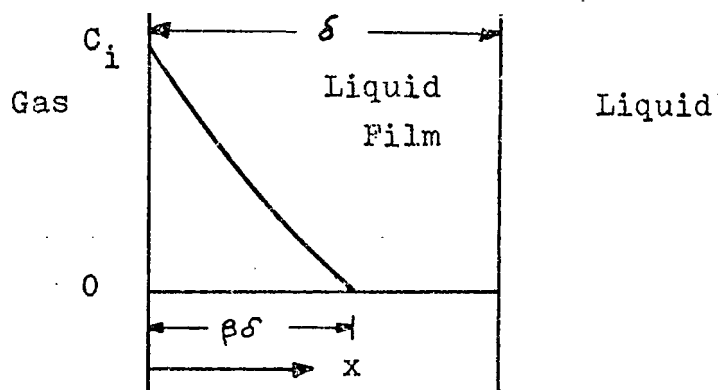


Fig. 4.4 Concentration Gradient for a Very Fast Reaction During Gas Absorption

$$\mathcal{D} \frac{d^2C}{dx^2} = kC \quad (4-71)$$

where

x = axial distance

k = reaction rate constant

C = concentration of dissolved gas reactant in
liquid film

\mathcal{D} = diffusivity of dissolved gas reactant through
liquid film

The corresponding boundary conditions are

$$(1) \quad x = 0 \quad C = C_i \quad (4-72)$$

$$(2) \quad x = \delta \quad C = C_b \quad (4-73)$$

where

δ = film thickness

C_i = interface concentration of reactant A

C_b = concentration of reactant A in liquid bulk

$$C_i > C_b$$

A solution for Equation (4-71) can be obtained readily in the form of

$$C = A_1 \sinh \alpha x + A_2 \cosh \alpha x \quad (4-74)$$

where

$$\alpha = \sqrt{k/\mathcal{D}}$$

The boundary conditions (4-72) and (4-73) can be substituted in Equation (4-74) yielding the following

expression for the concentration of reactant A within the liquid film,

$$C = \frac{C_b \sinh \alpha x + C_i \sinh \alpha (\delta - x)}{\sinh \alpha \delta} \quad (4-75)$$

The rate of diffusion of solute A into the liquid is obtained from

$$N_A = -D \frac{dC}{dx} \Big|_{x=0} = \frac{D(-C_b + C_i \cosh \alpha \delta)}{\sinh \alpha \delta} \quad (4-76)$$

Also the rate of diffusion of solute A into the bulk of the liquid is obtained by substituting $x = \delta$:

$$N_A' = -D \frac{dC}{dx} \Big|_{x=\delta} = \frac{D(C_i - C_b \cosh \alpha \delta)}{\sinh \alpha \delta} \quad (4-77)$$

Of the solute A entering the liquid phase, the fraction ϵ reaching the liquid bulk without reacting is given by

$$\epsilon = \frac{C_i - C_b \cosh \alpha \delta}{C_i \cosh \alpha \delta - C_b} \quad (4-78)$$

The reacted fraction ϵ of solute A for C_b equal to zero is shown in Fig. 4.3.

For a very slow reaction, i.e., $\delta \sqrt{k/D} \rightarrow 0$, all the absorbed reactants enter the liquid bulk without reaction. For a fast reaction, the solute disappears very quickly as it moves across the liquid film. For a very fast reaction, the dissolved A is entirely consumed by the reaction within the liquid film as shown in Fig. 4.4.

The boundary conditions for such a situation are

$$(1) \ x=0 \quad C = C_i \quad (4-72)$$

$$(2) \ x=\beta\delta \quad C = 0, \quad 0 < \beta \leq 1 \quad (4-79)$$

The solution of Equation (4-71) with the above boundary conditions is

$$C = \frac{C_i \sinh \alpha(\beta\delta - x)}{\sinh \alpha\beta\delta} \quad (4-80)$$

Next, consider the case where a liquid reactant A diffuses through the liquid film toward the gas phase. Its gas-liquid interface can be illustrated by Fig. 4.5. The rate equation, boundary conditions, and solution for this case are identical to Equations (4-71), (4-72), and (4-73) for gas-absorption accompanied by chemical reaction except that the concentration in liquid bulk, C_b is greater than that at the gas-liquid interface, C_i . For a very slow reaction, i.e., $\delta\sqrt{k/D} \rightarrow 0$, all the reactants diffused from the liquid bulk are evaporated into the gas bubble without reaction. For a fast reaction, the solute disappears very quickly as it moves across the liquid film. For a very fast reaction, the dissolved A is entirely consumed by the reaction within the liquid film as shown in Fig. 4.6. The boundary conditions for such a case will be

$$(1) \ x = \beta\delta \quad C = 0 \quad (4-79)$$

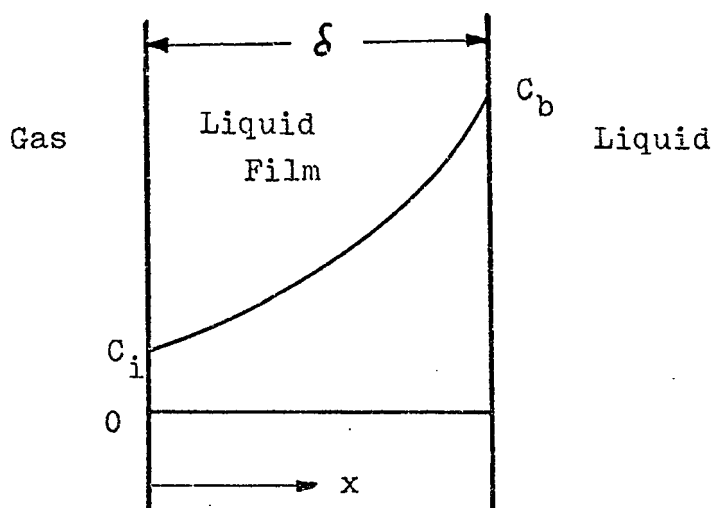


Fig. 4.5 Concentration Gradient for Liquid Evaporation with Chemical Reaction

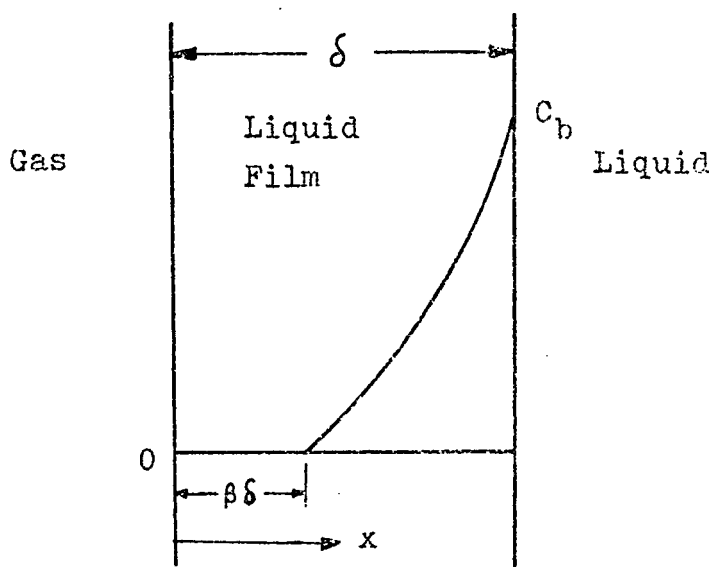


Fig. 4.6 Concentration Gradient for A Very Fast Reaction During Liquid Evaporation

$$(2) \quad x = \delta \quad C = C_b \quad (4-73)$$

The solution of Equation (4-71) with the above boundary conditions can be solved readily:

$$C = \frac{C_b \sinh \alpha (x - \beta \delta)}{\sinh \alpha \delta (1 - \beta)} \quad (4-81)$$

There is no reactant A entering the gas bubble and Equation (4-81) can be obtained from a more general solution of Equation (4-75) by proper substitution.

Finally, consider a combined case in which the reactant A is supplied from both gas bubble and liquid bulk. For a very fast reaction, the reactant A coming from the gas bubble completely disappears in the film at $x = \beta \delta$ and that coming from the liquid bulk disappears at $x = \xi \delta$ as shown by Fig 4.7. Since this is a combination of Fig 4.3 and Fig 4.5, the solutions for the concentration gradients are identical to Equations (4-80) and (4-81) except that the fraction β shown in Equation (4-81) should be replaced by ξ . The complete solution for this case are as follows:

$$\begin{cases} C = \frac{C_i \sinh \alpha (\beta \delta - x)}{\sinh \alpha \beta \delta} & 0 \leq x \leq \beta \delta & (4-82a) \\ C = 0 & \beta \delta \leq x \leq \xi \delta & (4-82b) \\ C = \frac{C_b \sinh \alpha (x - \xi \delta)}{\sinh \alpha (1 - \xi) \delta} & \xi \delta \leq x \leq \delta & (4-82c) \end{cases}$$

A special case for the above equations is applied when

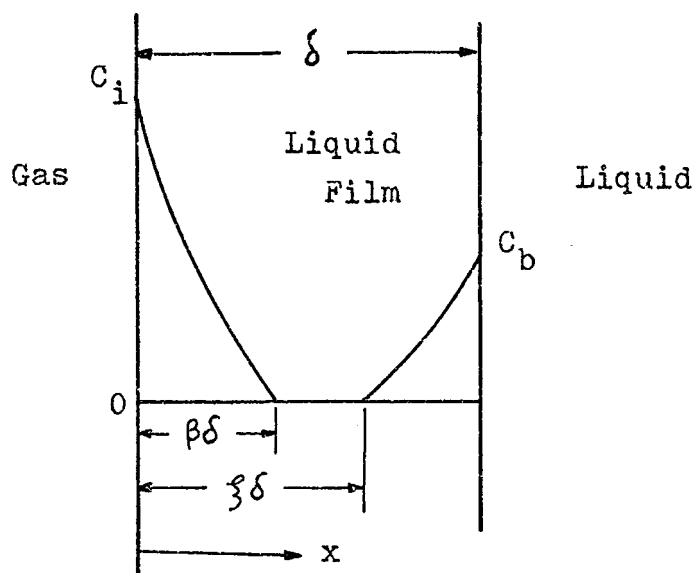


Fig. 4.7 Concentration Gradient for A Moderate Fast Reaction with Reactant Coming from both Gas Bubble and Liquid Bulk

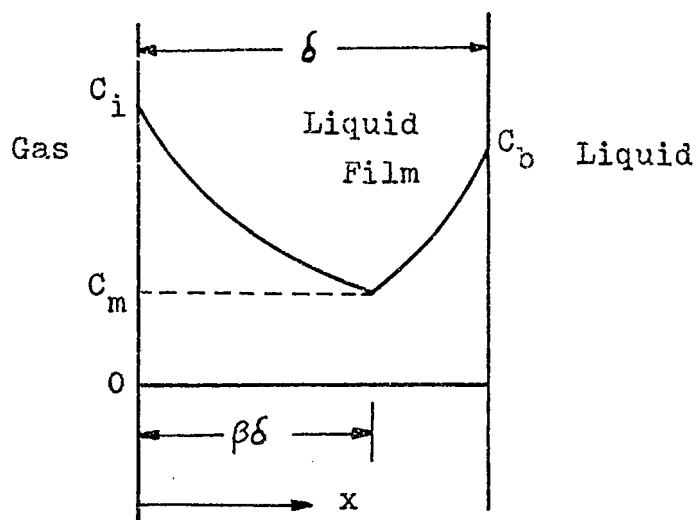


Fig. 4.8 Concentration Gradient for A Moderate Slow Reaction with Reactant Coming from both Gas Bubble and Liquid Bulk

the two concentration curves become zero at the same point, i.e., $\xi = \beta$. The solutions become

$$\left\{ \begin{array}{l} C = \frac{C_i \sinh \alpha(\beta\delta - x)}{\sinh \alpha\beta\delta} \end{array} \right. \quad 0 \leq x \leq \beta\delta \quad (4-83a)$$

$$\left\{ \begin{array}{l} C = \frac{C_b \sinh \alpha(x - \beta\delta)}{\sinh \alpha\delta(1 - \beta)} \end{array} \right. \quad \beta\delta \leq x \leq \delta \quad (4-83b)$$

For moderate reaction rate, the two concentration curves will intersect at a point $\beta\delta$ and have same concentration, C_m as shown by Fig. 4.8. The boundary conditions for such a situation include the following two sets:

$$\text{Set 1} \quad \left\{ \begin{array}{l} x = 0 \\ x = \beta\delta \end{array} \right. \quad \begin{array}{l} C = C_i \\ C = C_m \end{array} \quad \begin{array}{l} (4-72) \\ (4-84) \end{array}$$

$$\text{Set 2} \quad \left\{ \begin{array}{l} x = \beta\delta \\ x = \delta \end{array} \right. \quad \begin{array}{l} C = C_m \\ C = C_b \end{array} \quad \begin{array}{l} (4-84) \\ (4-73) \end{array}$$

The solution of Equation (4-86) and the above boundary conditions can be obtained readily as

$$\left\{ \begin{array}{l} C = \frac{C_m \sinh \alpha x + C_i \sinh \alpha(\beta\delta - x)}{\sinh \alpha\beta\delta}, \quad 0 \leq x \leq \beta\delta \quad (4-85a) \\ C = \frac{C_m \sinh \alpha(\delta - x) + C_b \sinh \alpha(x - \beta\delta)}{\sinh \alpha\delta(1 - \beta)}, \end{array} \right.$$

$$\beta\delta \leq x \leq \delta \quad (4-85b)$$

Again, if C_m is equal to zero, Equations (4-85a) and (4-85b) can then be reduced to a special case whose

solutions are represented by Equations (4-83a) and (4-83b).

Now, if the interface area of all the bubbles in the system is a cm^2/cm^3 clear liquid volume, the rate of mass produced and/or consumed by reaction in the liquid film surrounding the bubbles will be

$$W_f = \int_0^\delta akC \, dx \quad (4-86)$$

A more general form of the reactant concentration gradient, i.e., Equation (4-85a) and (4-85b), is substituted into Equation (4-86) to yield the rate of mass generation or consumption within the liquid films.

$$\begin{aligned} W_f &= \int_0^\delta akC \, dx = ak \int_0^{\beta\delta} \left[\frac{C_m \sinh \alpha x + C_i \sinh (\beta\delta - x)}{\sinh \alpha\beta\delta} \right] dx \\ &\quad + \int_{\beta\delta}^\delta \left[\frac{C_m \sinh \alpha(\delta - x) + C_b \sinh \alpha(x - \beta\delta)}{\sinh \alpha\delta(1 - \beta)} \right] dx \\ &= \frac{ak}{\sinh \alpha\beta\delta} \left[\frac{C_m}{\alpha} \cosh \alpha x - \frac{C_i}{\alpha} \cosh \alpha(\beta\delta - x) \right]_0^{\beta\delta} \\ &\quad + \frac{ak}{\sinh \alpha\delta(1 - \beta)} \left[-\frac{C_m}{\alpha} \cosh \alpha(\delta - x) + \frac{C_b}{\alpha} \cosh \alpha(x - \beta\delta) \right]_{\beta\delta}^\delta \\ &= \frac{ak}{\alpha \sinh \alpha\beta\delta} \left[C_m (\cosh \alpha\beta\delta - 1) - C_i (1 - \cosh \alpha\beta\delta) \right] \\ &\quad + \frac{ak}{\alpha \sinh \alpha\delta(1 - \beta)} \left[-C_m \{1 - \cosh \alpha\delta(1 - \beta)\} + \right. \\ &\quad \left. C_b \{ \cosh \alpha\delta(1 - \beta) - 1 \} \right] \end{aligned}$$

$$= \frac{ak(C_m + C_i)(\cosh \alpha \beta \delta - 1)}{\alpha \sinh \alpha \beta \delta} + \frac{ak(C_m + C_b)[\cosh \alpha \delta (1 - \beta) - 1]}{\alpha \sinh \alpha \delta (1 - \beta)} \quad (4-87)$$

It will be of interest to predict the behavior, by the above equation, of the system under extreme conditions.

If the diffusional mass transfer rate is very large compared to the reaction rate, the mass transfer resistance will be very small such that $\delta \rightarrow 0$. With $\delta \rightarrow 0$, Equation (4-87) can be reduced to zero:

$$\begin{aligned} \lim_{\delta \rightarrow 0} \int_0^{\delta} akc \, dx &= \lim_{\delta \rightarrow 0} \frac{ak(C_m + C_i)(\cosh \alpha \beta \delta - 1)}{\alpha \sinh \alpha \beta \delta} \\ &+ \lim_{\delta \rightarrow 0} \frac{ak(C_m + C_b)[\cosh \alpha \delta (1 - \beta) - 1]}{\alpha \sinh \alpha \delta (1 - \beta)} \\ &= \frac{ak(C_m + C_i)}{\alpha} \lim_{\delta \rightarrow 0} \frac{\cosh \alpha \beta \delta - 1}{\sinh \alpha \beta \delta} + \frac{ak(C_m + C_b)}{\alpha} \lim_{\delta \rightarrow 0} \frac{\cosh \alpha \delta (1 - \beta) - 1}{\sinh \alpha \delta (1 - \beta)} \\ &= \frac{ak(C_m + C_i)}{\alpha} \lim_{\delta \rightarrow 0} \frac{\alpha \beta \sinh \alpha \beta \delta}{\alpha \beta \cosh \alpha \beta \delta} + \frac{ak(C_m + C_b)}{\alpha} \lim_{\delta \rightarrow 0} \frac{\alpha (1 - \beta) \sinh \alpha \delta (1 - \beta)}{\alpha (1 - \beta) \cosh \alpha \delta (1 - \beta)} \\ &= 0 \end{aligned}$$

This means that the production or consumption is almost none within the liquid film and that all the reactions take

place in the liquid bulk if the diffusional mass transfer rate is extremely large.

On the other hand, if the reaction rate is extremely high compared with the diffusion rate, Equations (4-82a), (4-82b) and (4-82c) can be substituted into Equation (4-86) giving:

$$\begin{aligned}
 \int_0^{\delta} akC \, dx &= \frac{akC_i}{\sinh \alpha \beta \delta} \int_0^{\beta \delta} \sinh \alpha (\beta \delta - x) \, dx + \int_{\beta \delta}^{\delta} 0 \, dx \\
 &+ \frac{akC_b}{\sinh \alpha \delta (1-\beta)} \int_{\beta \delta}^{\delta} \sinh \alpha (x - \beta \delta) \, dx \\
 &= \frac{-akC_i}{\alpha \sinh \alpha \beta \delta} \left[\cosh \alpha (\beta \delta - x) \right]_0^{\beta \delta} \\
 &\quad + \frac{akC_b}{\alpha \sinh \alpha \delta (1-\beta)} \left[\cosh \alpha (x - \beta \delta) \right]_{\beta \delta}^{\delta} \\
 &= \frac{akC_i (\cosh \alpha \beta \delta - 1)}{\alpha \sinh \alpha \beta \delta} + \frac{akC_b [\cosh \alpha \delta (1-\beta) - 1]}{\alpha \sinh \alpha \delta (1-\beta)} \\
 &\hspace{15em} (4-88)
 \end{aligned}$$

If there is no liquid feed, i.e., $C_b = 0$, the overall amount of reactant consumed within the film will depend on gas-liquid interfacial solubility C_i only, and no reactant diffuses into the liquid bulk from the vapor bubbles. On the contrary, if there is no vapor feed, i.e., $C_i = 0$, there will be no reactant appearing in the generated vapor bubbles.

4.5.2 Reaction in Liquid Bulk

Since the liquid portion of the feed contains a reactant, ethyl alcohol, the reaction also takes place continuously in the liquid bulk. The rate of mass production and consumption in the liquid bulk is designated W_B and can be expressed as follows.

$$W_B = kC_b(v - a\delta) \quad (4-89)$$

where v is the clear liquid volume. It should be noted that the volume of liquid bulk excluding the film is represented by $(v - a\delta)$.

4.5.3 Overall Rates of Mass Production or Consumption

Since a component is consumed or produced both within the liquid film and in the liquid bulk, its overall mass rate of production or consumption can be expressed as

$$W_T = W_f + W_B$$

Substituting Equations (4-87) and (4-89) into the above yields

$$W_T = \frac{ak(C_m + C_i)(\cosh \alpha\beta\delta - 1)}{\alpha \sinh \alpha\beta\delta} + \frac{ak(C_m + C_b)[\cosh \alpha\delta(1-\beta) - 1]}{\alpha \sinh \alpha\delta(1-\beta)} + kC_b(v - a\delta) \quad (4-90)$$

If the reaction rate for a unit volume is designated by R_T , then

$$W_T = R_T v \quad (4-91)$$

Equating Equations (4-90) and (4-91) gives

$$R_T = \frac{1}{v} \left\{ \frac{ak(C_m + C_i)(\cosh \alpha \beta \delta - 1)}{\alpha \sinh \alpha \beta} + \frac{ak(C_m + C_b)[\cosh \alpha \beta (1 - \beta) - 1]}{\alpha \sinh \alpha \delta (1 - \beta)} + kC_b(v - a\delta) \right\}$$

or,

$$R_T = kC_b \left(1 - \frac{a\delta}{v} \right) + \frac{ak(C_m + C_i)(\cosh \alpha \beta \delta - 1)}{\alpha v \sinh \alpha \beta} + \frac{ak(C_m + C_b)[\cosh \alpha \delta (1 - \beta) - 1]}{\alpha v \sinh \alpha \delta (1 - \beta)} \quad (4-92)$$

4.5.4 Mass Transfer Effects Correction Factors

In order to account for the mass transfer effects, a mass transfer correction factor is introduced to the following intrinsic rate expression,

$$R_T = \eta k C_T \quad (4-93)$$

where

η : mass transfer correction factor on the intrinsic rate expression

k : intrinsic rate constant

C_T : concentration measured from an overall liquid sample

Equating the exact solution, Equation (4-92) and the defining equation, Equation (4-93) gives

$$\eta = \frac{C_b}{C_T} \left(1 - \frac{a\delta}{v}\right) + \frac{a(C_i + C_m)(\cosh \alpha\beta\delta - 1)}{\alpha C_T \sinh \alpha\beta\delta} + \frac{a(C_m + C_b)[\cosh \alpha\delta(1-\beta) - 1]}{\alpha^v C_T \sinh \alpha\delta(1-\beta)} \quad (4-94)$$

Equation (4-94) contains three terms which represent the mass transfer effects on reaction rates, namely film thickness, interfacial area, and interfacial concentration. These three terms, δ , a and C_i cannot be measured directly and separately. Therefore, it is convenient and practical that the correction factor, η , is introduced to lump the three unmeasurable variables into one.

As the values of the liquid film thickness, the interfacial area, and the interfacial concentrations are affected by the system operating conditions, the mass transfer effects correction factor is characterized by the same system parameters. These parameters are numerous and include those related to physical dimensions and shape of the apparatus, operating and flow conditions, and transport properties of the system. It is too ambitious to study the effects of all the parameters on the correction factors. For the present study, therefore, the number of the parameters of which the effects are to be investigated is limited to four. These variables are:

1. Initial system temperature and surrounding temperature, T_o
2. Total feed rate, F
3. Relative ratio of feed vapor to total feed, ψ
4. System temperature, T

Thus, the correction factor, η , can be expressed by

$$\eta = \eta(T_o, F, \psi, T) \quad (4-95)$$

It is noted that the first three variables, T_o , F , and ψ change from one experimental run to another but are set equal to certain constant values during a given run. The system temperature T is a time-dependent function during each run. It is assumed that η -function is a product of two separate functions as follows:

$$\eta = \eta(T_o, F, \psi, T) = \eta_s(T_o, F, \psi) \cdot \eta_T(T) \quad (4-96)$$

The above approach is useful because one function η_s , which is not time-dependent, is separated from the other η_T , which is time-dependent. It is further assumed that the temperature dependent function, η_T , is related to temperature in a functional relationship similar to the Arrhenius Equation, namely,

$$\eta_T(T) = e^{-E_\eta/RT} \quad (4-97)$$

where

$$R = \text{gas constant} = 1.987 \text{ cal/g-mole-}^\circ\text{C}$$

Substituting Equation (4-97) into Equation (4-96) gives

the following expression for the mass transfer coefficient factor:

$$\eta = \eta_s \eta_T = \eta_s e^{-E_\eta/RT} \quad (4-98)$$

It is recalled that the Arrhenius Equation relates the reaction rate constant k to temperature as follows

$$k = k_o e^{-E_o/RT} \quad (4-99)$$

Substituting Equation (4-98) and (4-99) into Equation (4-93) yields

$$\begin{aligned} R_T &= \eta k C_T = \left[\eta_s e^{-E_\eta/RT} \right] \left[k_o e^{-E_o/RT} \right] C_T \\ &= \eta_s k_o e^{-(E_\eta + E_o)/RT} \end{aligned}$$

or

$$R_T = K_m e^{-E_m/RT} C_T \quad (4-100)$$

where

$$E_m = E_\eta + E_o \quad (4-100a)$$

$$K_m = \eta_s k_o \quad (4-100b)$$

Furthermore, if an intrinsic reaction rate equation

$$R_T = k_m C_T \quad (4-101)$$

is adopted for expressing the overall reaction rate which indicates not only the reaction kinetics but also the mass transfer effects, the constant, k_m , can

be represented by the Arrhenius-type equation

$$k_m = K_m e^{-E_m/RT} \quad (4-102)$$

It is emphasized that the terms, k_m , E_m , and K_m , as defined by their respective equations, include the variables representing the contributions from both reaction kinetics and mass transfer.

4.5.5 Pseudo-High-Order Reactions

As discussed earlier, the chemical reactions encountered in this study are more complex and pseudo-high-order reactions. The mathematical analysis and models for the rate expressions including mass transfer effects for such reactions will be extremely complex but the basic approach in deriving Equations (4-100) to (4-102) may be extended to the high-order reactions. Thus,

For Reaction 1 — Esterification

$$R_{1,T} = k_{m,1} C_{1,T} C_{6,T} = K_{m,1} e^{-E_{m,1}/RT} C_{1,T} C_{6,T} \quad (4-103)$$

For Reaction 2 — Dehydration

$$R_{2,T} = k_{m,2} C_{1,T}^2 = K_{m,2} e^{-E_{m,2}/RT} C_{1,T}^2 \quad (4-104)$$

For Reaction 3 — Successive Reaction

$$R_{3,T} = k_{m,3} C_{1,T}^2 C_{6,T} = K_{m,3} e^{-E_{m,3}/RT} C_{1,T}^2 C_{6,T} \quad (4-105)$$

The rate equations should then be used to calculate the respective rates, R_i 's, in the series of equations derived in Section 4.4.1 through 4.4.10.

4.6 Relationship between the Vapor and Liquid Composition

Both chemical reaction and mass transfer affects the vapor-liquid relationship of a reaction-distillation system. The effects of chemical reaction on a vapor-liquid equilibrium system reflect in the activity coefficients while the effects of mass transfer deviate the system from vapor-liquid equilibrium. In order to reduce the mass transfer effects to the minimum and consequently to obtain a perfectly or nearly perfectly mixed tray as assumed previously, a micro-sieve distillation tray equipped with a high speed stirrer and three baffle plates is then employed. The micro-sieve tray (60-75) produces very tiny bubbles resulting in large interfacial area as well as excellent mixing. The stirrer and the baffle plates provide good mixing and good contact with the vapor bubbles as well as liquid droplets. Therefore, it is reasonable to consider that the sieve tray used in this study can be treated as an ideal tray and the vapor leaving the tray is momentarily in equilibrium with the liquid mixture on the tray.

The equilibrium mole fractions of component i in the vapor and liquid phases may be related by the following

definition.

$$y_i = K_i x_i \quad (4-106)$$

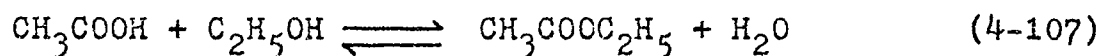
where

K_i = vapor-liquid equilibrium ratio

y_i = vapor mole fraction

x_i = liquid mole fraction

When a chemical reaction is present in the liquid phase, it proceeds until the chemical equilibrium is attained. The vapor-liquid concentration relationship which is sought for the distillation accompanied by chemical reaction is, in general, not that under the chemical equilibrium. Instead, the interest is to determine the relationship of vapor and liquid compositions while they are still under the influence of active chemical reaction. A typical example is the vapor-liquid equilibrium relationship obtained by Hirata and Komatsu (32,33,34), as mentioned previously in Section 2.1.2, for the esterification of acetic acid and ethyl alcohol.



For the present study, it is also assumed that there exists an instantaneous equilibrium at any moment between the vapor leaving the system and the liquid remaining in the system. The instantaneous temperature so measured is considered to be the bubble point of the liquid corres-

ponding to vapor-liquid equilibrium.

Component i in vapor and liquid are in equilibrium if, and only if, fugacity of vapor phase is equal to that of liquid phase.

$$f_i^V \equiv f_i^L \quad (4-108)$$

where

f_i^V = vapor phase fugacity

f_i^L = liquid phase fugacity

The vapor phase fugacity is related to the vapor phase mole fraction through the vapor phase fugacity coefficient ϕ_i by

$$f_i^V = \phi_i y_i P \quad (4-109)$$

where

ϕ_i = vapor phase fugacity coefficient

P = total system pressure

y_i = mole fraction of component i in vapor phase

The liquid phase fugacity f_i^L is related to the liquid phase mole fraction x_i by an activity coefficient and a standard-state fugacity. In this study, the liquid solution is extremely complex. As discussed in Section 4.2, it contains nine compounds as well as their associated ionic species. These ionic species are all initiated by the protons supplied by sulfuric

acid at the presence of water. The amount of free sulfuric acid in the liquid solution is essentially fixed for all the experimental runs at any instance. The amount of water is increased due to a continuous feed and a dehydration reaction but decreased due to a continuous evaporation. The resulting amount of water from the above three functions gives an almost constant water mole fraction in the liquid solution. Therefore, the effects of the liquid compositions of all the ionic species on the activity coefficients of the nine compounds in the system may have little variations. Therefore, it is reasonable, as a practical application, to set up vapor-liquid equilibria for this reaction-distillation system only based on the thermophysical properties of these nine compounds. That is, all the ionic species are included in their corresponding compound. Since all the compounds in the system are condensable, the following form given by Prausnitz, et al. (53) for the liquid fugacity coefficient of a condensable component is then adopted here.

$$f_i^L = \gamma_i x_i f_i^{\text{OL}} \exp \left(\int_{P^r}^P \frac{\bar{v}_i^L}{RT} dP \right) \quad (4-110)$$

where

f_i^{OL} = standard-state fugacity, i.e., fugacity of pure liquid i at temperature T adjusted to the reference pressure P^r

γ_i = activity coefficient of component i at temperature T adjusted to the reference pressure P^r
 \bar{v}_i^L = partial molal volume of i in the solution at temperature T.

The standard-state fugacity is given by

$$f_i^{oL} = p_i^o \phi_i^o \exp \left(\int_{p_i^o}^{P^r} \frac{v_i^L}{RT} dP \right) \quad (4-111)$$

where

p_i^o = saturated vapor pressure of pure liquid i
 ϕ_i^o = fugacity coefficient of pure vapor i at temperature T and pressure p_i^o , and
 v_i^L = molar liquid volume of pure component i at temperature T.

Since the solution in the system is far from critical conditions, v_i^L and \bar{v}_i^L are of negligible difference. Equations (4-110) and (4-111) can then be combined and simplified to

$$f_i^L = \gamma_i x_i p_i^o \phi_i^o \exp \left(\int_{p_i^o}^P \frac{v_i^L}{RT} dP \right) \quad (4-112)$$

Also, at low subcritical conditions, the liquid molar volume v_i^L may be considered to be independent of system pressure (53), Equation (4-112) may be further reduced to:

$$f_i^L = \gamma_i x_i p_i^o \phi_i^o \exp \left[\frac{v_i^L (P - p_i^o)}{RT} \right] \quad (4-113)$$

Substituting Equations (4-109) and (4-113) into Equation (4-108) gives the following vapor-liquid equilibrium relationship.

$$\phi_i y_i P = \gamma_i x_i p_i^o \phi_i^o \exp \left[\frac{v_i^L (P - p_i^o)}{RT} \right] \quad (4-114)$$

Equation (4-114) can now be incorporated with the defining equation, Equation (4-106) to yield the following expression for K_i :

$$K_i = \frac{y_i}{x_i} = \frac{\gamma_i p_i^o \phi_i^o \exp \left[\frac{v_i^L (P - p_i^o)}{RT} \right]}{\phi_i P} \quad (4-115)$$

The exponential term, $\exp (v_i^L (P - p_i^o)/RT)$, in the above equation is called Poynting factor. At atmospheric pressure, the highest calculated Poynting factor is 1.009 for ethyl alcohol at 130 °C. This term can then be simply set to unity. Also at the low pressure the vapor mixture may be considered to be an ideal gas and ideal solution. Thus, the vapor fugacity coefficient in the mixture, ϕ_i , may also be set to unity without significant error.

With the assumptions that $\phi_i = 1.0$ and $\exp \left[\frac{v_i^L (P - p_i^o)}{RT} \right] = 1.0$, Equation (4-115) can now be reduced to the following working equation

$$K_i = \frac{\gamma_i p_i^o \phi_i^o}{P} \quad (4-116)$$

It is noted that fugacity coefficient of pure vapor, ϕ_i^o

cannot be omitted from the above equation because its value for ethyl alcohol at the highest operating temperature, 125.4 °C is only 0.837, which is 16.3 % below unity. The three-parameter general correlations by Prausnitz, et al. are used for estimating the fugacity coefficients of pure vapors. Their correlations are shown in Appendix A.12. For vapor pressures, p_i^0 , the Antoine Equation given in Appendix A.5 is used. Its three constants are either obtained from the literature or fitted from vapor pressure data by the computer program BSOLFIT given in Appendix C.5.

In this study, the instantaneous vapor and liquid compositions are measured experimentally. Thus, K_i -values are obtained from experiments. The only undetermined quantity in Equation(4-116), liquid activity coefficient, can then be calculated from the following rearranged form of Equation (4-116).

$$\gamma_i = \frac{K_i P}{\phi_i^0 p_i^0} = \frac{y_i P}{x_i \phi_i^0 p_i^0} \quad (4-117)$$

However, there are some difficulties when using the above equation for calculating activity coefficients of either very volatile diethyl ether or four very nonvolatile components, namely acrylamide sulfate, sulfuric acid, ammonium bisulfate and acrylamide. For very volatile diethyl ether, its liquid mole fraction,

x_i , can not be measured accurately. For the four very nonvolatile compounds, their vapor mole fractions, y_i , can not be determined properly either. These are all due to the facts that diethyl ether is not detectable in the liquid phase and the four very nonvolatile compounds are not found in the vapor condensate. Since the activity coefficients of diethyl ether and all the nonvolatile compounds are not important for vapor-liquid equilibrium calculations, it is expeditious to lump all the very nonvolatile compounds as a pseudo-component and to treat diethyl ether as a gaseous product from dehydration. The pseudo-component is designated as very nonvolatile material. Summarizing, the liquid mixture to be considered for correlating liquid activity coefficients, as will be shown in Chapter 6, contains the following five readjusted components.

Readjusted Component Identity Number	Component Name
1	Ethyl Alcohol
2	Ethyl Acrylate
3	Water
4	ϕ -Ethoxy-ethyl propionate
5	Very Nonvolatile Material

4.7 Numerical Method for Solution of Unsteady-State Distillation Accompanied by Chemical Reactions

The mathematical model for the semi-batch distillation accompanied by chemical reaction is represented

by a series of differential equations developed in Chapter 3. Because of its complexity, an analytical method for simultaneously solving this set of equations is not available. Therefore, a numerical method is applied. As happened so often the system has more unknowns than the number of equations. It then demands a trial-and-error integrating procedure. Holland (36) has proposed the θ -method for solving an unsteady-state distillation in absence of chemical reaction with a constant holdup. His method is not applicable to the present problem since the liquid holdup on the tray is not constant and the reaction rate expressions are nonlinear here. A new convergence method is proposed in this study to solve the model developed for the unsteady-state distillation accompanied by chemical reaction.

4.7.1 Reduction of Unknown Variables in Working Equation

In order to reduce the number of unknown variables, and to rewrite the model into forms for easier numerical solutions, the following relationships are introduced to Equations (4-55) through (4-59) and (4-63) through (4-66),

(1) Vapor composition

$$V_{i,OUT} = y_i V_{OUT} \quad (4-118)$$

(2) Vapor - liquid equilibrium

$$y_i = \frac{\gamma_i p_i^{\circ} x_i}{P} \quad (4-119)$$

(3) Liquid molal holdup

$$M_i = x_i M \quad (4-120a)$$

or

$$x_i = \frac{M_i}{M} = \frac{M_i}{\sum_{i=1}^9 M_i} \quad (4-120b)$$

(4) Reaction rates

$$R_1 = R_{1,T} = K_{m,1} e^{-E_{m,1}/RT} C_{1,T} C_{6,T} \quad (4-103)$$

$$R_2 = R_{2,T} = K_{m,2} e^{-E_{m,2}/RT} C_{1,T}^2 \quad (4-104)$$

$$R_3 = R_{3,T} = K_{m,3} e^{-E_{m,3}/RT} C_{1,T}^2 C_{6,T} \quad (4-105)$$

(5) Concentration

$$C_{i,T} = \frac{M_i}{V} \quad (4-121)$$

After substitutions and certain rearrangements, Equations (4-55) through (4-59) and (4-63) through (4-66) can be rewritten to the following set of equations

$$\frac{dM_1}{dt} = L_{1,IN} + V_{1,IN} - \frac{\gamma_1 p_1^{\circ}}{P} \frac{V_{OUT} M_1}{M} - \left[K_{m,1} e^{-E_{m,1}/RT} \left(\frac{M_1 M_6}{V} \right) + 2K_{m,2} e^{-E_{m,2}/RT} \frac{M_1^2}{V} + 2K_{m,3} e^{-E_{m,3}/RT} \frac{M_1^2 M_6}{V^2} \right]$$

(4-122)

$$\frac{dM_2}{dt} = - \frac{\gamma_2 p_2^0 \phi_2^0}{P} \frac{M_2 V_{OUT}}{M} + K_{m,1} e^{-E_{m,1}/RT} \frac{M_1 M_6}{v} \quad (4-123)$$

$$\begin{aligned} \frac{dM_3}{dt} = L_{3,IN} + V_{3,IN} - \frac{\gamma_3 p_3^0 \phi_3^0}{P} \frac{M_3 V_{OUT}}{M} + \\ K_{m,2} e^{-E_{m,2}/RT} \frac{M_1^2}{v} \end{aligned} \quad (4-124)$$

$$\frac{dM_4}{dt} = - \frac{\gamma_4 p_4^0 \phi_4^0}{P} \frac{M_4 V_{OUT}}{M} + K_{m,2} e^{-E_{m,2}/RT} \frac{M_1^2}{v} \quad (4-125)$$

$$\frac{dM_5}{dt} = - \frac{\gamma_5 p_5^0 \phi_5^0}{P} \frac{M_5 V_{OUT}}{M} + K_{m,3} e^{-E_{m,3}/RT} \frac{M_1^2 M_6}{v^2} \quad (4-126)$$

$$\begin{aligned} \frac{dM_6}{dt} = - K_{m,1} e^{-E_{m,1}/RT} \frac{M_1 M_6}{v} - K_{m,3} e^{-E_{m,3}/RT} \frac{M_1^2 M_6}{v^2} \\ (4-127) \end{aligned}$$

$$\frac{dM_7}{dt} = 0 \quad (4-128)$$

$$\begin{aligned} \frac{dM_8}{dt} = K_{m,1} e^{-E_{m,1}/RT} \frac{M_1 M_6}{v} + K_{m,3} e^{-E_{m,3}/RT} \frac{M_1^2 M_6}{v^2} \\ (4-129) \end{aligned}$$

$$\frac{dM_9}{dt} = 0 \quad (4-130)$$

It is noted that 9 unknowns ($V_{i,OUT}$) are eliminated and replaced by a new unknown, total vapor rate (V_{OUT}).

The above equations can be substituted into Equation (4-67) to yield another equation for the total mass change.

$$\frac{dM}{dt} = L_{IN} + V_{IN} - V_{OUT} - K_{m,3} e^{-E_{m,3}/RT} \frac{M_1^2 M_6}{v^2} \quad (4-131)$$

The values of heats of reaction needed in Equation (4-69) can be calculated from heats of formation by applying Hess' law. The heats of formation are obtained from literature or estimated by reliable correlations. All the determined heats of reaction along with related data sources and correlation methods are given in Appendix A.10. The reaction rate equations and the heat of reaction expressions are substituted into Equation (4-69) to yield the following new equation for the temperature change with time:

$$\begin{aligned} \frac{dT}{dt} = \frac{1}{MC_p} & \left[L_{IN} h_{IN} + V_{IN} H_{IN} - V_{OUT} H_{OUT} + \right. \\ & (-\Delta H_{R,1}) K_{m,1} e^{-E_{m,1}/RT} \frac{M_1 M_6}{v} + \\ & (-\Delta H_{R,2}) K_{m,2} e^{-E_{m,2}/RT} \frac{M_1^2}{v} + (-\Delta H_{R,3}) K_{m,3} \cdot \\ & \left. e^{-E_{m,3}/RT} \frac{M_1^2 M_6}{v^2} - U_i a_i (T - T_o) - h_s \frac{dM}{dt} \right] \quad (4-132) \end{aligned}$$

Again, the liquid enthalpy and vapor enthalpy required in the above equation are obtained from literature or estimated from the reliable correlations. Appendix A.7 and Appendix A.8 have detailed discussions on these two items.

Since the clear liquid volume, v , is required for calculating the reaction rates for all the three reactions, it is necessary to formulate its rate equation. The difference between the feed rate and the leaving vapor rate contributes most of variation in the clear liquid volume. Assuming excess volume induced from mixing and composition changes by chemical reactions is negligible small compared to the above mentioned factor, the rate of change of the clear liquid volume can be represented by the following equation:

$$\frac{dv}{dt} = \sum_{i=1}^5 \frac{F_i}{\rho_i} - \sum_{i=1}^5 \frac{V_{i,OUT}}{\rho_i} \quad (4-133)$$

where

ρ_i = liquid density for component i at the
temperature of the reacting liquid mixture

$F_i = L_{i,IN} + V_{i,IN}$ = total feed rate for component i

In order to compare the measured vapor molal condensates by the mathematical model, it is then necessary to write rate equations for the vapor condensates of individual components as well as of the total mixture. Let N_i be the instantaneous vapor condensate of component i and N_T the instantaneous total accumulated vapor condensate. Then the relationship between N_i and $V_{i,OUT}$ can be expressed by the following definition:

$$\frac{dN_i}{dt} = V_{i,OUT} \quad (4-134)$$

The above definition can be incorporated with the definitions of Equations (4-118) and (4-119) to give the following working equations for the rates of change of N_i and N_T :

$$\frac{dN_i}{dt} = \left(\frac{\gamma_i p_i^0 \phi_i^0}{P} \frac{M_i}{M} \right) V_{OUT}, \quad i = 1, \dots, 5 \quad (4-135)$$

to (4-139)

$$\frac{dN_T}{dt} = V_{OUT} \quad (4-140)$$

Now, it can be summerized that there are 19 unknowns ($M_1, \dots, M_9, N_1, \dots, N_5, T, M, v, N_T, V_{OUT}$) to be solved simultaneously from 18 equations which can be recapitulated as follows.

$$\frac{dM_i}{dt} = f_i = f_i(M_1, \dots, M_9, N_1, \dots, N_5, T, M, v, N_T, V_{OUT}), \quad i = 1, \dots, 9 \quad (4-141)$$

to (4-149)

$$\frac{dT}{dt} = f_{10} \quad (4-150)$$

$$\frac{dM}{dt} = f_{11} \quad (4-151)$$

$$\frac{dv}{dt} = f_{12} \quad (4-152)$$

$$\frac{dN_i}{dt} = f_{12+i}, \quad i = 1, \dots, 5 \quad (4-153)$$

to (4-157)

$$\frac{dN_T}{dt} = f_{18} \quad (4-158)$$

The boundary and initial conditions given for the solution are the initial liquid compositions, the inlet liquid and vapor compositions and surrounding or oil bath temperature.

A trial procedure begins with an assumed value for V_{OUT} which is the total vapor outlet flow. Then, the integrations and solutions are obtained for the remaining 18 variables by the Runge-Kutta method. The details are given in the next section.

Trial- and-error procedure requires a means of checking whether the assumed value is correct. For this solution, the criterion is that the sum of the component compositions in the outlet vapor must be equal to unity.

$$\sum_{i=1}^5 y_i = 1.0 \quad (4-159)$$

Substituting Equation (4-119) into the above equation yields

$$\sum_{i=1}^5 \frac{\gamma_i^0 p_i^0 \phi_i^0 x_i}{P} = 1.0 \quad (4-160)$$

If an error function α is defined,

$$\alpha = \sum_{i=1}^5 \frac{\gamma_i p_i^0 \phi_i^0 x_i}{P} - 1.0 \quad (4-161)$$

A set of solutions ($M_1, \dots, M_9, T, M, v, N_1, \dots, N_5, N_T$) is obtained when an iteration of the trial-and-error procedure reaches an α -value within the allowable tolerance ϵ . The trial-and-error procedure is best illustrated by the flow diagram given in Fig. 4.9.

4.7.2 Runge-Kutta Method

The Runge-Kutta method (8) has been used widely for obtaining satisfactory numerical solutions for differential equations. It is also used in this study for solving the above 18 simultaneous differential equations. Let t_z and t_{z+1} represent, at the $(z+1)$ th integration step, the previous time and the elapsed time respectively. The Runge-Kutta method makes use of the values of $x_{i,z}^0$ and t_z to predict $x_{i,z+1}^0$ values where x^0 stands for any of the 18 dependent variables. It is based on Taylor's series of expansion of x_i^0 about t . The evaluation of the terms which are higher than the fourth order is not necessary for most applications, and the Runge-Kutta fourth-order method is discussed here.

In order for a uniform and easy discussion of the

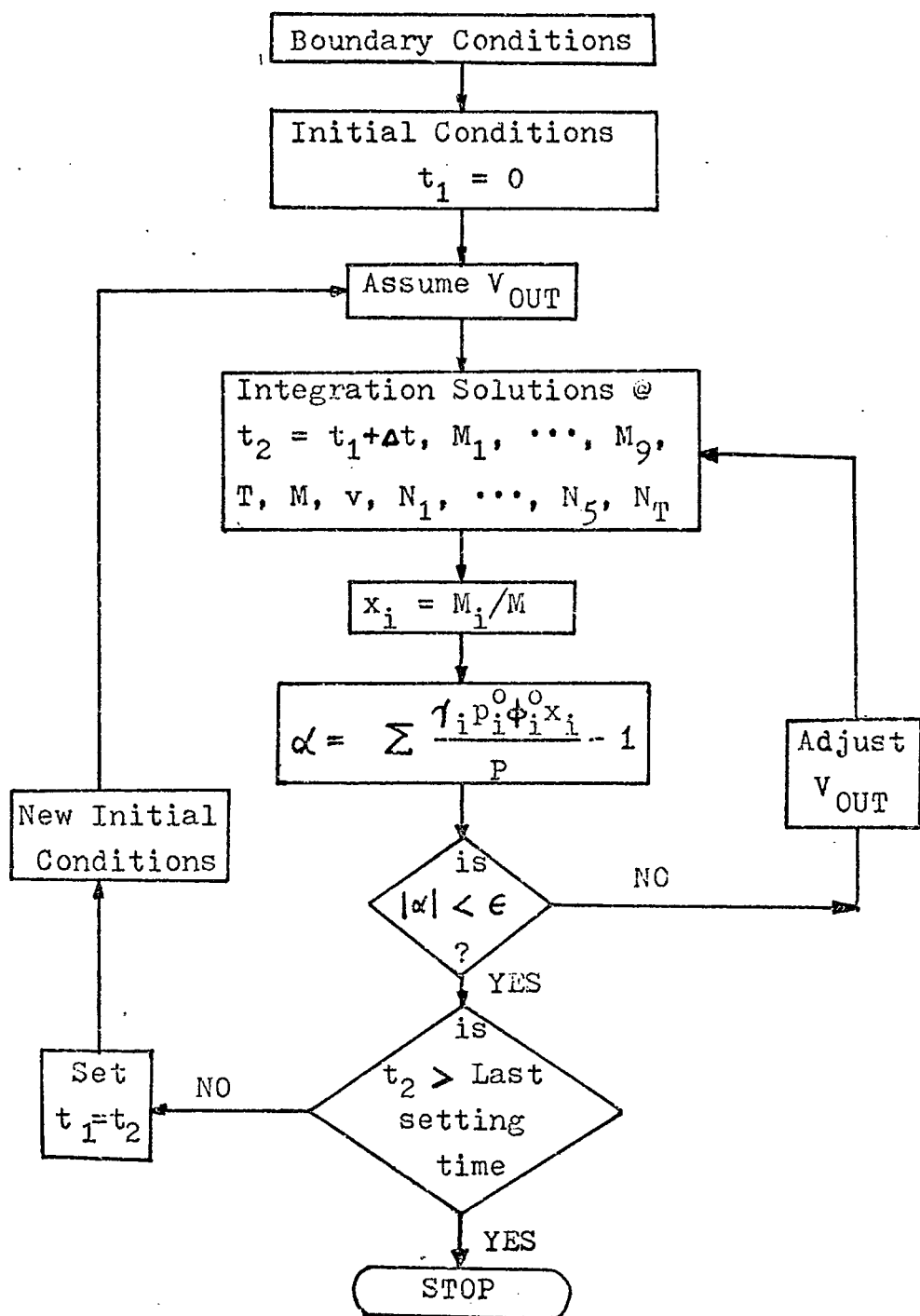


Fig. 4.9 Flow Diagram for Integration Procedures by Trial-And-Error

procedures, the 18 dependent variables are represented by the above mentioned mathematical terms, x_i^0 as follows.

$$\begin{aligned} x_1^0 &= M_1 \\ &\vdots \\ x_9^0 &= M_9 \\ x_{10}^0 &= T \\ x_{11}^0 &= M \\ x_{12}^0 &= v \\ x_{13}^0 &= N_1 \\ &\vdots \\ x_{17}^0 &= N_5 \\ x_{18}^0 &= N_T \end{aligned}$$

Then, a general representation of a working equation can be written for variable x_i^0 :

$$\frac{dx_i^0}{dt} = f_i(x_i^0, v_{OUT}, t) \quad (4-162)$$

Then, the Runge-Kutta formula can be represented as

$$x_{i,z+1}^0 = x_{i,z}^0 + \frac{\Delta t}{6}(G_{i,1} + 2G_{i,2} + 2G_{i,3} + G_{i,4}) \quad (4-163)$$

where

Δt = Size of integration step

$$G_{i,1} = f(t_z, x_{i,z}^0, v_{OUT,z}) \quad (4-164)$$

$$G_{i,2} = f(t_{z+\frac{1}{2}}, x_{i,z}^0 + \frac{1}{2}\Delta t G_{i,1}, v_{OUT,z+\frac{1}{2}}) \quad (4-165)$$

$$G_{i,3} = f\left(t_{z+\frac{1}{2}}, x_{i,z}^0 + \frac{1}{2} \Delta t G_{i,2}, V_{OUT,z+\frac{1}{2}}\right) \quad (4-166)$$

$$G_{i,4} = f\left(t_{z+1}, x_{i,z}^0 + \Delta t G_{i,3}, V_{OUT,z+1}\right) \quad (4-167)$$

With the exception of $V_{OUT,z+1}$, $V_{OUT,z+\frac{1}{2}}$, the values of individual terms in the right-hand sides of the above equations are available from the calculated results of the previous step. The first assumption is made for the value of $V_{OUT,z}$ which is then designated as $v^{(1)}$. If the very small time interval Δt is chosen so that V_{OUT} can be represented as a linear function of time, then

$$V_{OUT,z+\frac{1}{2}} = \frac{1}{2} (V_{OUT,z} + V_{OUT,z+1})$$

or

$$V_{OUT,z+\frac{1}{2}} = \frac{1}{2} (V_{OUT,z} + v^{(1)}) \quad (4-168)$$

Thus, $x_{i,z+1}^0$ can be calculated by Equation (4-163) after $G_{i,1}$, $G_{i,2}$, $G_{i,3}$, and $G_{i,4}$ are determined by Equations (4-164) through (4-167). It is noted that during the course of computation, the computation requires values for vapor pressure, activity coefficient, and reaction rate constants. These values will be obtained by appropriate correlations which are given later in Chapter 6.

When a set of $x_{i,z+1}^0$'s is obtained, the value of the error function α is calculated by Equation (4-161). If the absolute value of α is less than the tolerance, then the trial procedure is terminated for the $(z+1)$ th

step. The last assumed value of V_{OUT} and the last calculated values of x_i^0 's are the desired solutions. These values are then used as the starting values for another series of trial-and-error calculations for the next time interval. However, if the absolute value of the calculated error function is greater than the tolerance, a new series of V_{OUT} must be assumed and the new iterative computations by the Runge-Kutta equation should be repeated. How quickly a good convergence can be obtained will depend on the method of assigning the next assumed value of $V^{(2)}$.

4.7.3 Convergent Method

The convergent method is essentially a linear interpolation (or extrapolation) of the previous results. Mathematically, it can be stated that

$$V^{(k+2)} = \frac{V^{(k)} \alpha^{(k+1)} - V^{(k+1)} \alpha^{(k)}}{\alpha^{(k+1)} - \alpha^{(k)}} \quad (4-169)$$

In order to avoid unreasonable extrapolation at the beginning of using the above equation, the first iterative pair of error functions, $\alpha^{(k)}$ and $\alpha^{(k+1)}$ must satisfy the following criterion:

$$\alpha^{(k)} \alpha^{(k+1)} < 0 \quad (4-170)$$

These error functions can be obtained by repeatedly adjusting the first assumed value of $v^{(1)}$ until a pair of assumed values of $v^{(k)}$ and $v^{(k+1)}$ can produce a pair of error functions to satisfy the above mentioned criterion. The adjusting function employed is expressed as follows:

$$v^{(m+1)} = (1 + \beta)^m v^{(1)} \quad m = 1, \dots, k \quad (4-171)$$

where m is number of adjustments on $v^{(1)}$ and β is an arbitrary value having the same sign with that of $\alpha^{(1)}$.

Chapter 5 Experimental Investigation

5.1 Experimental System

5.1.1 Design of Experimental System to Meet the Process Requirements

A general system of the semi-batch distillation accompanied by chemical reaction was illustrated previously in Figure 4.1. The experimental scheme proposed here is developed to meet the conceptual design. The first task in designing the experimental system is to provide the mechanisms whereby the following three operating parameters can be measured consistently and accurately.

- (1) Initial and Constant Surrounding Temperature, T_0
- (2) Feed Flow Rate, F
- (3) Relative Ratio of Feed Vapor to Total Feed, ψ

A constant temperature bath is used to satisfy the first condition. In order to avoid any operating difficulty later, the initial temperature of each experimental run is adjusted to the surrounding temperature. The initial liquid holdup on the reaction-distillation tray is made up of the very nonvolatile reactant, acrylamide sulfate. The separately prepared acrylamide sulfate is charged to and kept in the reaction-distillation tray until its temperature becomes equal to the surrounding temperature,

with the maximum tolerance of 0.02°C . When this tray temperature is reached, the other reactant, ethyl alcohol, is introduced to the tray.

A variable-speed pump is used to feed the liquid, ethyl alcohol, the more volatile reactant, from a storage container to a preheater. The feed rate of the liquid ethyl alcohol is measured by a rotameter installed in front of the preheater. The second design condition is thus met. The preheater is a simple tube submerged in the oil bath. The ethyl alcohol is heated and partially vaporized. While it passes through the preheater, the tiny vapor bubbles and liquid droplets are dispersed into the reaction-distillation tray through the perforations. The bubbles and droplets stir and mix the liquid hold-up on the tray with the aid of a high-speed stirrer such that an assumption of a complete mixing on the tray can be justified.

Although the tube preheater is simple it has a certain limitation. For a given liquid feed rate, a given oil bath temperature and a given tube length and material, there is a definite corresponding ratio of vapor to feed. The heat input to the preheater cannot be manipulated independently. In order to provide different ratios, two different types of tubes are used. A copper tubing is used to provide a high heat flux and consequently a

high vapor to feed ratio while a glass tubing is adopted for a low vapor to feed ratio.

A large oil bath is selected so that a constant temperature can be maintained even though there is a constant transfer of heat from the oil to the preheater. Furthermore, the cold feed to the preheater is installed far away from the reaction-distillation tray. This is done because most of heat flux from the oil to the preheater occurs in this region and consequently a constant oil temperature in the vicinity of the reaction-distillation zone can be further guaranteed.

The left section of Figure 5.1 is an illustration of the experimental setup to measure the above three operating variables. As soon as ethyl alcohol is mixed with acrylamide sulfate in the reaction-distillation tray, the three reactions, i.e., esterification, dehydration, and successive reaction, take place immediately. In order to satisfy the assumption that the tray is a perfect tray, a stirrer driven by a motor and three baffle plates are furnished. Uniform temperature and concentration distribution in the liquid holdup are obtained with these assistances. The instantaneous liquid temperature is measured by a thermocouple and the instantaneous liquid sample is obtained by a syringe as shown in

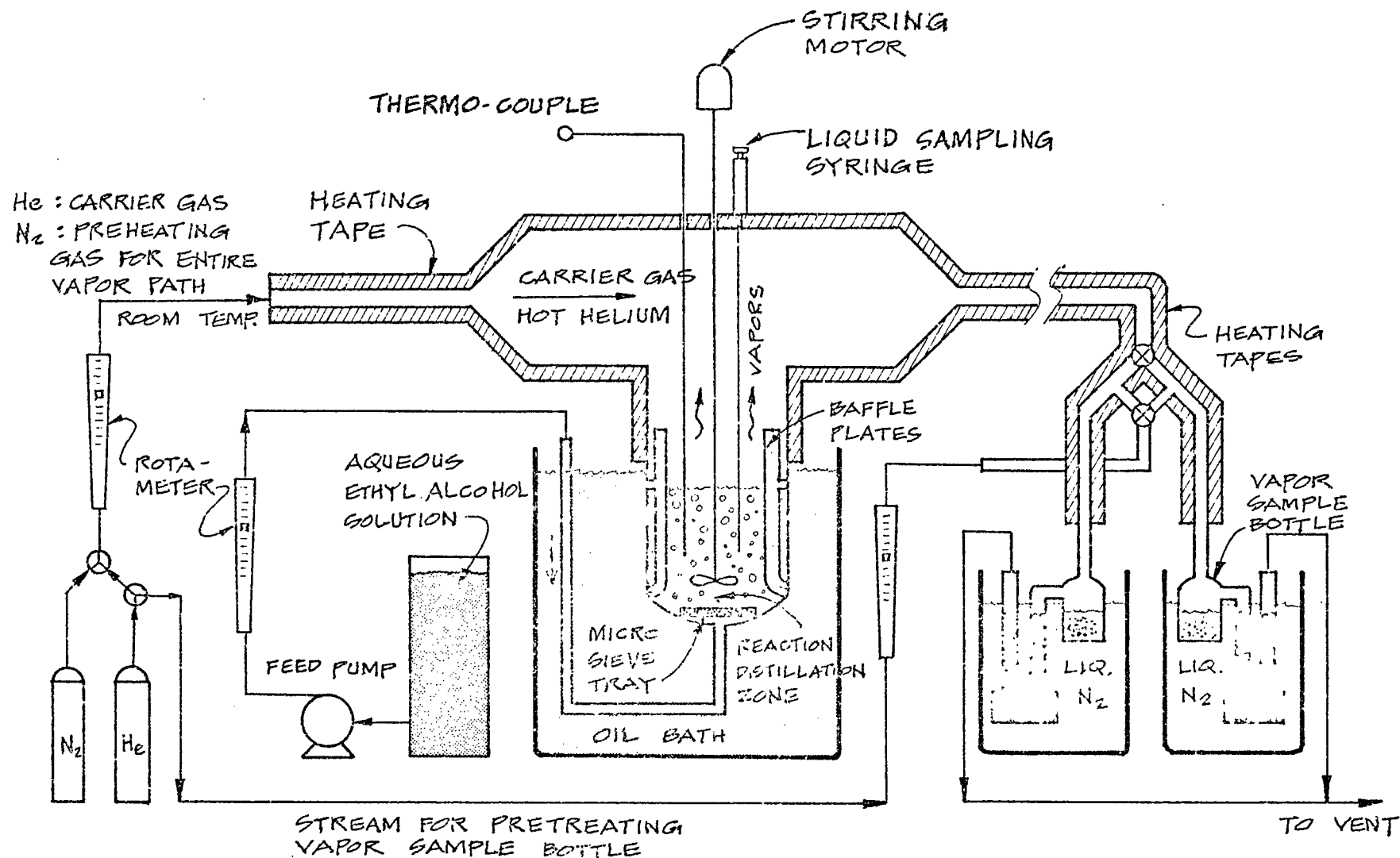


Fig. 5.1 Flow Scheme

Fig. 5.1. The remaining section of Fig. 5.1 shows a special design for sampling a vapor condensate. Its concentration is not only dependent on time but also affected by chemical reactions. Details of its flow scheme are discussed in the next section as follows.

5.1.2 Experimental Arrangement for Vapor Sampling

The reaction products as well as unreacted ethyl alcohol may absorb enough heat to be vaporized. The conventional method to obtain a vapor sample is first to use a water cooler to condense this vapor stream. However, in this study, the vapor condensate collected must be an instantaneous sample corresponding to the liquid sample withdrawn. The vapor travelling time from the vapor-liquid interface to the sample bottle of the vapor condensate must be accurately measured. The conventional water cooler can not provide a substantial temperature driving force to make a very fast condensation. The condensation involves complicated heat and mass transfer. Furthermore, the conventional method often leaves a certain amount of vapor condensate in the condensation tube and causes a mass loss. Therefore, the vapor condensate collected by the conventional method cannot closely relate to the vapor which leaves the vapor-liquid interface. A special design for sampling a time-dependent vapor condensate is then required for this study.

The present method of vapor condensate sampling includes two specific features, one using helium as a carrier gas and the other liquid nitrogen as a cooling medium for the condenser. The use of helium as a carrier gas reduces the time lag for the vapor sample to reach the condenser. Liquid nitrogen (B.P., -195°C) provides a large temperature driving force to condense the vapor sample quickly without condensing the helium carrier gas. Furthermore, liquid nitrogen is the least expensive cryogenic liquid available.

Helium is supplied by a pressurized helium tank as shown on the left-hand side of Fig. 5.1. A rotameter is used to measure its flow rate. The boundary of the mathematical model considered in this study is only large enough to enclose the liquid holdup. Once the vapor leaves the liquid holdup and is heated up to a slightly higher temperature to keep it from refluxing back to the system, the vapor temperature beyond the boundary will have negligible effect on the system energy and material balances. In order to prevent the condensation before the vapor reaches the condenser the vapor temperature in the vapor stream is raised about 5°C higher than the liquid temperature. To maintain this temperature in the upper section of the equipment the carrier gas was preheated before it is introduced to the system. All the rest of the vapor path is also maintained at about the same high

temperature to avoid vapor condensation before it reaches the sample bottle. The heat required for maintaining high temperature in these sections is supplied by heating tapes. Since these temperatures do not enter into the system analysis, accurate temperature controlling devices are not required.

During preparation for an experiment, all the vapor and gas lines are cold. Since helium is too expensive to be used to warmup the system, a much less expensive nitrogen gas of intermediate grade is then used for this service. A three-way valve has been equipped for selecting either nitrogen or helium for different operating requirements.

The vapor sample bottle is immersed in liquid nitrogen and functions as a vapor condenser. It has two stages. The connecting tube between the two stages must be free in the air. Since liquid nitrogen is extremely cold, most of vapor condensate can be trapped in the first stage. The remaining small amount of uncondensed vapor components is crystalized and filtered by a section of fine fiberglass in the second stage. Finally, the non-condensable helium gas is discharged through the vent. It is noted that if the connecting tube between the two stages is also immersed

in liquid nitrogen, vapor will be crystalized gradually inside the tube until it completely block the vapor passage. This, of course, will lead to an explosion causing ruptures of part of the equipment.

Although two vapor sample bottles are connected to the hot vapor line, only one of them is in service at any particular instant. The other is prepared ready for next vapor sampling. Since liquid nitrogen can also condense the oxygen in air, the helium is used to purge the air in the vapor sample bottle before the latter is used to collect the vapor condensate. The purge helium line is shown at the bottom of Fig. 5.1. Its flow rate can also be measured by a rotameter.

The complete experimental system of semi-batch distillation accompanied by chemical reaction is shown in Fig. 5.1.

5.2 Chemicals

5.2.1 Reactants and Related Chemicals

1. ACRYLAMIDE

The highest purity grade of acrylamide manufactured by Eastman Kodak Company is used in this experiment. It is a white crystalline solid with a melting point of 84.5°C . Since its vapor pressure is only 20 mm-Hg at 130°C compared to 3360-mm Hg for ethyl alcohol at the same temperature, it is then treated as a nonvolatile component in the system. It is thermally stable and has a long shelf life as compared with some other vinyl monomers, if the environmental temperature does not exceed its melting point. For example, even after 24 hours at 80°C , a pure sample shows little or no polymer formation (2). However, to maintain its highest purity for a long period, all the samples are stored at 5°C in a refrigerator.

Molten acrylamide polymerizes vigorously with evolution of heat (2). Even for a small amount, it is recommended that the solid acrylamide should not be heated above the melting point without due precautions. In this study, acrylamide is dissolved in concentrated sulfuric acid to form the molecular complex, acrylamide sulfate. The temperature of the acrylamide

sulfate solution may be above the melting point of acrylamide without any polymer formation. It is assumed that if the molal quantity of sulfuric acid is in excess of that of acrylamide, all the acrylamide is converted into acrylamide sulfate. That is, the amount of free acrylamide in such a acrylamide sulfate solution is negligible.

2. SULFURIC ACID

As mentioned previously in Section 4.2.3. if a large amount of water is presented in the acrylamide sulfate solution, esterification between acrylamide sulfate and ethyl alcohol will produce appreciable amount of by-product, acrylic acid. This by-product can be reduced to a negligible amount by reducing the water quantity in the acrylamide sulfate solution. Thus, the concentrated sulfuric acid must be used for preparing acrylamide sulfate.

A 89.6 Wt % sulfuric acid solution is used for all the experimental runs in this study. This concentration is within the range recommended by Hardman et. al. (27). The small amount of water in the acid is used mostly to dissociate protons (H^+) from the sulfuric acid which in turn initiates the formation of acrylamide sulfate.

The above-mentioned sulfuric acid solution is made

by diluting the 95-98 Wt % sulfuric acid of Fisher Scientific Company. The water used for dilution is specially treated. Deionized water is redistilled twice with the addition of 0.5 Wt % potassium permanganate solution. The potassium permanganate solution can destroy some organic compounds in the water which are not removed by an ion exchanger. The redistilled water has been tested by a gas chromatographer, which shows no trace of peaks other than that of water.

The diluted sulfuric acid is titrated by a dilute sodium hydroxide solution. Since the acid concentration of the sulfuric acid solution in the experiments is very high, a sulfuric acid solution sample for the concentration determination is prepared in two stages. The first stage is to take about 3 grams of the 95-98 % sulfuric acid and dilute it by adding about 50 ml of water. All these quantities can be accurately measured by the electronic balances available in the University of Houston Chemical Engineering Department. Then take a known volume of this newly diluted sulfuric acid solution and titrate it by a dilute sodium hydroxide solution.

The normality of the dilute sodium hydroxide solution can be determined from a standard acid solution. This standard acid solution is prepared by dissolving a known amount of potassium phthalic acid in a known

amount of water. The potassium phthalic acid used here is obtained from Matheson, Coleman & Bell.

Since sulfuric acid has very strong tendency to absorb moisture from the air, it is recommended that this prepared 89.6 Wt % sulfuric acid be stored in a desiccator. The sulfuric acid stored even for a month in the desiccator has shown no change in concentration.

3. ETHYL ALCOHOL

Pure ethyl alcohol manufactured by Commerical Solvents Corporation can be obtained from the University of Houston Chemistry Department store room.

Ethyl alcohol is the major reactant for esterification. It is prepared as a 86 Wt % aqueous solution. The small amount of water presented in the feed stream is to make up the water evaporated from the liquid hold-up. Without this small amount of water in the feed stream, a reduction of water in the liquid holdup reduce the amount of protons which is necessary for the formation of acrylamide sulfate. The lack of the protons may lead to other serious side reactions. The concentration of aqueous ethyl alcohol solution used in this study is also within the range recommended by Hardman et. al. (27).

5.2.2 Reaction Products and Related Chemicals

1. ETHYL ACRYLATE

Ethyl acrylate is the major product of this reaction system.

It can be easily polymerized at the time when it is produced by esterification. Therefore, a small amount of polymerization inhibitor, hydroquinone (about 0.5 Wt %) must be added into the acrylamide sulfate solution to prevent the polymerization. Both ethyl acrylate and hydroquinone are manufactured by Eastman Kodak Company.

2. DIETHYL ETHER

Diethyl ether is a trace by-product of this system. An analyzed reagent grade of diethyl ether from Matheson, Coleman & Bell is adopted for blank test in gas chromatography.

3. β -ETHOXY-ETHYL PROPIONATE

β -Ethoxy-ethyl propionate is another trace by-product in the system. Since it is not available commercially, all its properties including its relationship with other components in the gas chromatography

must be estimated. Accuracies of these estimated quantities have little effect on the entire system's behavior because it is a trace component in the system.

5.2.3 Chemicals for Gas Chromatography

1. CARBOWAX 1000

The columns in gas chromatography used in this study are prepared by the author. Three types of chemicals are required for packing a gas chromatographic column. They are used as stationary phase, support and solvent. For selection of stationary phase, McReynolds' book, "Gas Chromatograph Retention Data " (47) has been referred. The column must be able to separating 1-propanol and acetone in addition to all the five volatile components in the system. 1-Propanol is used as a reference compound while acetone is a solvent for the vapor sample. Detailed functions for these two additional compounds in the samples will be discussed later in this Chapter. Comparing the retentions times for the above seven components in the McReynolds' book, it is found that Carbowax 1000 is the most suitable stationary phase and is, therefore, adopted for this study.

2. CHROMOSOB W 80/100

According to Horvath (14), almost any analytical problem in gas chromatography can be solved with columns made of diatomaceous supports. The acid washed chromosorb is a common diatomaceous support. It is chosen as column support for this system. Small particle size of the support increases the pressure drop along the column. However, it can provide more surface area for the same total amount of support. Selection of particle size should then be judged from these two factors. It is found that 80/100 mesh acid washed chromosorb can provide desired separation and is then used in this system.

3. ETHYLENE CHLORIDE

Selection of solvent in correspondance with a stationary phase is specified in most of commercial catalogs of gas chromatographic columns. The solvent is used to dissolve the stationary phase and then to coat it on the column support. For carbowax 1000, ethylene chloride should be used. The manufacturers of the above mentioned chemicals are listed as follows.

Carbowax 1000	Variant Aerograph
Chromosorb W 80/100	Fisher Scientific
Ethylene Chloride	Fisher Scientific
Acetone	Fisher Scientific
1-Propanol	Fisher Scientific

4. HELIUM

In addition to the above three chemicals, helium is used as a carrier gas in gas chromatography. A helium with minimum 99.995 % purity is used in this work. It is also used as carrier gas for the vapor sampling system. The gas is a product of Union Carbide.

5.2.4 Miscellaneous Chemicals

1. SILICONE FLUID

Dow Corning 200 dielectric silicon fluid has low vapor pressure, low viscosity, moderate heat capacity and high dielectric constant at high temperature. It is recommended by the manufacturer to be used as heating medium of a high-temperature oil bath. The silicon fluid is supplied by Lubri-Kote Company, Houston, Texas.

2. LIQUID NITROGEN

Liquid nitrogen is used to condense vapor samples as mentioned previously in Section 5.1. A liquid nitrogen tank with a capacity of 160 liters is used in this experiment. It is manufactured by Union Carbide and supplied by IWECCO, Houston.

3. GLYCERINE

Glycerine with 99+% purity is used in this work for

calibrating overall heat transfer coefficient and relative ratio of feed vapor to total feed. This compound is obtained from Curtin Scientific Company, Houston. It has extremely low vapor pressure (1.5 mm Hg at 130 °C) and is infinitely miscible with water and ethyl alcohol. Therefore, it can absorb these feed vapors with negligible amount of vapor loss above the liquid surface. The heat of condensation of the feed vapor is used principally to increase the temperature of glycerine. From the temperature rise of glycerine, the relative ratio of feed vapor to total feed can be determined. Detailed techniques of using glycerine for determining the relative vapor ratio will be presented later in Section 5.4.

5.3 Major Experimental Units of the System

5.3.1 Reaction-Distillation Tray and Its Accessories

The reaction-distillation tray and its accessories are illustrated in Fig. 5.2. The reaction-distillation tray is the portion below the Teflon gasket as shown in the figure. The wall of the reaction-distillation tray is a 2" standard pyrex pipe, i.e., it has an inside diameter of 2.068" and wall thickness of 0.125". A micro-sieve Pyrex disc with pore sizes of 60-75 μ , is fitted onto the bottom of the pipe as the distilla-

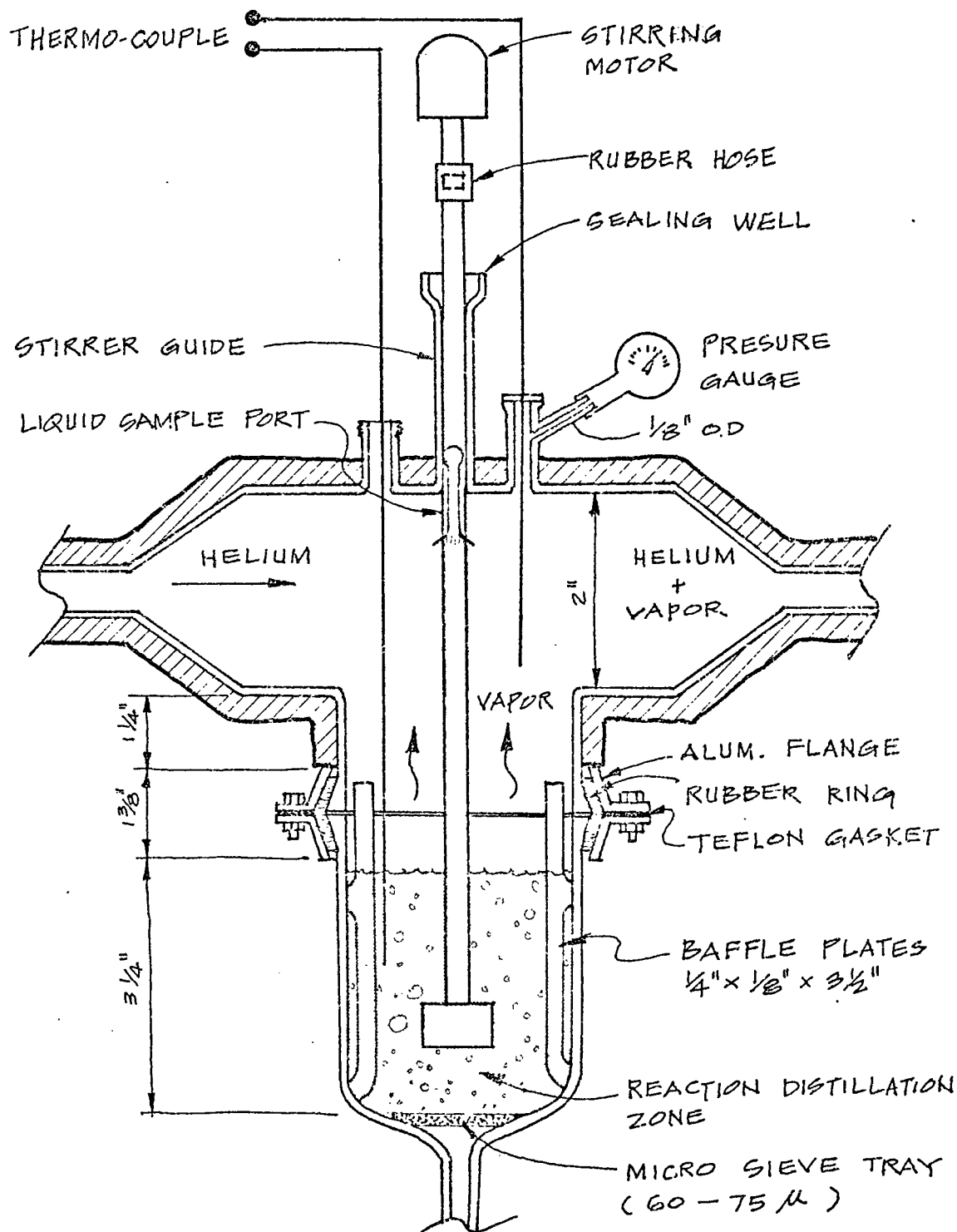


Fig. 5.2 Reaction-Distillation Tray
and Its Accessories

tion tray. The disc has a thickness of $1/8$ " and diameter of 20 millimeters. Below the disc, the 2" pipe is connected to a capillary glass tubing with 1.0- mm inside diameter and $1/4$ " outside diameter. A stirrer is suspended above the sieve tray. This stirrer is housed in a stirrer guide and driven by a motor. Detailed descriptions on the stirrer guide and the motor will be presented later in this section. This stirrer is employed to provide good mixing in the liquid holdup. Its 10-mm shaft is equipped with four symmetric flat blades, each of which is 15° declined from the vertical line. This decline in blades enables the liquid to make up-and-down mixing. The blade is 7 mm wide, 10 mm long and sweep out a circle of 24-mm diameter making the ratio of stirrer radius to the pipe inside diameter of about 1 : 2.1. The stirrer is positioned so that the blades are 1.5" above the sieve distillation plate. To improve mixing, 3 glass baffle plates are provided. Each baffle is $1/4$ " wide, $1/8$ " thick and 3.5" long. The clearance between the baffle plate and the pipe wall is $1/8$ " to avoid mixing dead spots. The baffle plates are connected to the pipe wall only at two points as shown in Fig. 5.2. At the stirring speed of about 1000 rpm, as used in this system, very uniform temperature and concentration distributions can be obtained. The temperature distribution can be tested by

moving the thermocouple positions while the concentration distribution of the liquid is directly obtained by sampling at two different positions simultaneously by sampling syringes. Details on temperature measurement and liquid sampling will be discussed later in this chapter.

The portion above the Teflon gasket up to the top edge of the larger horizontal pipe is the area for vapor withdrawal. It looks like a T-shape pipe joint. The vertical part is a 2" glass pipe flange and the horizontal part right on the top of the flang is a 2" glass pipe. Total length of the 2" horizontal pipe is 5 inches. At each of its two ends, the pipe is reduced conically and then connected to a 1/2" glass tubing. At the left-hand side the 1/2" glass tubing is only 1.5" long. It is connected to a 1/4" copper tubing by a reducing union. The copper tubing is enclosed in a heating tape and served as a preheater for the carrier gas, helium. The preheated helium carries the up-coming vapor and leaves this vapor withdrawal section. It then enters the 1/2" horizontal tubing at the right hand side of the unit, and eventually goes to the vapor sample unit. In order to prevent vapor from condensation, the larger pipe portion is surrounded by a heating mantle obtained from Curtin Scientific Company. The rest of small tubings (1/2" & 1/4") are all wrapped by heating tapes.

All the temperatures along the vapor path are manually controlled by transformers. This operation is justified because the purpose is not to obtain accurate temperatures but to get temperatures greater than dew points of the entire gas-vapor stream.

On the center top of the large horizontal pipe, there are one stirrer guide and three vertical ports. As mentioned early in this section, the stirrer guide is used to house the stirrer for stable operation. Silicon fluid is used as lubricating fluid, and sealing material in this gap. The silicon fluid may flow down along the stirrer shaft and enter the reaction-distillation tray due to high-temperature operation and partial dissolution of silicon fluid in organic compounds. To prevent it from contaminating the liquid mixture, a small Teflon holder is installed on the stirrer rod right beneath the stirrer guide to hold the grease as shown in Fig. 5.3. Since the thermal expansion of Teflon is much higher than that of glass, the hole at the bottom of the Teflon grease holder must be small enough such that at the operation temperature, it still can tightly hold on the glass rod. Therefore, the installation of the Teflon holder on the glass rod must be performed at a temperature higher than the system operating temperature. This device is very helpful for avoiding the grease contamination in a reaction system in-

volving organic vapors. In this experiment, the accumulated grease is only about 0.2 ml compared to more than 100 ml vapor condensate for a complete run. The amount of vapor dissolved in the grease is even smaller and thus negligible.

The stirrer is driven by a reversible and variable-speed (0-6000 rpm) motor with 1/40 horse power. Both motor and speed controller are manufactured by G. K. Heller corporation. A short piece of thick rubber tubing is used to connect the stirrer rod and the motor shaft. The rubber tubing used here is to reduce the stress of stirrer rod on the stirrer guide and to avoid breaking stirrer shaft or stirrer guide.

The port on the left-hand side among the three vertical ports are the largest one. It is 5/8" in diameter, and 1.125" in height, and used as the feed entrance of acrylamide sulfate at the beginning of each run. It is also used as a thermocouple path. The other two ports are both 1/4" diameter and 1" high. The center port is a path way for liquid sampling syringe and the right-hand port is used as a thermocouple path. The midpoint of the right-hand port is connected to a glass tubing of 1/8" O.D. and 1" long. This 1/8" glass tubing is connected to a pressure guage (0-5 psig) by a flexible Tygon tubing for measuring the operating pressure of the reaction-distillation system.

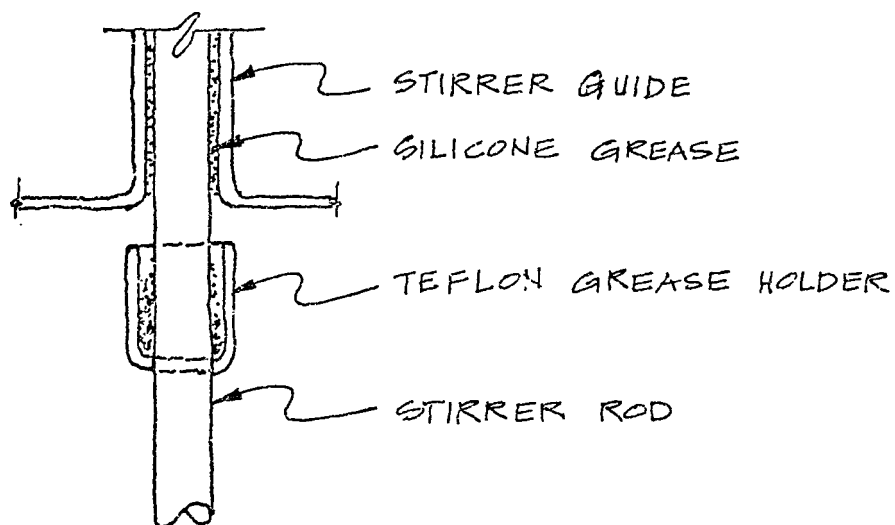


Fig. 5.3 Teflon Grease Holder

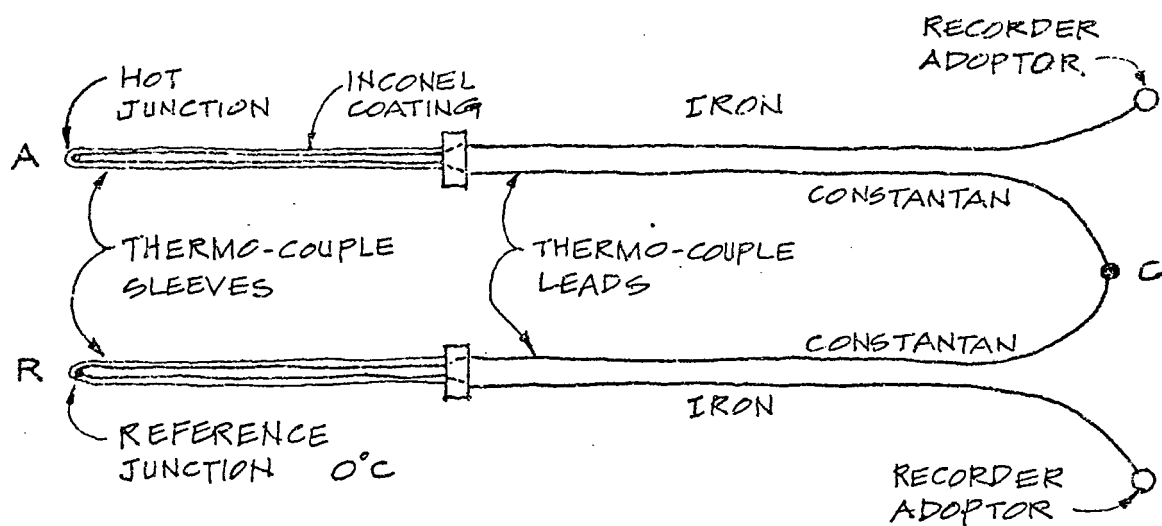


Fig. 5.4 Thermocouples

5.3.2 Temperature Measuring System

5.3.2.1 For Reaction-Distillation Tray and Its Accessories

Two sets of iron-constantan thermocouples are used for measuring the temperatures in the liquid holdup as well as in the vapor withdrawal area. These two sets have the same configuration as shown in Fig. 5.4. Each set contains a hot junction, a reference junction, two sleeves, two leads, and two recorder adaptors.

The reference junction is immersed in a tubing containing Dow Corning dielectric silicon fluid. Since the tubing is immersed in an insulated ice bath, the temperature of the silicon fluid can achieve a stable 0 °C reference temperature after an overnight immersion of the tubing in the ice bath. It is noted that the direct immersion of thermocouple in the ice bath sometimes may lead to inaccurate reference temperature if the ice bath contains impurities, especially ionic impurities.

The hot junction is immersed in the reaction-distillation tray. Since the reaction system is very corrosive, coating metal on the hot junction as well as on the thermocouple sleeves must be properly selected. It is found from the experiment that type-316 or type-347 stainless-steel coating can be completely destroyed

in only one run. However, inconel, an nickle alloy, has excellent resistance to this reaction system. Throughout the entire experiments, only one inconel-coated thermocouple is used without replacement.

Two constantan cords from the thermocouple leads must be welded together at point C as shown in Fig. 5.4. Thus, when the hot junction is immersed in a hot fluid, the difference in conductance between the two metals will produce a net thermo-electrical current. This current is then detected and converted into voltage by a "Honeywell 19" two-pen recorder. For iron-constantan thermocouple, 0.05 mv is equivalent to about 1 °C if the reference temperature is 0 °C. The conversion table for the iron-constantan thermocouple used in this system is given in Table B.1 of Appendix B.

The hot junction for measuring the liquid temperature is located at about one third of total liquid height from the liquid surface. At the first ten minuites of each run, the bottom temperature is about 1 °C higher than that at the above-mentioned location. This is because all the heat of reaction cannot be dispersed fast enough and is absorbed in the liquid phase in this section. However, after the initial period, a uniform temperature throughout the liquid holdup can be achieved with the same apparatus described in Section 5.2. The mathematical model for semi-batch distillation accompanied by

chemical reactions deals with the above operating period of uniform temperature distribution.

The hot junction for measuring the temperature of the carrier gas-product vapor is located at the intersection between the center of the 2" horizontal pipe and the right-hand edge of the vertical 2" pipe. This location was considered as an ideal point for obtaining average temperature of the gas-vapor mixture.

5.3.2.2. For Isothermal Oil Bath

Since oil bath temperature is constant throughout a run, it is not necessary to use thermocouple for measuring temperature. A calibrated thermometer is then employed for measuring the temperature of silicon fluid in the oil bath. Deionized boiling water (100°C) and deionized ice water (0°C) are the two checking points for this calibration.

5.3.2.3 For Cryogenic Temperature

Temperatures of the carrier gas, helium, in the vapor sample bottle are well below the ice point. They can not be measured by any thermometers. But the thermocouples presented in Section 5.3.2.1 can be used for this purpose

with a minor modification. The required modification is to shift the zero reference point on the Honeywell 19 Recorder from one end of the recorder chart to the other end. Thus, negative voltages can be shown on the recorder charts. Conversion of this negative voltage to a corresponding cryogenic temperature is also given in Table B. 1 of Appendix B.

5.3.3 Preparation of Nonvolatile Reactant, Acrylamide Sulfate

The molal ratio of acrylamide to sulfuric acid used for preparing acrylamide sulfate for all experimental runs is about 1:1.2. For comparison, each run uses about one mole of acrylamide. This acrylamide sulfate solution is prepared separately outside the reaction-distillation tray as described below.

The weighed concentrated sulfuric acid (89.6 Wt %) of desired quantity is heated in a 250-ml glass beaker over an electric heater. The temperature of the sulfuric acid can be increased rapidly up to 60-70 °C under agitation. The temperatures are measured by the calibrated thermometer described in Section 5.3.2, which is mainly used for measuring the oil bath temperature. Then, the weighed acrylamide of desired quantity is gradually added also under agitation into the sulfuric acid in about 30 seconds. Because heat is evolved from the reaction be-

tween these two components as well as supplied by the electrical heater, the liquid temperature can be further increased up to 115-125 °C after all the desired quantity of acrylamide is added. The temperature is normally about 10 °C above the desired oil bath temperatures. Since the prepared acrylamide sulfate must be fed through a glass funnel, which is normally at room temperature, the liquid temperature is then decreased down to about the oil bath temperature. Whenever there are differences between these two temperatures, it is necessary to wait for about 25 minutes before the absolute difference between the two temperatures becomes less than an allowable error of 0.02 °C. Then, an initial liquid temperature equal to the oil bath temperature (surrounding temperature) can then be reached.

As mentioned earlier, ethyl acrylate from esterification between acrylamide sulfate and ethyl alcohol may polymerize as soon as vinyl group is freed from the molecular complex, i.e., acrylamide sulfate. Thus, 0.2 Wt % of hydroquinone is then added into the acrylamide sulfate solution before feeding ethyl alcohol into the reaction-distillation tray.

5.3.4 Volatile Reaction Feed System

Volatile reactant, ethyl alcohol is prepared as an 86 Wt % aqueous solution. Sufficient amount of ethyl alcohol solution for one run is stored in a 250-ml

calibrated glass cylinder. The solution is first pumped from the cylinder and its rate measured by a rotameter. It is then preheated by the heat from the hot silicon fluid in the oil bath before entering the reaction-distillation tray. Details on the storages, cylinder pumping device, rotameter and feed preheater are described as follows.

5.3.4.1 Storage Cylinder and Flow Rate Measurement

A capillary glass tubing with outside diameter of $1/4$ " and inside diameter of 1 mm is immersed into the ethyl alcohol solution in the cylinder. Its open end is located 1 centimeter above the bottom of the cylinder. The other end is outside of the cylinder. It is reduced and then connected to a flexible Tygon tubing with outside diameter of $1/8$ " and wall thickness of $1/32$ ". This Tygon tubing is extended to a pump for pumping the solution from the cylinder to the reaction-distillation tray.

When suction is obtained from the pump, the ethyl alcohol solution will enter the open end of the capillary tubing. The solution level instantaneously reduced in the cylinder can then be read from the readings marked on the cylinder.

With the amount of the solution consumed and the corresponding time measurement, the feed rate of the solution can be determined. Thus, this storage cylinder

with calibrated volume serve as a storage tank as well as a device for fine flow rate measurement.

However, this device can not be used for controlling the desired flow rate. A rotameter is installed for presetting the desired flow rate for each run. The rotameter is located right after the discharge stream from the feed pump. Gilmount No. 260 flowrator is used for this service. Its calibration will be presented later in details in Section 5.4.

5.3.4.2 Feed pump

A polystaltic pump manufactured by Bucher Instruments is very suitable for delivering continuous small liquid stream ranged from 2 ml/hr to 1000 ml/hr. In this system, the observed flow rates are ranged from 60 to 120 ml/hr, which are well covered by the capacity of this pump.

The pump has four parallel rotating stainless-steel cylinders. On each rotating cylinder, there are ten stainless-steel bearings. All the cylinders are attached to a variable internal motor, whose rate can be controlled by a dial on the top panel of the pump as shown in Fig.5.5. The Tygon tubing mentioned in the previous section is pressed against on five of the ten bearings for each rotating cylinder. The liquid solution then moves in the same direction of the rotating cylinder

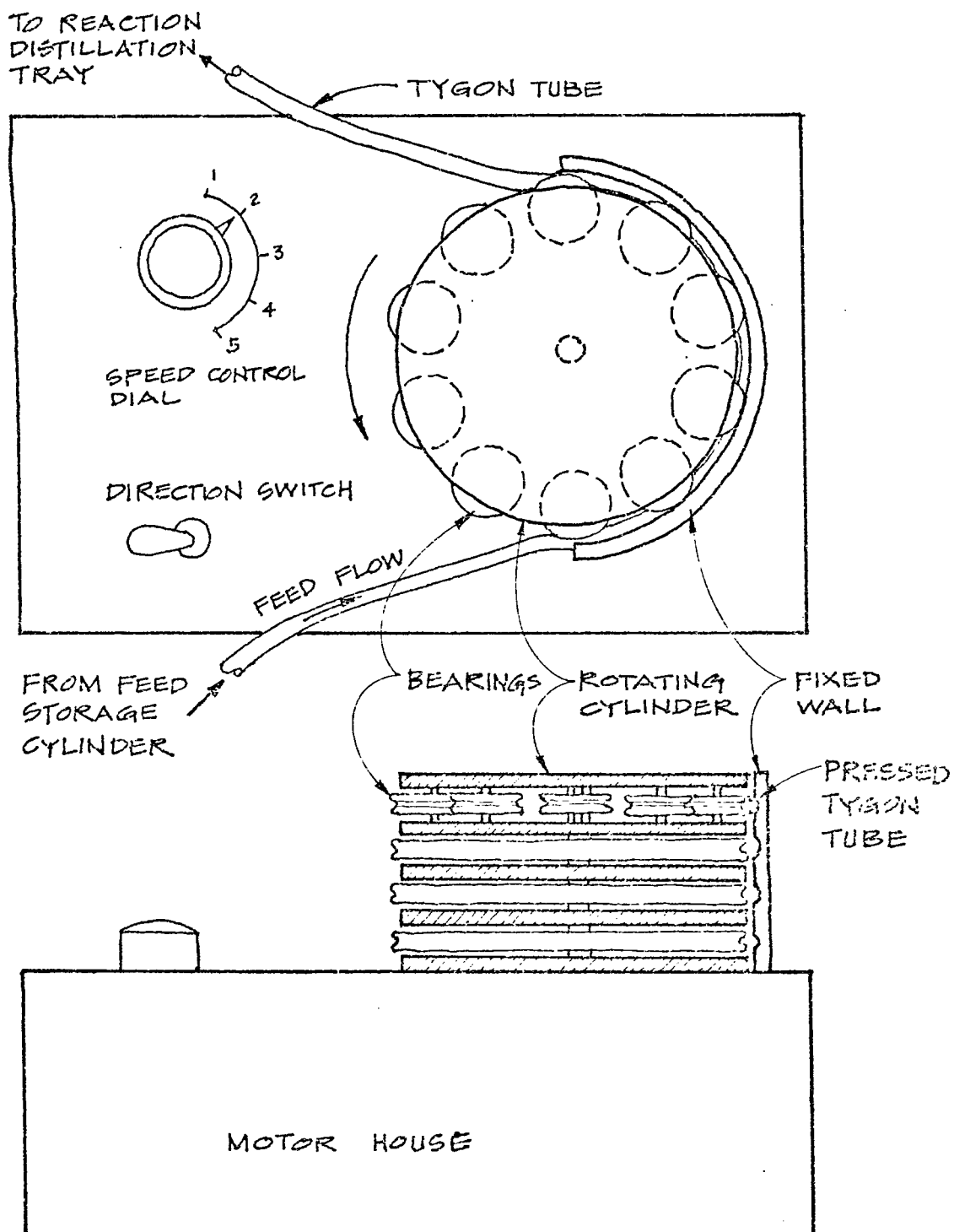


Fig. 5.5 Feed Pump

when the five bearings press the Tygon tubing against a fixed vertical wall. Although the flow pattern produced by polystaltic pump is slightly peristaltic, the amplitude of the peristalsis is constant and very small. For example, for ethyl alcohol fed at 2 ml/min or 120 ml/hr the rotameter reading is 60 ± 0.2 . The peristaltic duration is only 0.4 seconds. Therefore, this flow pattern can be considered to be constant and stable. Though there are four rotating cylinders, only one of them is in use at any time.

5.3.4.3 Feed Preheater

For the best feed rate measurement, aqueous ethyl alcohol solution is fed to the system in liquid state at room temperature. The solution is then preheated to the desired relative ratio of vapor to total feed. As mentioned in previous sections, the solution is preheated by the heat from the hot silicon fluid in the oil bath. Heat transfer surface is a glass tubing wall, or a copper tubing wall, or both of them in series. If low relative ratio of vapor to total feed is desired, only a segment of glass tubing directly connected to the bottom of the reaction-distillation tray is used as preheater. This preheater is illustrated in Fig. 5.6.a. The heating section is an eleven-inch long capillary glass tubing with inside diameter of 1 mm and outside diameter of $1/4"$. The free end of the heating tubing is connected by a swageloc elbow

union to an upward glass tubing of the same size. The other end of the upward glass tubing is reduced to a size such that it can be fitted and connected to the 1/8" tygon tubing extended from polystalic pump. It is noted that the free end of the heating glass tubing must be kept in a position that the elbow union is still underneath the surface of the oil bath. This is because the free end of the glass tubing should be connected to a copper tubing for high relative ratio of vapor to total feed. If the union is exposed to the air, the vapor from the copper tubing will be condensed. Heat loss caused by this false installation will lead to serious error in determining relative ratio of vapor to total feed. The preheater for higher relative ratio of vapor to total feed is illustrated in Fig. 5.6.b.

In addition to the glass heating tubing mentioned early in this section, a 48" long of spiral copper tubing with outside diameter of 1/4" is used to increase vapor ratio in the feed stream. At the downstream of the copper tubing, a pressure gauge of 5 psig is attached on the tubing to measure the pressure of the feed stream at this point. For a given oil bath temperature and a selected flow rate, there is a corresponding pressure. This pressure can be kept almost constant throughout a run im-

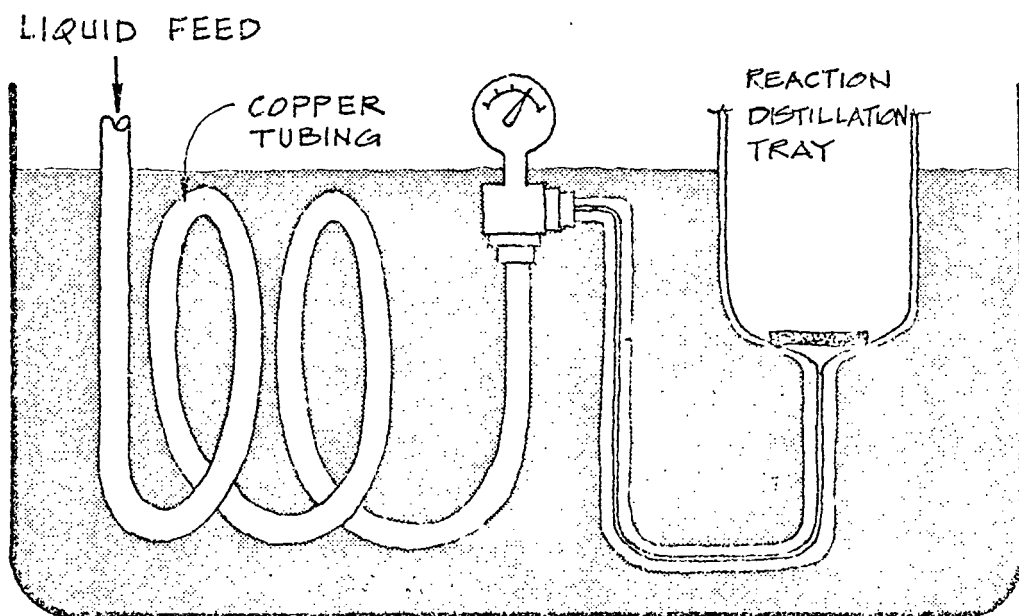


Fig. 5.6b Feed Preheater for High Relative Ratio of Vapor to Total Feed

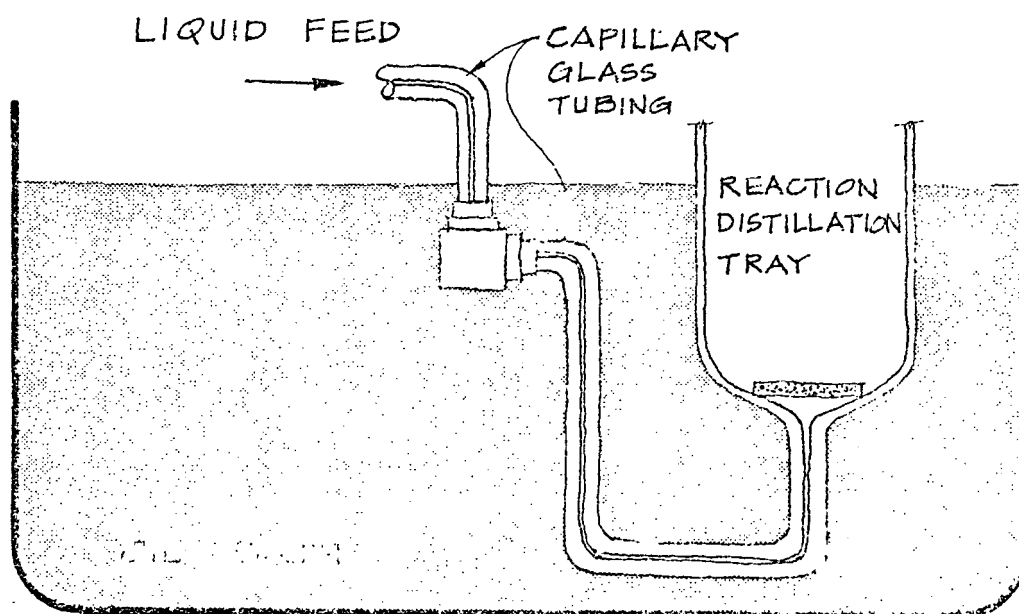


Fig. 5.6a Feed Preheater for Low Relative Ratio of Vapor to Total Feed

plying that the feed flow rate can be steadily maintained. Calibration of relative ratio of vapor to total feed will be presented later in Section 5.4.

5.3.5 Vapor Sampling System

Vapor sampling system starts from the cylinder with carrier gas helium to the vapor sample bottles immersed in liquid nitrogen. Helium is delivered by pressure drop at a fixed flow rate for all experimental runs. The rate is set at 4.5 standard cubic ft per hour or 2170 ml/min. Since the total volume in the helium path from the vapor withdrawal section to the vapor sample bottle is 250 ml, the above-mentioned carrier gas rate then reflects a time lag of only 0.11 minutes compared a total of about 120 minutes of operation time for each run. The error caused by the time lag of vapor sample to liquid sample can then be reduced to minimum.

Vapor withdrawal section has been described in Section 5.3.1. Here the discussion is devoted to vapor condensation in liquid nitrogen, which is contained in a 1200 ml dewar for good insulation.

Two-stage sample bottles are used for trapping vapor sample by liquid nitrogen and shown in Fig. 5.7. The first stage is a small glass bottle with very thin wall thickness. It has a diameter of 1.125" and height of 2", which can be used to contain vapor condensate up to

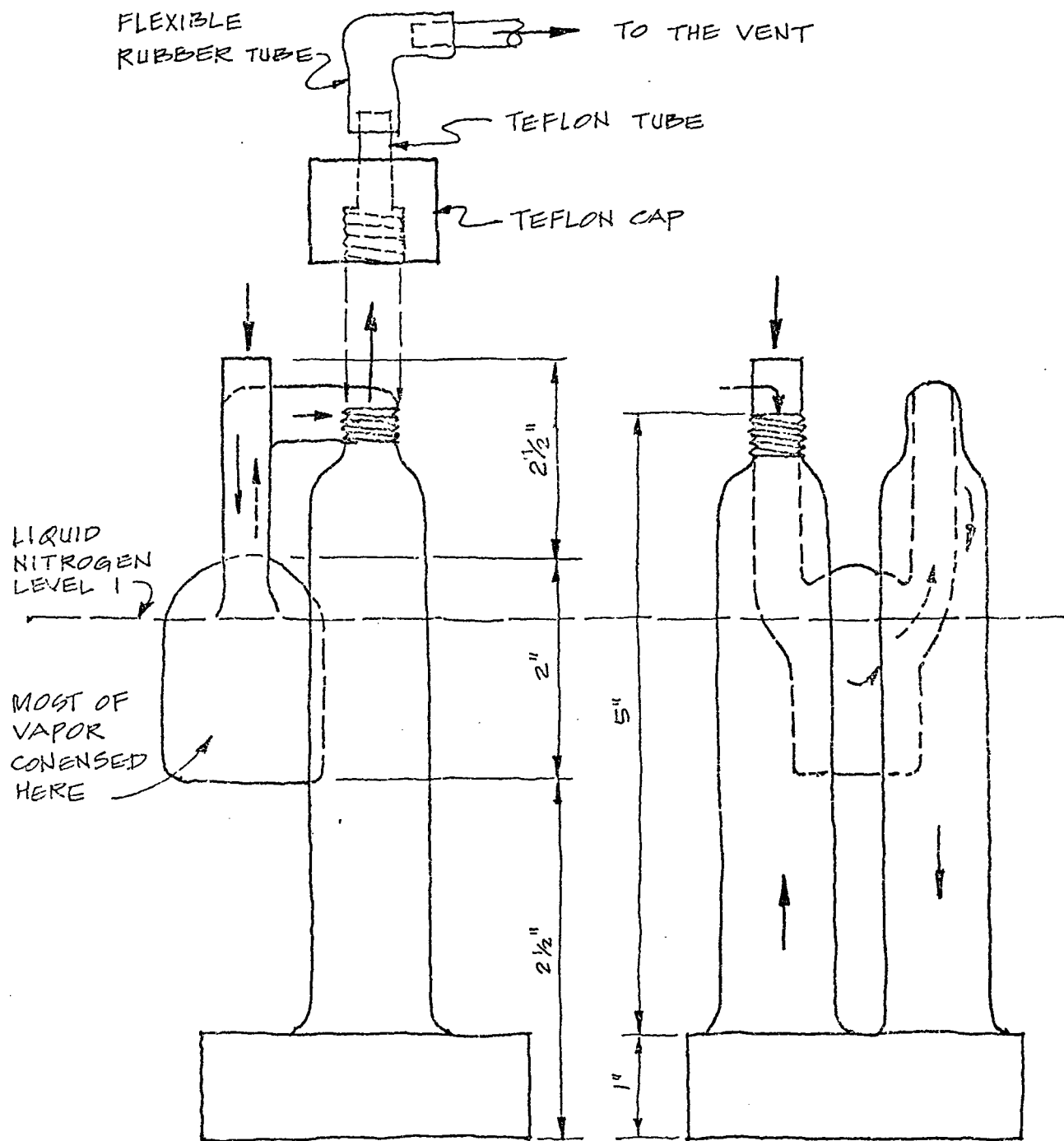


Fig. 5.7 Vapor Sample Bottle

25 ml. Two inlet and outlet glass arms are connected to both sides of the upper edge of the bottle and extended straight upward. The inlet arm has a flat opening end which can be attached onto the hot tubing extended from the vapor withdrawal section. The outlet arm of the first-stage bottle is connected by a U tube to the second-stage bottle.

The second-stage bottle has two parallel vertical glass tubings with an outside diameter of 1" and a length of 5". They are on tops of a shallow cylinder of 3" in diameter and 1" in height. This shallow cylinder is designed to allow the entire sample bottle sitting stably on the table or weighing pan. One of the two vertical tubes is, of course, connected to the above-mentioned U tube and the other is connected to a flexible rubber tube by a special Teflon cap. The female screw in the Teflon cap is fitted to the male screw on the glass tube for connection. A hole is punched on the center of the teflon cap. Then a small segment of teflon tubing with outside diameter slightly greater than the hole is forced into the hole for tight connection between the teflon tube and teflon cap. The free end of the teflon tube is then connected to a vent gas line by a piece of flexible rubber tube. The sample of the vent gas can then be taken by a gas sampling syringe at the flexible rubber tube for analysis.

Within the two parallel vertical tubes and the shallow cylinder, fine glass fiber is packed for filtration purpose. The outlet temperature of the exhausted gas in the bottle beneath liquid nitrogen level is measured to be -192°C by the thermocouple described in Section 5.3.2.3. At such cryogenic temperature all the vapors in the system become crystals. Although most of vapors are condensed in the first stage of the vapor sample bottle, the rest of vapor may become particles suspending in the helium stream. These particles can not be adsorpted simply by glass wall. Therefore, fine glass fiber must be provided for a complete collection of all the vapor components by filtration.

Since the product vapor mixture is a continuous stream, the sampling devices should permit an immediate shift of the vapor stream from one sample bottle to another without any mass loss. Therefore, two vapor sample bottles must be connected in parrallel to the hot helium-vapor line for this purpose. The devices are illustrated in Fig. 5.8.

The down-stream tubing for hot helium-vapor stream from the reaction-distillation tray extends for 13 inches before bended vertically downward for 3 inches. A small port is installed at the elbow as a path way for thermocouple. The port is covered by a silicon rubber cap for sealing. The vertical tube is then connected to a three-

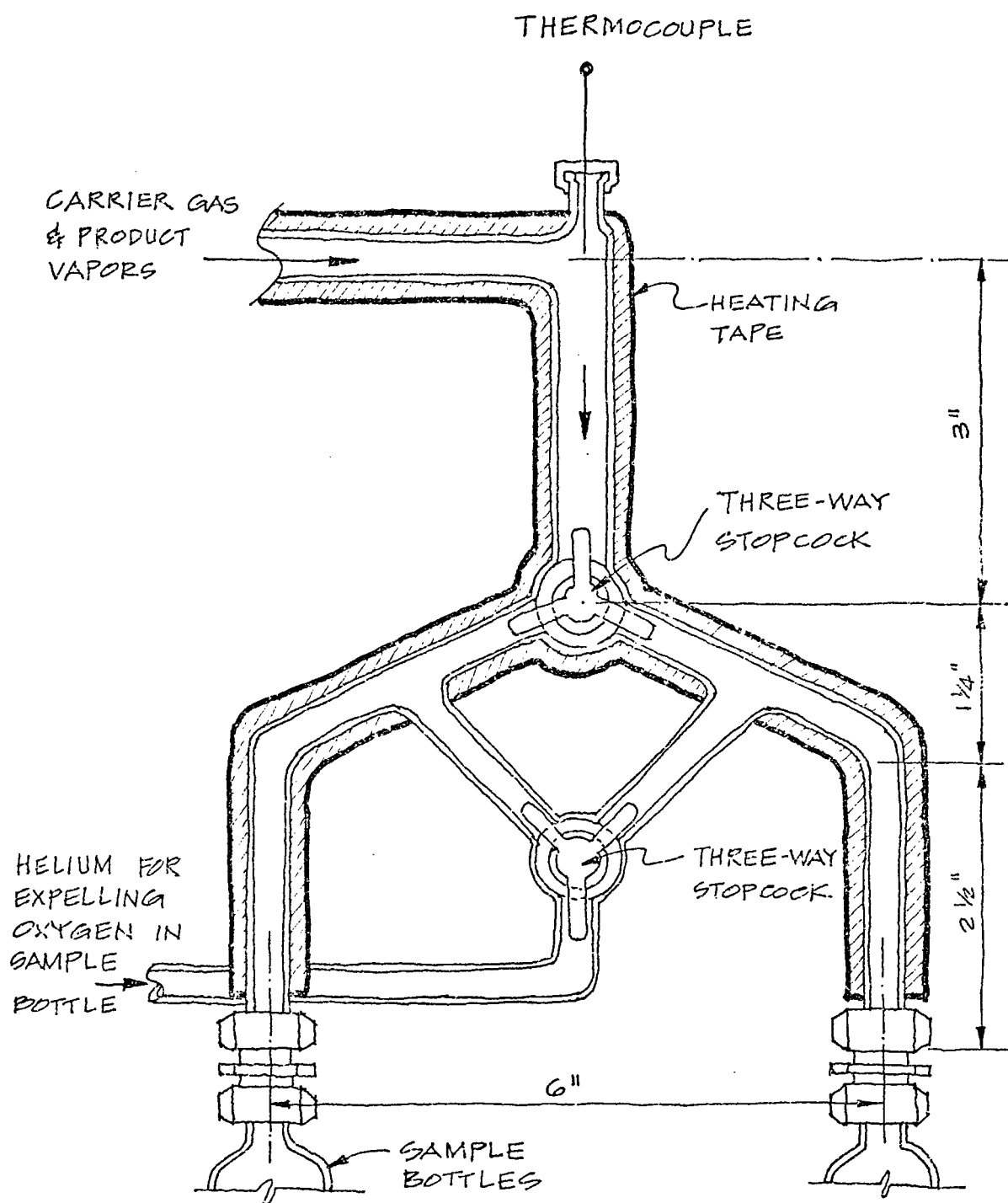


Fig. 5.8 Device for Gas Flow Shift

way stopcock. The other two ways of the stopcock are connected to two symmetric glass tubes with 30° declination. The declined tubes are then bended downward vertically for adopting two vapor sample bottles by tubing unions.

At the center points of the two declined tubes, the declined tubes are connected to another set of three-way stopcock unit. The free end of its three paths is connected to helium gas cylinder by a flexible rubber tubing. The purpose of this device is to expel air in the vapor sample bottle by helium before it is surrounded by liquid nitrogen because oxygen in the air is condensable at liquid nitrogen temperature. The flow rate of this helium stream can also be measured by a rotameter.

It is noted that the glass tubing in the regions with hot vapor stream are wrapped by heating tape to prevent vapor from condensing on the tubing walls.

5.3.6 Liquid Sampling System

As the reaction-distillation tray is immersed in an oil bath, liquid samples should be taken from the sample port located on the top of the 2" horizontal pipe as shown in Fig. 5.2. The distance between the liquid holdup and the sample port requires a syringe with an 8"-long needle. Cast stainless-steel of type-316 is used as the material of the needle. It has much better cor-

rosive resistance to the reacting liquid mixture than the weld type-316 stainless steel used for coating on thermocouple as mentioned previously. For more than one-hundred liquid samplings no visible corrosion on the needle, i.e., no visible reduction in needle diameter, is found.

To overcome high liquid head in the long syringe needle, a Glenco gas-tight glass syringe is used. It has a maximum capacity of 10 ml with an adapter fitted to Hamilton syringe needle with gauge number of 18. The strong suction of this gas-tight syringe greatly reduces the time required for taking a liquid sample.

Since acrylamide and ammonium bisulfate in the system are in solid state at room temperature. If the syringe needle is not preheated before liquid sampling, these two compounds will be crystalized inside the needle as soon as the needle is pulled from the hot liquid holdup. The crystallized compounds block the path way of the needle and make sampling become completely impossible. Thus, a copper tubing with a sealed end is used for preheating the needle. The copper tubing is immersed in the hot oil bath and has an outside diameter of $1/8$ " and a length of 8". For similar reason, another piece of copper tubing immersed in the oil bath is also used to preheat the glass syringe to avoid crystallization in the syringe. This copper tubing has a larger diameter

of 7/8" and a shorter length of 6". The syringe and syringe needle must be inserted into the above mentioned two heating tubes at least 5 minutes before taking liquid sample. Thus, the temperatures of the syringe and the syringe needle can become high enough to maintain the liquid sample as a clear brown liquid solution. The liquid sample is then injected into a liquid sample bottle. The liquid sample bottle is illustrated in Fig. 5.9. It is a 1/2" x 2" cylindrical vial. A silicon rubber stopper with reversible sleeve provides path way for syringe needle and simultaneously gives an excellent seal for the bottle.

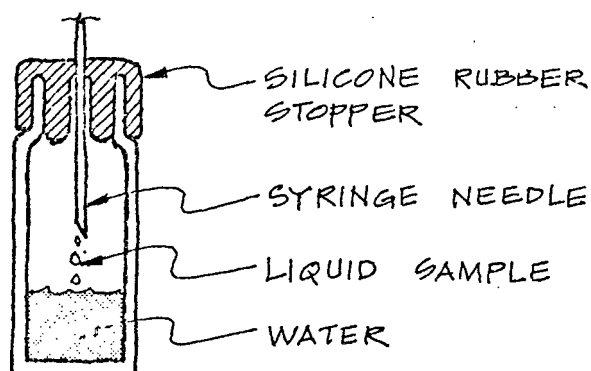


Fig. 5.9 Liquid Sample Bottle

In order to terminate reactions in the liquid sample, cold water is used to quench the liquid sample. Since the liquid sample becomes partially crystallized at low temperature, this cold water also becomes a good solvent for dissolving all solid compounds in the liquid sample. As the bottle is entirely closed, injection of liquid sample will increase the internal pressure of the bottle. This increased internal pressure reduces sample injection rate and even pushes away the rubber stopper. Therefore, all the liquid sample bottles are partially vacuumed in advance by a gas-tight syringe to provide fast sample injection rate and to secure the rubber stopper.

During the sample injection, the needle tip must not be in touch with cold water in the bottle. Otherwise, nonvolatile compounds may be crystallized in the needle to block the sample path way. As soon as the sample is injected into the water, the sample bottle is shaken violently to speedup quench function as well as dissolution of solid compounds in the sample. A clear liquid solution is then obtained, and immersed in ice bath for sample analysis.

5.3.7 Sample Analysis by Gas Chromatography

Gaw Mac Model 69-500 Gas Chromatography is used in this system for sample analysis. Its detector is a thermal conductivity cell. Although a hydrogen flame

ionization detector is more sensitive to organic compounds, it cannot be used here because the system contains water. Its oven can house two columns of same size, and same packed material for producing same chromatograms. As mentioned in Section 5.2, gas chromatographic columns used in this work are self prepared. Since good separation for the components in a sample greatly depend on the quality of a packed column, preparation of the packed column is then presented first in this section.

5.3.7.1 Preparation of Packed Column

Carbowax 1000 and Chromosob W 80/100 have been selected previously as stationary phase and support respectively. The next step is to coat Carbowax 1000 on Chromosorb W 80/100. A desired amount of Carbowax 1000 is dissolved in the solvent, methylene chloride, in a flask. The corresponding amount of Chromosorb W, which makes 35 Wt % of Carbowax 1000 on this support, is placed in a shallow porcelain dish. Then pour the methylene chloride solution in the Chromosorb W with constant and mild stirring. The solvent is then gradually evaporated from the dish, where heat is supplied from a heater underneath it. The temperature of the heater is generally controlled slightly below the boiling point of the solvent. For this case, temperature is adjusted at

about 40-50 °C. As soon as the coated support is completely solvent free, it is then ready for being packed into a column.

According to Horváth (14), small-diameter columns with inside diameters from 2-3 mm are most adequate for analytical purpose. Thus, the tube used in this work have outside diameter of 1/8" and inside diameter of 3/32", which is equivalent to 2.4 mm. Two six-foot stainless-steel tubes of the above mentioned size are then cleaned and dried for column packing. The method of packing the coated support into the stainless-steel tubes is illustrated in Fig. 5. 10.

The method employs a vacuum pump to provide a suction force such that the support can be forced into the tube. It is used here because it is easy to operate and its low pressure drop across the column does not seriously crush the particles of the support.

The tube is declined 45-60 ° from the floor. On its top, it is connected to a small glass funnel by a small segment of flexible Tygon tube. To pack the column, the packing material is fed into the column from the funnel. At the bottom of the tube, it is connected to one end of a Nupro filter by a tube union. The other end of the filter is further connected to the vacuum pump. In the filter, the filtration is performed by a 50-60 μ sintered metal which prevents the packing material

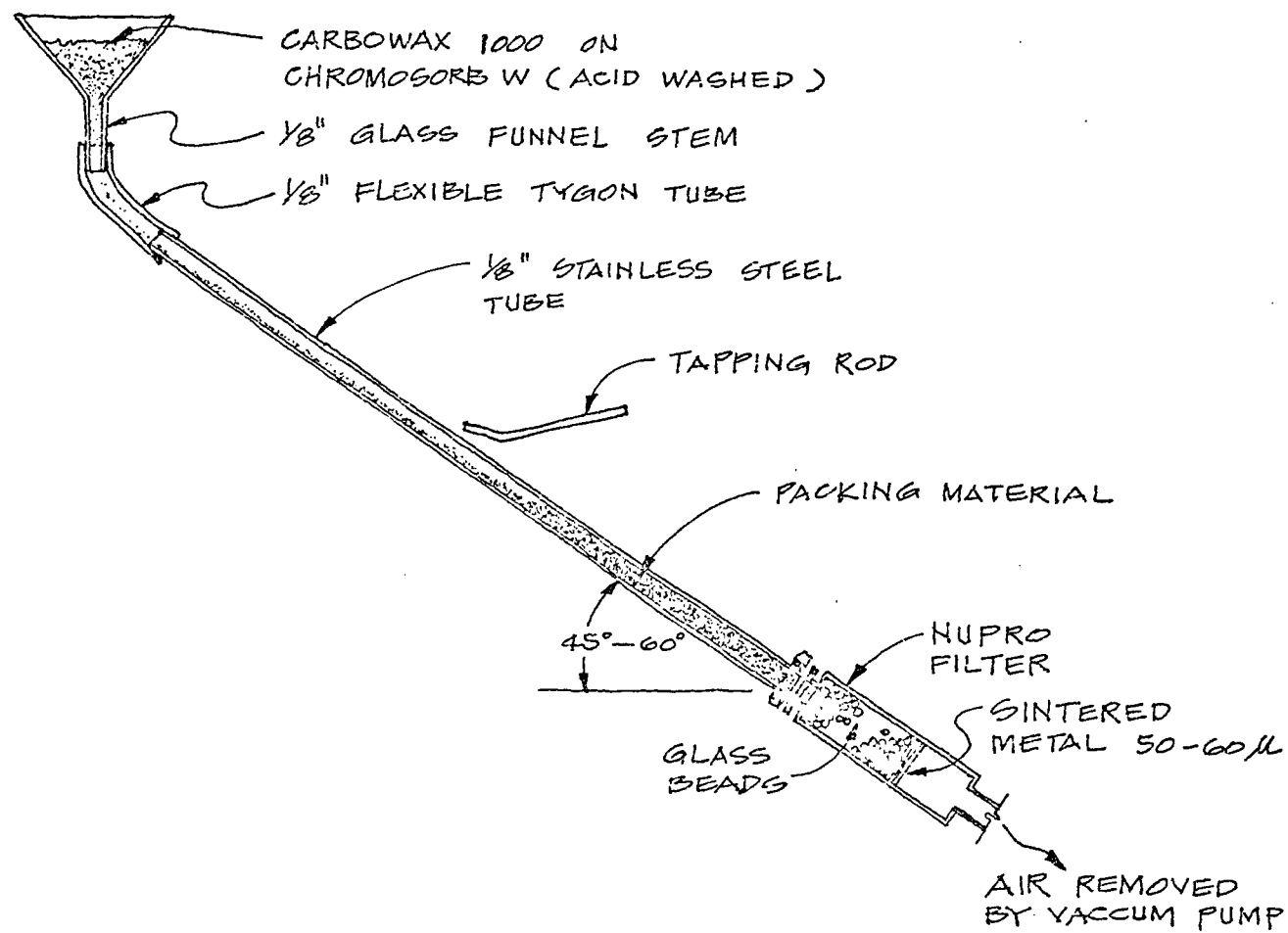


Fig. 5.10 Device for Column Packing

from entering the vacuum pump. The upper space of the filter is filled with glass beads to serve as the filtration media and thus reduce the amount of the packing material falling into the filter. Although pressure drop presents the entire column tube, the small inside diameter of the tube reduces incoming flow rate of the support. Therefore, tapping must be applied by a metal bar on the tube. It is better to tap the tube up-and-down lightly until the packing is finished. The packed column is then removed from the packing system and inserted with fine glass fiber on both of its ends. All the procedures are then repeated for packing the another column. Finally, both of the column tubes are bent into coils and connected by Swagelog tube fittings onto the tube adaptors in the column oven of the gas chromatography.

Now, the next step is to condition the prepared columns. At first, each column is only connected to the sample injection chamber. The other end is let free to avoid the contamination of detector filament at the beginning of column conditioning. Helium of 99.995 % is used as carrier gas. The flow rate is set at 30 ml/min. The oven temperature is adjusted at 125 °C, maximum suggested temperature for the Carbowax 1000. The column is then operated overnight at the above mentioned conditions. Next, the column is attached to the tube adaptor in the oven, which is connected to the detector. The detector temperature is set at 110 °C while the oven

temperature is reduced from 125 °C to 100 °C and the carrier gas is increased from 30 ml/min to 50 ml/min with a gauge pressure of 60 psig. The current of the detector filament is set at 180 ma at 110 °C detector temperature. The current may be adjusted slightly higher or lower than 180 ma depending upon the size of the sample. After another 24 hours, a stable base line can be obtained and no impurities can be observed from the chromatograms. The column is then ready for sample analysis. It is operated isothermally.

5.3.7.2 Sample Analysis

1. Vapor Sample:

Most of vapor sample is in solid state when it is removed from the liquid nitrogen bath. The vapor sample bottle is then flushed by warm water until the entire vapor sample becomes liquid state. This step takes about 30 seconds. The bottle is then weighed by an electronic balance to get total weight of the sample. Since some vapor sample is caught in glass fiber, about 60-ml acetone per sample is added into the bottle to extract it out and also to mix uniformly all the vapor sample.

For better results, 1-propanol is used as reference compound in gas chromatographic analysis. The amount of this reference compound must be known. It can be

calculated from the difference between the weights of bottle before and after the addition of 1-propanol. A typical gas chromatogram for a vapor sample is shown in Fig. 5.11. Very clear peak separation among all the components including acetone and 1-propanol in the sample bottle can be observed. This demonstrates that the prepared column is excellent for analyzing the compounds in this system. The peak area for each compound is measured by a Hudron planimeter. The measured area for each peak should be divided by the attenuator shown on the top of the peak. The resulting areas for all the compound then has the same basis.

Although water peak has a long tailing because of its high polarity, its relatively small quantity in the entire sample does not produce a significant effect on analysis for major compounds such as ethyl acrylate and ethyl alcohol. The area ratio of a component to 1-propanol as measured above does not reflect actual weight ratio between the two components. Therefore, relationship between area ratio and weight ratio for a component to the reference compound, 1-propanol must be determined from blank test on gas chromatography. Calibration between these ratios will be presented later in Section 5.4.

2. Liquid Sample

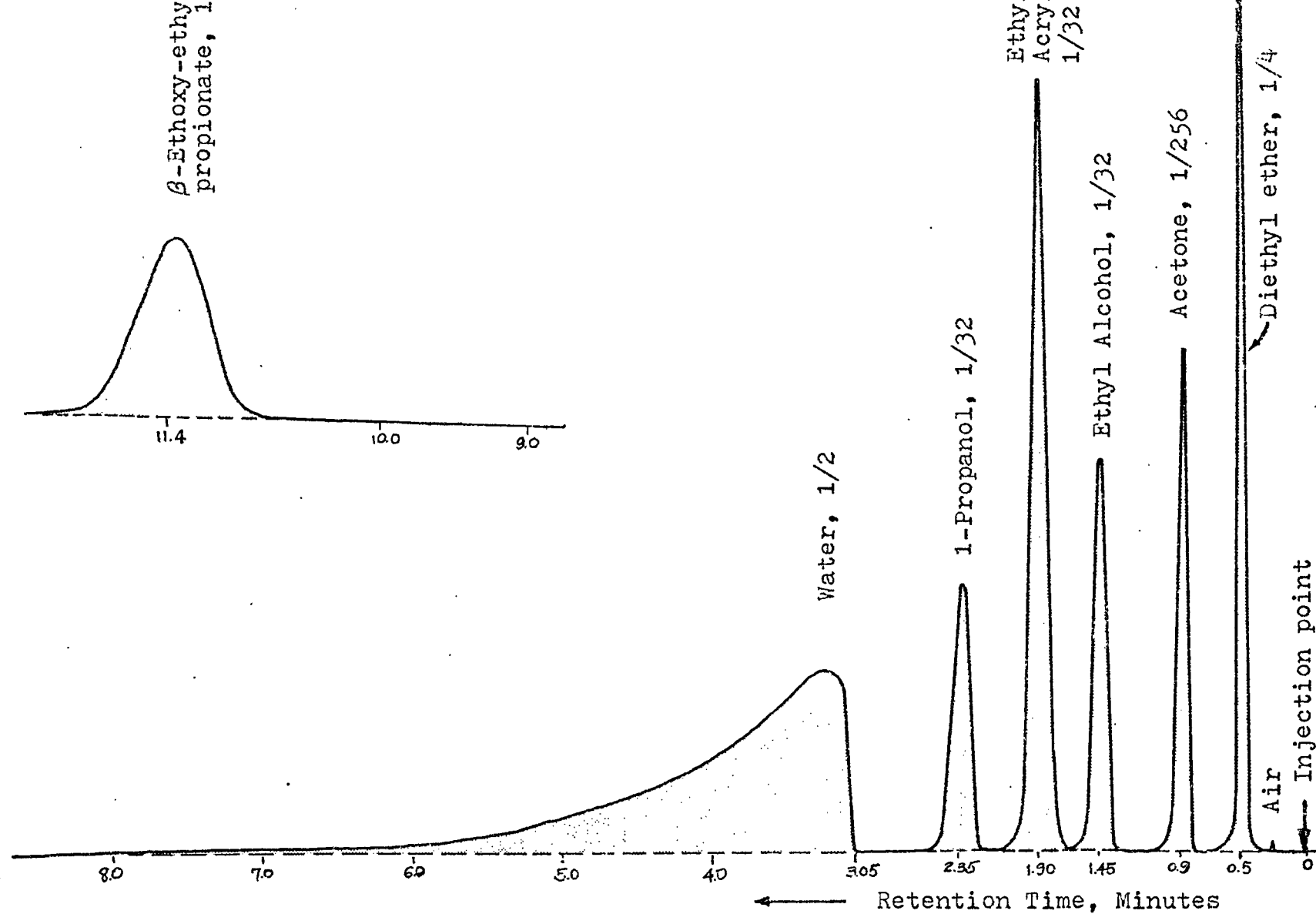


Fig. 5.11 Gas Chromatographical Analysis of A Typical Vapor Sample

The molal quantities in the liquid holdup are calculated from the instantaneously stoichiometric balance on the basis of the accumulated feed quantities, vapor condensate, and reaction relationship. Therefore, only relative ratios among ethyl alcohol, ethyl acrylate, diethyl ether, and β -ethoxy ethyl propionate are needed to be determined. No reference compound is used in liquid sample because the presence of sulfuric acid in the liquid sample can cause serious side reactions with 1-propanol, and thus produces unclear gas chromatograms.

A typical gas chromatogram for a liquid sample is shown in Fig. 5.12. A slight shift in base line is caused by the deposit of nonvolatile compounds and sulfuric acid. This shift may be assumed to have negligible error in determination of relative areas among the different peaks. Because of the effect of sulfuric acid, inorganic non-volatile compounds, the peak of ethyl alcohol has a tailing effect which overlaps the peak of ethyl acrylate. The relationship between the two over-lapped compounds has been determined by blank test. The shaded area all belongs to ethyl alcohol and that of the unshaded peak belongs to ethyl acrylate. Since large amount of water is used to quench the liquid sample and to dissolve its solid compound, the peak of water in the gas chromatographic chart is then very large. Since the quantity of water

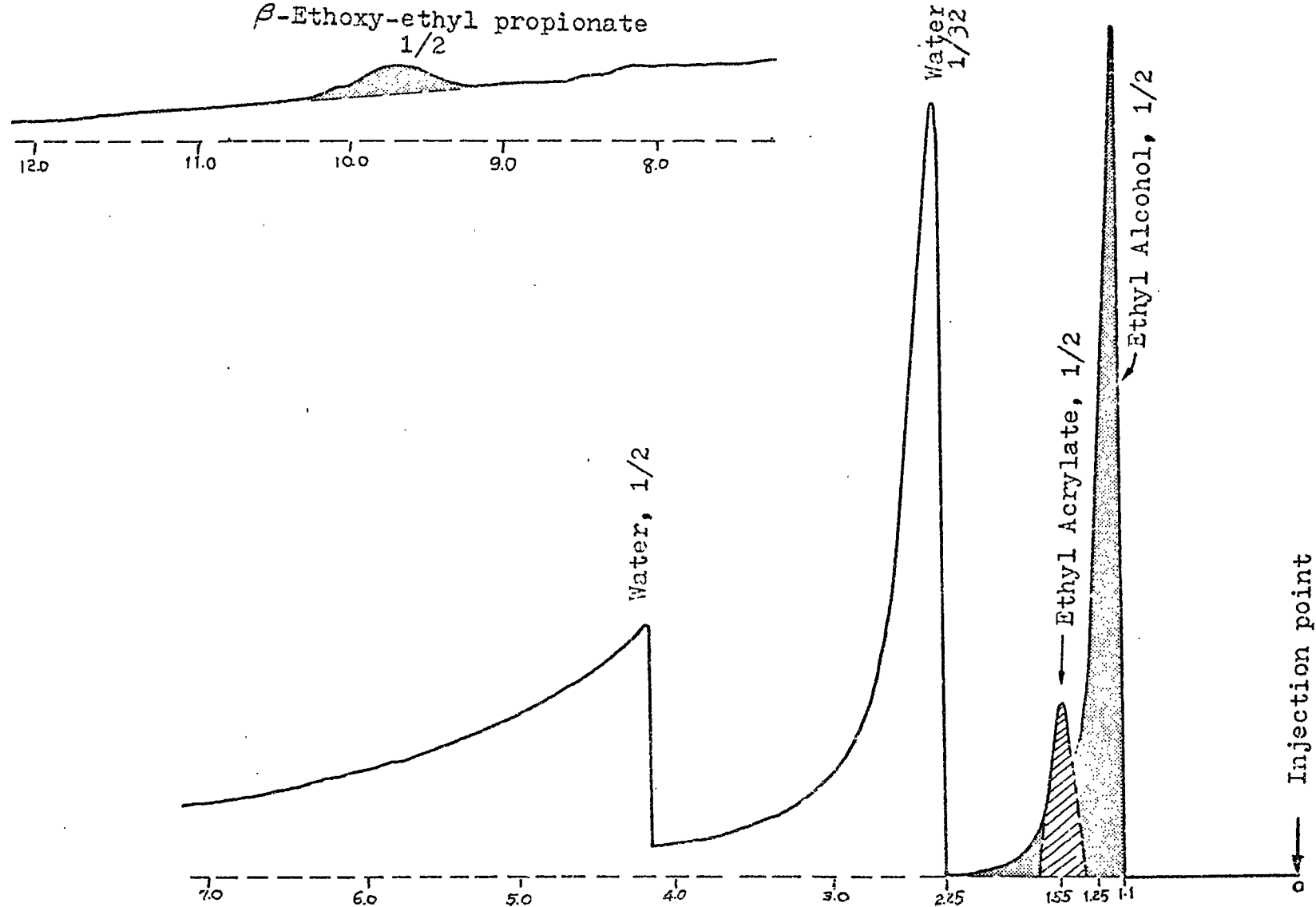


Fig. 5.12 Gas Chromatographical Analysis of
A Typical Liquid Sample

produced can be calculated from the amount of diethyl ether produced, its peak in this chromatogram is not used to determine its quantity. It is noted that diethyl ether does not show on the chart of the liquid sample. All the diethyl ether produced in the reaction is evaporated and appears in the vapor condensate sample. Calibration of gas chromatographical area ratio as a function of actual weight ratio will be presented in Section 5.4.

5.4 Equipment Calibration

Several equipment used in the experimental system are calibrated by the procedures described below.

5.4.1 Feed Flow Rate

The feed flow rate is one of the three operating parameters in the system. It is measured by a Roger Gilmont rotameter. For calibration purpose, a three-way stopcock is equipped on the top of the rotameter. One of the two outlets of the stopcock goes to the reaction-distillation tray. The other is a free end. During calibration, this free end is attached by a glass cylinder as a collection bottle while aqueous ethyl alcohol solution flow through the rotameter. For a preset rotameter reading, an accumulated amount of ethyl alcohol solution is weighed with respect to the measured time

interval. Then the mass flow rate of the feed can be calculated for its corresponding reading on the rotameter. If a volume flow rate is preferred, the density of the prepared aqueous alcohol solution can be used to convert the mass flow rate into the volume flow rate. All the calibrated volumetric feed rate for the Gilmont rotameter is given in Fig. B.2 of Appendix B.

5.4.2 Overall Heat Transfer Coefficient Across the Wall of the Reaction-Distillation Tray

Boiling water, boiling ethyl alcohol and nonvolatile glycerine are the three materials used to simulate the liquid mixture in the reaction-distillation tray. Overall heat transfer coefficient for each of the above three materials across the wall of the reaction-distillation tray is measured separately. Since the variations among the three sets of measured overall heat transfer coefficient are small, their average value is then used as a simulated overall heat transfer coefficient for the reaction-distillation liquid mixture. Detailed techniques for measuring the above three sets of overall heat transfer coefficients are described as follows.

5.4.2.1 Overall Heat Transfer Coefficient of Boiling Water in the Reaction-Distillation Tray

A fixed amount of water is preheated up to about

90 °C and then put into the reaction-distillation tray. The oil bath temperature is set higher than the boiling point of water such that water in the reaction-distillation tray can be heated up to its boiling point and also kept boiling at the boiling point. It is noted that no water is fed into the reaction-distillation tray during this measurement. Thus, all the heat transferred across the wall of the reaction-distillation tray contributes to evaporate water vapor. The amount of heat transferred can then be calculated from water vaporization rate and heat of vaporization of water by the following equation:

$$Q = \lambda_{H_2O} V_{H_2O} \quad (5-1)$$

where

Q = heat transfer rate across the wall of the reaction-distillation tray

V_{H_2O} = vapor mass flow rate of water, i.e. vaporization rate

λ_{H_2O} = heat of vaporization of water

From the definition of overall heat transfer coefficient

Q can be alternatively represented by

$$Q = U_i a_i (T_o - T) \quad (5-2)$$

where

a_i = inside heat transfer area of the reaction-distillation tray

U_i = overall heat transfer coefficient referred
to inside heat transfer area

T_o = oil bath temperature

T = liquid temperature in the reaction-distillation
tray

Equating the above two equations and removing the term, $a_i(T_o - T)$ to the other side give the following working equation for U_i :

$$U_i = \frac{\lambda_{H_2O} V_{H_2O}}{a_i(T_o - T)} \quad (5-3)$$

The water vapor rate, V_{H_2O} , can be calculated from the amount of water vapor condensate collected within a measured time interval. The experimental apparatus introduced in Section 5.3.6 for vapor sampling can be used to measure water vapor condensate, and a stop watch to measure the time interval. If the temperature driving force, $(T_o - T)$, which is constant throughout a measuring period, is not large, evaporation rate will be small. And, if the temperature driving force is too small, amount of water evaporated will be too small. This may reduce the accuracy in calculated total heat transfer rate across the wall of the reaction-distillation tray. Therefore, three oil bath temperatures, 105 , 110 and 115 °C,

which can provide moderate temperature driving forces, are used. Before calculating heat transfer area, a_i , the aerated volume must be determined first.

The aerated water volume is calculated from the following equation:

$$v_a = \frac{(W_o - W_c/2)}{\rho} \times \epsilon \quad (5-4)$$

where

v_a = aerated water volume

W_o = amount of water in the reaction-distillation tray at the beginning of measurement

W_c = amount of water vapor condensate collected at the end of measurement

ρ = water density at 100 °C

ϵ = volumetric ratio of aerated water to clear water

The term, ϵ , is predetermined to be 1.06. The procedures are described below. The clear water volume is calculated from water quantity and water density. The aerated volume is obtained by first measuring the height of the aerated water and then using the calibration chart given in Fig. B.3 of Appendix B for the volume of aerated water.

When the aerated volume, v_a , is determined from Equation (5-4), its corresponding heat transfer area, which can not be directly measured in this reaction-distillation system, can be obtained from a calibration curve also given in Fig. B.3. For computer calculations in the program

MODEL, this calibration curve has been fitted by a polynomial equation. The program MODEL is a computer simulation for the mathematical model of semi-batch distillation accompanied by chemical reaction.

Now, all the terms on the right-hand side of Equation (5-3) are known, the overall heat transfer coefficient, U_i , can then be calculated. Since the reaction-distillation liquid is mixed by a stirrer at about 1000 rpm, the overall heat transfer coefficient of the boiling water is also measured at the same stirring speed. The measured results are listed as follows.

$T_o, ^\circ\text{C}$	$(T_o - T), ^\circ\text{C}$	$U_i, \text{ cal/min-}^\circ\text{C-cm}^2$
105	5	0.180
110	10	0.184
115	15	0.185

An average value of $0.183 \text{ cal/min-}^\circ\text{C-cm}^2$ for the above three quantities is then used to represent the overall heat transfer coefficient of boiling water in the reaction-distillation tray.

5.4.2.2 Overall Heat Transfer Coefficient of Boiling Ethyl Alcohol in the Reaction-Distillation Tray

The method and equations given in the previous

section are also used here to measure overall heat transfer coefficient of boiling ethyl alcohol in the reaction-distillation tray. Three oil bath temperatures, 85, 90 and 95 °C are used to provide temperature driving forces close to those shown in the previous section. It is noted that boiling point of ethyl alcohol is 78.4 °C. The results are listed as follows.

T_o , °C	$(T_o - T)$, °C	U_i , cal/min-°C-cm ²
85	6.6	0.150
90	11.6	0.152
95	16.6	0.152

An average value of 0.151 cal/min-°C-cm² is then used to represent the overall heat transfer coefficient of boiling ethyl alcohol in the reaction-distillation tray.

5.4.2.3 Overall Heat Transfer Coefficient of Nonvolatile Glycerine in the Reaction-Distillation Tray

Vapor pressure of glycerine is very small. Therefore, during the determination of overall heat transfer coefficient using glycerine, there is no vaporization of glycerine in the reaction-distillation tray. All the heat transferred from the oil bath then contributes to increase the temperature of glycerine. The glycerine is also completely mixed in a similar manner as used in

the two previous cases. For any instant, the energy balance require that the rate changes of heat transfer and internal energy increase should be equal. Thus,

$$M \frac{dE}{dt} = U_i a_i (T_o - T) \quad (5-5)$$

At atmospheric pressure, the differential internal energy, dE , may be approximated by

$$dE = d(h - pv) \approx dh = C_p dT$$

Substituting the above relationship into Equation(5-5)

yields

$$MC_p \frac{dT}{dt} = U_i a_i (T_o - T)$$

If the temperature range is narrow, an average heat capacity \bar{C}_p , may be used to replace C_p without any significant error. Then the above equation can be readily integrated to give the following working equation for overall heat transfer coefficient:

$$U_i = \frac{M \bar{C}_p \ln \frac{T_o - T_1}{T_o - T_2}}{a_i (t_2 - t_1)} \quad (5-6)$$

where

1 =subscript to represent the initial conditions

2 =subscript to represent the final conditions

\bar{C}_p =average heat capacity

Two oil bath temperatures, 105 and 115 °C are used and the temperature rise for glycerine is in the range of 70 to 85 °C. The results are listed as follows.

$T_o, ^\circ\text{C}$	$U_i, \text{ cal/min-}^\circ\text{C-cm}^2$
115	0.149
105	0.145

An average value of 0.147 cal/min-°C-cm² is then used to represent overall heat transfer coefficient of non-volatile glycerine in the reaction-distillation tray.

5.4.2.4 Overall Heat Transfer Coefficient of the Reaction-Distillation Liquid Mixture

The reaction-distillation liquid mixture contains both volatile components such as ethyl alcohol and water, and very nonvolatile components such as sulfuric acid and ammonium bisulfate. Therefore, a simulated overall heat transfer coefficient calculated from an average of the above three experimental overall heat transfer coefficients is then used for the reaction-distillation liquid holdups. The calculated average value is 0.16 cal/min-°C-cm². Since the liquid inside the reaction-distillation tray is boiling and under a vigorous stirring, its resistance to heat transfer should be much smaller than that of the silicon film on the outside wall of the reaction-distillation system. The silicon fluid is very nonvolatile and stirred

mildly. The silicon film on the outside of the glass wall and the glass wall itself are the major components of the overall heat transfer resistance. This is verified by the fact that the overall heat transfer coefficients determined by using the three different fluids in the system are about the same. Therefore, the use of an average overall heat transfer coefficient is justified.

5.4.3 Relative Ratio of Vapor to Total Feed

The relative ratio of vapor to total feed is used to calculate the inlet enthalpy of the feed stream. According to the definition of the system, the inlet enthalpy of the feed stream should be that at the micro sieve tray entry, or more precisely, right before its mixing with the liquid holdup. Because of the glass-blowing technique, the feed glass tube is connected to the bottom of the reaction-distillation tray as a whole piece. Thus, the feed enthalpy is best measured with the same preheater (feed tubing) and under the same operating conditions as used in the reaction-distillation system except that glycerine is used as liquid holdup. The incoming aqueous ethyl alcohol solution is absorbed into glycerine without chemical reaction. When the vapor in the feed stream is absorbed by glycerine, an appreciable amount of heat will be released because the absorbed vapor is condensed into the liquid holdup. This released heat of conden-

sation will then increase the temperature of glycerine. The overall heat transfer coefficient across the wall of the reaction-distillation tray with such an additional insulation by Teflon sheet is then measured by the same procedures described in Section 5.4.2.3. The new measured overall heat transfer coefficient is $0.056 \text{ cal/min-}^{\circ}\text{C-cm}^2$, which is much smaller than the original $0.16 \text{ cal/min-}^{\circ}\text{C-cm}^2$.

The instantaneous energy balance around the reaction-distillation tray can be represented by

$$\frac{d}{dt}(Mh) = V_{IN}H_{IN} + L_{IN}h_{IN} + U_i a_i (T_o - T)$$

For a small measuring period, average liquid holdup, heat capacity, and heat transfer area may be employed. Then, the above equation can be reduced to the following equation:

$$\bar{M}\bar{C}_p \frac{dT}{dt} = V_{IN}H_{IN} + L_{IN}h_{IN} + U_i \bar{a}_i (T_o - T)$$

Integration of the above equation yield:

$$\frac{V_{IN}H_{IN} + L_{IN}h_{IN}}{U_i \bar{a}_i} = \frac{T_2 - T_1 e^{-\alpha \Delta t}}{1 + e^{-\alpha \Delta t}} - T_o \quad (5-7)$$

where

$$\alpha = \frac{U_i \bar{a}_i}{\bar{M}\bar{C}_p}$$

Δt = measured time interval

T_1 = temperature of glycerine before absorbing ethyl alcohol solution

T_2 = temperature of glycerine at the end of a measuring period

At a high ethyl alcohol concentration, equilibrium compositions of vapor and liquid very close. Therefore, it may be assumed that the vapor composition is the same as the feed composition. Thus, the inlet enthalpy can be expressed as a function of heat of vaporization, total feed rate and relative ratio of vapor to total feed as follows:

$$V_{IN}H_{IN} + L_{IN}h_{IN} = (\psi\lambda + h_F)F$$

where

ψ = relative ratio of vapor to total feed

F = total feed rate

λ = heat of vaporization of feed stream

h_F = liquid enthalpy for total feed at the exit temperature of the preheater

Substituting the above equation into Equation (5-7) and rearranging the equation will give the following working equation to determine the relative ratio of vapor to total feed.

$$\psi = \frac{U_i a_i}{\lambda F} \left[\frac{T_2 T_1 e^{-\alpha \Delta t}}{1 + e^{-\alpha \Delta t}} - T_0 \right] - \frac{h_F}{\lambda} \quad (5-8)$$

As mentioned in Section 5.3.4.3, glass tubing is used for generating a low relative ratio of vapor to total feed and copper tubing plus the above mentioned

glass tubing is used to generate a high relative ratio of vapor to total feed. For each set of operating conditions, i.e., oil bath temperature, feed rate, and tubing material, the experiments are repeated twice.

The average value of ψ 's determined by Equation (5-8) is plotted in Fig. B.4. of Appendix B and its smoothed curve is used as the calibration for relative ratio of vapor to total feed. Figure B.4 shows that at a higher flow rate, the relative ratio of vapor to total feed is smaller if the other operating conditions such as the oil bath temperature and tubing material do not change. Though an increase in inside flow rate can increase the inside film heat transfer rate, it is too small to affect an overall heat transfer coefficient.

5.4.4 Relation between Weight Ratio and Area Ratio in Gas Chromatography

As mentioned in Section 5.3.5. 1-propanol is used as the reference compound in gas chromatographical analysis. Therefore, for each volatile compound except β -ethoxy ethyl propionate in the system, several samples with different weight ratios to 1-propanol are prepared for blank test. The peak areas of the test compound and 1-propanol from the chromatographical analysis are then integrated by a Hudron planimeter. The weight ratios are then plotted against the corresponding area ratios

as shown in Fig.B.5 of Appendix B. It is found that ethyl acrylate and ethyl alcohol have the constant relationships between the ratios. But the similar relationships for water and diethyl ether are functions of weight ratios. As mentioned in Section 5.2, β -ethoxy-ethyl propionate can not be purchased from commercial sources for use in a blank test. Since the system contains only a trace amount of this by-product, any error introduced by a simplifying assumption is negligible. It is assumed that the weight and the area ratios for this compound are the same.

All the smoothed curves in Fig. B.5 have been fitted into polynomial equations and used by the computer program LABDATA. That is, all the gas chromatographical analysis obtained from area ratios into actual weight ratios by these polynomial equations is in the program LABDATA.

5.4.5 Heat of Reaction for the Reaction between Acrylamide and Sulfuric Acid

Heat of reaction for the reaction between acrylamide and sulfuric acid is required for calculating heat of formation of molecular complex, acrylamide sulfate. Then the heat of formation of acrylamide sulfate is used to calculate the heats of reaction for esterification and successive reaction on the basis of Hess' law. The heat of reaction between acrylamide and sulfuric acid is

measured as follows.

A 250-ml beaker containing 131.3 grams of sulfuric acid solution of 89.6 Wt %, which is equivalent to 1.2 moles of pure sulfuric acid, is immersed in the oil bath at 80 °C. Temperature of sulfuric acid is finally reached at 80 °C. Then, 71.1 grams or 1 mole of acrylamide at the room temperature, 25 °C, is added into the sulfuric acid solution under continuous stirring. The released heat from the reaction between sulfuric acid and acrylamide not only melts crystalline acrylamide but also raise the temperature of the formed acrylamide sulfate solution to 89.2 °C. The heat of reaction is then equal to the heat required to melt acrylamide and raises temperatures of acrylamide from 25 °C to 89.2 °C and sulfuric acid from 80 °C to 89.2 °C. The calculation procedures are given as follows.

1. Heat of Fusion of Acrylamide:

General correlation for heat of fusion has been unsuccessful. However, entropies of fusion of homologous compounds are generally very close while those of heterogenous compounds are widely apart as shown below.

Paraffins	Entropy of Fusion cal/g-mole-°K
n-Hexane	17.51
n-Heptane	18.37

Naphthene

Cyclohexane	2.28
-------------	------

1,cis'-2-Dimethyl Cyclohexane	1.76
-------------------------------	------

Aromatics

Benzene	8.43
---------	------

Toluene	8.83
---------	------

Therefore, the best estimate for heat of fusion is to use the entropy of fusion of a homologous compound with known heat of fusion or entropy of fusion. The closest compound to acrylamide with known heat of fusion is cyanamide (52). It is then used to estimate the heat of fusion of acrylamide as follows.

Compound	Melting Point °C	Heat of Fusion Kcal/g-mole
Cyanamide	44	2.09
Acrylamide	84.5	x

$$x = 2.09 \times \frac{273.2 + 84.5}{273.2 + 44} = 2.36 \text{ Kcal/g-mole}$$

2. Sensible Heat:

For pure sulfuric acid

$$\bar{C}_p = 0.38 \text{ cal/g-}^\circ\text{C}$$

$$h_1 = 131.3 \times 0.896 \times 0.38(89.2 - 80) \times 10^{-3}$$

$$= 0.41 \text{ Kcal/g-mole acrylamide}$$

For water

$$\bar{C}_p = 1.0 \text{ cal/g-}^\circ\text{C}$$

$$h_2 = 131.3 \times (1 - 0.896) \times 1.0(89.2 - 80) \times 10^{-3}$$

$$= 0.12 \text{ cal/g-mole acrylamide}$$

For acrylamide

$$\bar{C}_p = 0.60 \text{ cal/g-}^\circ\text{C}$$

$$h_3 = 71.1 \times 0.60 \times (89.2 - 25.0) \times 10^{-3}$$

$$= 2.73 \text{ Kcal/g-mole acrylamide}$$

3. Heat of Reaction:

Difference in heat capacities between the reactant and the product is assumed to be negligible. Then heat of reaction for this reaction, Reaction 4 is equal to the sum of the above four energy terms:

$$\Delta H_{R_4} = \lambda_f + h_1 + h_2 + h_3$$

$$= 2.36 + 0.41 + 0.12 + 2.73$$

$$= 5.62 \text{ Kcal/g-mole acrylamide}$$

5.5 Experimental Procedures

5.5.1 Preparatory Work

1. Turn on the gas chromatographic equipment at least 48 hours before sample analysis.

2. Prepare vapor sample bottle following the method given in Section 5.3.5.

3. Prepare liquid sample bottle following the method given in Section 5.3.6

4. Before the addition of silicon fluid into the oil bath, assemble experimental apparatus according to the flow scheme shown in Fig. 5.1.

5. Add silicon fluid into the oil bath, turn on the heater and the stirrer, and set the desired temperature of the oil bath.

6. Feed nitrogen gas into the vapor withdrawal system for preheating the system.

7. Turn on heating tapes and heating mantle along the vapor withdrawal line and set the desired temperature.

8. It takes at least an hour before the constant temperatures both in the oil bath and the vapor withdrawal system are reached.

9. Preheat the liquid sample syringe and syringe needle following the method given in Section 5.3.6.

10 Shift the above nitrogen gas to carrier gas helium.

11. Feed the auxiliary helium into the vapor sample bottles to expel air in the bottles.

12. Two minutes later, pour liquid nitrogen into the 1200 ml dewar to immerse vapor sample bottles about 1/2" below the U tube of the bottle.

13. Another three minutes later, close the auxiliary helium stream and open the carrier gas helium stream.

14. Prepare nonvolatile reactant, acrylamide sulfate solution following the method given in Section 5.3.3

15. Pour the above prepared acrylamide sulfate solution into the reaction-distillation tray through the largest vertical port.

16. Seal the largest vertical port by a large Teflon stopper equipped with a silicon-Teflon rubber, and seal other two vertical ports with silicon rubber stopper with reversible sleeves.

17. Insert thermocouples through the above mentioned silicon-Teflon rubber or silicon rubber stopper for measuring liquid and carrier gas temperatures.

18. As soon as the temperature in the liquid holdup (acrylamide sulfate solution) become the same as oil bath temperature, or the difference between the two temperatures becomes less than 0.02°C , the system is ready for conducting an experiment on semi-batch distillation accompanied by chemical reaction.

5.5.2 Reaction-distillation Experiment and Vapor Liquid Sampling

19. First close the feed line to the reaction-distillation tray but open the flow path to the glass cylinder. The latter is used for the feed rate adjustment and calibration.

20. Turn on the feed pump and adjust its variable dial for the rotameter reading equivalent to the desired flow rate.

21. As soon as the desired flow rate is obtained, turn the three-way stopcock to shift the feed flow from the glass cylinder to the reaction-distillation tray.

22. Notice that a sudden decrease in rotameter reading can be observed at this moment because a sudden vaporization occurs in the preheater and consequently increases the pressure drop across the micro-sieve tray. Therefore, readjust the dial on the feed pump immediately. It takes only 5 to 15 seconds to get another steady and constant flow at the desired flow rate.

23. At the desired sampling time, take the liquid sample by a Glenco gas-tight syringe through the liquid sample port.

24. Inject the liquid sample into the cold liquid sample bottle to quench immediately the reaction.

25. Immerse the liquid sample bottle in an ice bath to keep it from reacting. Then take the vapor sample by shifting the helium-product vapor stream into a previously empty bottle for next vapor sampling. The shifting can be accomplished by turning the three way stopcock on the upper part of the gas-shifting device shown in Fig. 5.8.

26. Remove the vapor sample bottle with the vapor condensate from the gas-shifting device. Seal the bottle with a silicon rubber stopper and then flush the bottle surface with tap water until all the frozen solids are melted.

27. Clean the contaminated syringe and syringe needle used in Steps 23 and 24 for liquid sampling. If spare syringes and syringe needles are enough for a complete experimental run, this step can be skipped. Otherwise, a longer time period between two samplings must be allowed because this step requires at least 5 minutes. The cleaned syringe and syringe needle are then preheated following the method given in Section 5.3.6.

28. Replace the liquid nitrogen-containing dewar, which was used to condense the previous vapor sample, by an empty dewar. Attach a new empty vapor sample bottle on the gas-shifting device. The empty dewar should be adjusted so that the empty vapor sample bottle can be suspended right above its center bottom.

29. Blow auxiliary helium stream through the empty vapor sample bottle to expel the air in it for about two minutes. Then, pour liquid nitrogen into the dewar to pre-cool the vapor sample bottle. The liquid nitrogen level should be about one centimeter below the horizontal connecting tube in the sample bottle.

30. Repeat Steps 23 through 29 for next set of liquid and vapor samplings until the end of an experimental run.

31. Remove reaction residue from the reaction-distillation tray and then clean all the experimental apparatus for next experimental run.

32. Finally, analyze all the collected vapor and liquid samples by the gas chromatography following the methods given in Section 5.3.7.2.

Chapter 6 Analysis of Experimental Data and Correlation of Operating Parameters

6.1 Treatment of Experimental Data

Data obtained from the experiments described in the previous chapter include the following:

- (1) Composition analyses of vapor and liquid samples by gas chromatograph
- (2) Accumulated vapor condensate for each vapor sample
- (3) Instantaneous liquid temperature

The above data were obtained for different sets of operation conditions. Three operating parameters discussed in Chapter 4 define the conditions for each experimental run. These operating parameters are:

- (4) Initial and constant surrounding temperature
- (5) Feed rate of aqueous alcohol solution
- (6) Relative ratio of vapor to total feed

Among the above six different data, values of items (4) and (6) are used for energy balance calculations only. For the system investigated in this study, the energy balance calculations are required for solving the mathematical model of the semi-batch distillation accompanied by chemical reaction. The energy balance based on the mathematical model will be discussed in next chapter.

Thus, data analysis presented in this chapter will deal with the remaining four items, i.e., Items (1), (2), (3) and (5). These are required for correlating "chemical" vapor-liquid equilibria and reaction rates. The correlations, in turn, provide numerical values for verifying the mathematical model as discussed in Chapter 7.

6.1.1 Vapor and Liquid Compositions

The individual vapor molal quantities of a vapor sample can be calculated from its total weight and gas chromatographical analysis obtained in the previous chapter. The required calibration curves for converting the relative area ratios to the weight ratio of a component to 1-propanol are given in Fig. B.5 of Appendix B. The vapor molal quantities for a compound determined above at different time intervals are then added to get the accumulated vapor molal quantity. The derivative of the smoothed curve of this accumulated quantity at any moment then becomes its instantaneous molal flow rate. The individual accumulated vapor molal quantities can be typically represented by Run 1 and plotted in Fig. 6.1.a. The results show that the relative content of the main product, ethyl acrylate, is very high at the early stage due to an active esterification, and becomes smaller than those of ethyl alcohol and water at the end of the run due to a continuous feed of the later two compounds and a much less active esterification. Very low contents in diethyl ether

and β -ethoxy-ethyl propionate indicate that the two side reactions, dehydration and successive reaction, are very minor.

The total vapor molal quantities calculated from the above individual molal condensates, and the liquid hold-up temperatures are plotted as a function of time and shown in Figs. 6.1.b through 6.4 for the nine experimental runs made in this study. During the first ten minutes of the reaction between acrylamide sulfate and ethyl alcohol, the amount of vapor condensate collected in the vapor sample bottle is negligibly small. A rapid temperature rise of the liquid holdup is observed for this time period. These phenomena indicate that the reacting liquid mixture during the first ten minutes is still below its bubble point. Therefore, the heat released from chemical reactions are absorbed entirely by the liquid mixture to raise its temperature.

When the temperature reaches its maximum value it indicates that the liquid mixture has reached its bubble point. Then, the additional release of heat of reaction is consumed by vaporizing the volatile product and other components. The accumulation of the vapor condensate becomes noticeable. After this maximum point, the liquid bubbling temperature, starts to decline as more of the relatively cold ethyl alcohol is fed into the system and as the liquid composition changes because of reactions. Heat of reactions is sufficient enough to vaporize products and other volatile compounds. The vapor condensate

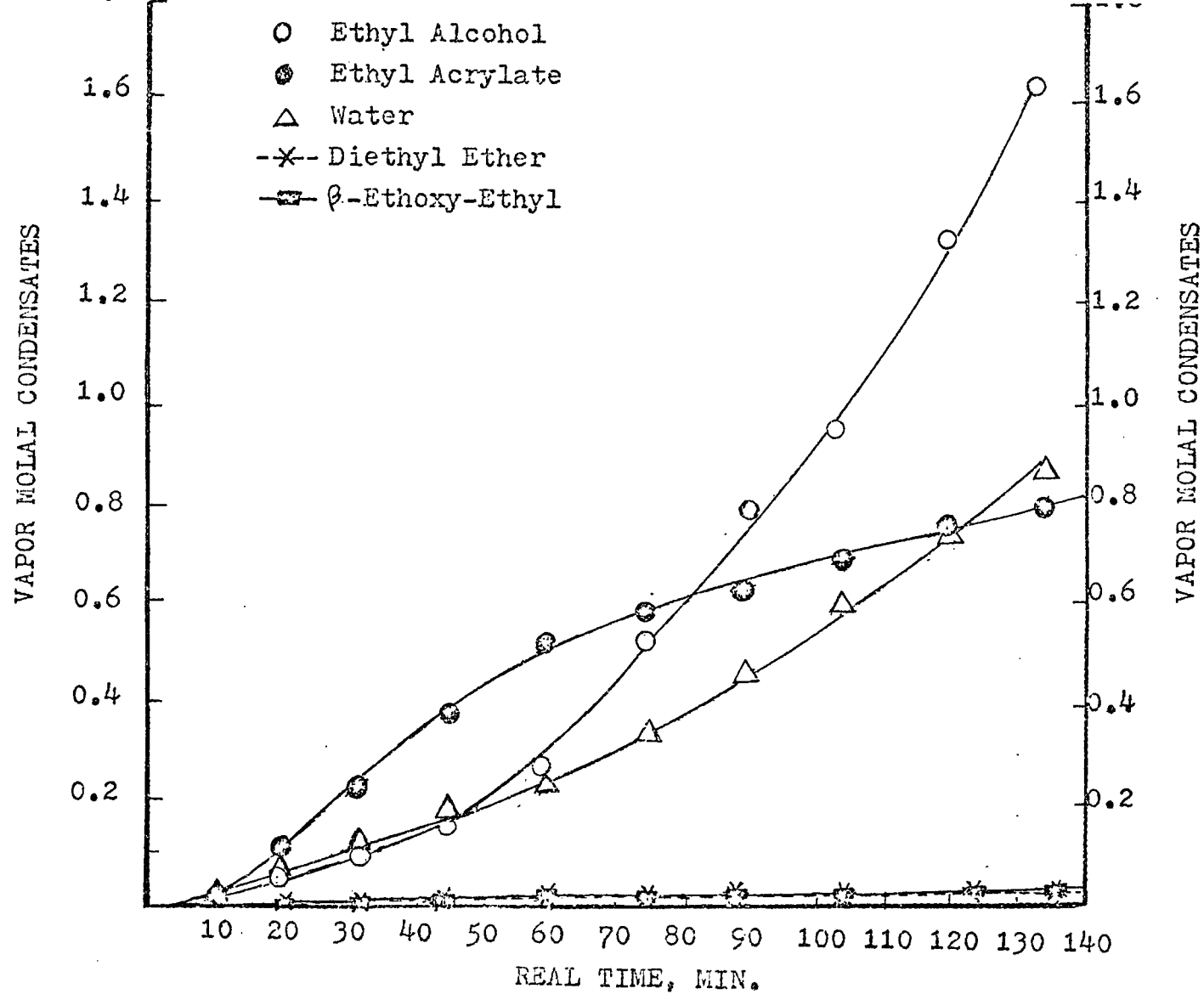


Fig. 6.1.a Individual Vapor Molal Condensates for Five Volatile Components

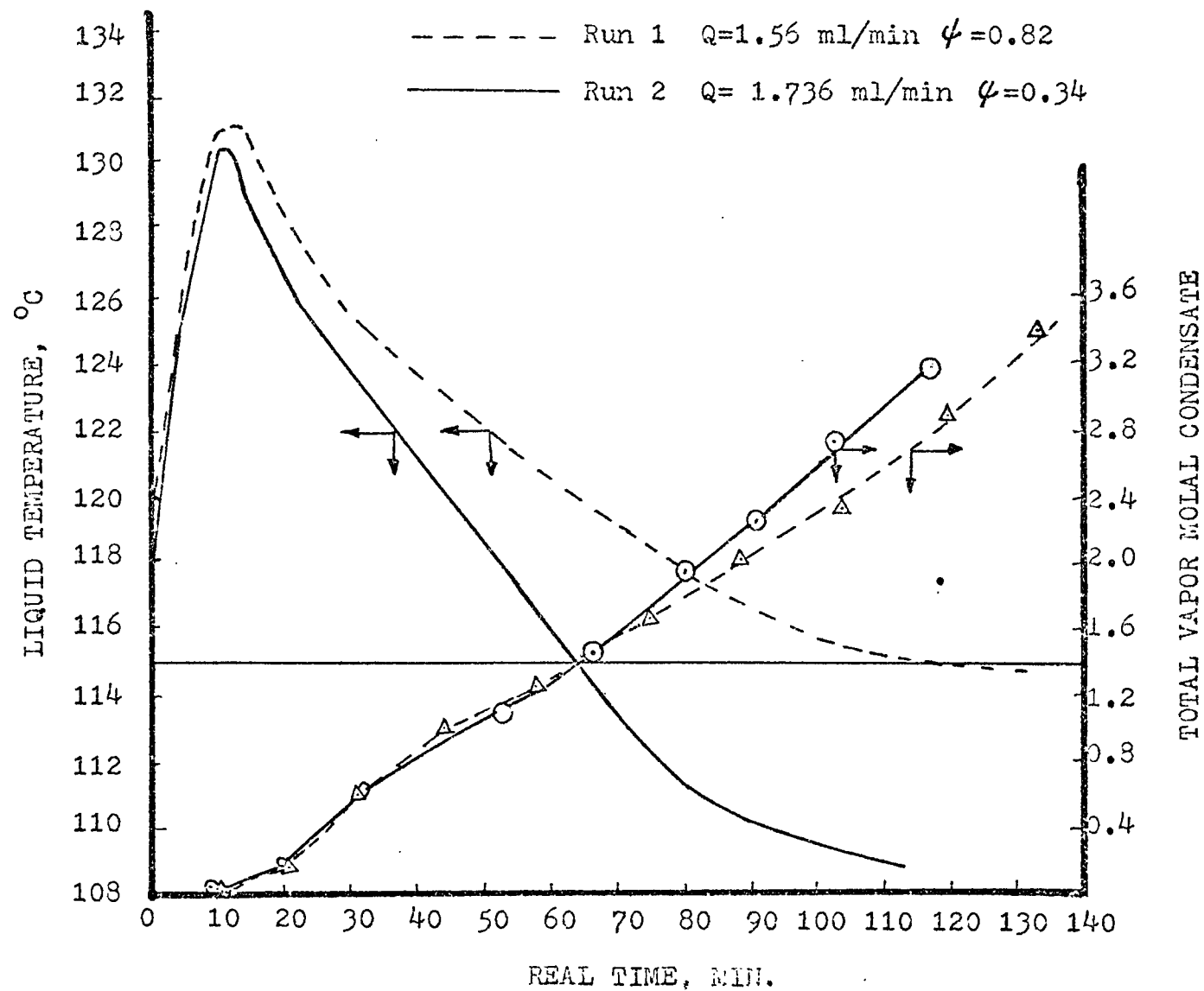


Fig. 6.1.b Liquid Temperature and Total Vapor Molal Condensate Vs. Real Time, Runs 1 & 2

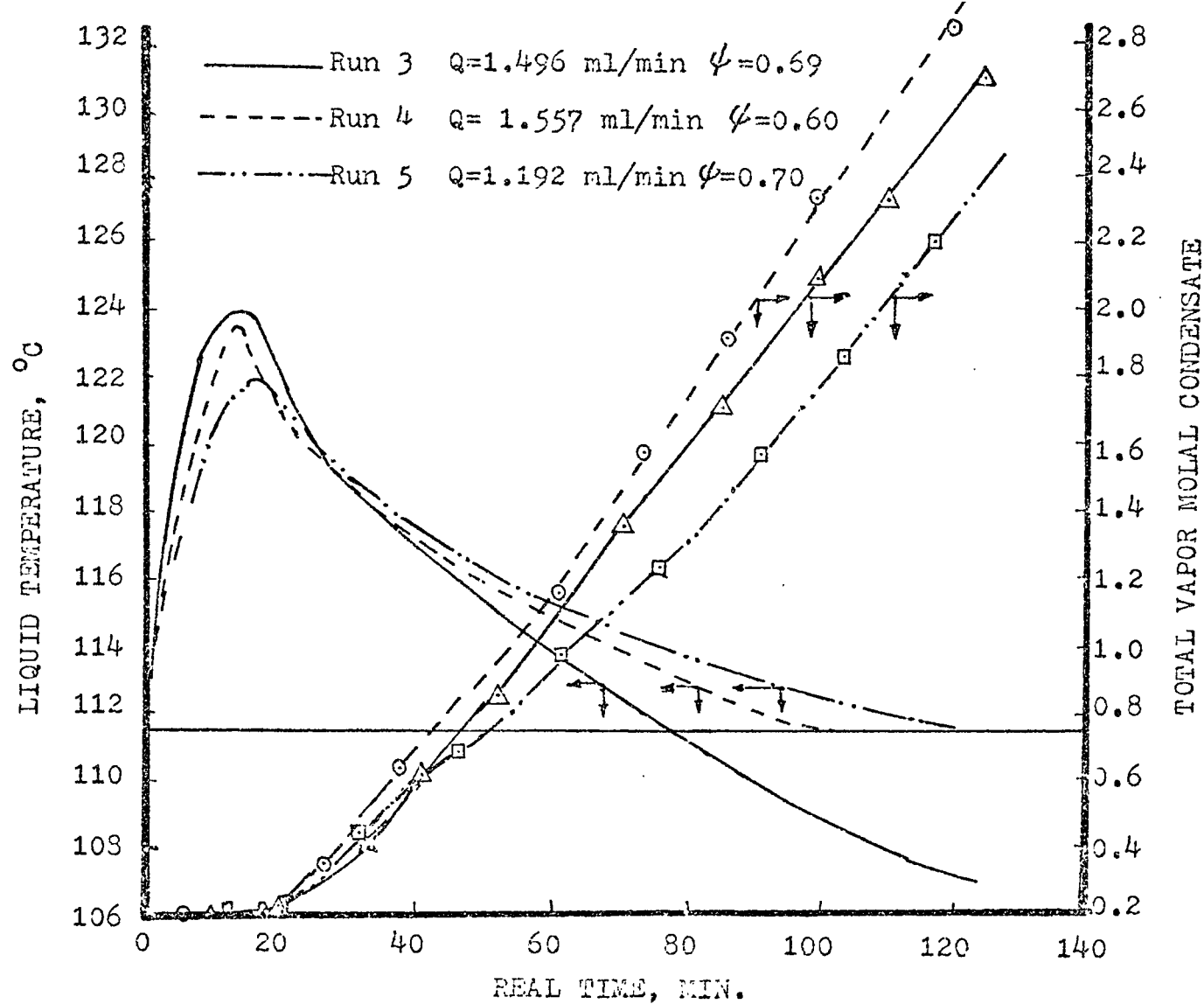


Fig. 6.2 Liquid Temperature and Total Vapor Molal Condensate Vs. Real Time, Run 3, 4, & 5

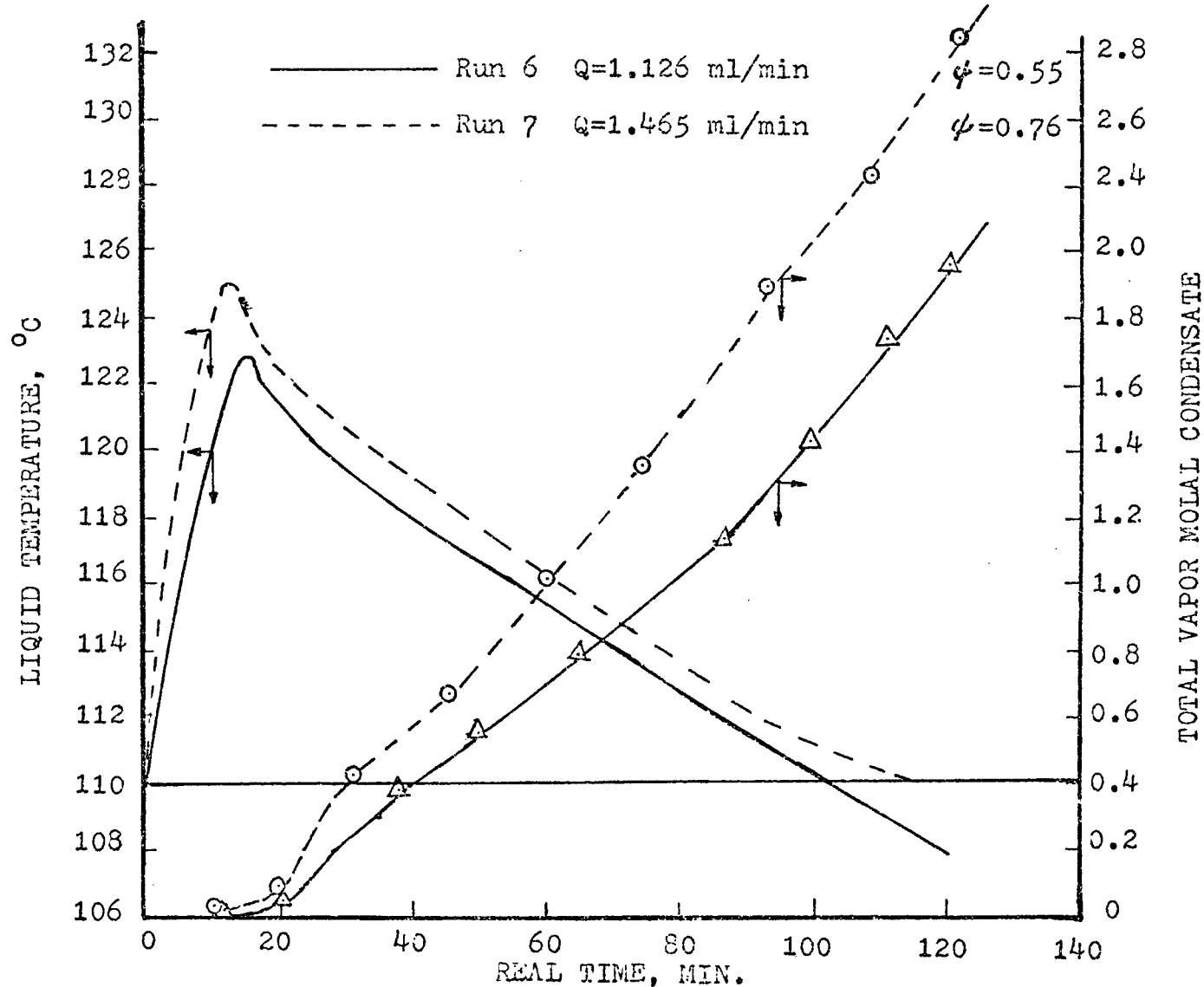


Fig. 6.3 Liquid Temperature and Total Vapor Molal Condensate Vs. Real Time, Runs 6 & 7

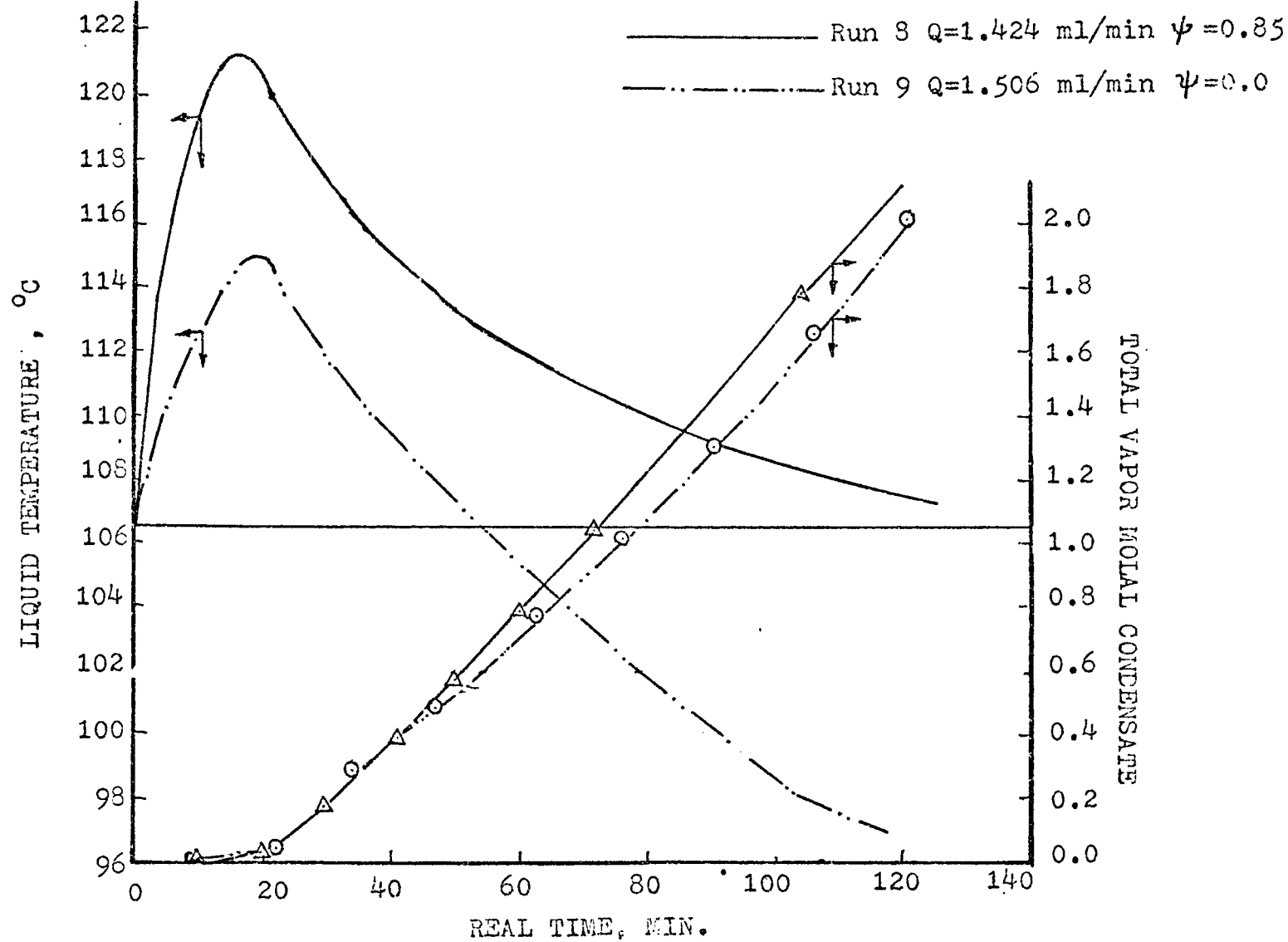


Fig. 6.4 Liquid Temperature and Total Vapor Molal Condensate Vs. Real Time, Runs 8 & 9

is accumulated steadily almost at a constant rate, Runs 1 through 9 exhibit the similar behavior. Generally, the higher the feed rate and the higher the relative ratio of vapor to total feed, the higher the maximum temperature obtained. This is because a higher feed rate yields a higher reaction rate and consequently releases more heat of reaction. The higher relative ratio of vapor to total feed provides a larger inlet enthalpy.

In order to make sure all the collected vapor samples are obtained from a boiling liquid, the data points used for evaluating the semi-batch distillation accompanied by chemical reaction are those after the maximum liquid temperature of each run. Since, usually, the maximum temperature is reached after the second sampling, the third sampling time is taken as the zero time in the data correlation and analysis.

Since the variation of accumulated vapor molal quantities, as a function of time, is rather moderate, they can be properly fitted into a polynomial equation. Then, the instantaneous vapor molal flow rate for each component is obtained as the derivative of its corresponding polynomial equation.

As mentioned in Chapter 5, there is a certain time lag, though small, between the vapor and liquid sampling.

This time lag can be calculated from the vapor molal flow rate. The total vapor molal flow rate is first calculated as the sum of all the individual molal flow rates. Since the system is operated at atmospheric pressure, the ideal gas law can be used to convert total vapor molal flow rate into total vapor volumetric flow rate. Other information required is the carrier gas (helium) flow rate and the volume of the entire vapor flow path. It is found that the time lag between vapor generation and vapor collection is between 0.24 to 0.41 minutes for all the experimental runs of this study. These time lags are relatively small. However, these time lags are not ignored but are taken into account for correcting the sampling time. For the mathematical model analysis, the vapor and liquid samples should be at equilibrium.

6.1.2 "Chemical" Vapor-Liquid Equilibria

Molal quantities determined in the previous section can be used to determine instantaneous vapor and liquid compositions at the vapor-liquid interface. With the calculated vapor and liquid compositions, the corresponding K-value for "chemical" vapor-liquid equilibrium can be readily determined.

From the above determined K-value, liquid activity

coefficient can be calculated by Equation (4-117) which is repeated below

$$\gamma_i = \frac{K_i P}{\phi_i^0 P_i^0} = \frac{y_i P}{x_{ii}^0 P_i^0} \quad (4-117)$$

The vapor pressure, P_i^0 , can be calculated from Antoine constants given in Table A.5 and fugacity coefficient, ϕ_i^0 , from the correlations of Prausnitz and his coworkers as given in Appendix A.12. The activity coefficients calculated from Equation (4-117) for all the five volatile components in the system are correlated by the methods presented later in Section 6.2.1.

6.1.3 Reaction Rates

Ethyl acrylate, the main product of the reaction system, appears in both liquid and vapor phases. Therefore, its overall production rate should be equal to the sum of its rate of flow to the vapor condensate and its rate of accumulation in the liquid holdup. The volume of the liquid holdup is equal to its original volume plus the net change. The net change is the difference between the liquid volume of the entering feed under the tray conditions and the volume of the accumulated vapor condensate. With these information, the reaction rate can be calculated.

For determination of the dehydration rate, i.e.,

R_2 for the second reaction, numerical values of the vapor molal flow rate of diethyl ether are only required. Diethyl ether is totally vaporized and it is not detectable in the liquid mixture. For the successive reaction, i.e., the third reaction, its reaction rate can be calculated from the vapor molal flow rate and accumulation rate of β -ethoxy ethyl propionate in the liquid. A procedure similar to that for esterification can be used. The liquid concentrations of all the components in the liquid mixtures can be determined analytically as discussed in Chapter 5. The rate and the liquid composition data are substituted into Equation (4-103) through (4-105) to obtain three corresponding rate constants, $k_{m,1}$, $k_{m,2}$, and $k_{m,3}$. If these three rate constants can be properly correlated as a function of the three operating parameters, the reaction rates under different operating conditions can be estimated. The correlations of the reaction rate constants will be presented in Section 6.2.2.

Based on the methods described above computer program LABDATA was prepared and used to treat all the laboratory data. The program listing input data and calculated results for all the above experimental results are given in Appendix C.1.

6.2 Correlations of Parameters

6.2.1 Correlation of Activity Coefficient for "Chemical" Vapor-Liquid Equilibria

The conventional correlation of activity coefficients must satisfy the Gibbs-Duhem equation, the basic thermodynamic relation to treat the nonideality of a liquid solution. However, in this study, the activity coefficients of several compounds and their associated ionic species can not be measured. These compounds include the very volatile compound, diethyl ether, and the four very nonvolatile compounds, namely acrylamide sulfate, sulfuric acid, ammonium bisulfate and acrylamide. As mentioned in Section 4.6, the purpose of this correlation is to predict accurate vapor mole fractions from the known liquid compositions. A hypothetical liquid solution, containing four volatile components, namely ethyl alcohol, ethyl acrylate, water and -ethoxyethyl propionate, and one pseudo-component, "very nonvolatile material", is then used as the basis of this correlation. The pseudo-component, "very nonvolatile material", is a lumped parameter obtained from lumping together the four very nonvolatile compounds and their associated ionic species.

Even for a hypothetical liquid solution, a conventional correlation equation which can satisfy the

Gibbs-Duhem equation can make better prediction of activity coefficient than an arbitrary function. Therefore, a good correlation equation for the activity coefficients of the four volatile components may be selected from the five well-known correlations of Wilson, van Laar, Margules, Wohl, and Hala (11).

Sabylin and Aristovich (55) made a comparison of the five correlations with the "physical" equilibrium data of 30 ternary and 4 quaternary systems. It was concluded that the Wilson equation gives the best prediction while the Wohl and Hala equations are least successful in predicting good multicomponent data. The superiority of the Wilson equation to predict multicomponent data from the binary data, implies that the mixing rule and the function forms proposed by Wilson are also superior. The Wilson method is then adopted here as the basis for developing the correlation for the multicomponent "chemical" vapor-liquid equilibria.

6.2.1.1 Working Equation

The Wilson equation for a multicomponent system can be represented by the following equation.

$$\ln \gamma_i = 1 - \ln \left(\sum_{j=1}^N \Lambda_{ij} x_j \right) - \sum_{k=1}^N \frac{x_k \Lambda_{ki}}{\Lambda_{kj} x_j} \quad (6-1)$$

where

$$\Lambda_{ij} = \frac{v_j^L}{v_i^L} \exp \left[- \frac{(\lambda_{ij} - \lambda_{ii})}{RT} \right] \quad (6-1a)$$

In equation (6-1a), v_i^L and v_j^L are the liquid molal volumes of the pure components i and j and $(\lambda_{ij} - \lambda_{ii})$ is an empirically determined energy term. Since the temperature range for this reaction-distillation system is small, the Wilson constant, Λ_{ij} , is treated as a constant, independent of both temperature and pressure. It is noted that the binary Wilson constants (Λ_{kj} and Λ_{jk}) are the only parameters appear in Equation (6-1). The parameters, Λ_{ii} , Λ_{jj} , Λ_{kk} , etc., should be equal to unity.

In order to clearly understand the characteristics of the Wilson equation, its simplest form, that is the binary form, may be examined. For a binary mixture, Equation (6-1) is reduced to

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{12}}{\Lambda_{21}x_1 + x_2} \right) x_2 \quad (6-2a)$$

$$\ln \gamma_2 = -\ln(x_1 + \Lambda_{21}x_1) - \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{12}}{\Lambda_{21}x_1 + x_2} \right) x_1 \quad (6-2b)$$

If a mixture is an infinitely diluted solution of component 1 its composition can be expressed as

$$x_1 \longrightarrow 0,$$

and

$$x_2 \longrightarrow 1.$$

With the relationships, equations (6-2a) and (6-2b) are reduced to

$$\ln \gamma_1 = - \ln \Lambda_{12} + 1 - \Lambda_{21} \quad (6-3a)$$

$$\ln \gamma_2 = 0 \quad (6-3b)$$

The activity coefficient of a component at an infinite dilution is then a function of Λ_{12} and Λ_{21} while the activity coefficient of pure component is unity.

For an ideal solution $\Lambda_{12} = \Lambda_{21} = 1$. Thus, deviation of the parameters from unity is an indication of the nonideality of the solution. If both Λ_{12} and Λ_{21} are greater than unity, γ_1 becomes less than unity according to Equation (6-3a). That is, the solution exhibits negative deviations from ideality. However, if they are both less than unity, positive deviations from ideality can be observed. It is possible that one parameter may exceed unity and the other less than unity for cases where deviations from ideality are not large.

Although the Wilson equation used in this work is an empirical form, the relationship between the calculated activity coefficients and the Wilson constants should have the same characteristics as discussed above.

6.2.1.2 Data Regression

For a five-component system, total number of required Wilson binary constants is $5 \times (5-1) = 20$, which excludes all the unity terms, $\Lambda_{11}, \Lambda_{22}, \dots$, and Λ_{55} . Now, the desired correlating equation, Equation(6-1) has twenty undetermined constants. These twenty constants can be obtained from regression of experimental data by SUBROUTINE BSOLVE, which is suitable for either linear or nonlinear fit of the experimental data by the method of least-squares. This subroutine employs either the Newton Raphson Method or the Steepest Descent Method for obtaining convergent solutions. There are two other computer programs developed and used in this study. One is SUBROUTINE FUNC, which is used to calculate the activity coefficient based on the given functions. The other is SUBROUTINE DERIV which calculates the partial derivative of activity coefficient. The form of functions used in this work is the general simultaneous equation, Equation (6-1). Since the number of undetermined constants is very large, it will be too cumbersome to list all the twenty individual derivatives calculated by SUBROUTINE DERIV. Instead, they are grouped into the following three general cases.

Case 1:

$$\frac{\partial \ln \gamma_i}{\partial \Lambda_{ik}} = - \frac{x_k}{\sum_{j=1}^N \Lambda_{ij} x_j} + \frac{x_i x_k}{\left(\sum_{j=1}^N \Lambda_{ij} x_j \right)^2} \quad (6-4a)$$

where $k \neq i$

Case 2:

$$\frac{\partial \ln \gamma_i}{\partial \Lambda_{ki}} = - \frac{x_k}{\sum_{j=1}^N \Lambda_{kj} x_j} + \frac{\Lambda_{ki} x_i x_k}{\left(\sum_{j=1}^N \Lambda_{kj} x_j \right)^2} \quad (6-4b)$$

where $k \neq i$

Case 3:

$$\frac{\partial \ln \gamma_i}{\partial \Lambda_{km}} = \frac{\Lambda_{ki}^{-x_k} x_m}{\sum_{j=1}^N \Lambda_{kj} x_j} \quad (6-4c)$$

where $k \neq m \neq i$

All the above subroutines are included in the program "CHEMACT" which is listed in Appendices C.3.1 - C.3.3. The input data and constants for the program are also shown in the Appendices.

By the definition as given in Equation (6-1a), Λ_{ij} must be a positive value. Therefore, the lower bound of Λ_{ij} is set equal to zero during the data regression. Since the range of experimental temperatures are only between 90 °C and 130 °C, the difference of temperature effects on activity coefficients are very small compared to the effects of composition on the solution nonideality. Since the system is operated at constant pressure, γ_i can be treated here as a function

of only composition. With the above assumptions, the fitted values of Λ_{ij} by the program CHEMACT are as follows,

Λ_{12}	0.0709	Λ_{21}	0.494
Λ_{13}	0.	Λ_{31}	1.41
Λ_{14}	0.	Λ_{41}	0.
Λ_{15}	0.677	Λ_{51}	13.2
Λ_{23}	0.	Λ_{32}	9.11
Λ_{24}	0.271	Λ_{42}	0.
Λ_{25}	0.	Λ_{52}	0.
Λ_{34}	10.9	Λ_{43}	0.0269
Λ_{35}	6.02	Λ_{53}	3.91
Λ_{45}	0.	Λ_{54}	6.91

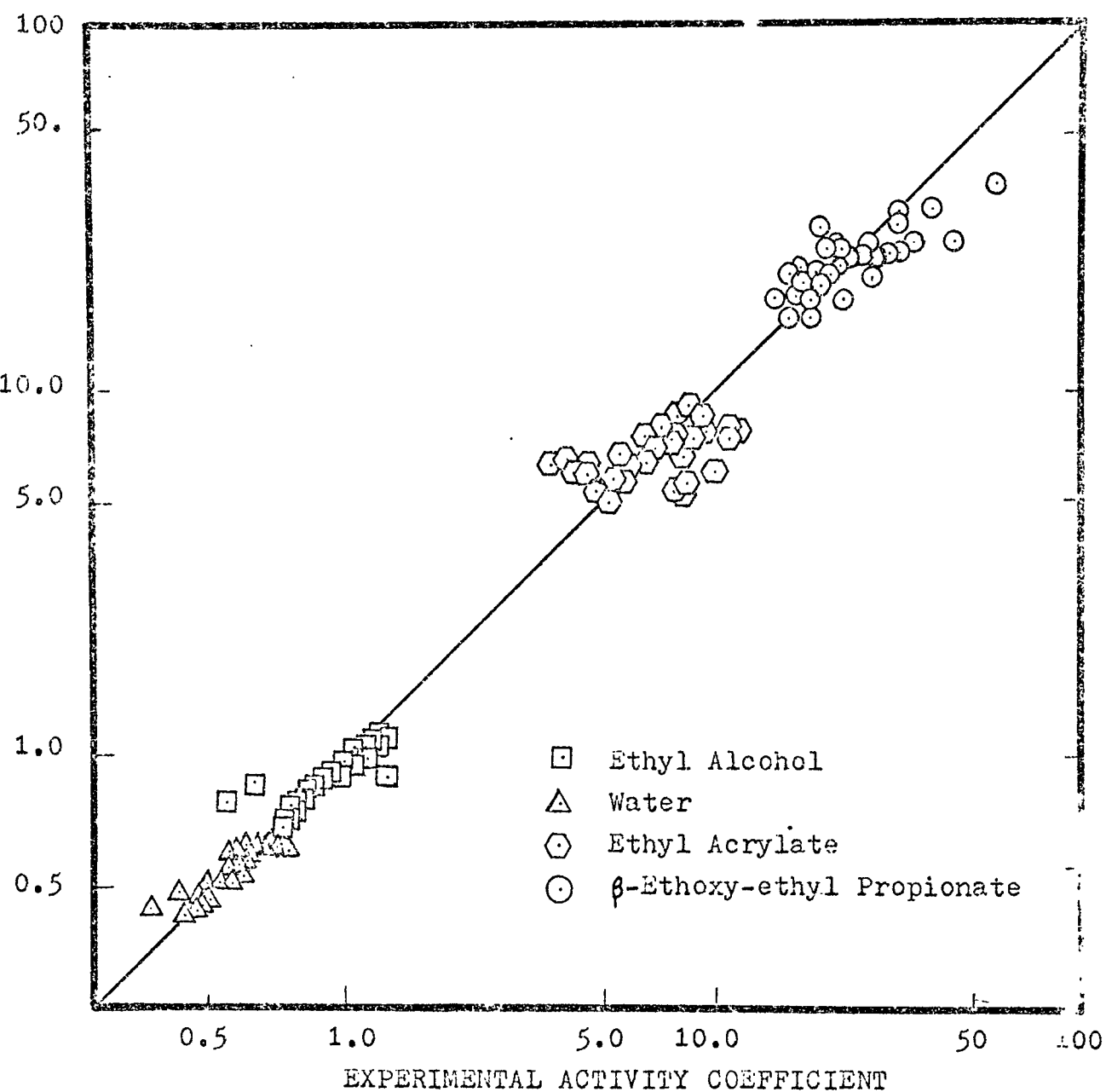


Fig. 6.5 Comparison of Calculated Activity Coefficients by The Wilson's Equation To Experimental Activity Coefficients

The calculated activity coefficients using the above coefficients and Wilson's equations are plotted against the experimental values as shown in Fig.6.5. The agreement between the calculated values and the experimental data are satisfactory, especially for the reactant ethyl alcohol and the most polar component, water. Larger deviation can be seen for the activity coefficient of the two volatile products, ethyl acrylate and β -ethoxy ethyl propionate. This larger deviation may be explained as follows. The mole fractions of these two products in the reacting liquid are very small, only up to 0.0525 for ethyl acrylate and 0.0076 for β -ethoxy ethyl propionate. It is not unusual that the percentage error for measuring a very small quantity is larger than that for measuring a large quantity. Furthermore, determination of a smaller peak area from the gas chromatograph also has an inherent larger percentage reading error.

Since the liquid mixture contains mostly the non-volatile material, the activity coefficients of the four volatile components are affected by their molecular relationships to this nonvolatile material. Water is a very polar compound. Its presence helps sulfuric acid to generate proton for promoting the

formation of acrylamide sulfate. Its affinity to the nonvolatile liquid mixture is then very high and thus its activity coefficient is the smallest among the four volatile components. These low water activity coefficients can be characteristically represented by the fitted Wilson constants for the binary pair of water and nonvolatile material. The constants are $\Lambda_{35}=6.02$ and $\Lambda_{53}=3.91$. As discussed earlier high values of Λ_{ij} give low γ_i . This is consistent with water activity coefficient determined for water here. For reactant ethyl alcohol, activity coefficients in the pair with the nonvolatile material are such that Λ_{51} is greater than unity while Λ_{15} is less than unity. For the main product, ethyl acrylate, $\Lambda_{25}=\Lambda_{52}=0$. This indicates that ethyl acrylate has very large activity coefficients, which are not affected by the liquid compositions of the system components. Instead, this large product activity coefficient is affected by the large heat of reaction of the system as explained below.

During the production of ethyl acrylate, a large amount of heat of reaction is released (please see the calculation by Hess' Law as given in Appendix A.10). If ethyl acrylate were a nonvolatile material, this heat

would be uniformly distributed in the liquid solution through a mechanical mixing resulting in the rise of liquid temperature. However, ethyl acrylate is a volatile component with low heat of vaporization. The heat of reaction immediately becomes available as the heat of vaporization for the reaction product. Therefore, the vapor stream becomes very rich in ethyl acrylate. The liquid temperature is reduced because the part of its enthalpy is also used to vaporize ethyl acrylate.

For the by-product, β -ethoxy ethyl propionate, its binary Wilson constants with nonvolatile material are $\Lambda_{45}=0$ and $\Lambda_{54}=6.91$. Since its mole fraction in the liquid is extremely small, its activity coefficient may be considered at infinite dilution. At infinite dilution, its activity coefficient in a binary system may be represented by Equation (6-3) and repeated below with corresponding subscript:

$$\ln \gamma_4 = -\ln \Lambda_{45} + 1 - \Lambda_{54}$$

Although Λ_{54} is much greater than unity, it is still a small term compared to $-\ln \Lambda_{45}$ where Λ_{45} approaches zero. Therefore, the calculated γ_4 is the largest among the four components. This unusually large activity coefficient for by-product β -ethoxy-ethyl propionate is another indication of substantive effect of chemical reaction on vapor-

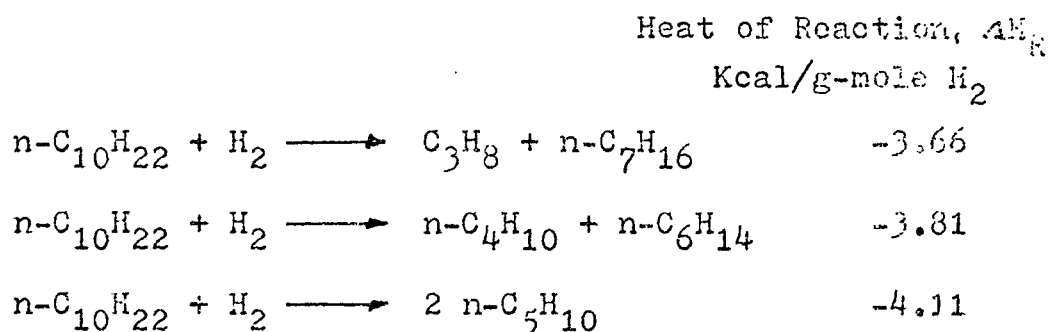
liquid equilibria.

In a "physical" vapor-liquid equilibrium system, the activity coefficients in a multicomponent mixture, as mentioned in Chapter 2, are generally developed from the data of its constituent binary systems. Therefore, the activity coefficients of its any two constituents have the same relative order-of-magnitude as they are in a binary mixture. However, in a "chemical" vapor-liquid equilibrium system, such as the one used in this study, a reverse order of magnitude for some binary pair can be observed.

As an example, the binary system of ethyl acrylate and ethyl alcohol is considered. The activity coefficients of ethyl acrylate calculated from the present "chemical" vapor-liquid equilibrium data fall between 3 and 12. They are much higher than those of ethyl alcohol, which are between 0.45 to 1.4. However, the activity coefficients of these two compounds calculated from the "physical" vapor-liquid equilibrium data of Loginova, et al. (43) show a reverse trend. The activity coefficients of ethyl alcohol are between 1.0 to 9.45, while those of ethyl acrylate are between 0.53 to 2.56.

Based on the above analysis of the present experimental data and on the comparison between the Chao-Seader

"physical" vapor-liquid equilibrium correlation and the Grayson-Streed "chemical" vapor-liquid equilibrium correlation, given in Section 2.1, it can be concluded that chemical reaction do have a definite effect on vapor-liquid equilibrium. One of the causes yielding, definite effect of chemical reactions on vapor-liquid equilibrium is the release of the heats of reactions. For Grayson Streed hydrocracking system, the reaction kinetics are extremely complicated. However, the exothermic reactions of the system can be typically represented by the hydrocracking of n-decane as shown below:



The average heat of reaction for hydrocracking of n-decane is then equal to -3.86 Kcal per gram mole of hydrogen consumed. This heat of reaction per gram mole of hydrogen consumed is somewhat different if the reactant is a different type of hydrocarbon such as naphthene or aromatic, or a different size of hydrocarbon such as n-heptane or n-hepta-decane.

If hydrogen consumption is very large for a hydro-

cracking system, the exothermic heat of reaction per mole of a heavy hydrocarbon must be very large, implying that this system has a high reaction conversion. Hydrocracking can be performed thermally. It can be further promoted at the presence of a catalyst. Since these two types of operation have different reaction kinetics, resulting in different conversions, their heats of reaction are then different and so are their effects of chemical reaction on "chemical" vapor-liquid equilibrium. Therefore, for a reactor effluent from a catalytic bed, the vapor-liquid equilibrium pattern right after the catalytic bed may be different from that at a remote separation zone without the presence of catalyst. When measuring "chemical" vapor-liquid equilibria for such a system, it is recommended that the residence time and the variation in "chemical" vapor-liquid equilibrium from the catalytic bed to the separation zone should be taken into account.

6.2.2 Reaction Rate Constants

The reaction rate constants, $k_{m,1}$, $k_{m,2}$ and $k_{m,3}$ defined in Section 4.5.4 can be expressed in the following Arrhenius type equations:

$$k_{m,1} = K_{m,1} e^{-E_{m,1}/RT}$$

$$k_{m,2} = K_{m,2} e^{-E_{m,2}/RT}$$

$$k_{m,3} = K_{m,3} e^{-E_{m,3}/RT}$$

Taking the logarithm of the above three equations gives the

following general form:

$$\log k_{m,i} = \log K_{m,i} - \frac{E_{m,i}}{2,303 RT}, \quad i=1, \dots, 3 \quad (6-5)$$

For each experimental run, $k_{m,i}$ are then plotted against $1/(2.303 RT)$ on semilog graph paper which is shown as Fig. 6.6 for esterification reaction. It is observed that for the first hour of operation, i.e., the first 5-6 experimental points, the above plot yields straight lines. Furthermore, these straight lines are parallel to each other indicating that the activation energy for all the nine experimental runs are the same for the first five to six data points. This is a significant experimental confirmation of the assumption made for this study. For the rest of each experimental run, the reaction rate is greatly reduced and the temperature is decreased as the time progresses. This phenomenon is an indication of more active side reactions near the end of an experimental run. The possible side reaction may be the decomposition of acrylamide sulfate and the formation of alkyl sulfates $(C_2H_5)_2SO_4$ and $C_2H_5HSO_4$, which are generally the transition components for the formation of diethyl ether.

For the first five to six points of each run, a universal activation energy can now be introduced to

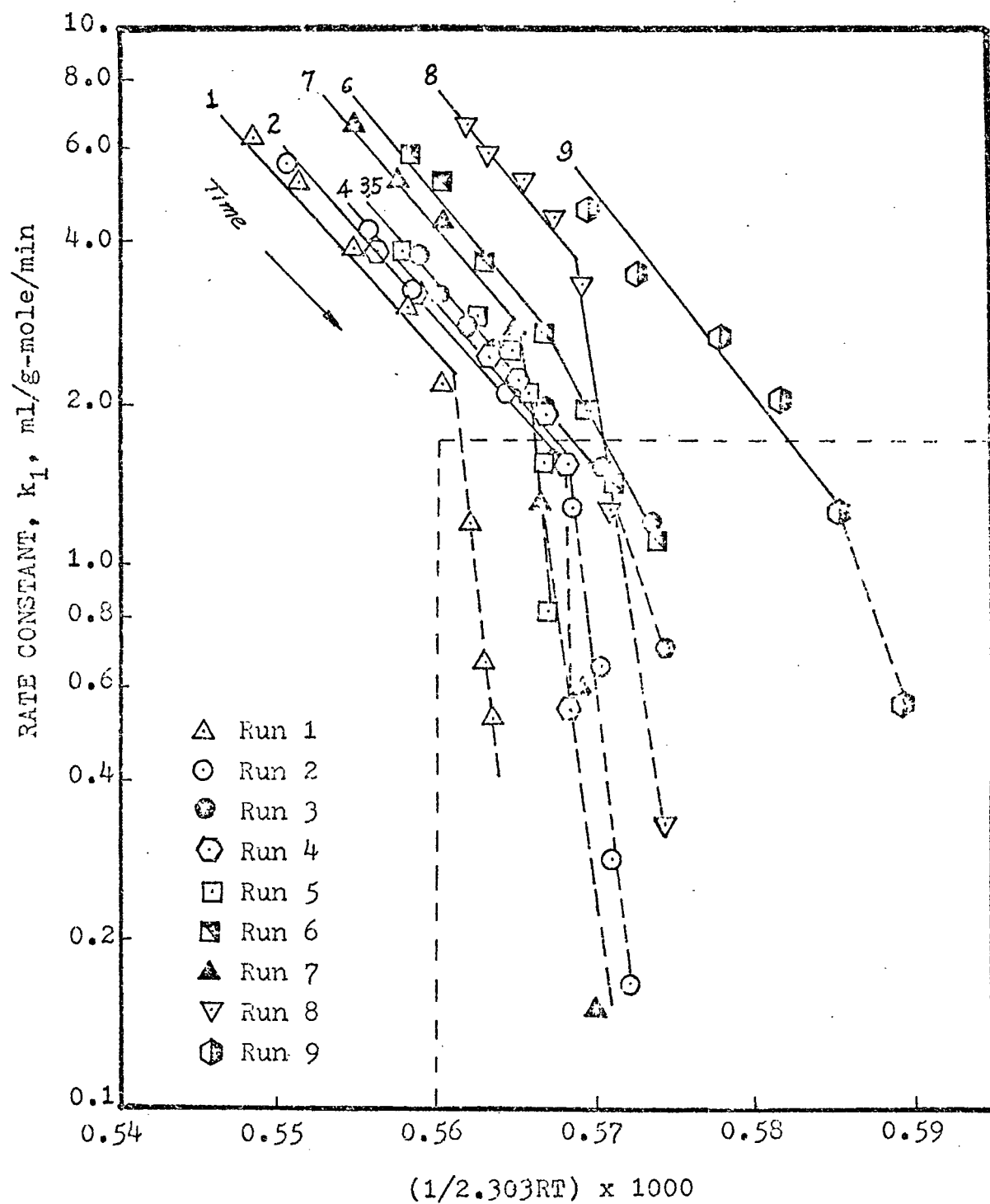


Fig. 6.6 Esterification Rate Constant k_1 Vs. Reciprocal of Temperature

make further simplification. The procedures are stated below.

For a data point in the run s , Equation (6-5) is rewritten, with the activation energy in Kcal/(g-mole), as

$$\log K_s - \frac{1000 E_s}{2.303R T_{s,j}} = \log k_{s,j}, \quad s=1, \dots, n_s \quad (6-6)$$

where

n_s = number of experimental runs

E_s = universal activation energy in Kcal/(g-mole)

Define $\zeta_{s,j} = 1000/(2.303RT_{s,j})$

$\Phi_{s,j} = \log k_{s,j}$,

and

$F_s = \log K_s$.

Equation (6-6) can then be reduced to

$$F_s - E_s \zeta_{s,j} = \Phi_{s,j}, \quad s=1, \dots, n_s \quad (6-7)$$

The difference between the experimental and calculated values of $\log K_s$ for the data point j in the run s is equal to that between right-hand side and left-hand side of Equation (6-7). Mathematically it can be represented as follows:

$$\epsilon_{s,j} = \Phi_{s,j} - F_s + E_s \zeta_{s,j} \quad (6-8)$$

The variation for all the data points, where the universal activation energy concept can be applied, is written according to the definition:

$$\sigma^2 = \sum_{s=1}^{n_s} \sum_{j=1}^{n_j} \epsilon_{s,j}^2 \quad (6-9)$$

where

σ^2 = variation

n_s = number of runs = 9

n_j = number of data points for run s.

Substituting Equation (6-8) into Equation (6-9) gives the following working equation

$$\sigma^2 = \sum_{s=1}^{n_s} \sum_{j=1}^{n_j} (\Phi_{s,j} - F_s + E \ell_{s,j})^2 \quad (6-10)$$

The least-squares method requires that

$$\frac{\partial \sigma^2}{\partial E} = 0 \quad \text{and} \quad \frac{\partial \sigma^2}{\partial F_s} = 0, \quad s=1, \dots, n_s$$

The corresponding $(n_s + 1)$ simultaneous linear equations can now be obtained by differentiating Equation (6-10) with the above $(n_s + 1)$ constraints:

$$2 \sum_{s=1}^{n_s} \sum_{j=1}^{n_j} (\Phi_{s,j} - F_s + E \ell_{s,j}) \ell_{s,j} = 0 \quad (6-11)$$

and

$$2 \sum_{j=1}^{n_j} \sum_{s=1}^{n_s} (\Phi_{s,j} - F_s + E \ell_{s,j}) = 0, \quad s=1, \dots, n_s \quad (6-12)$$

Equation (6-11) can be further simplified as follows:

$$\sum_{s=1}^{n_s} \sum_{j=1}^{n_j} \ell_{s,j} \Phi_{s,j} - \sum_{s=1}^{n_s} \sum_{j=1}^{n_j} \ell_{s,j} F_s + E \sum_{s=1}^{n_s} \sum_{j=1}^{n_j} \ell_{s,j}^2 = 0 \quad (6-13)$$

From Equation (6-12),

$$\sum_{j=1}^{n_j} \Phi_{s,j} - n_j F_s + E \sum_{j=1}^{n_j} \zeta_{s,j} = 0$$

or

$$F_s = \frac{\sum_{j=1}^{n_j} \Phi_{s,j} + E \sum_{j=1}^{n_j} \zeta_{s,j}}{n_j} \quad (6-14)$$

Substituting Equation (6-14) into Equation (6-13) gives the following solution for E, the universal activation energy:

$$E = \frac{\sum_{s=1}^{n_s} \sum_{j=1}^{n_j} \zeta_{s,j} \Phi_{s,j} - \sum_{s=1}^{n_s} \left(\sum_{j=1}^{n_j} \zeta_{s,j} \right) \left(\sum_{j=1}^{n_j} \Phi_{s,j} \right)}{\sum_{s=1}^{n_s} \left(\sum_{j=1}^{n_j} \zeta_{s,j} \right)^2 / n_j - \sum_{s=1}^{n_s} \sum_{j=1}^{n_j} \zeta_{s,j}^2} \quad (6-15)$$

The value of the universal activation energy, E, is obtained by the above equation with all the experimental data points. Then Equation (6-14) can be used to determine F_s for each run. The frequency factor, $K_{m,1}$ is simply calculated as 10^{F_s} .

The above procedures for data reduction are also used for the dehydration and the successive reactions. These procedures have been programmed into the computer program RXNRATE which is given in Appendix C.4. The reduction of all the experimental data by the computer

program RXNRATE yields the activation energies and frequency factors for the three reactions of all the experimental runs. They are summarized in Table 6.1. As shown in Table 6.1 the average percentage errors for the three reactions are small, which justify and confirm the appropriateness of the proposed rate expressions for the three chemical reactions dealt in this study.

The above data reduction has shown that a specific behavior of each experimental run can be represented by a single factor, namely Frequency Factor. Thus, the different effects of interface mass transfer on reaction rate can now be discussed quantitatively in terms of the frequency factors. Furthermore, since the interface properties such as interface concentration, film thickness, etc, cannot be measured directly, the frequency factor be used to represent the overall effects of these properties on the reaction behavior. As discussed earlier the interfacial properties are functions of the three operating parameters, i.e., the initial and surrounding temperature, the feed rate of aqueous ethyl alcohol solution, and the relative ratio of vapor to total feed. These operating conditions for all the experimental runs are listed in Table 6.2.

The frequency factor may now be quantitatively related to the operating parameters as follows, assuming

Table 6.1 Arrhenius Constants

		Esteri- fication	Dehydration	Successive Reaction
Activation Energy E, Kcal/g-mole		35.56	47.97	52.88
Frequency Factors	Units Run No. s	$K_{s,1} \times 10^{-17}$ l/g-mole-min	$K_{s,2} \times 10^{-23}$ l/g-mole-min	$K_{s,3} \times 10^{-25}$ l ² /(g-mole) ² - min
	1	2.59	1.01	3.51
	2	2.93	0.93	2.70
	3	3.08	1.82	5.35
	4	3.12	3.21	5.02
	5	3.85	2.60	6.25
	6	3.96	2.11	3.71
	7	4.02	1.69	3.37
	8	7.41	7.11	13.79
	9	10.21	3.60	17.95
Average Percent- age Error of $K_{s,i}$		3.77	6.29	12.6

$$k_{s,1} = K_{s,1} e^{-35560/RT}$$

$$k_{s,2} = K_{s,2} e^{-49970/RT}$$

$$k_{s,3} = K_{s,3} e^{-52880/RT}$$

$$R = 1.987 \text{ cal/g-mole-}^{\circ}\text{K}$$

$$T = \text{temperature in } ^{\circ}\text{K}$$

that each parameter has independent influence.

$$K_{s,i} = g_1(T_o) g_2(F) g_3(\psi) \quad (6-16)$$

where

$K_{s,i}$ = frequency factor for reaction i and run
number s

T_o = initial and surrounding temperature

F = feed rate

ψ = vapor fraction of feed stream

g_1 , g_2 , and g_3 = independent functions

It is assumed that each independent function, g_1 , has two constants to represent the effects of its corresponding parameter. The following function form is found to be very suitable,

$$g_1(\zeta) = (\zeta + b_1)^{b_2}$$

where

$$\zeta = T_o, F \text{ or } \psi.$$

With the above relation, Equation (6-16) can be rewritten as

$$K_{s,i} = b_7 (T_{IN} + b_1)^{b_2} (F + b_3)^{b_4} (\psi + b_5)^{b_6} \quad (6-17)$$

where the constant b_7 is an adjusting factor to match the relative magnitudes between $K_{s,1}$ and three g_i 's.

Although there are only nine frequency factors to fit seven constants for the above equation, the

Table 6.2 Operating Parameters

Run Number	Initial Temp., °C	Feed Rate, ml/min	Vapor* Fraction
1	115	1.56	0.82
2	115	1.736	0.34
3	111.5	1.496	0.69
4	111.5	1.558	0.60
5	111.5	1.192	0.70
6	110.0	1.147	0.55
7	110.0	1.465	0.76
8	106.0	1.26	0.85
9	106.0	1.506	0.0

* Relative Ratio of Vapor to Total Feed

operating temperatures in the nine runs have covered the applicable reaction temperature range. Therefore, these nine experimental runs were considered to be sufficient to demonstrate how the basic information required for this study can be obtained. The constants in Equation (6-17) are determined by the computer program BSOLFIT. The program is developed on the basis of the BSOLVE techniques, which was described in Section 6.2.1 and is listed in Appendix C.5. The working equations for the three reactions with appropriate constants obtained by the computer program BSOLFIT with the data of Table 6.1 and 6.2 are given as follows.

Esterification:

$$K_{m,1} = 0.196(T_o - 104)^{-0.571} \times (F + 0.911)^{-0.501} \times (\psi + 0.0447)^{-0.13} \times 10^{18} \text{ l/(g-mole)-min} \quad (6-18)$$

Dehydration:

$$K_{m,2} = 1.31(T_o - 103)^{-1.14} \times (F - 0.661)^{-0.258} \times (\psi + 0.01)^{0.131} \times 10^{23} \text{ l/(g-mole)-min} \quad (6-19)$$

Successive Reaction:

$$K_{m,3} = 7.22(T_o - 104)^{-0.885} \times (F - 0.164)^{1.84} \times (\psi - 0.749)^{-0.4} \times 10^{25} \text{ l}^2\text{/(g-mole)}^2\text{-min} \quad (6-20)$$

The calculated frequency factors from Equations (6-18) to (6-20) are plotted in Figures 6.7 - 6.9 and compared to the experimental frequency factors listed in Table 6.1. For the esterification reaction, the agreement is very satisfactory. However, for the dehydration and the successive reactions it is only fair. The experimental runs with intermediate operating conditions exhibit larger deviations. Thus, the simple correlation model as given by Equation (6-17) may be inadequate for the correlation of these two reactions. Fortunately, these two reactions are minor compared with the esterification reaction. Therefore, a somewhat larger error in their frequency factors would not significantly affect the prediction of the system behavior. Therefore, their fitted equations, Equations (6-19) and (6-20) may still be adopted by for the simulation studies which will be presented in the next chapter.

Since Equation (6-18) can accurately predict the frequency factors for the main reaction, esterification, it can be used to discuss the effects of operating conditions on the frequency factor. The major advantage of this equation is to express the three operating parameters, T_0 , F , and ψ as separated variables. If any two of the three operating conditions are kept constant, the effect of the third operating condition can be readily

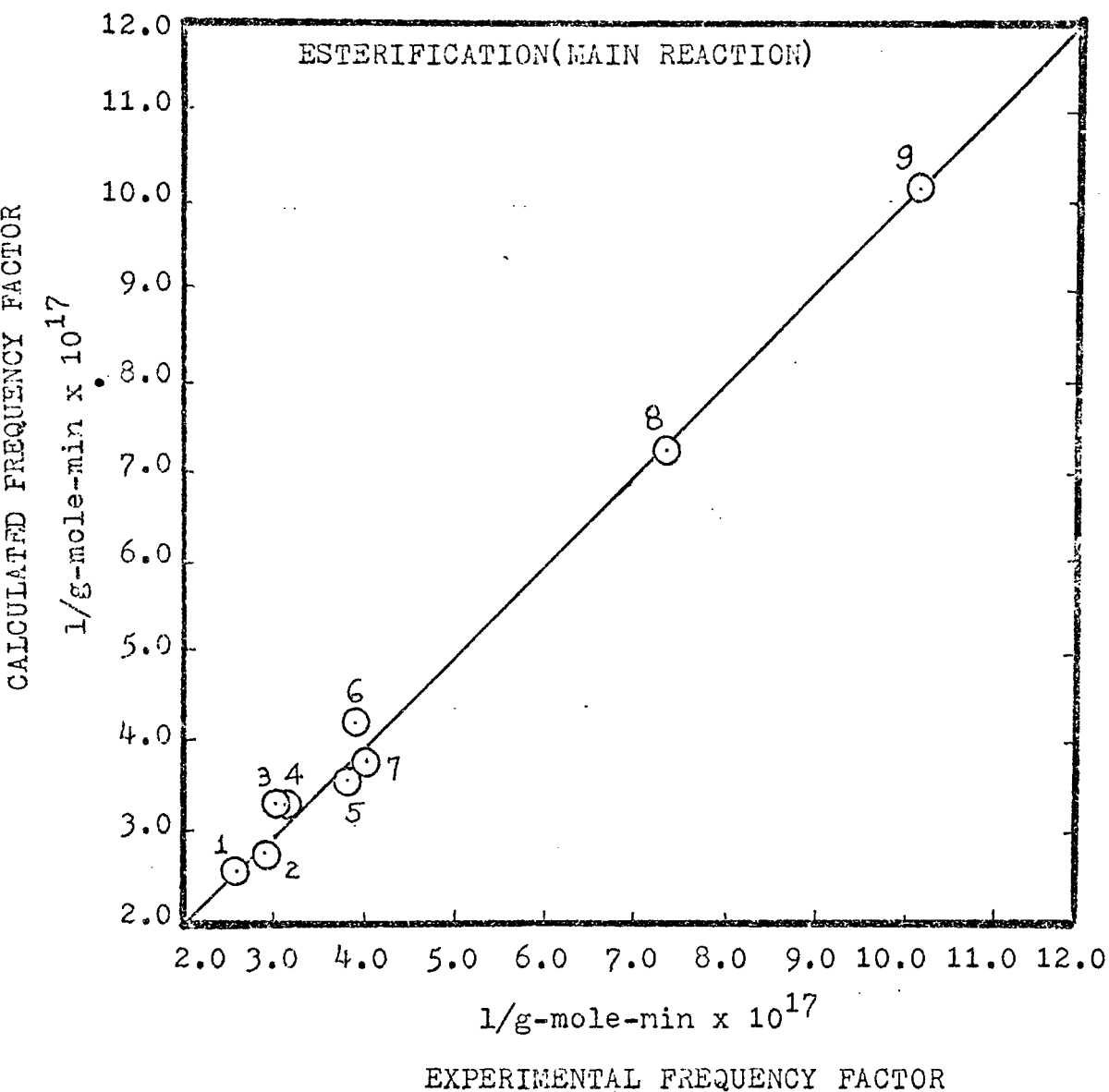


Fig. 6.7 Comparison of Frequency Factors for Esterification

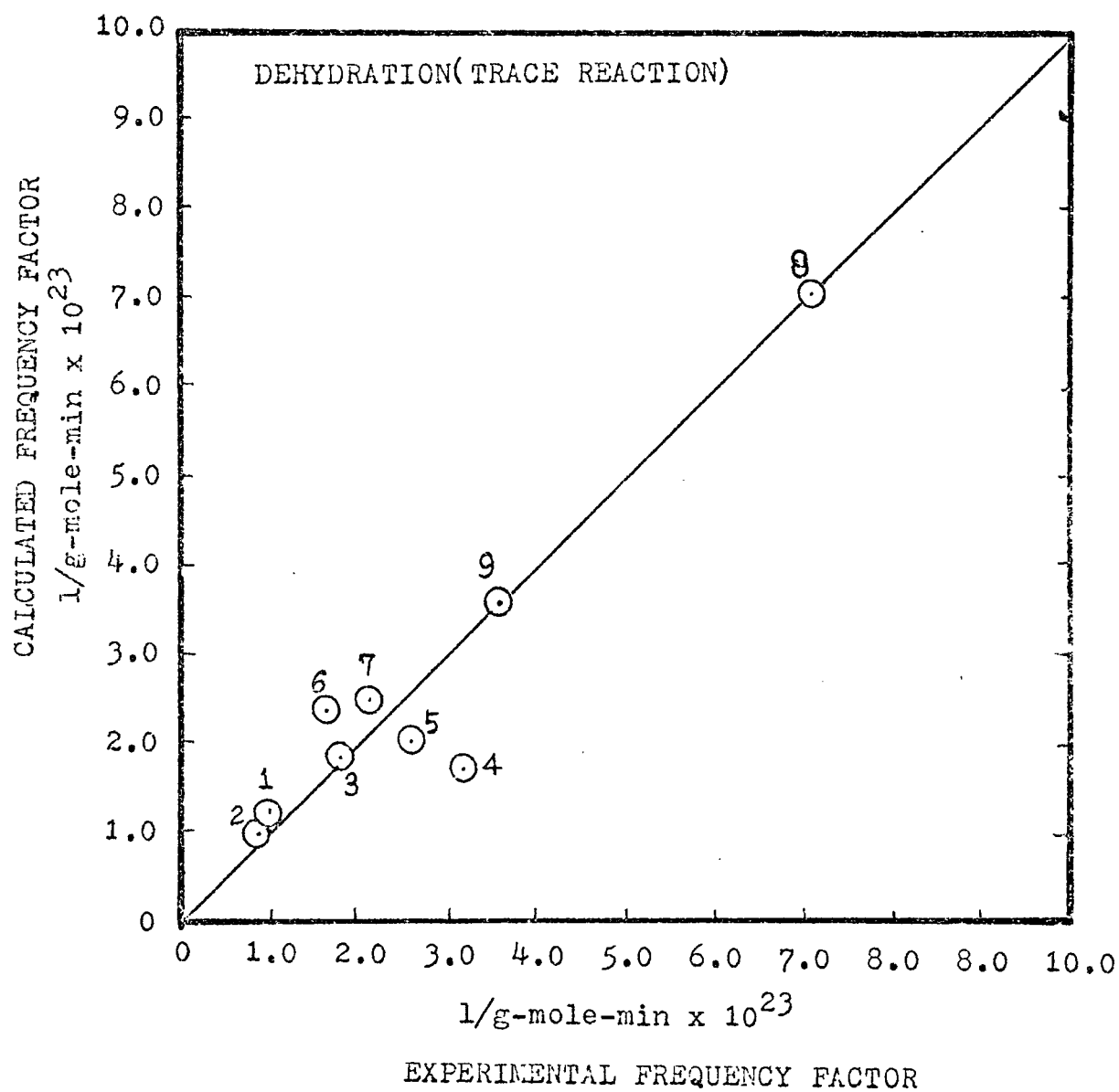


Fig. 6.8 Comparison of Frequency Factors for Dehydration

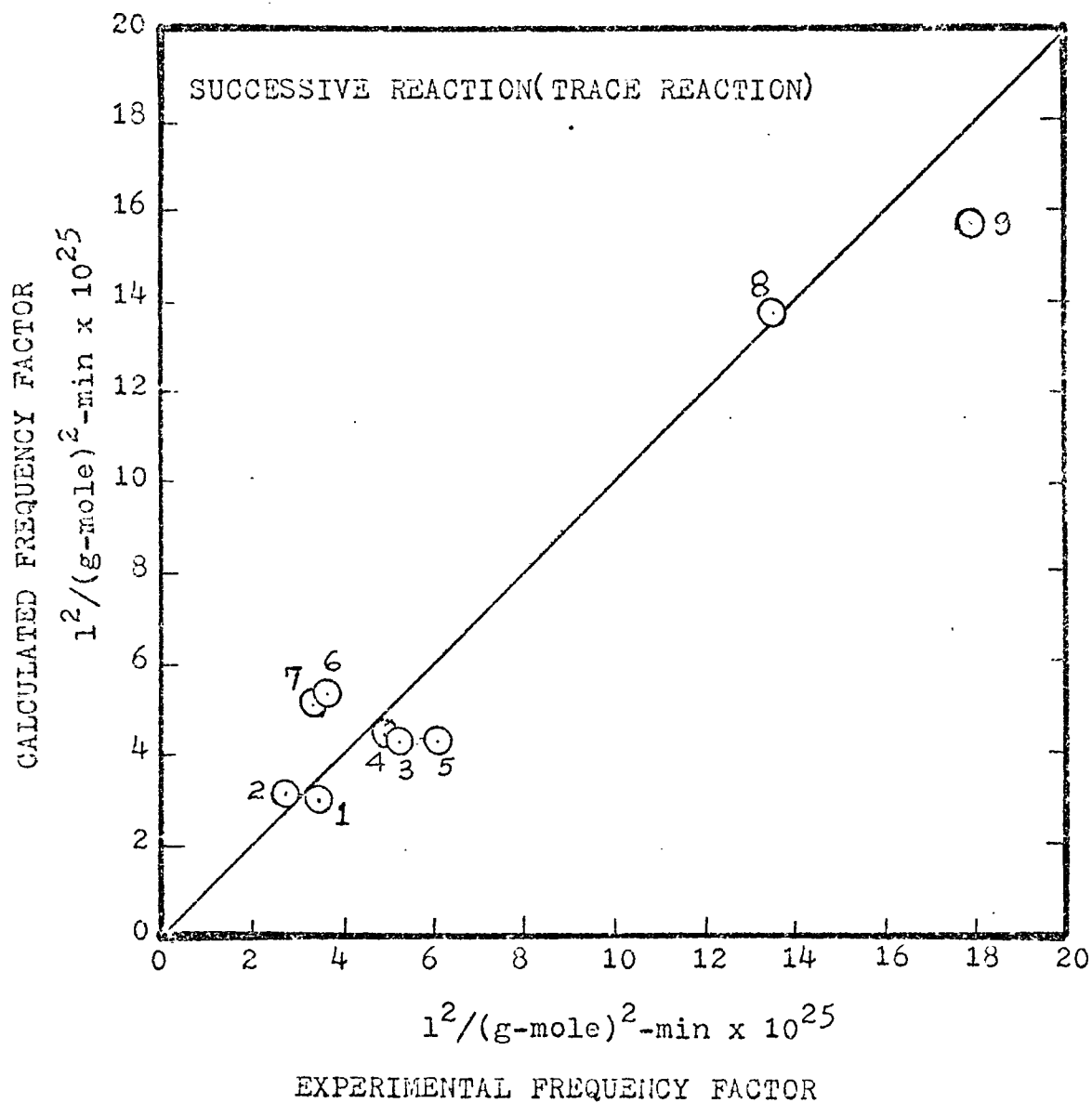


Fig. 6.9 Comparison of Frequency Factors for Successive Reaction

derived from Equation (6-18) as an independent parameter. If the effect is expressed as the ratio of frequency factors of Condition 2 to Condition 1, the three independent effects can be expressed as follows:

$$\left(\frac{K_{T,2}}{K_{T,1}} \right)_{F,\psi} = \left(\frac{T_{o,2} - 104}{T_{o,1} - 104} \right)^{-0.571} \quad (6-21)$$

$$\left(\frac{K_{F,2}}{K_{F,1}} \right)_{T_o,\psi} = \left(\frac{F_2 + 0.911}{F_1 + 0.911} \right)^{-0.501} \quad (6-22)$$

$$\left(\frac{K_{\psi,2}}{K_{\psi,1}} \right)_{T_o,F} = \left(\frac{\psi_2 + 0.0447}{\psi_1 + 0.0447} \right)^{-0.13} \quad (6-23)$$

where subscripts 1 and 2 stand for Condition 1 and Condition 2, and subscripts T, F, and ψ stand for T_o , F and ψ , respectively. If Condition 1 is taken as the operating condition giving the smallest frequency factor and Condition 2 giving the largest frequency factor within the boundary of the operating conditions used by this study, then the largest independent effects by the three operating parameters can be determined from the above three equations. The results are summarized in Table 6.3. These results demonstrate that the frequency factor is most sensitive to the initial and surrounding temperature, T_o , and least affected by the volatile reactant feed rate, F. If the initial and surrounding temperature is

Table 6.3 Largest Independent Effect of Operating
Conditions on the Frequency Factors

<u>Independent Operating Parameter</u>			<u>Condition 1</u>	<u>Condition 2</u>	<u>Ratio of Frequency Factors K_2/K_1</u>
<u>Name</u>	<u>Symbol</u>	<u>unit</u>			
Initial and Surrounding Temperature	T_o	$^{\circ}\text{C}$	115	106	2.65
Volatile Re- actant Feed Rate	F	ml/min	1.127	1.736	1.13
Ratio of Vapor to Total Feed	ψ	-	0.85	0.0	1.48

increased from 106 °C to 115 °C, the frequency factor will be reduced by a factor of 2.65. This implies that the reaction occurs mostly in the liquid film due to a high reaction rate at a high temperature. If the vapor fraction in the total feed is reduced from 0.85 to zero, the frequency factor will be increased by a factor of 1.48. This implies that the film reaction is reduced to the minimum by introducing a totally liquid feed stream. The volatile reactant feed rate mostly contributes to increasing the concentration of the volatile reactant, ethyl alcohol, in the liquid holdup. Its effect on the frequency factor is then small.

Chapter 7 Verification of Theoretical Model and Parametric Evaluation

7.1 Theoretical Solutions

Two conditions must be met and satisfied for any theoretical model to predict the system behavior accurately. First, the model must be developed on the sound theoretical foundation. Secondly, the physical and chemical data to be applied and used in the model must be accurate. Thus, before analysing the system behavior predicted by the model, the preparation of accurate physical and chemical data will be discussed.

7.1.1 Physical and Chemical Data Required for System Analysis

The physical and chemical data required in this system consist of two groups. One group is the data related mainly with material balance equations and the other for energy balance.

The data for material balance are essentially those related to

- (1) Chemical vapor-liquid equilibria
- (2) Chemical reaction rates

The correlations of the above data, with the experimental

data obtained by this work, were discussed in details in Chapter 6. They will not be repeated here.

The data for energy balance equations include:

- (1) Liquid and vapor enthalpies
- (2) Heats of reactions
- (3) Overall heat transfer coefficient

As mentioned in Chapter 3 heat of solution is assumed to be negligibly small compared to heats of reactions or latent heats of vaporization. Therefore, the enthalpy of a mixture, either liquid or vapor, is determined by adding the enthalpies of individual components. The enthalpy of a pure liquid component is calculated from heat capacity data according to the definition with datum temperature of 0 °C. If liquid heat capacity, C_p , is related to temperature by the following polynomial equation:

$$C_p = a_1 + a_2T + a_3T^2 + a_4T^3 \quad (7-1)$$

where

C_p = liquid heat capacity in cal/g-°C

T = temperature, °C

a_1 , a_2 , a_3 and a_4 = constants for a component,

then liquid enthalpy can be readily obtained as

$$h = a_1T + (1/2)a_2T^2 + (1/3)a_3T^3 + (1/4)a_4T^4 \quad (7-2)$$

Therefore, only liquid heat capacity data are required for obtaining the constants, a_1 , a_2 , a_3 and a_4 . The data regression by the least-square method is made using the computer program POLYFIT, as described in Appendix C.6. The computer program employs the Gauss elimination method to solve simultaneous linear equations.

The liquid heat capacity data for ethyl alcohol (15), ethyl acrylate (17), water (52), diethyl ether (16), and sulfuric acid (52) are available in the literature. For other compounds of which data are not available in the literature, reliable correlations are used. For example, the method of Johnson and Huang (39, 52) is used for predicting the liquid heat capacities at 20 °C. The method is based on the idea of additive contribution from constituent atomic groups. The correlation is relatively accurate, with 5 and 16 per cent average and maximum deviations. For estimation of the heat capacities at temperature other than 20 °C, the Watson expansion factor (23) method is employed. Estimation of liquid heat capacities for the components without available literature data are discussed in details in Appendix A.7. All the constants of Equation (7-1), determined by the program POLYFIT from either available literature data or the above mentioned estimated data, are listed in Table 7.1.

Table 7.1 Liquid Enthalpies and Heat Capacities

$$C_p = a_1 + a_2 T + a_3 T^2 + a_4 T^3$$

$$h = a_1 T + a_2 T^2/2 + a_3 T^3/3 + a_4 T^4/4$$

$$C_p = \text{cal/g-}^\circ\text{C} ; h = \text{cal/g} ; T = ^\circ\text{C}$$

<u>Component Name</u>	<u>a_1</u>	<u>$a_2 \times 10^3$</u>	<u>$a_3 \times 10^5$</u>	<u>$a_4 \times 10^7$</u>	<u>Ref.</u>
Ethyl Alcohol	0.53150	2.2012	0.72024	-	(15)
Ethyl Acrylate	0.45560	0.48312	0.17086	-	(17)
Water	1.0060	-0.31738	0.34230	-	(52)
Diethyl Ether	0.53002	0.97143	1.10120	-	(16)
β -Ethoxy-ethyl Propionate	0.44220	1.0364	0.26786	-	(Est.)
Acrylamide Sulfate	0.51106	-2.6872	2.5080	-0.46642	(Est.)
Sulfuric Acid	0.47483	-5.4866	4.1811	-0.81692	(52)
Ammonium Bisulfate (Solid)	0.42665	-2.3368	1.7822	-0.34821	(Est.)
Acrylamide	0.56106	1.1766	0.19831	0.017361	(Est.)

The vapor enthalpy can be treated as the ideal gas enthalpy because the system is operated at atmospheric pressure. The ideal gas enthalpy of a volatile component, except β -ethoxy-ethyl propionate, at the boiling point is equal to the sum of the heat of vaporization and the liquid enthalpy at that temperature. The vapor enthalpy at other temperatures is calculated from the heat capacity data following the similar procedure as employed for determining the liquid enthalpy. Vapor heat capacities and heats of vaporization for ethyl alcohol (15), ethyl acrylate (17), water (52), and diethyl ether (16) are available in the literatures.

The heat capacity or the enthalpy data for β -ethoxy-ethyl propionate are not available in the literature. They are, therefore, calculated by the correlations. The Giacomini method (21) is used for estimating heat of vaporization at its normal boiling point. The method has an average error of 3 % and maximum error of 10 % (52). For the estimation of heat of vaporization at other temperatures, the Watson temperature correlation is used. It is relatively accurate with 4.7 % average error for 247 organic compounds (21). For detailed procedures of the estimation, refer to Appendix A.8.

All the vapor enthalpy data determined from the procedures stated above are then fitted into poly-

nomial equations by the program POLYFIT. The fitted constants along with the vapor enthalpy equation are listed in Table 7.2.

The second set of data needed for energy balance calculations is heat of reaction. As mentioned in the previous chapter, Hess' law is used to calculate heat of reaction. To utilize Hess' law, heats of formation for all the reactants and the products must be obtained first. Since neither experimental data nor estimation methods are available for obtaining the heat of formation of the molecular complex, acrylamide sulfate, a special procedure is then used to calculate its heat of formation.

As mentioned in Section 5.4.5, heat of reaction for Reaction 4, the formation of acrylamide sulfate from acrylamide and sulfuric acid, or Equation (4-1), is measured to be -5.62 Kcal/g-mole. Then from this heat of reaction, heat of formation for the molecular complex, acrylamide sulfate can be estimated from the following equation according to Hess' law:

$$H_{f,6} = H_{f,7} + H_{f,9} + \Delta H_{R,4} \quad (7-3)$$

where

H_f = heat of formation

Table 7.2 Vapor Enthalpies at 1 Atm.

$$H = a_1 + a_2 T + a_3 T^2 + \dots$$

T = temperature, °C

H = ideal gas enthalpy, cal/g

Component	a_1	a_2	$a_3 \times 10^5$	$a_4 \times 10^7$	Ref.
Ethanol	227.0	0.3630	33.973		(15)
Ethyl Acrylate	96.0	0.2387	67.20	-0.132	(16)
Water	597.6	0.4200	0.102		(52)
Diethyl Ether	90.0	0.3450	0.375		(16)
β -Ethoxy-ethyl Propionate	79.7	0.3695	- 6.211	8.929	(Est.)

6,7,9 = subscripts for acrylamide sulfate, sulfuric acid, acrylamide, respectively

$$\Delta H_{R,4} = -5.62 \text{ Kcal/g-mole.}$$

The heat of formation for sulfuric acid, at 25 °C, $H_{f,7}$, is available in the literature (48) while the heat of formation of acrylamide at 25 °C is estimated from the method of Anderson, Beyer and Watson (22). The ABW method is the only available method, which contains heat of formation of a basic amide group, formamide (HCONH_2). If the estimation starts from formamide, instead of other simpler atomic groups as used by other estimation methods, the estimation error can then be reduced to minimum. Therefore, this method is adopted in this work for estimating heat of formation of acrylamide. After the heat of formation of acrylamide sulfate is determined, by Equation (7-3), heats of reaction for all the three major reactions can then readily be calculated from the following equations by utilizing Hess' law.

- (1) For esterification, or Reaction 1, or Equation (4-2)

$$\Delta H_{R,1} = H_{f,2} + H_{f,8} - H_{f,6} - H_{f,1} \quad (7-4)$$

- (2) For dehydration, or Reaction 2, or Equation (4-3)

$$\Delta H_{R,2} = H_{f,3} + H_{f,4} - 2 H_{f,1} \quad (7-5)$$

- (3) For successive reaction, or Reaction 3, or Equation

(4-4)

$$\Delta H_{R,3} = H_{f,5} + H_{f,8} - 2 H_{f,1} - H_{f,6} \quad (7-6)$$

The contribution of the net heat capacity between reactants and products to the heat of reaction, for the above three reactions, is found to be very small compared to the calculated heat of reaction. Therefore, heats of reactions at 25 °C, determined from the heats of formations at 25 °C by the above three equations, are used for the entire temperature range.

All the required heats of formation shown in Equation (7-4) through (7-6) are listed in Table 7.3. Their literature sources or the methods of estimation used are given in Appendix A.9. The detailed procedures for determining the heats of reactions of the above three reactions are discussed in Appendix A.10. Table 7.4 is a summary of the heat of reaction determined and used in in this chapter for analysis of the mathematical model.

The last data required for energy balance calculations is overall heat transfer coefficient across the system wall. It is determined experimentally as described in details in Section 5.4.2.3.

7.1.2 Solution of Theoretical Model

Table 7.3 Heats of Formation

No.	Component	Phase	Kcal/g-mole	Ref.
1	Ethyl Alcohol	L	-66.35	(52)
2	Ethyl Acrylate	L	-92.46	(Est.)
3	Water	L	-68.32	(52)
4	Diethyl Ether	L	-65.2	(52)
5	β -Ethoxy-Ethyl Propionate	L	-160.81	(Est.)
6	Acrylamide Sulfate	L	-245.91	(Exp.)
7	Sulfuric Acid	L	-193.69	(52)
8	Ammonium Bisulfate	S	-238.99	(Est.)
9	Acrylamide	L	-46.6	(Est.)

Table 7.4 Heats of Reaction

Reaction No.	Reaction	Equation	Heat of Reaction Kcal/g-mole
1	Esterification	(4-2)	- 19.2
2	Dehydration	(4-3)	- 0.82
3	Successive Reaction	(4-4)	- 21.2
4	Equilibrium Reaction (Complex Formation)	(4-1)	- 5.62

As mentioned in Chapter 4 the Runge-Kutta fourth-order method was used for numerical solution of the proposed mathematical model. This method can be shown (8) to be convergent, that is,

$$\lim_{\Delta t \rightarrow 0} [y_i - y_i(t_i)] = 0 \quad (7-7)$$

where

t_i = independent variable

$y_i(t_i)$ = true solution

y_i = numerical solution

Δt = size of integration step

To obtain an exact solution $y_i(t_i)$ the size of integration step should be approaching zero, which is equivalent to requiring infinite integration steps. This is not practical. Instead, the size of an integration step is determined on the basis of considering both the desired accuracy and the computer time required to achieve this accuracy. Table 7.5 listed the calculated vapor condensate for Run No. 1, using four different integration steps, i. e., $\Delta t = 1, 2, 4$, and 8 minutes. Though no analytical solution can be obtained for comparison with these four sets of numerical solutions, the criterion of Equation (7-7) can be used to justify that the smaller the integration step the closer the numerical solution can approach the true solution. Significant differences

Table 7.5

Effect of Integration Step Size on
Calculated Total Molal Vapor Condensate

minutes	<u>Integration Step Sizes</u>			
	1 min.	2 min.	4 min.	8 min.
0	0.432	0.432	0.432	0.432
4	0.563	0.568	0.558	
8	0.676	0.678	0.676	0.665
12	0.789	0.789	0.784	
16	0.902	0.901	0.900	0.897
20	1.012	1.011	1.009	
24	1.121	1.120	1.119	1.110
28	1.229	1.227	1.225	
32	1.336	1.334	1.333	1.329
36	1.442	1.440	1.438	
40	1.549	1.547	1.545	1.533
44	1.657	1.654	1.651	
48	1.765	1.763	1.760	1.749
52	1.875	1.872	1.868	
56	1.986	1.983	1.979	1.964
60	2.098	2.095	2.090	
64	2.211	2.208	2.204	2.189
68	2.326	2.323	2.318	
72	2.443	2.440	2.434	2.418
76	2.561	2.558	2.552	
80	2.680	2.677	2.671	2.655

in vapor molal condensate between the 4-minute step size and the 8-minute step size can be observed. As the integration step size is reduced to 1 minute, the improvement from 2-minute step size becomes very small, for example, less than 0.08 % at $t = 80$ minutes. Therefore, the step size for the numerical integration was then selected as 2 minutes throughout this work, except a few severe cases such as adiabatic simulation where a smaller step size should be used for convergent solution.

7.2 Effects of System Parameters on Theoretical Solution

Among many independent parameters defining the system, three operating parameters are chosen as variables for the experimental investigations. They are initial and surrounding temperature, volatile reactant feed rate, and relative ratio of vapor to total feed. The effects of these three parameters on the system behavior will be discussed in details in this section. Furthermore, for a better understanding of the system characteristics, the system response to two other parameters, though not independent variables, will also be analysed. They are heat of reaction and overall heat transfer coefficient. For each of the above five system parameters, discussions are presented for the following three system responses:

- (1) Ethyl Acrylate Vapor Molal Condensate
- (2) Total Vapor Molal Condensate
- (3) Liquid Temperature

In a semibatch operation, the feed rate is generally limited to a certain range such that the system can be operated reasonably. For example, if the feed rate is too small, it will take a long time before the boiling point of the liquid mixture is attained. On the other hand if the feed rate is too large, the liquid holdup may increase rapidly such that liquid may overflow to the vapor flow path as entrainment. Since Run No. 1 is at a flow rate which is about in the middle of the appropriate flow range used in this study, all its system parameters are then used as the reference parameters for the discussion.

7.2.1 Effects of Heat of Reaction

Heats of reactions for this particular reaction system has been determined from Hess' law as described early in this chapter. Since heats of formation of several compounds required for such determinations are estimated, the calculated heats of reactions should have some degree of uncertainty. Because of this uncertainty, the analysis should be made to determine the effects if the estimated values of heat of reaction are erroneous.

The calculated value of heat of reaction for esterification is - 19.2 Kcal/g-mole. Five other values, namely -35, -30, -25, -10, and 0 Kcal/g-mole are chosen to determine the effect if the correct heat of reaction were not -19.2 Kcal/g-mole. No positive heat of reaction is used because the system being studied is exothermic.

Fig. 7.1 shows the plots of the liquid temperature as a function of time. For the case where the released heat of reaction exceeds 35 Kcal/g-mole, the liquid temperature becomes greater than 135 °C when time reaches 12 minutes. It has been experimentally verified that the acrylamide sulfate solution prepared in Section 5.3.3 decomposes near the vicinity of 135 °C. The decomposition can be detected easily by the smell of ammonia, one of the decomposed products. No actual measurements have been made for such decomposed vapors. If the absolute heat of reaction is lower, say at 30 Kcal/g-mole, the liquid temperature reaches the maximum which is slightly below 135 °C at $t=28$ minutes. Before reaching the maximum temperature, the system behavior is similar to the above "run-away" case. High heat of reaction forces out appreciable amount of volatile components and thus increases the bubble point of the liquid mixture.

After reaching the maximum temperature, more volatile

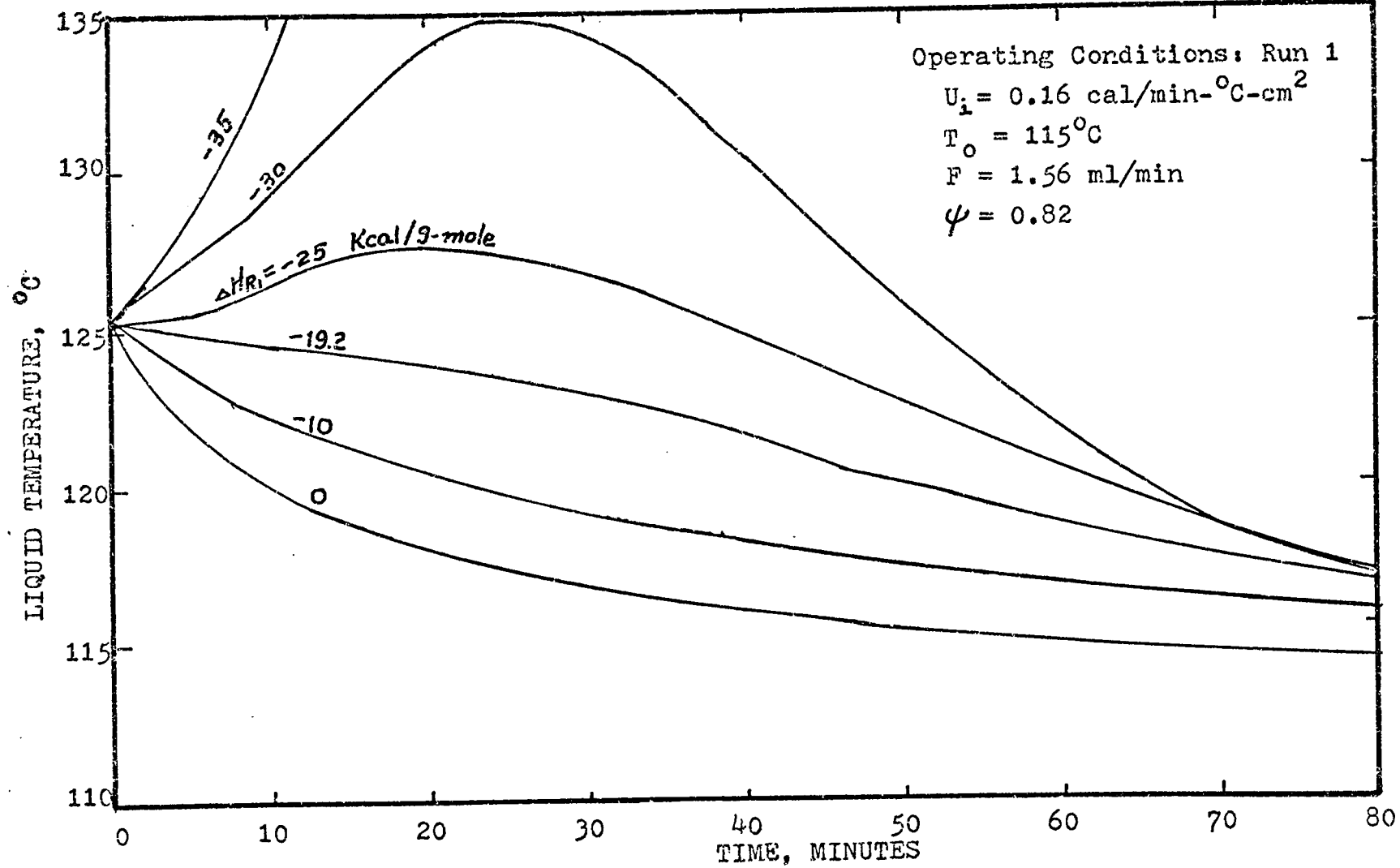


Fig. 7.1 Liquid Temperature — Effect of Heat of Reaction

components are either absorbed or produced in the liquid phase and more nonvolatile reactant (acrylamide sulfate) is consumed as time proceeds. Thus, the bubble point of the liquid mixture starts declining after the maximum temperature. If heat of reaction is small such that heat of generation is less than the net heat removal, the liquid temperature decreases continuously from the beginning of the run. This phenomenon can be recognized by the temperature lines of ΔH_R at -19.2, -10, and 0 Kcal/g-mole in Fig. 7.1. The effect of heat of reaction, as compared to its base value of -19.2 Kcal/g-mole can be summarized as

Difference in Heat of Reaction $\{\Delta H_{R,1} - (-19.2)\}$ Kcal/g-mole	Maximum Temperature Difference °C	Max. Temp. Difference per Unit Change of Heat of Reaction °C/(Kcal/g-mole)
-10.8	+11.7	1.08
- 5.8	+ 3.8	0.66
+ 9.2	- 3.8	0.41
+19.2	- 6.2	0.32

The results show that the maximum temperature difference per unit change of heat of reaction is least at zero heat of reaction and largest at the highest investigated heat of reaction of -35 Kcal/g-mole.

When the released heat of reaction is higher than 19.2 Kcal/g-mole, more ethyl acrylate can be produced and collected in the vapor condensate as shown in Fig. 7.2. This is because the reaction rate can be represented by the Arrhenius equation. As discussed earlier, the higher heat of reaction yields a higher liquid temperature which in turn results in a higher reacting rate. For the case of $\Delta H_{R,1} = -35$ Kcal/g-mole, it was stated that the liquid temperature reaches above 135 °C after 12 minutes of operation and that the product decomposition occurs. Therefore, no molal quantity of ethyl acrylate vapor condensate is shown in Fig. 7.2 after this point. For all the other selected heats of reaction, the molal quantities of ethyl acrylate vapor condensate are plotted up to $t = 80$ minutes so as to include all the data points used in Chapter 6 for correlating reaction rate expressions. At the operating time of 80 minutes, the difference of the collected amount of ethyl acrylate vapor condensate can be summarized as follows.

Difference in Heat of Reaction $H_{R,1} - (-19.2)$ Kcal/g-mole	Difference in Ethyl Acrylate Vapor Condensate Moles	Molal % Difference
-10.8	+0.112	+14.7
- 5.8	+0.045	+ 5.9
+ 9.2	-0.055	- 7.2
+19.2	-0.100	-13.1

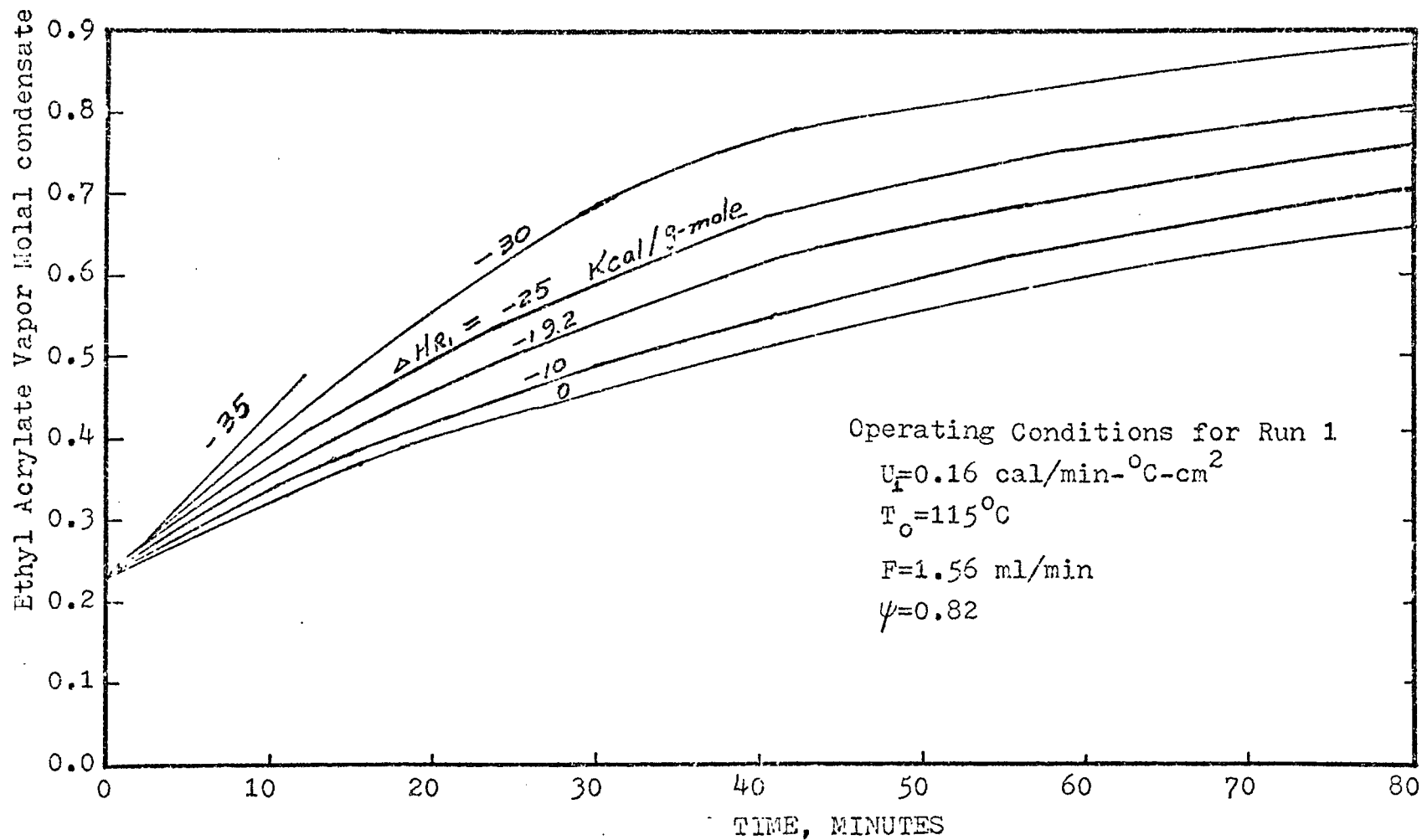


Fig. 7.2 Ethyl Acrylate Vapor Condensate —
Effect of Heat of Reaction

As shown in Fig. 7.3, during the early stage of the reaction, the variation of total vapor molal condensate is still appreciable, depending on the amount of heat of reaction released. This phenomenon reflects the high heat of reaction forcing out more volatile components from the liquid mixture. However, the differences are narrowed near the end of reaction because the esterification reaction rate becomes very small and consequently the effect of heat of reaction is greatly reduced.

7.2.2 Heat Transfer Coefficient

The overall heat transfer coefficient was measured previously as $0.16 \text{ cal/min-}^{\circ}\text{C-cm}^2$ using the similar fluids. If the system is operated adiabatically, i. e., no heat is transferred through the system boundary, the liquid temperature rises very rapidly and reaches 135°C in less than 8 minutes as shown in Fig. 7.4. If the insulation material can be adjusted to give an overall heat transfer coefficient of $0.08 \text{ cal/min-}^{\circ}\text{C-cm}^2$, the decomposition temperature of 135°C , may also be reached rapidly in about 17 minutes. However, such "run-away" temperatures are reached only when the initial and surrounding temperature (T_0) is high, or the relative ratio of vapor to total feed (ψ) is large, or both. Run 1 is operated under such conditions. For Run 9, the initial and surrounding temperature is

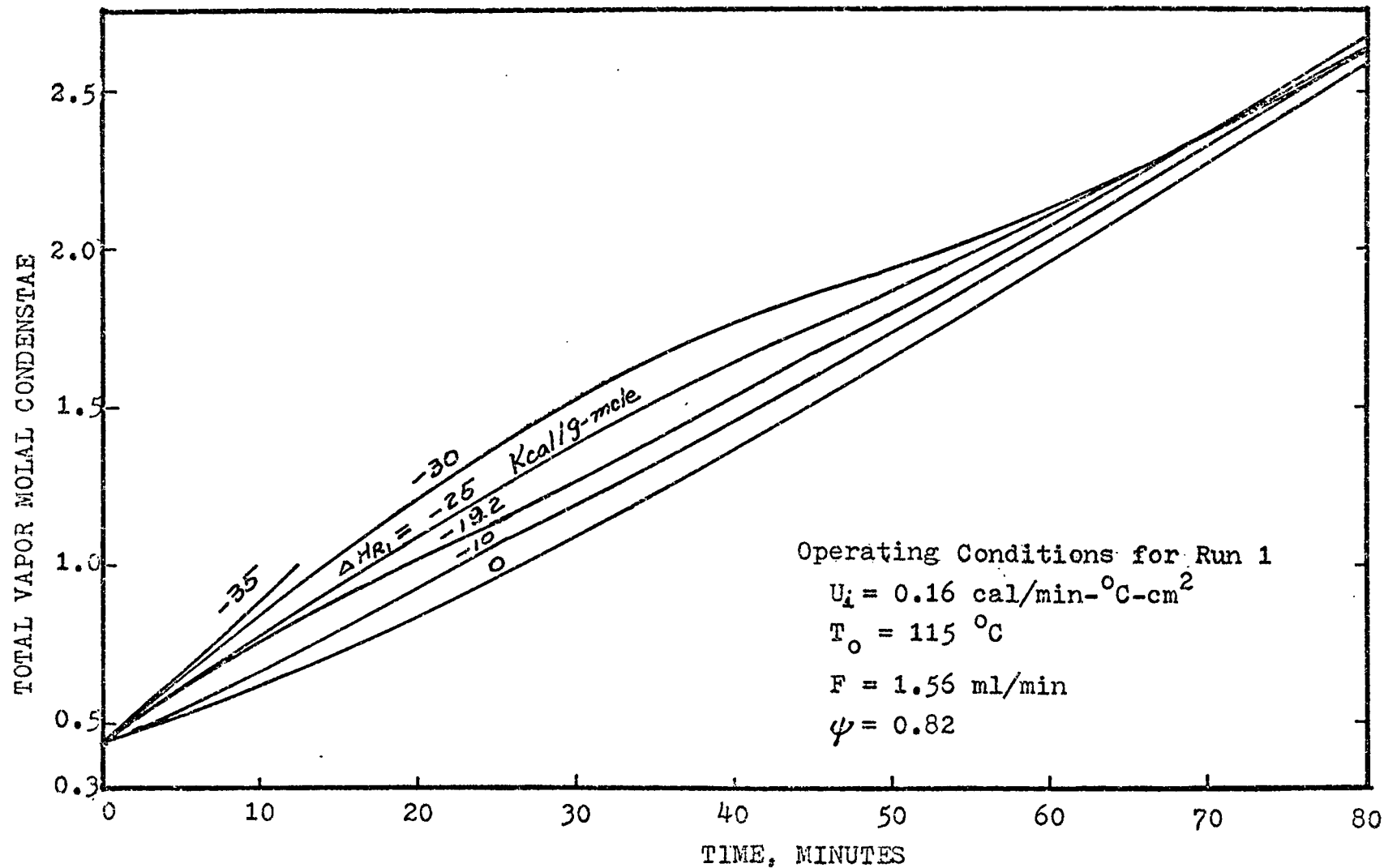


Fig. 7.3 Total Vapor Molal Condensate —
Effect of Heat of Reaction

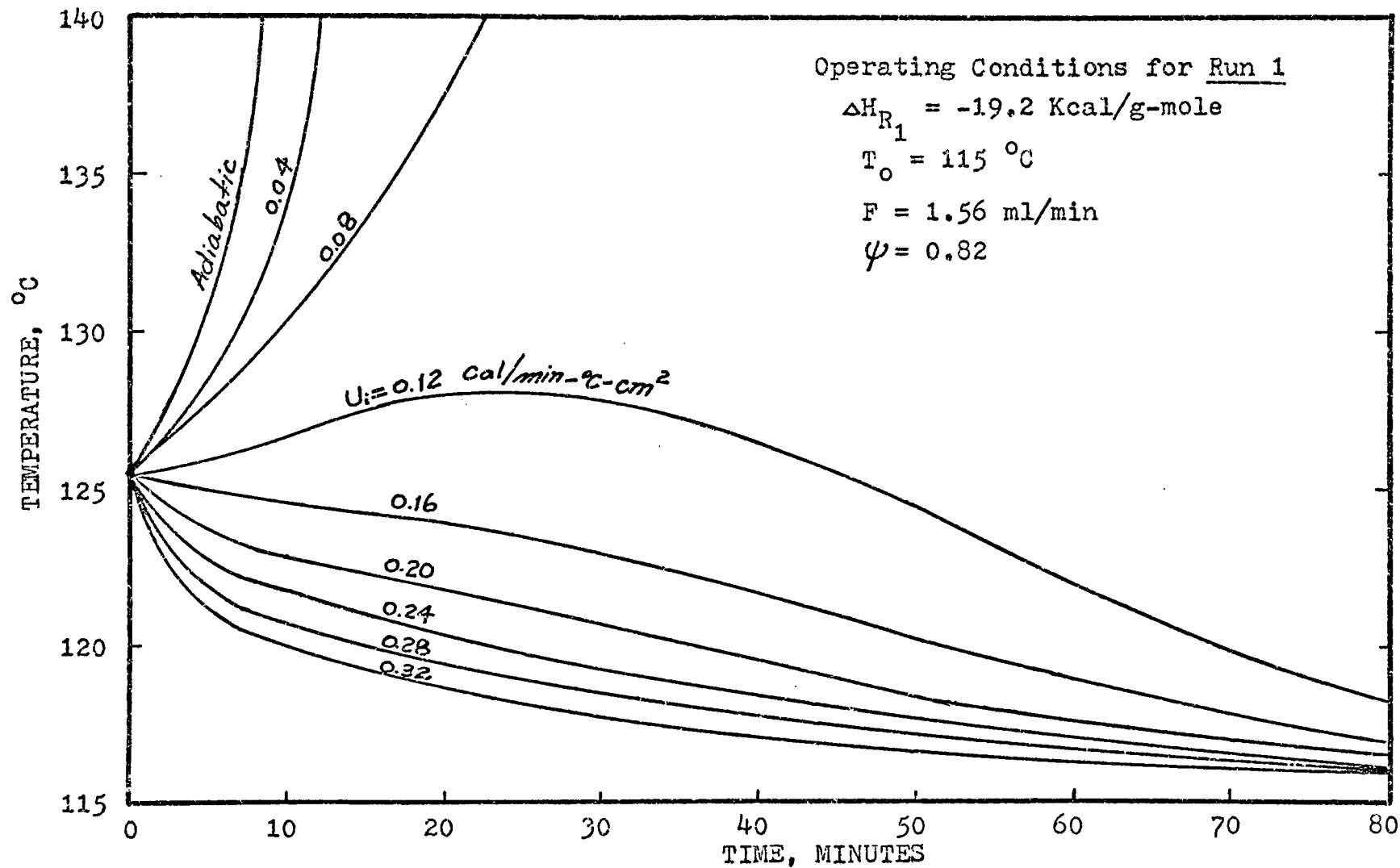


Fig. 7.4 Liquid Temperature — Effect of Overall Heat Transfer Coefficient

set to 106°C , and the relative ratio of vapor to total feed is zero, which are respectively lower than those of Run 1. As shown in Fig. 7.5 the maximum temperature is only 118.5°C even the system is operated adiabatically. Therefore, undesirable high operating temperatures can be avoided even for an adiabatic operation if the above mentioned two operating parameters are properly adjusted.

Now, return to Fig. 7.4. The overall heat transfer coefficient can be increased if the material of the pyrex wall of the reaction-distillation column is replaced by the corrosion-resistant metal such as inconel. Then, the liquid temperature will rapidly approach the surrounding temperature as shown by the lines of high overall heat transfer coefficients, ranged from $0.20\text{--}0.32\text{ cal/min-}^{\circ}\text{C-cm}^2$. As shown in Fig. 7.5, the liquid temperature may even go below the surrounding temperature. Usually this occurs only in the system where the feed is totally or nearly totally liquid.

If the overall heat transfer coefficient is small, the reaction temperature is higher, resulting in higher product yield. This phenomenon is illustrated in Fig. 7.6. The relation between product yield and overall heat transfer coefficient at the reaction time of 80 minutes can be summarized as follows.

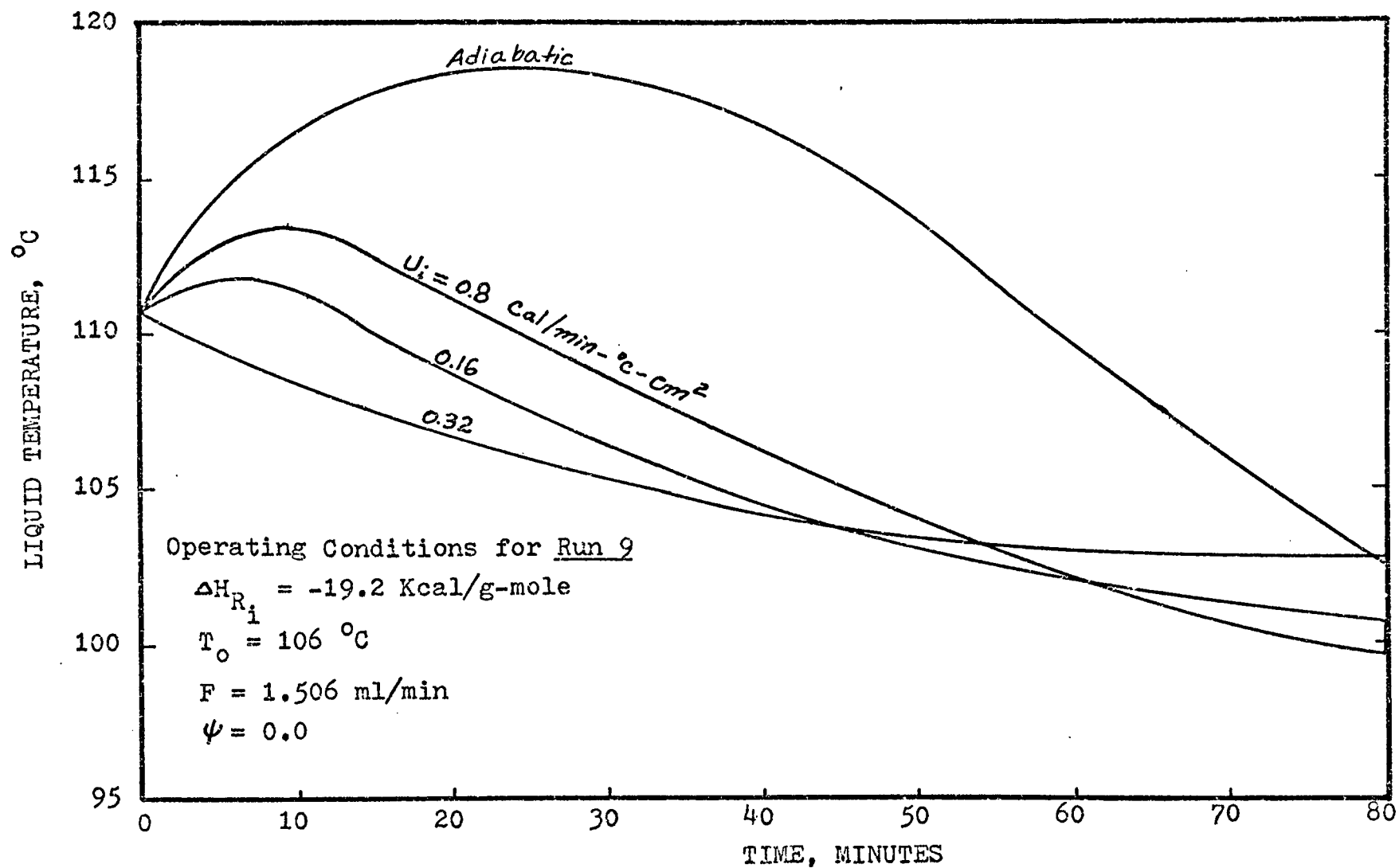


Fig. 7.5 Liquid Temperature — Effect of Overall Heat Transfer Coefficient

<u>U, cal/min-°C-cm²</u>	<u>Ethyl Acrylate, moles</u>
0.12	0.852
0.16(measured value)	0.752
0.24	0.701
0.32	0.678

During the early stage of reaction, small overall heat transfer coefficient leads to higher liquid temperature, which in turn forces out more volatile components from the liquid mixture to give a higher total vapor molal condensate as shown in Fig. 7.6. At the end of the reaction, all the liquid temperatures approach the surrounding temperature as illustrated by Fig. 7.4. Therefore, the effect of overall heat transfer coefficient on total vapor molal condensate is greatly reduced as shown in Fig. 7.7.

7.2.3 Initial and Surrounding Temperature, T_0

The initial temperature as discussed in Section 5.1.1 is set equal to the surrounding temperature to avoid further complicating the system. Fig. 7.8 gives the temperature history of the system at four different initial and surrounding temperatures, T_0 . For all the four cases, liquid temperature approaches to the surrounding temperatures. There is a temperature cross-over between the 110 °C and 106 °C lines. The cross-over is caused by two factors. One of them is frequency factor, and the other

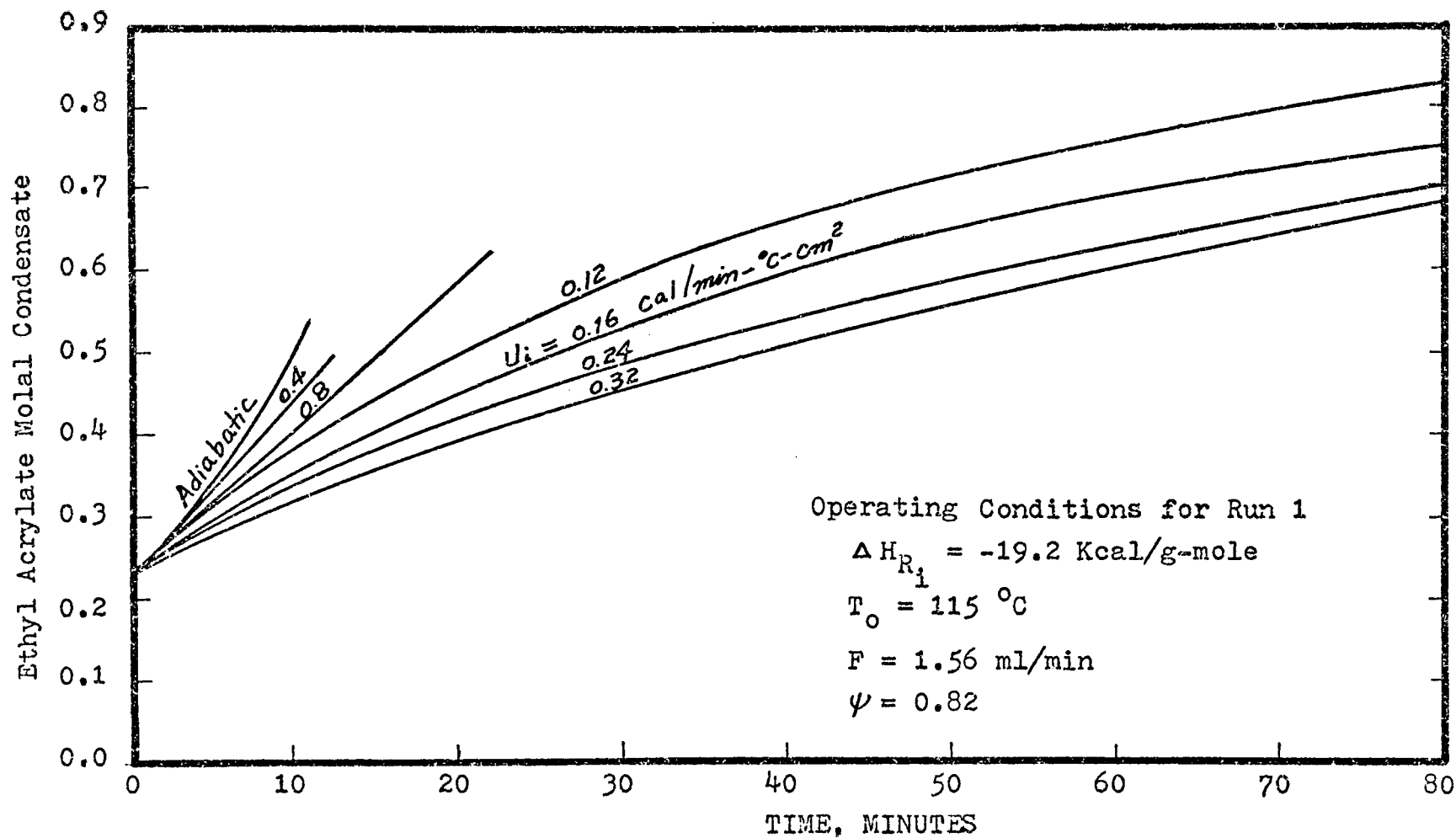


Fig. 7.6 Ethyl Acrylate Vapor Molal Condensate —
Effect of Overall Heat Transfer Coefficient

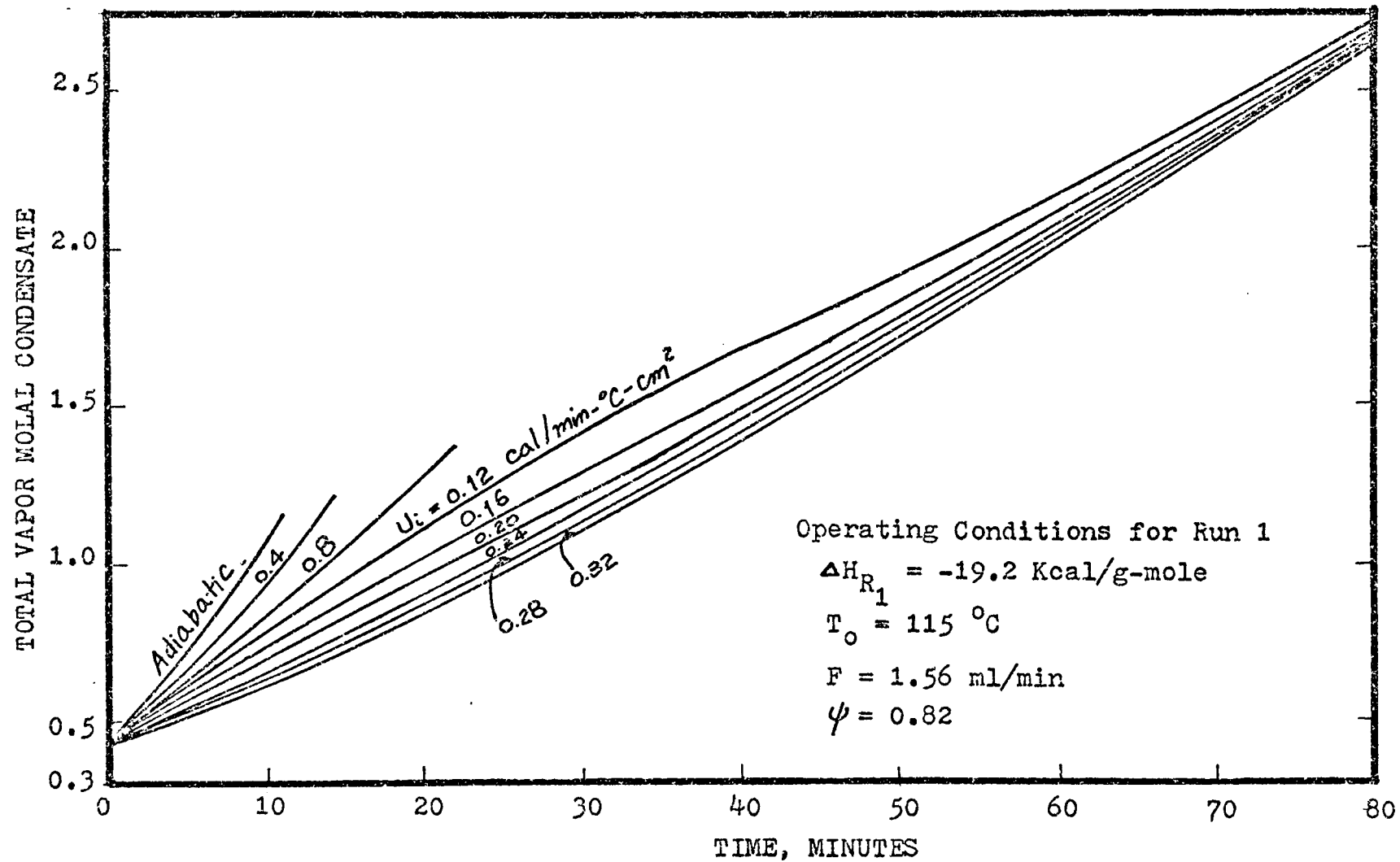


Fig. 7.7 Total Vapor Condensate — Effect of Overall Heat Transfer Coefficient

is heat loss. The ratio of the frequency factors of the 106°C case to the 110°C case can be calculated from Equation (6-29) as given in Chapter 6. It is found that the frequency factor for the 106°C case is 1.87 times that for the 110°C case. Therefore, during the early stage of reaction, the 106°C case produces more heat of reaction, resulting in a higher liquid temperature. As time proceeds, higher heat loss due to a higher temperature driving force across the reactor wall for the 106°C case rapidly brings down its liquid temperature line and then crosses over the 110°C line. If two sets of initial and surrounding temperature are very apart as in the cases of 115°C and 106°C , there is no cross-over because the less heat loss at 115°C can maintain higher liquid temperature during the run.

For this system, the reaction rate constant is higher for a lower initial and surrounding temperature. It is resulted from a higher frequency factor for this lower initial and surrounding temperature and a high starting liquid temperature, which in turn gives a high value for the Arrhenius exponential term. Therefore, the product yield at 106°C is very high as shown in Fig. 7.9.

At a higher surrounding temperature with a higher

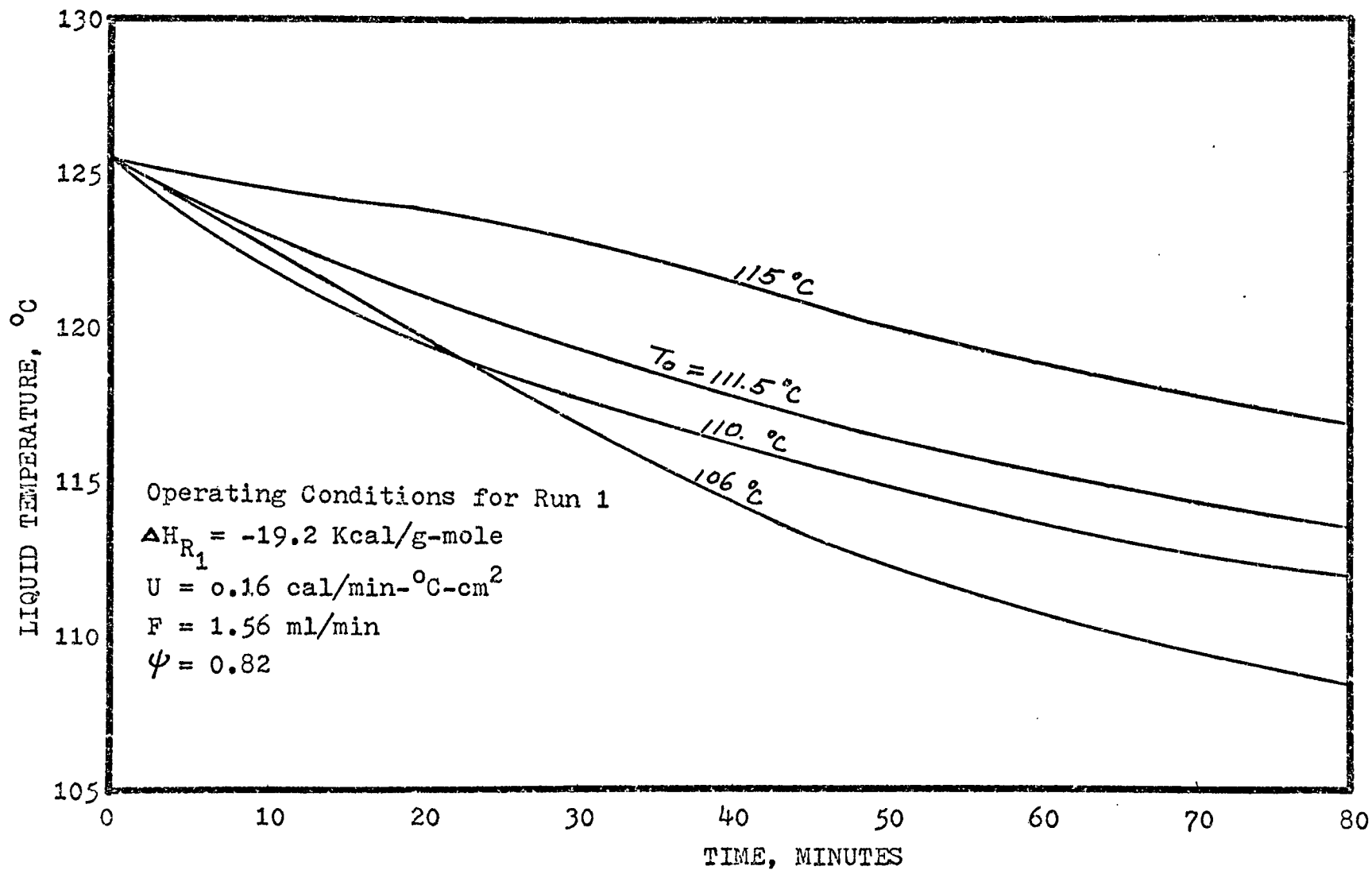


Fig. 7.8 Liquid Temperature — Effect of Initial and Surrounding Temperature

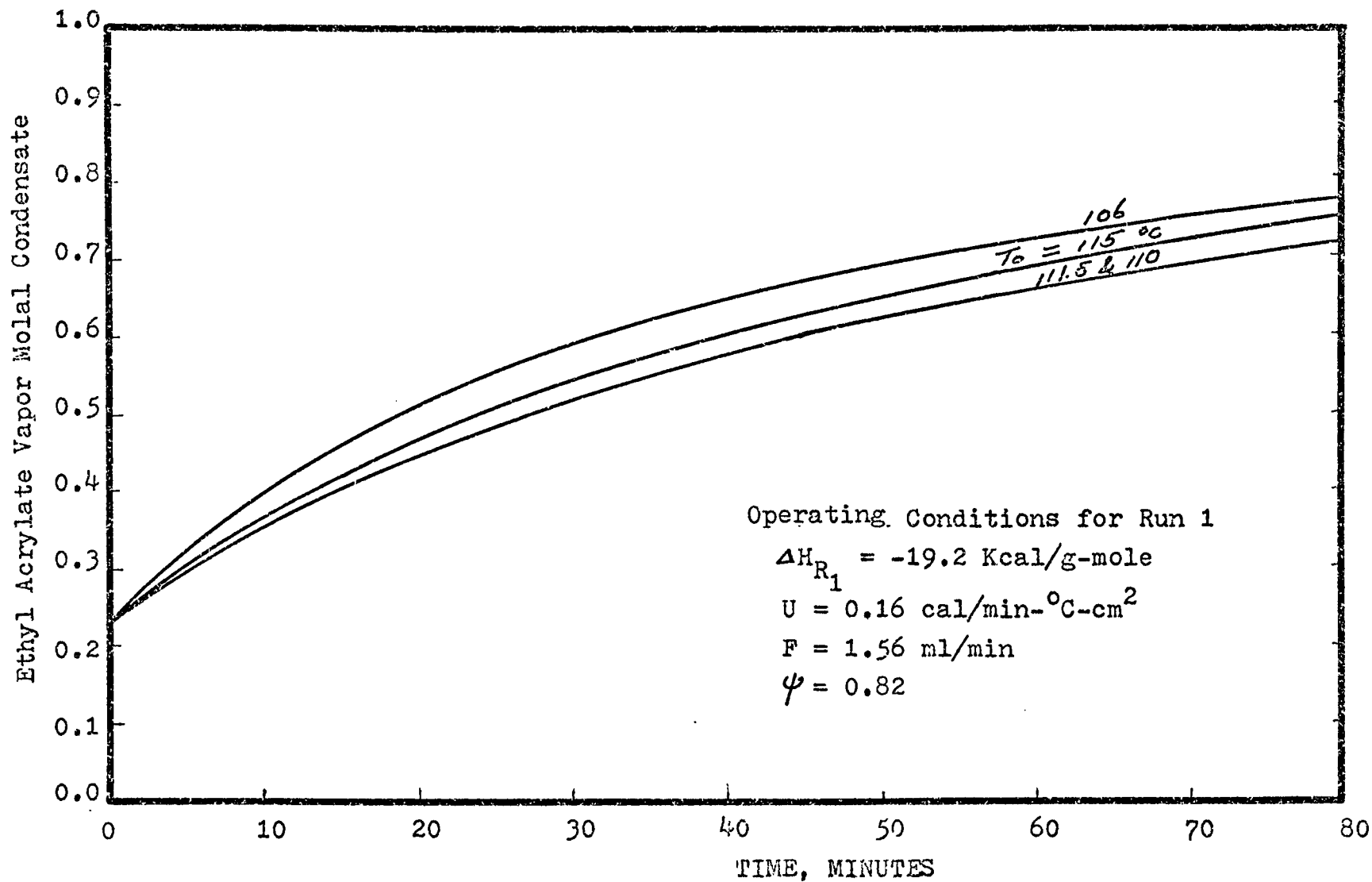


Fig. 7.9 Ethyl Acrylate Vapor — Effect of initial and Surrounding Temperature

initial temperature, the temperature driving force is small, consequently there is less heat loss through the wall of the reaction-distillation column. Therefore, the liquid temperature is higher and there is more volatile vapor leaving the liquid mixture as shown in Fig. 7.10.

7.2.4 Feed Flow Rate, F

As mentioned early in this section (7.1.3), feed flow rate can be neither too large nor too small for a semibatch system if the appropriate operating range is to be maintained. The selected flow rates in this study are between 1.0 and 2.0 ml/min. Since the feed flow rate during Run 1 is an intermediate rate, 1.56 ml/min., this flow rate along with the above mentioned feed rates are then used as the typical cases for the following discussions.

The liquid temperature during a run is plotted in Fig. 7.11 for three different rates. At the smallest feed rate, the liquid temperature in the early stage of reaction is the lowest. At the smallest feed rate, the concentration of ethyl alcohol in the liquid is lowest. Thus, its reaction rate is the slowest with release of the least heat of reaction. As the reaction continues,

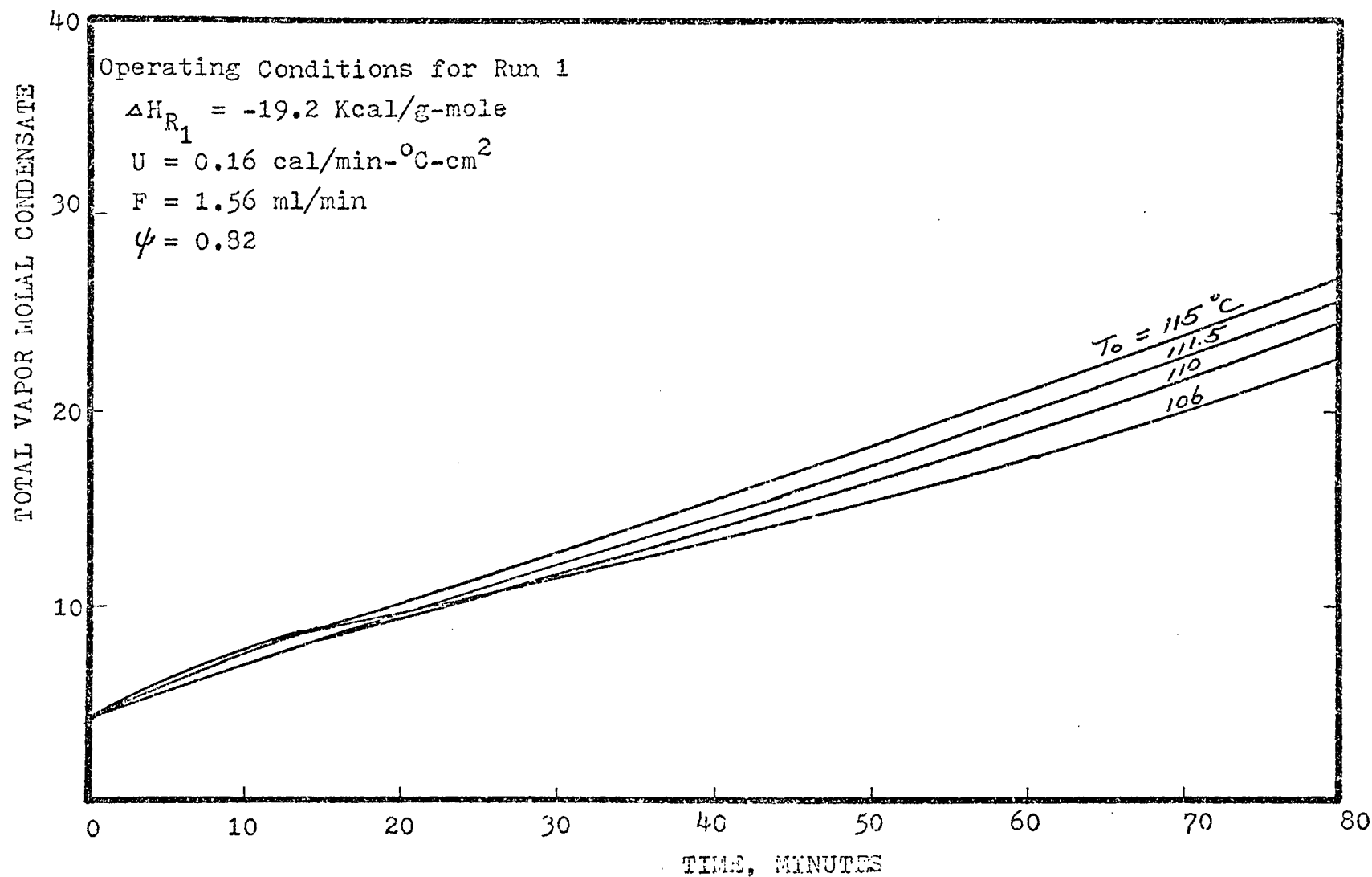


Fig. 7.10 Total Vapor Molal Condensate — Effect of Initial and Surrounding Temperature

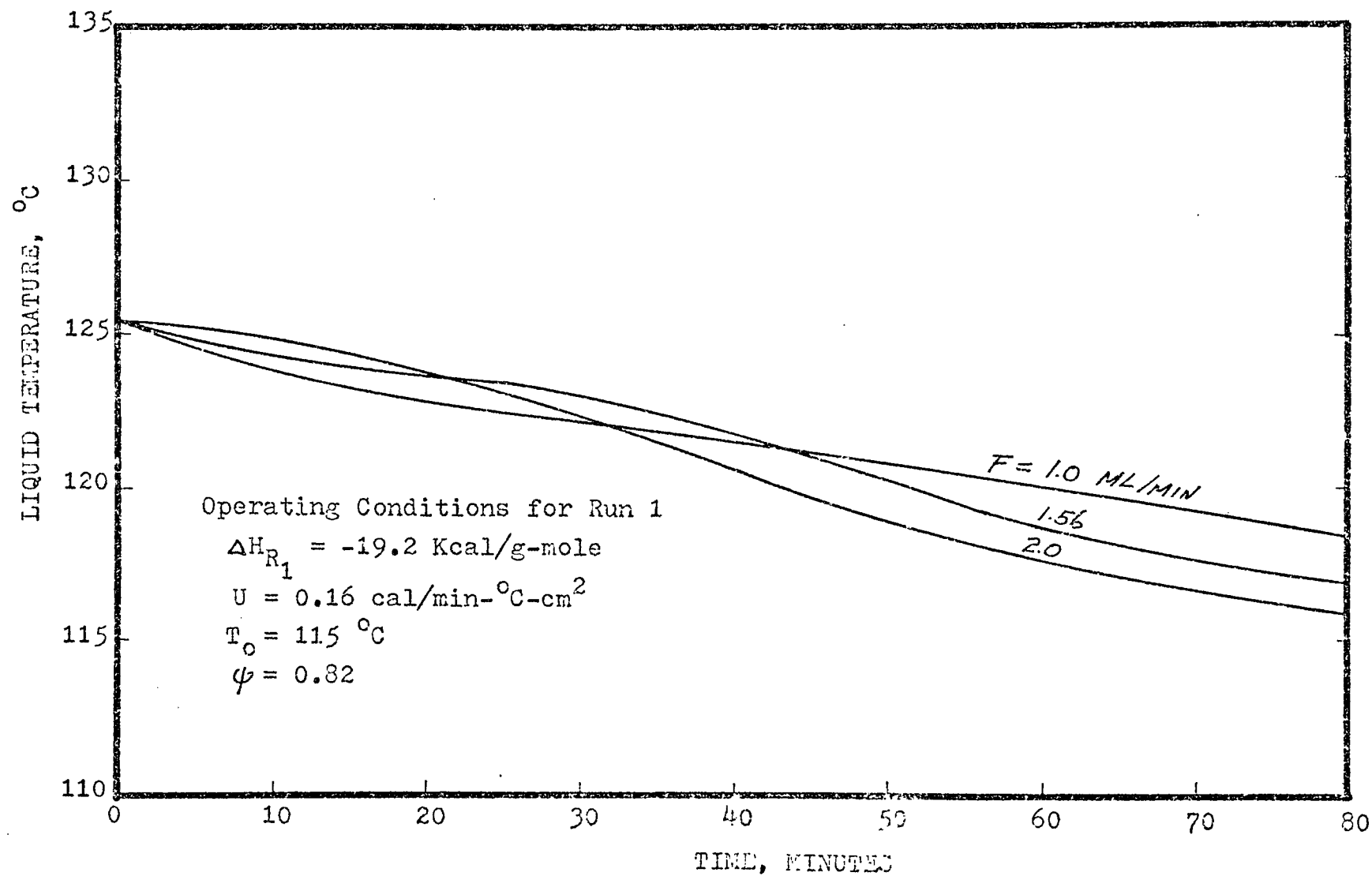


Fig. 7.11 Liquid Temperature —Effect of Feed Rate

the content of volatile components in the liquid mixture becomes much less. Therefore, its bubble point eventually becomes the highest among the three cases. This cross-over of the liquid temperature lines happens frequently; for example, the temperature cross-over between the cases of 1.56 and 2.0 ml/min. feed rates is at 21.5 minutes and similarly between 1.0 and 1.56 ml/min. at 42 minutes.

Since a high feed rate reduces the liquid temperature in the long run, it does not proportionately increase the product yield. Fig. 7.12 shows that the product yield at 2.0 ml/min. feed rate is slightly higher than that at 1.56 ml/min. during the first 60 minutes of operation. However, its yield becomes smaller after 60 minutes of operation. With little improvement in the product yield, this excessive increase of volatile components, introduced by the feed, will reduce the product concentration in the vapor condensate collected. Selection of a proper feed rate is, therefore, very important for obtaining the desired product concentration. However, it should be noted that many operating parameters interact and, therefore, the selection of feed rate should also be considered in accordance with other parameters, such as overall heat transfer coefficient, initial temperature, surrounding temperature and relative ratio of vapor to

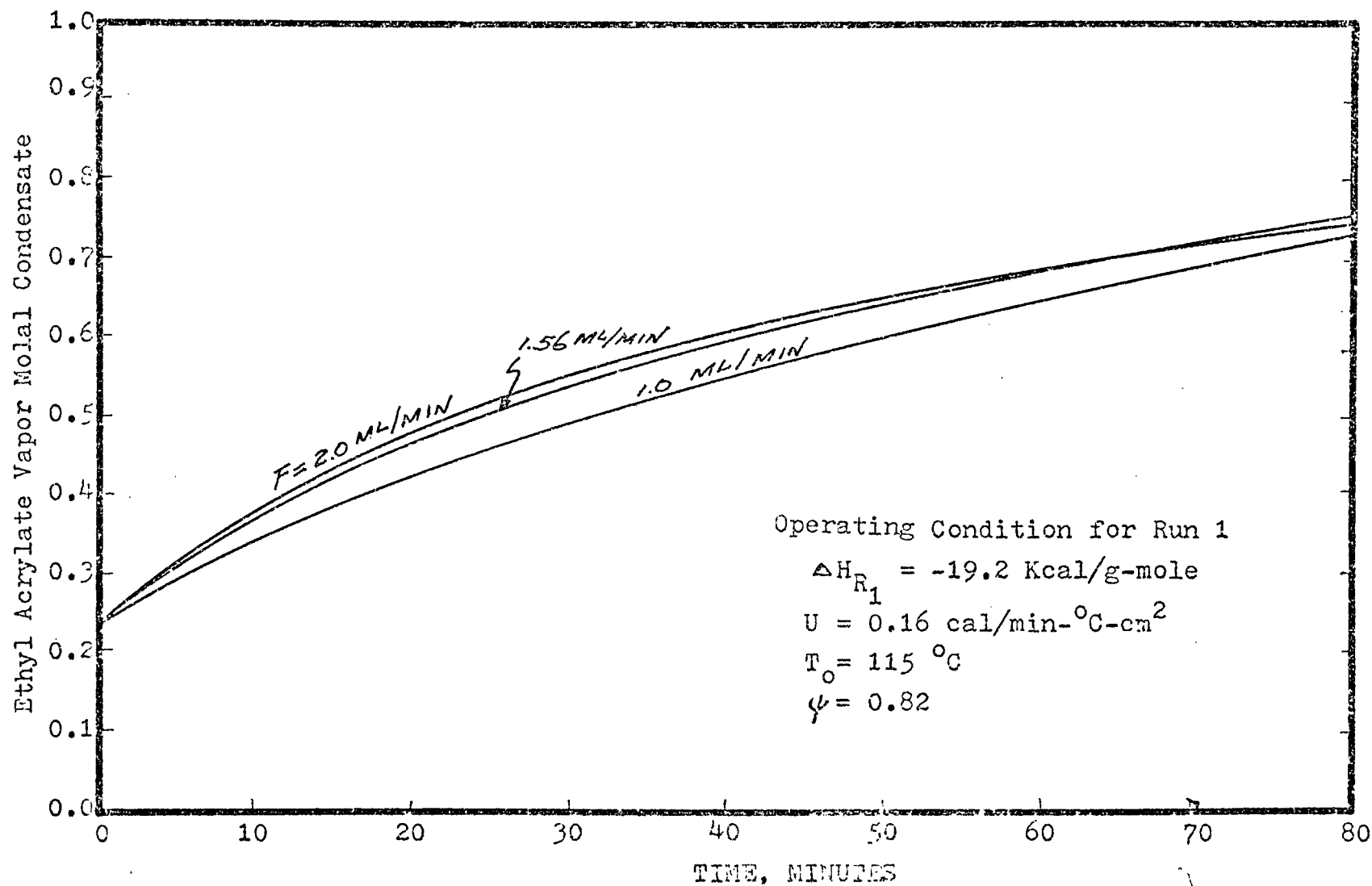


Fig. 7.12 Ethyl Acrylate Vapor Condensate — Effect of Feed Rate

total feed.

As can be expected, a higher feed rate, containing volatile components, produces more total vapor condensate. This is shown in Fig. 7.13. The difference in the amounts of accumulated total condensate at the different feed rates is very large compared to the similar variation in the product yield.

7.2.5 Vapor Fraction in the Total Feed

It has been shown earlier in Fig. 7.5. that the liquid temperature becomes less than the surrounding temperature if the feed is totally liquid. The illustration is shown for the case of a low initial and surrounding temperature of 106°C . However, a similar phenomenon can be observed for the run with a high initial and surrounding temperature of 115°C , as long as the relative ratio of vapor to feed rate is low. The latter is shown in Fig. 7.14. The liquid temperature becomes lower than the surrounding temperature, 115°C , at $t=20$ minutes if the feed stream is totally liquid. As the relative ratio of vapor to total feed is increased, the liquid temperature increases substantially, especially at $t=22$ minutes. No "run-away" temperature is reached because the outgoing vapor carries away some of this heat

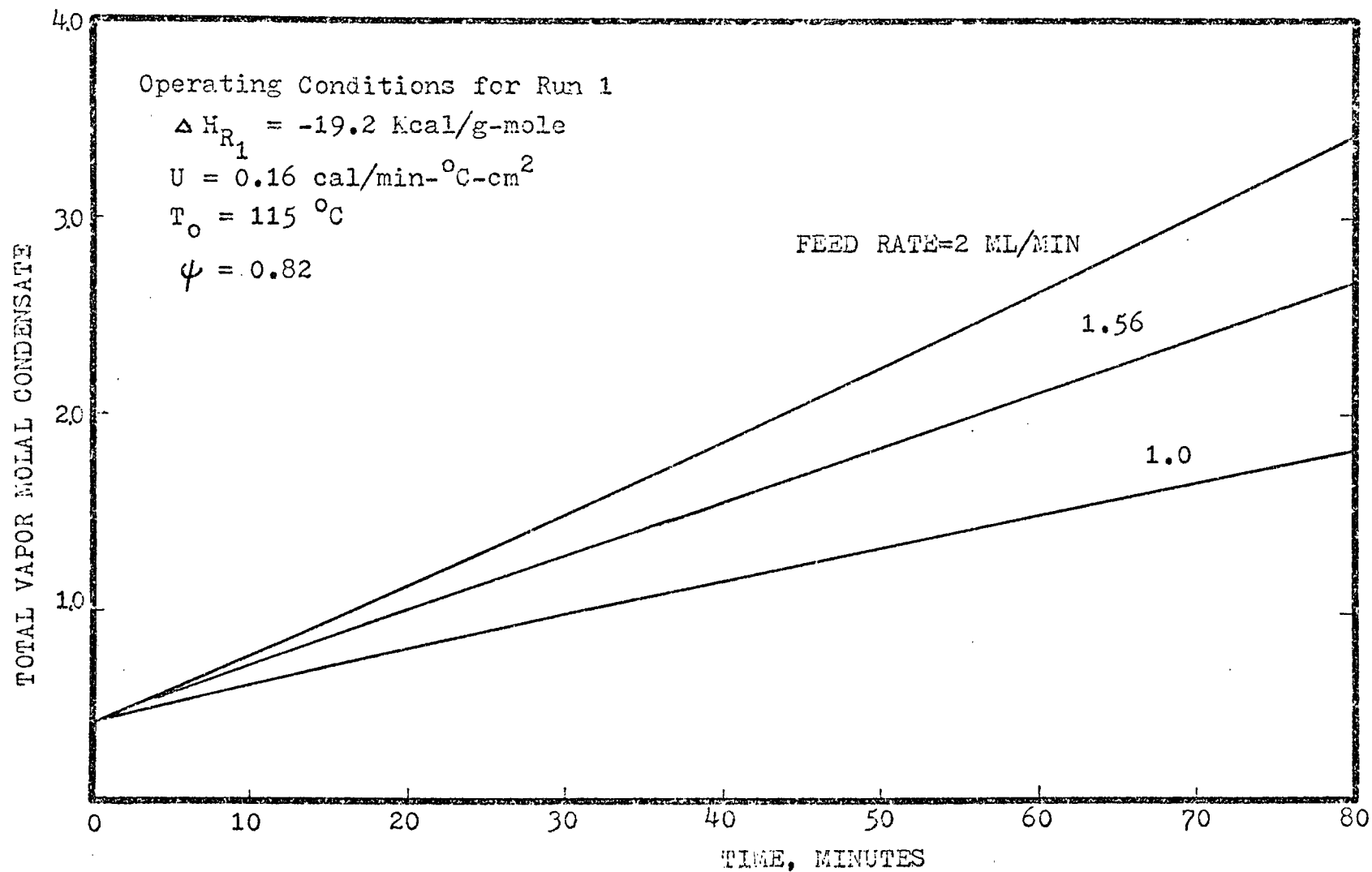


Fig. 7.13 Total Vapor Molal Condensate --- Effect of Feed Rate

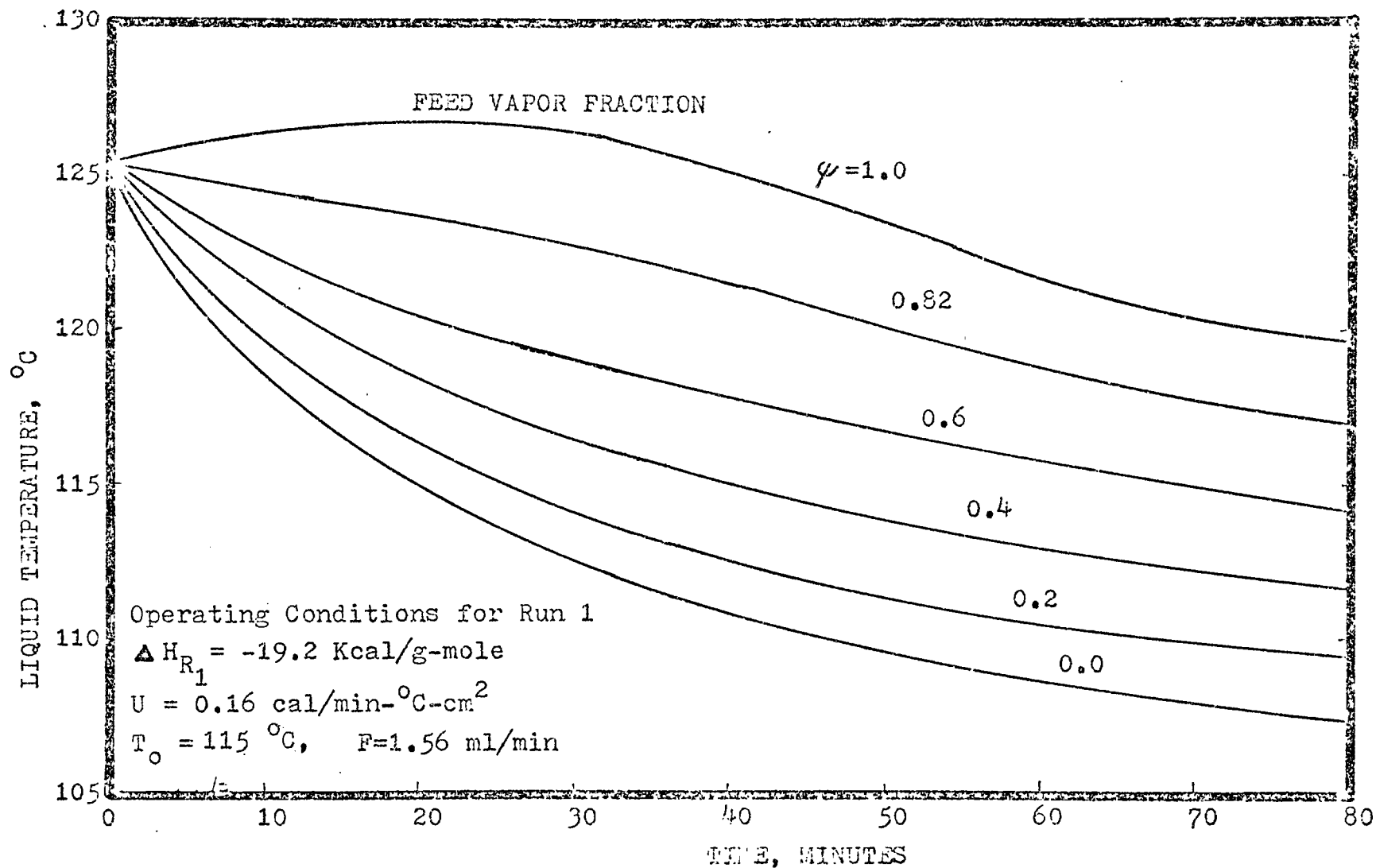


Fig. 7.14 Liquid Temperature — Effect of Feed Vapor Fraction

flow to maintain a moderate temperature operation. However, if the system is operated adiabatically and with the feed of totally vapor, the liquid temperatures may reach the "run-away" temperature of 135°C .

As shown in Fig. 7.14, the higher ψ the higher the liquid temperature. The corresponding product yield is then higher for the cases with higher ψ values, except the case of $\psi=0$. At low ψ , the ethyl alcohol concentration in the liquid is high. As discussed in Section 6.2.2, at low ψ , the frequency factor is also high. Therefore, a combination of low temperature, high frequency factor and high liquid concentration, as required for calculating reaction rate constant, may give a higher product yield at a lower ψ as shown in Fig. 7.15.

At the constant feed rate of $F=1.56\text{ ml/min.}$, the amount of total vapor condensate increases as the vapor fraction of the feed is increased. It can be reasoned simply that a feed with a higher content of vapor bring with it more heat which is in turn used for vaporization. This can be shown by Fig. 7.16.

7.3 Comparison of Theoretical and Experimental Results

The previous section has presented the parametric evaluations of the unsteady state system behavior, using

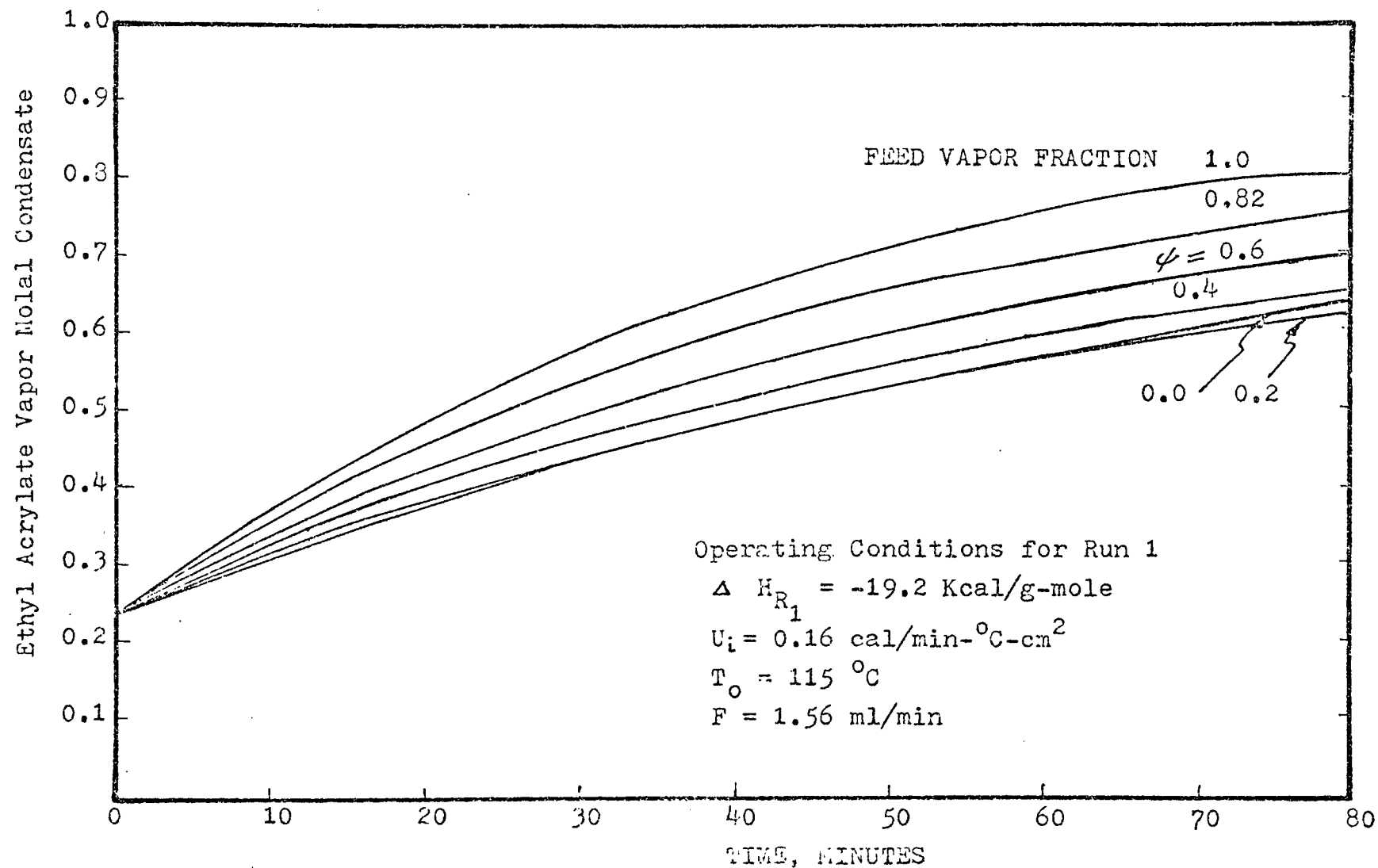


Fig. 7.15 Ethyl Acrylate Vapor Molal Condensate —
Effect of Feed Vapor Fraction

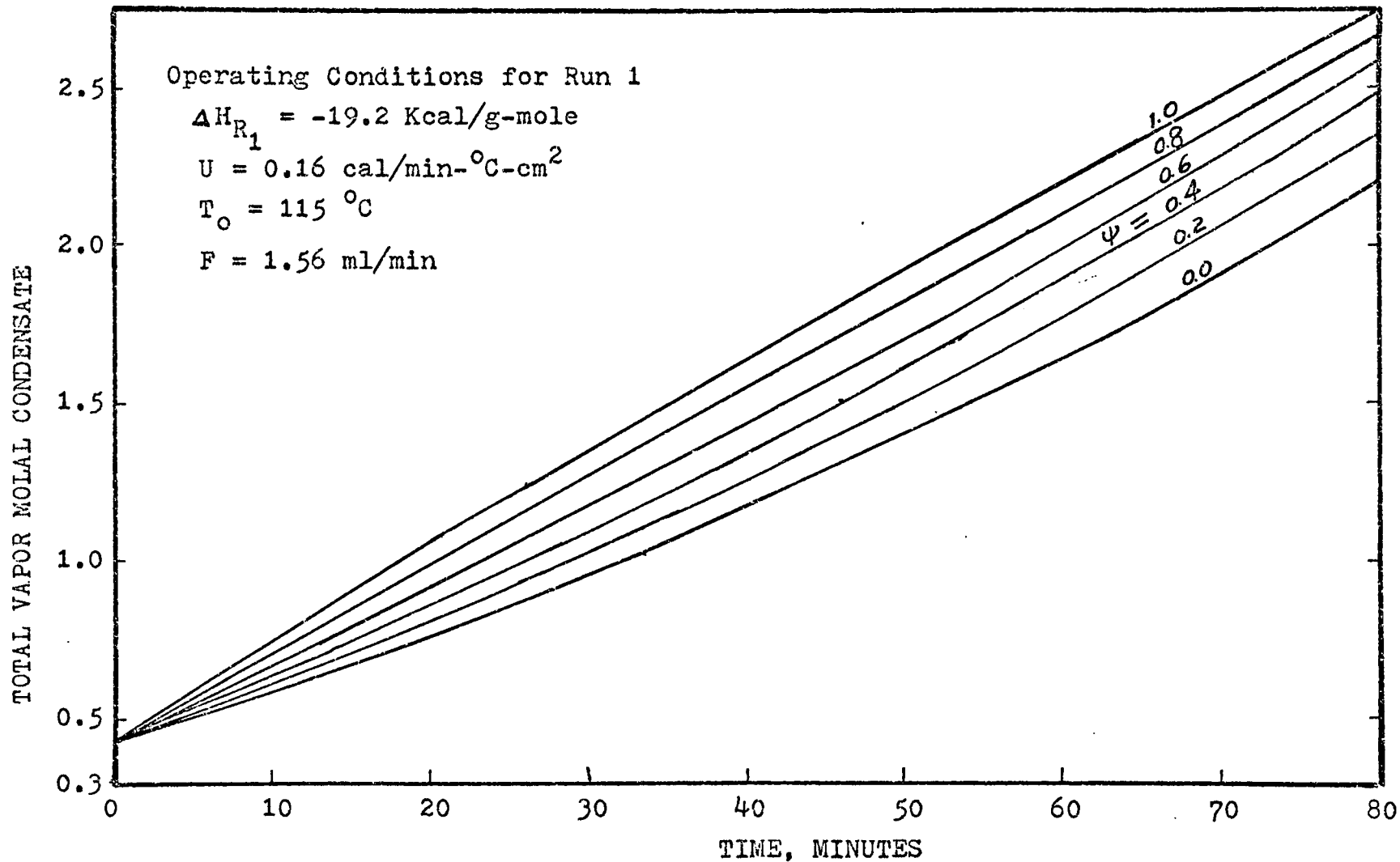


Fig. 7.16 Total Vapor Molal Condensate —
Effect of Feed Vapor Fraction

the proposed mathematical model. Now, the discussion should be extended to examine how accurately the proposed mathematical model represents and predicts the actual experimental results obtained in this study. The three operating parameters for all the nine experimental runs are given in Table 6.2, while their initial values are shown in the computer print-outs of the program LABDATA detailed in Appendix C.1.3.

Since the proposed theoretical model includes eighteen simultaneous differential equations, as presented in Chapter 4, eighteen initial conditions are required for the solution. These initial values are given, more conveniently, in the computer print-outs of the model simulation program, MODEL. They are included in Appendix C.2.3. Although there are eighteen dynamic quantities, as mentioned above, which can be used for comparing the theoretically calculated and experimentally measured values, only those with great importance are selected for presentation here. Among the selected are the accumulated vapor molal condensate and the liquid temperature. Since the liquid compositions provides useful information on the distribution of the volatile components between vapor and liquid as well as on the reaction conversion, they are also included in this comparative study.

7.3.1 Comparison on Vapor Molal Condensates

Since ethyl acrylate is the main product and ethyl alcohol is an important unreacted reactant in the vapor phase, they are the two vapor molal quantities of greatest importance. With the additional knowledge of the amount of total vapor molal condensate, the relative purity of ethyl acrylate in the condensate can be determined. Therefore, these three quantities are to be evaluated in this section. No discussions will be presented for the rest of components in the vapor, such as water, diethyl ether and β -ethoxy ethyl propionate, because water is not a product and the other two compounds are by-products with only trace quantities.

The comparisons between theoretically calculated and experimentally measured results for the above three important quantities are presented in Figures 7.17 - 7.25, one for each experimental run. The comparisons are made for the dynamic behavior of the system during the initial 80 minutes operation.

For the main reaction product, ethyl acrylate, the agreement between the theoretical and experimental values is very satisfactory except Run 9 where the theoretical calculations give an average error of 0.095 moles, i. e., approximately 23 %. It is noted that one of the original

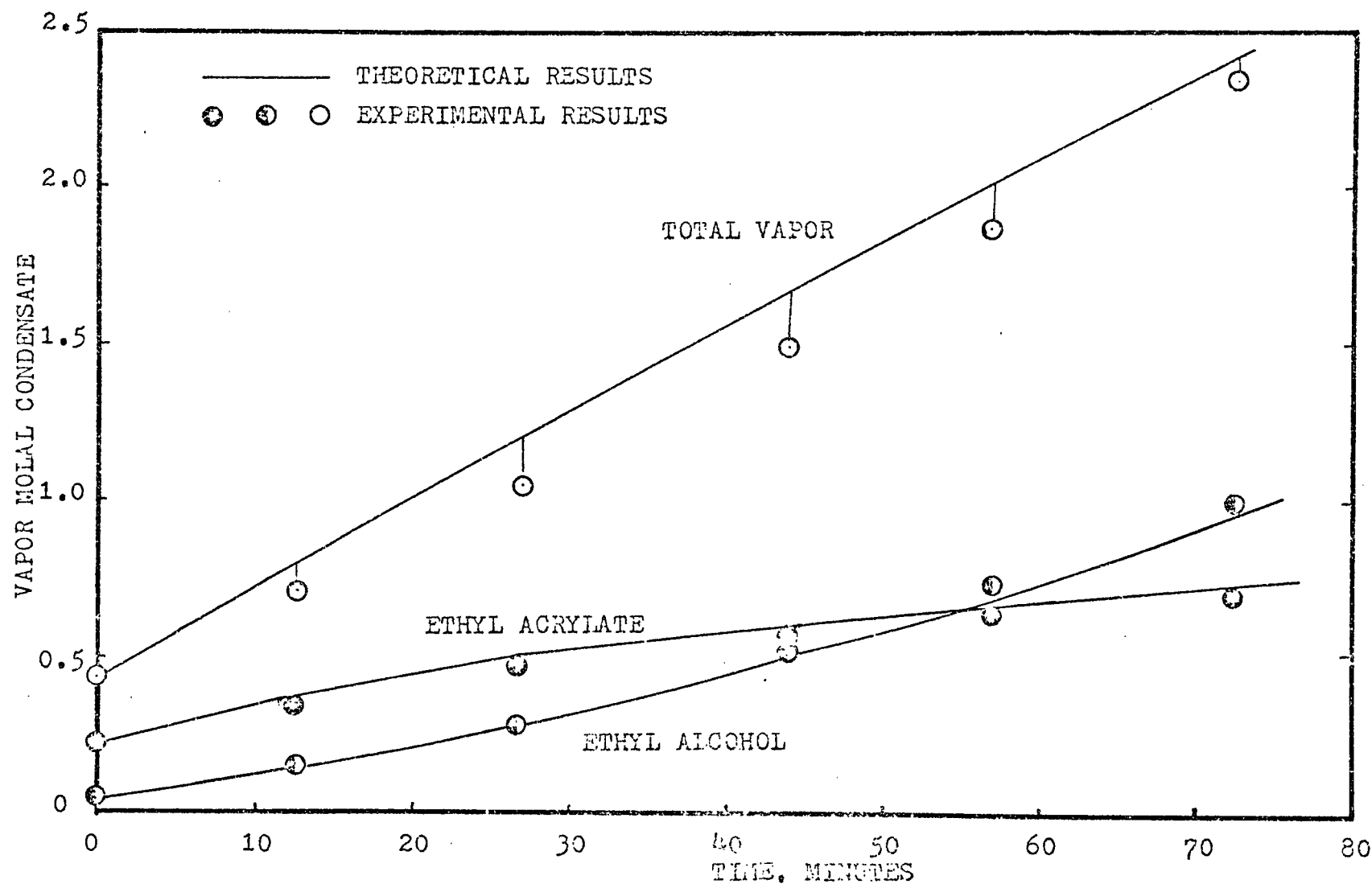


Fig. 7.17 Comparison of Theoretical Model and Experimental Results — Vapor Molal Condensate, Run 1

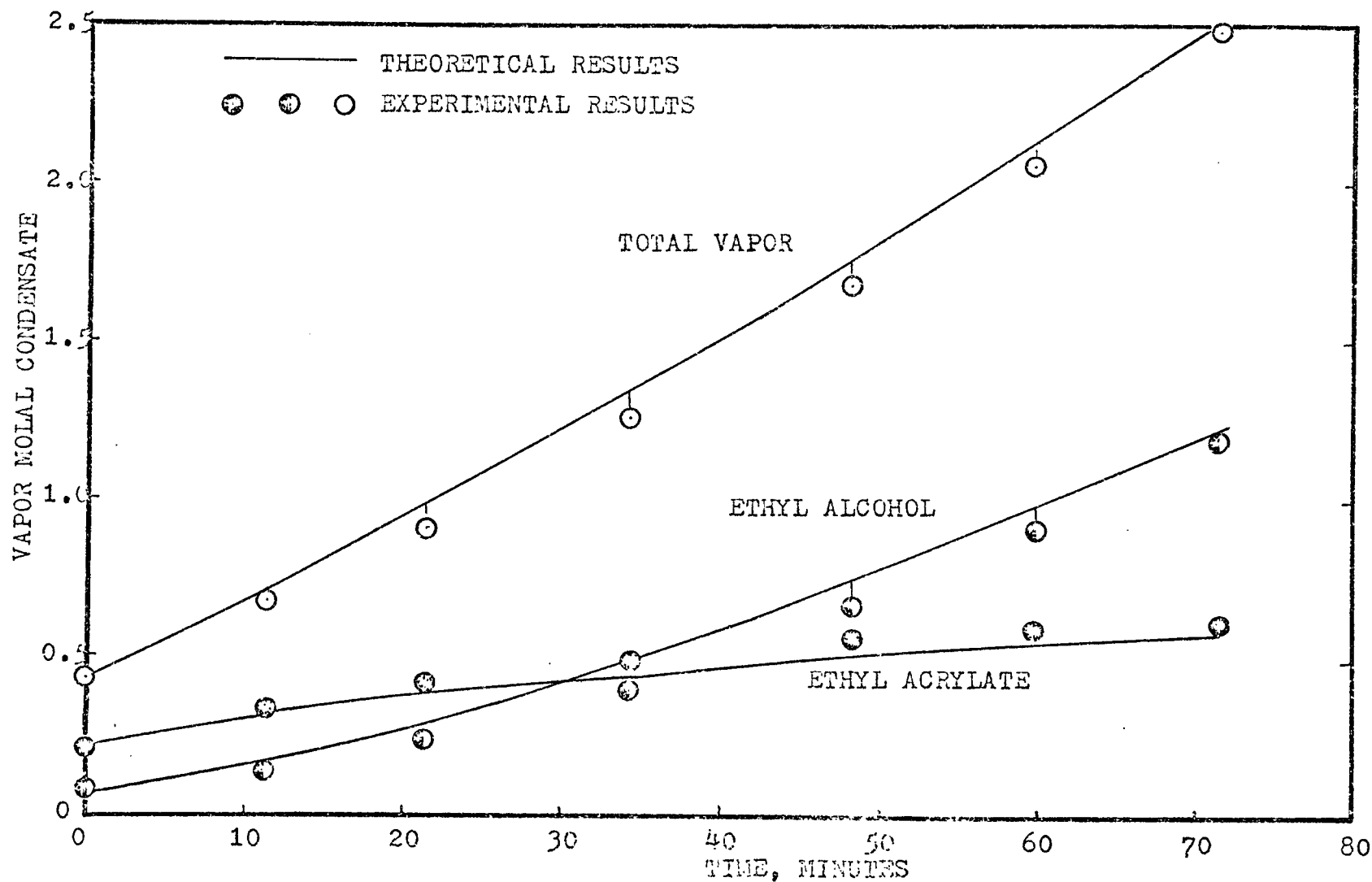


Fig. 7.18 Comparison of Theoretical Model and Experimental Results — Vapor Molal Condensate, Run 2

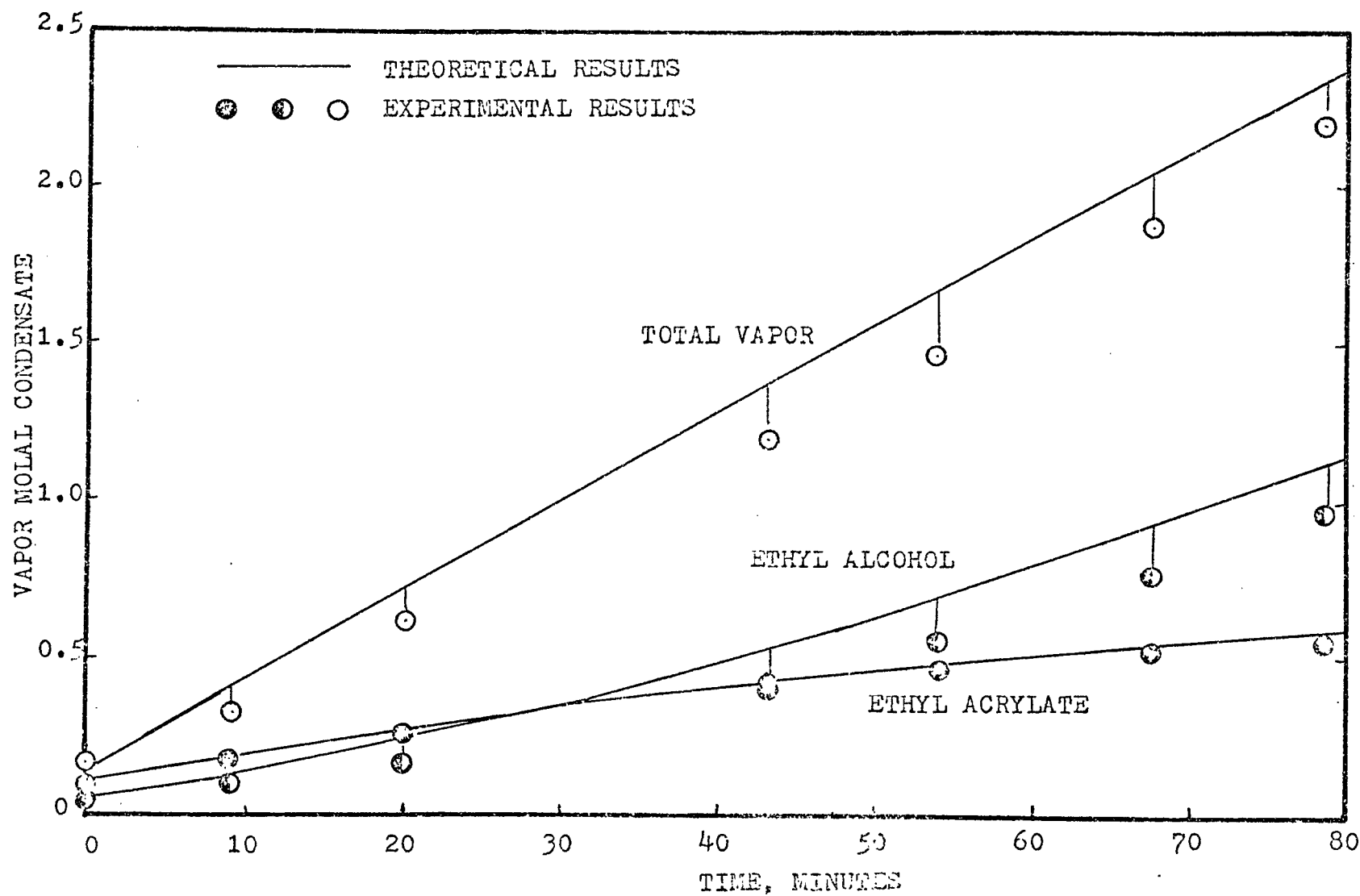


Fig. 7.19 Comparison of Theoretical Model and Experimental Results — Vapor Molal Condensate, Run 3

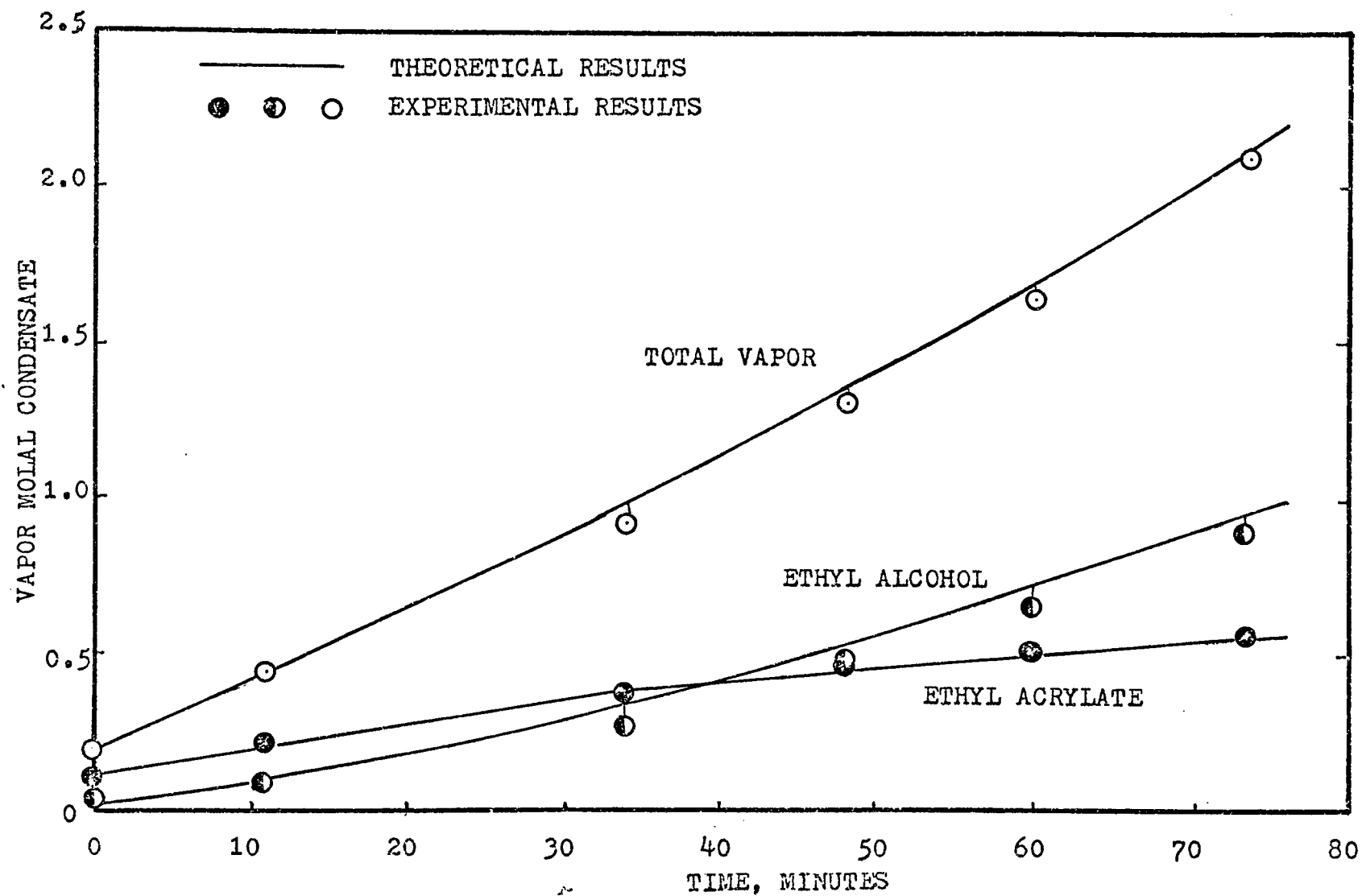


Fig. 7.20 Comparison of Theoretical Model and Experimental Results — Vapor Molal Condensate, Run 4

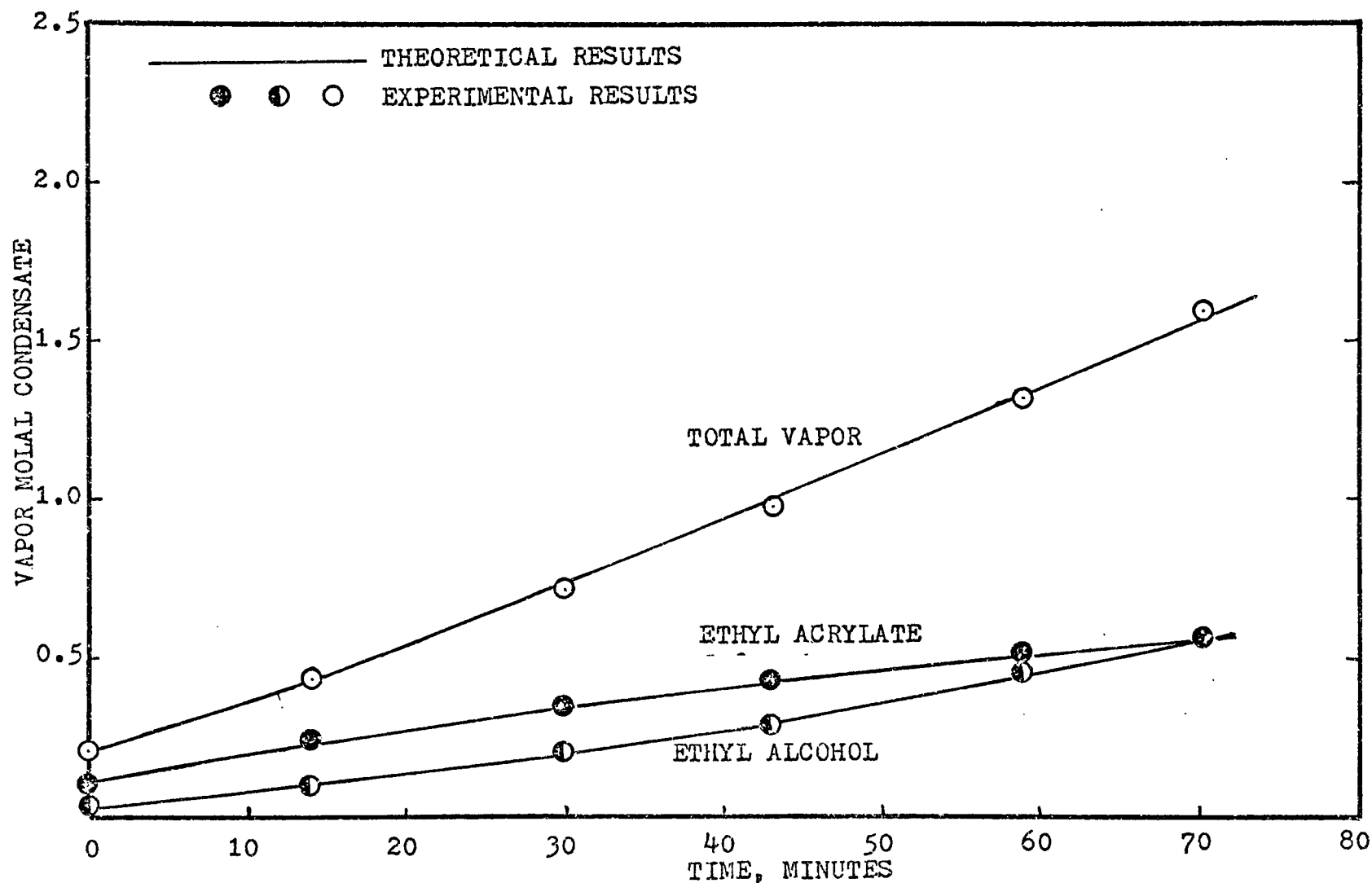


Fig. 7.21 Comparison of Theoretical Model and Experimental Results — Vapor Molal Condensate, Run 5

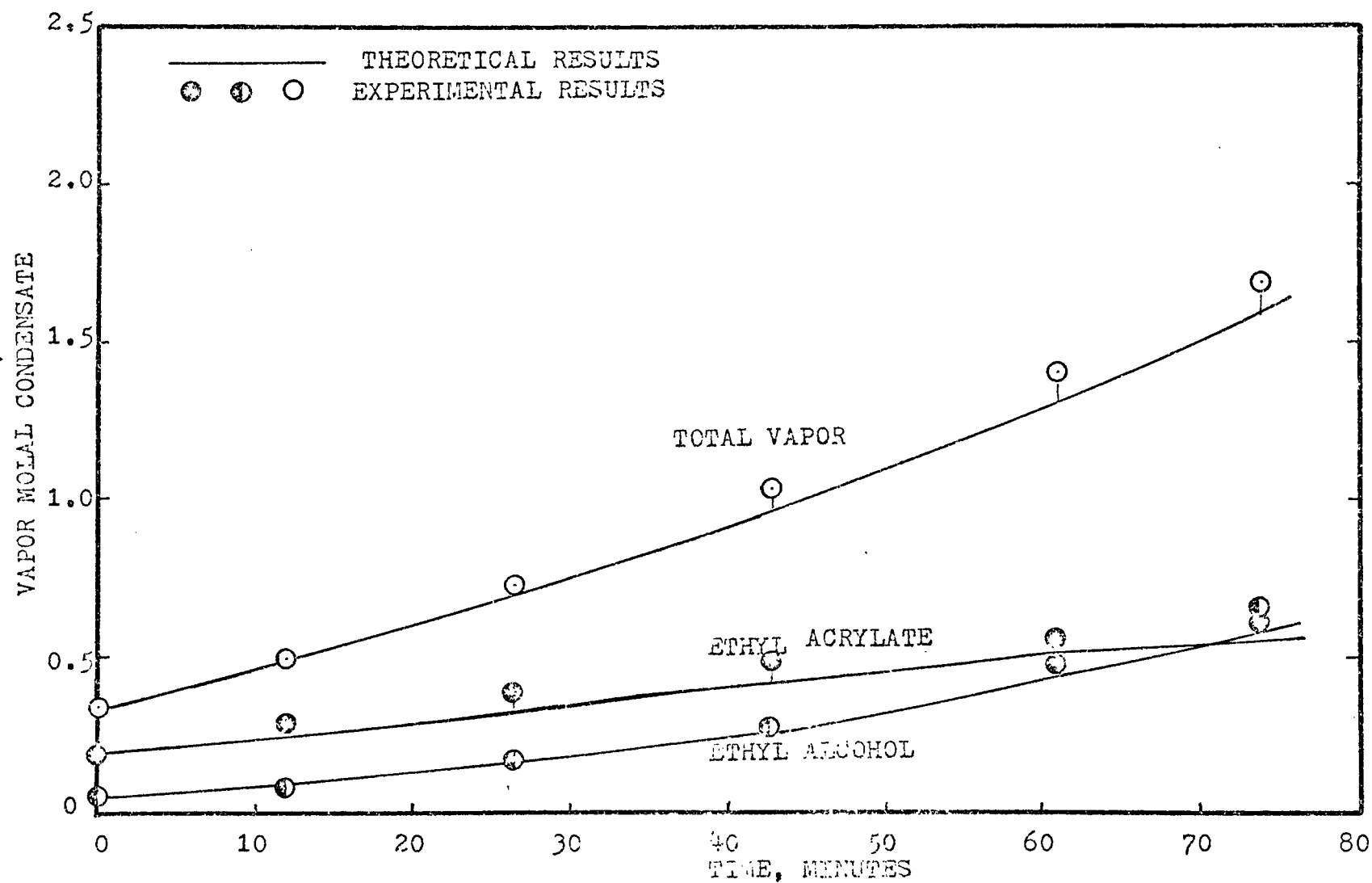


Fig. 7.22 Comparison of Theoretical Model and Experimental Results — Vapor Molal Condensate, Run 6

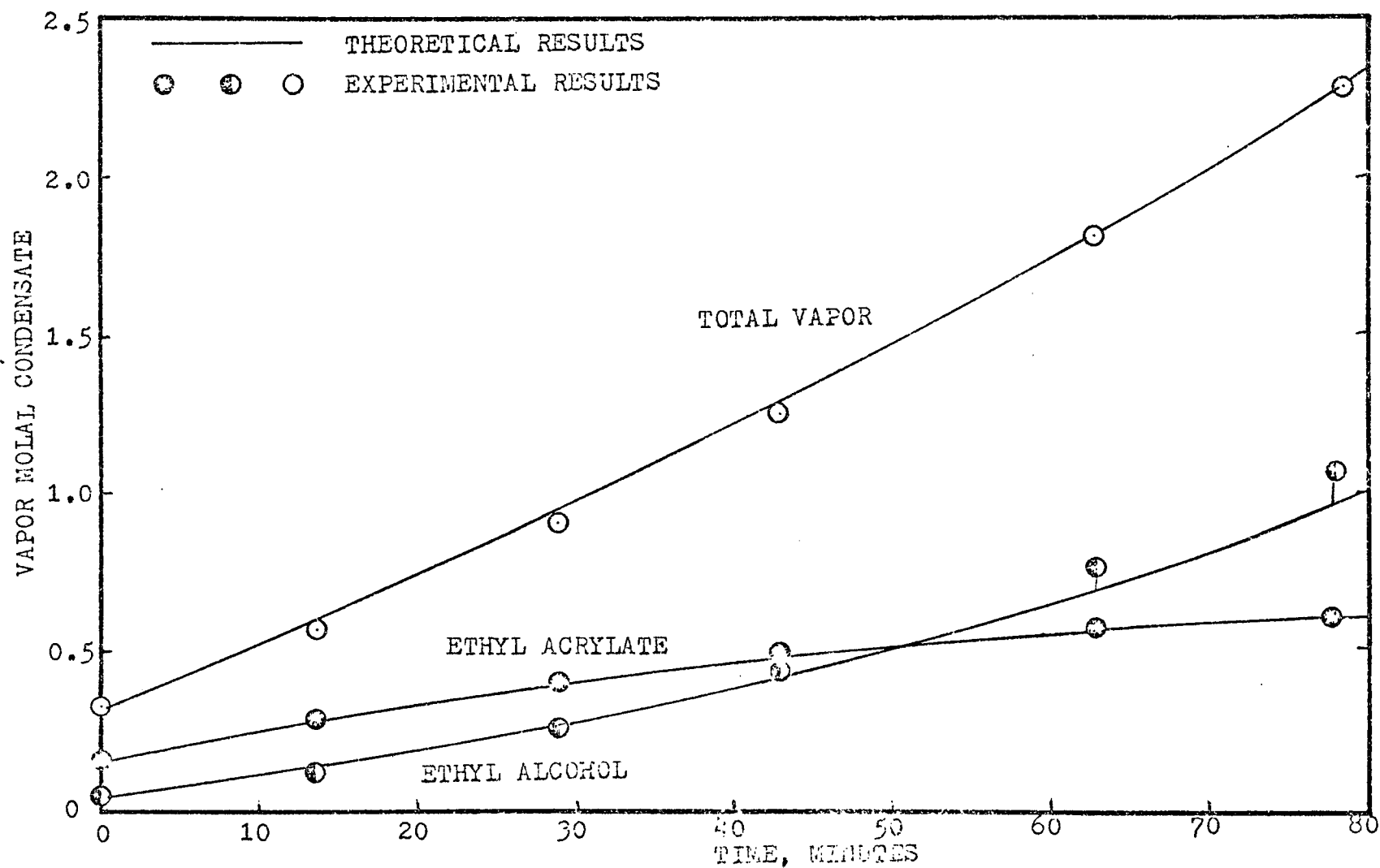


Fig. 7.23 Comparison of Theoretical Model and Experimental Results — Vapor Molal Condensate, Run 7

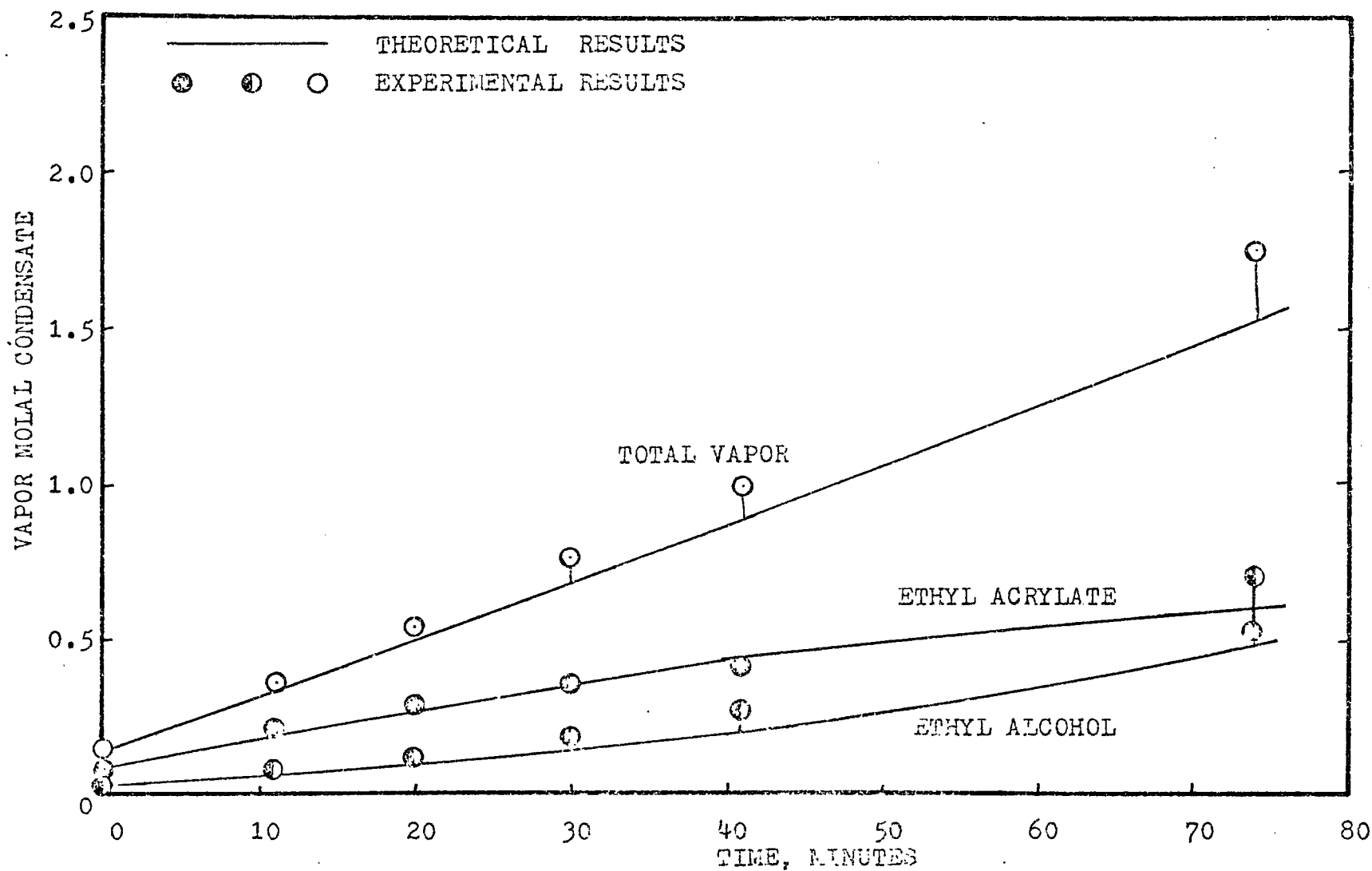


Fig. 7.24 Comparison of Theoretical Model and Experimental Results — Vapor Molal Condensate, Run 8

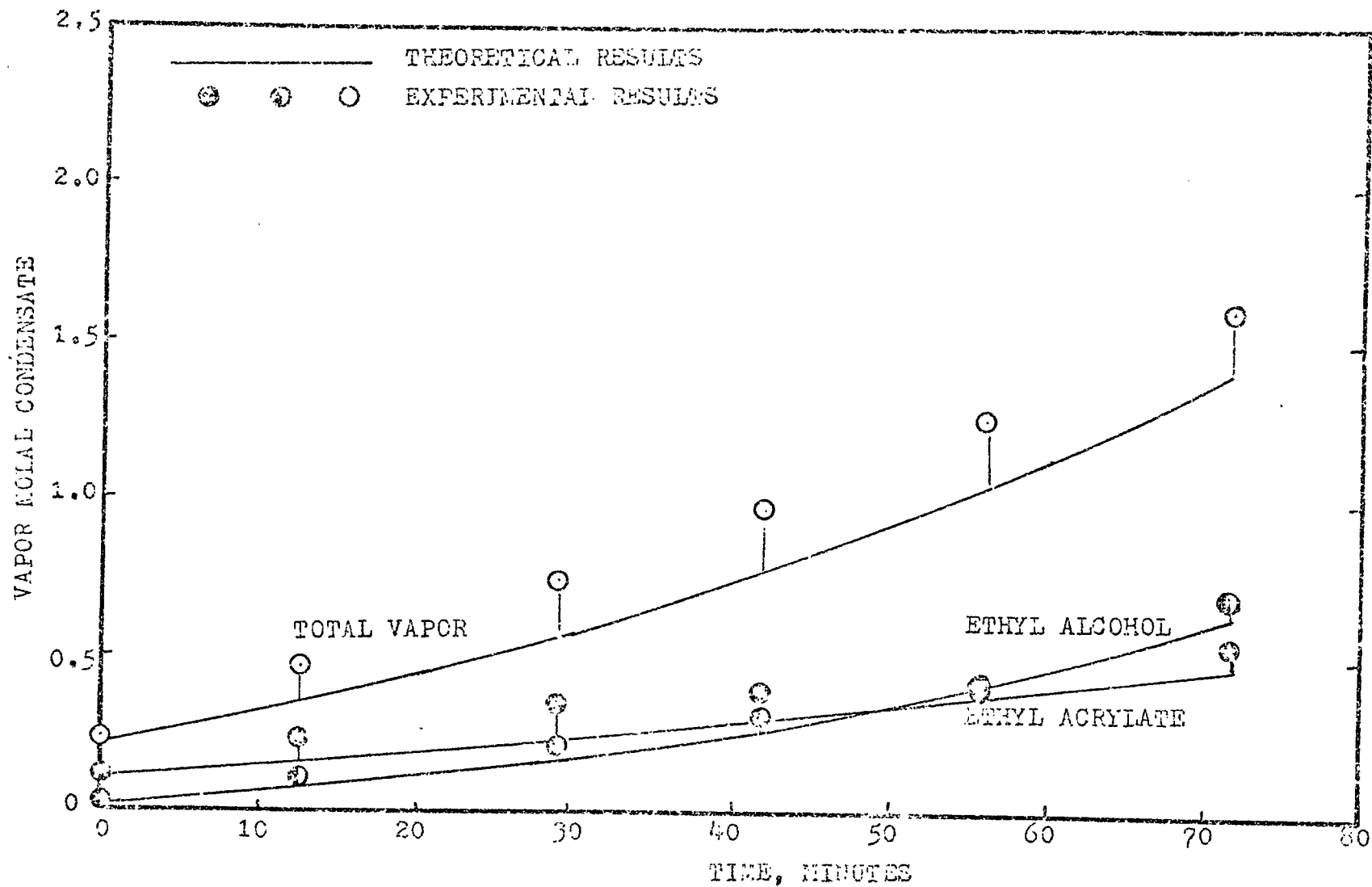


Fig. 7.25 Comparison of Theoretical Model and Experimental Results — Vapor Molal Condensate, Run 9

reactant, acrylamide, for all the nine runs was prepared to be in the range of 1.007 ± 0.021 gram moles. Therefore, the molal quantities shown on these graphs for ethyl acrylate essentially reflect total conversion of the reactant, acrylamide, to the main product, ethyl acrylate.

For ethyl alcohol, an unreacted volatile reactant, the theoretical prediction is also satisfactory except Run 3, where the quantity of the predicted vapor ethyl alcohol is 0.14 moles above the experimental data, 0.96 moles at $t=78.7$ minutes. This is equivalent to the discrepancy of 14.6 %.

The theoretical model also predicts fairly accurately the experimentally measured amount of the total vapor molal condensate. The average deviation is 7.9 % over the 47 data points covered in the nine runs. The maximum deviation occurs in Run 9 with an absolute average error of 19.5 % while the best prediction is seen in Run 5 with an absolute average error of only 1.2 %.

In view of the complexity of the mathematical model and of the reaction system, the agreement between the theoretical and the experimental results is excellent.

7.3.2 Comparison on Liquid Temperature

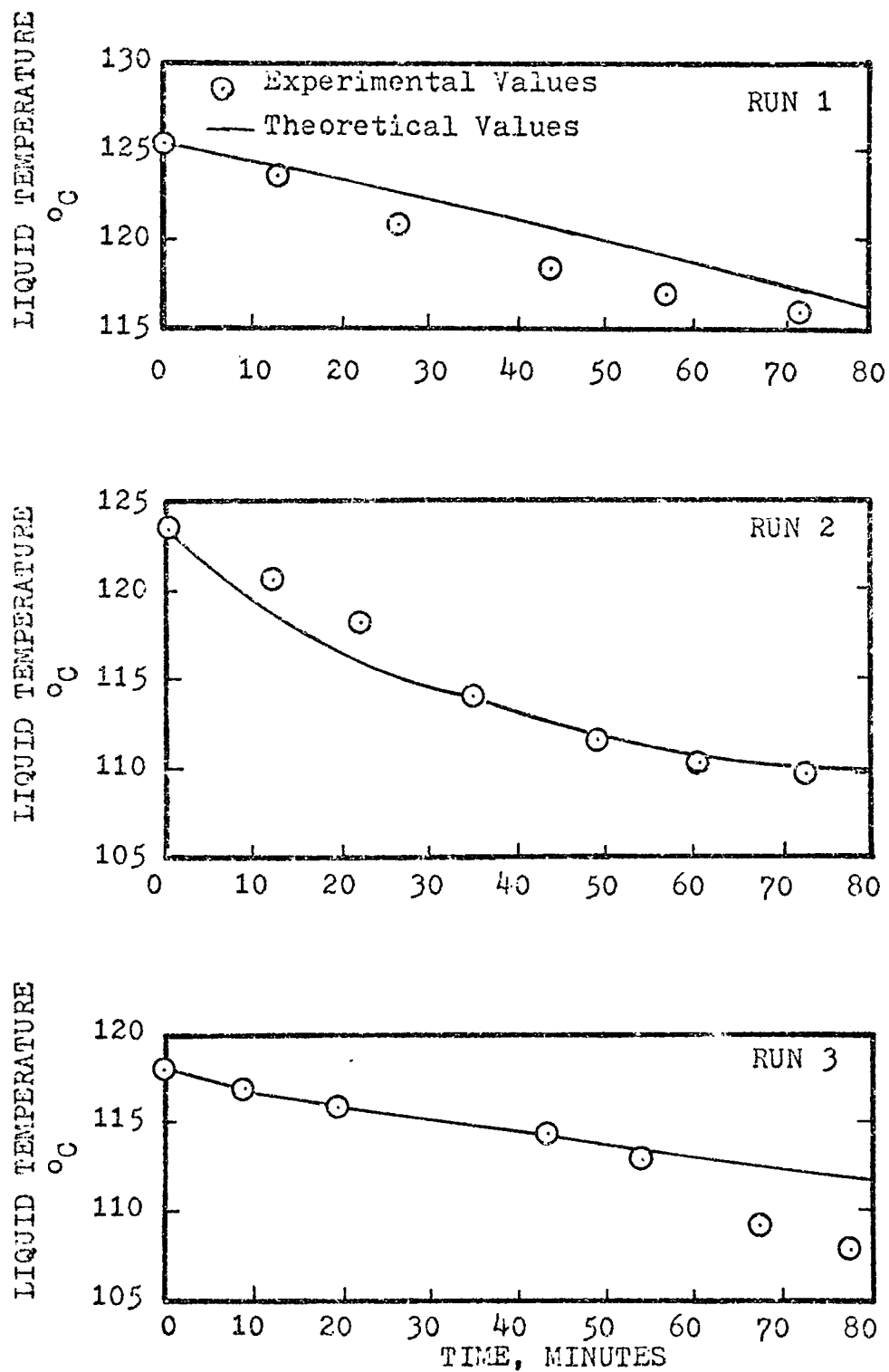


Fig.7.26 Comparison of Liquid temperature,
Run 1 to Run 3

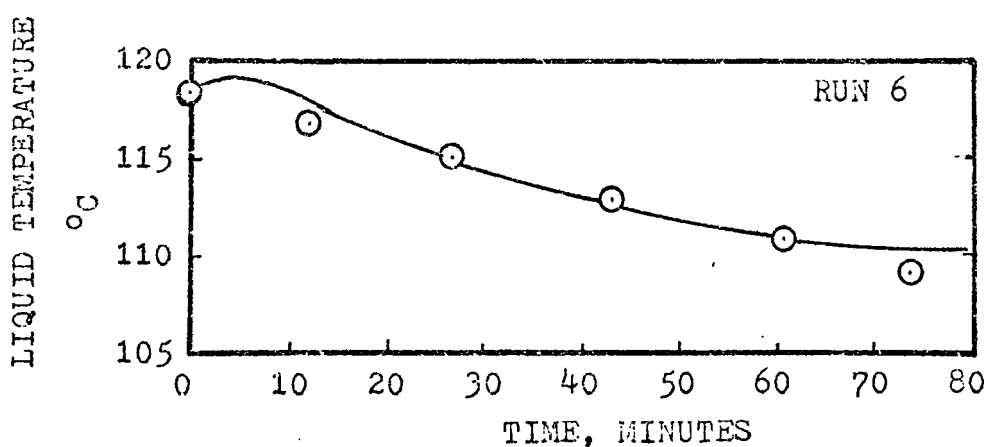
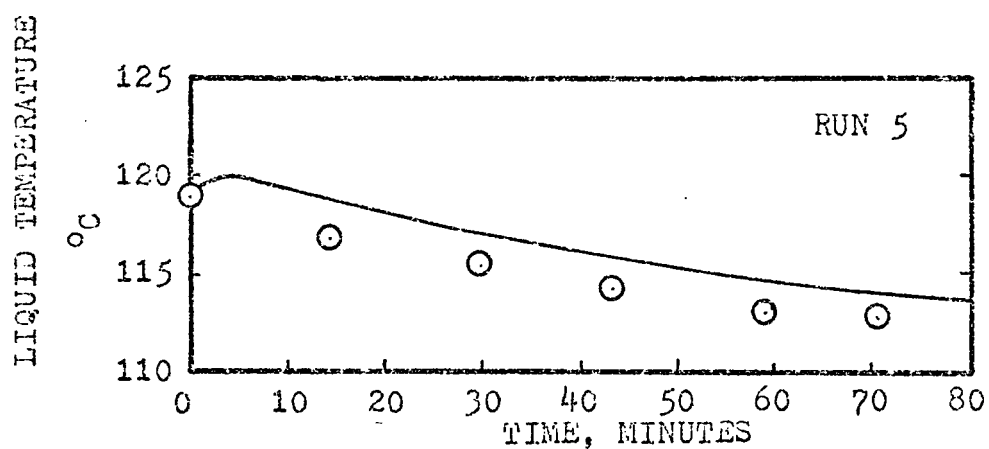
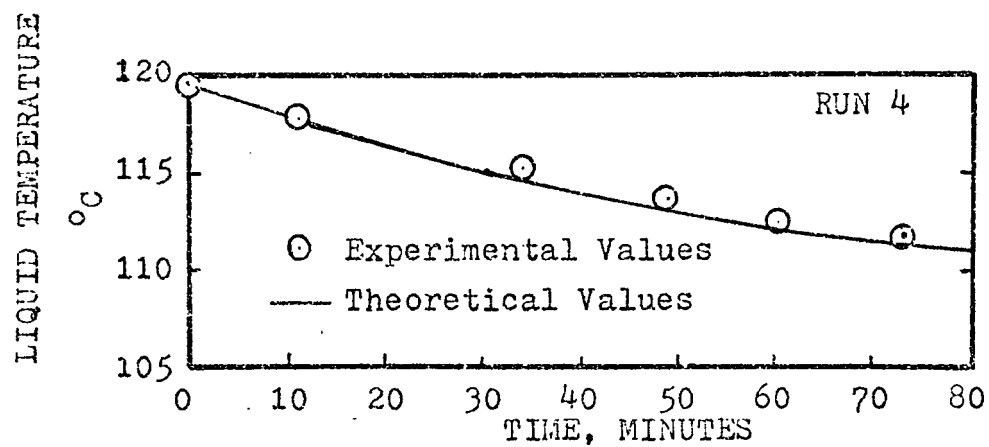


Fig. 7.27 Comparison of Liquid Temperature,
Run 4 to Run 6

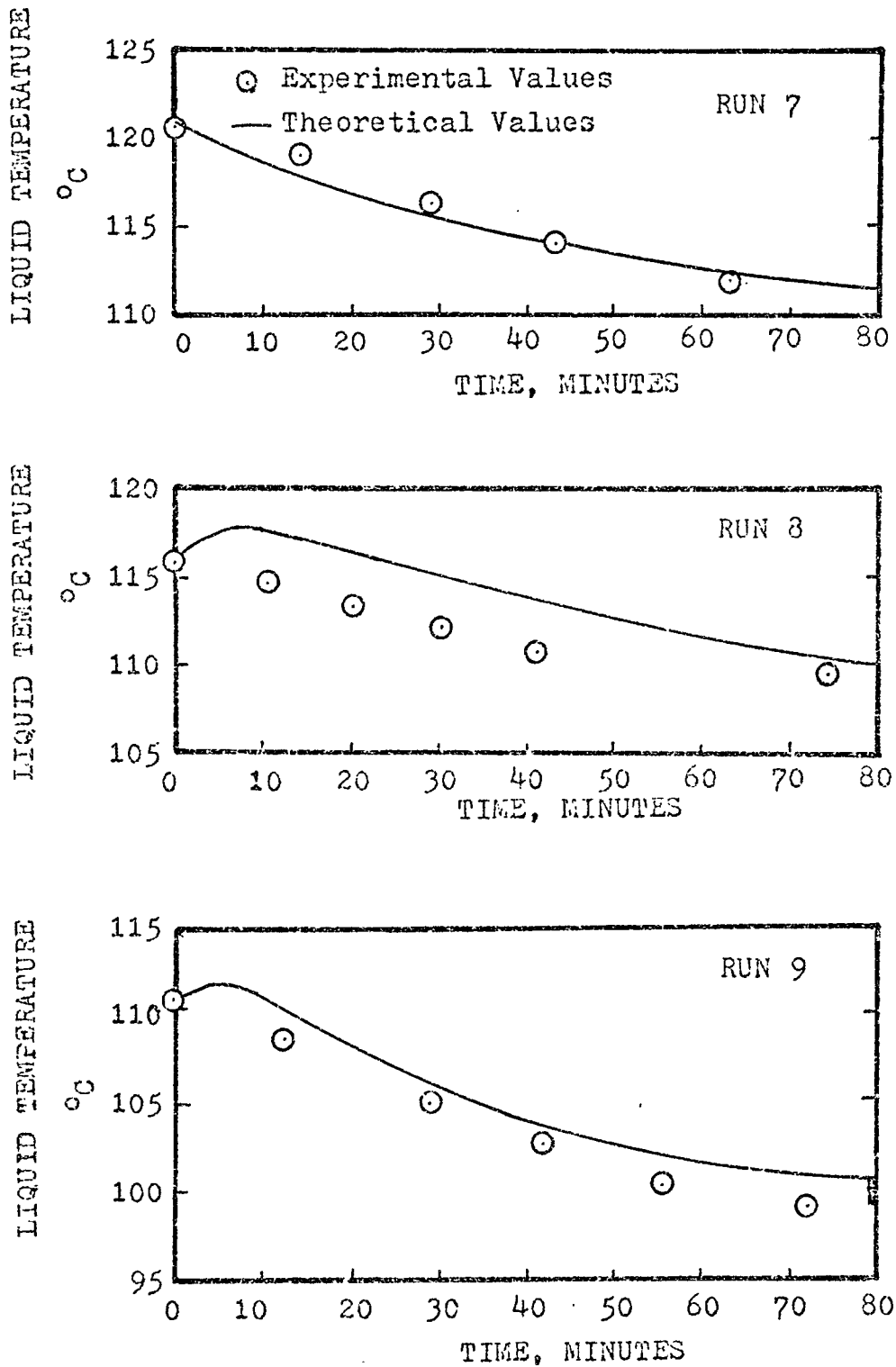


Fig. 7.28 Comparison of Liquid Temperature,
Run 7 to Run 9

The liquid temperature has significant effects on reaction rate and vapor-liquid equilibria, as demonstrated in the correlation work discussed in Chapter 6. Since the description of the physico-chemical system includes several energy terms such as heat of reactions, heat loss, enthalpy of feed stream and enthalpy of leaving vapor, an accurate prediction of the liquid temperature is dependent on the accuracy of the prediction or the measurement of these energy terms.

Comparison between theoretical and experimental liquid temperatures is given in Fig. 7-26 through 7-28 for all the nine runs. Although experimental temperature were measured continuously by a Honeywell 19 recorder, only discrete experimental temperatures at each sampling time are used here for comparison. The agreement for Runs 2, 3, 4, 6 and 7 are very satisfactory. For the other four Runs, 1, 5, 8 and 9, the predicted temperatures are 1 to 3 °C higher than the experimental values. As shown in the figures, once a higher predicted temperature is reached, the temperature profile remains high for a period of time because of consequential contribution from heats of reaction.

Maximum temperatures are predicted by the model for Run 5, 6, 8 and 9. This phenomenon indicates that net

accumulated energy estimated for the early stage of reaction is too high. As demonstrated in Section 7.2, the maximum temperatures can be obtained when the heat of reaction is high, or the overall heat transfer coefficient is small, or the relative ratio of vapor to feed is large.

Since the temperature deviations of 1 to 3 °C give very small errors in predicting the experimental molal quantities of vapor condensate as demonstrated by graphs, Figs. 7.17 - 7.25, these temperature deviations are considered to be insignificant and acceptable.

7.3.3 Comparison on Liquid Mole Fractions

If the agreement in total vapor molal condensate between the theoretical and experimental results of the total vapor condensate is satisfactory, the agreement on total liquid molal quantity should also be satisfactory. This is because the sums of the liquid and vapor quantities should be stoichiometrically constant for each component except of β -ethoxy-ethyl propionate which is presented in trace quantity. The variation of β -ethoxy-ethyl propionate quantity is not significant on the total picture.

The most severe test of the theoretical model is

whether it is able to predict the liquid composition. The comparison of liquid mole fractions of individual components can provide useful informations about distribution of volatile components between vapor and liquid as well as the conversion of reactants.

Since the theoretical model gives the best prediction for Run 7 and the worst prediction for Run 9 as to both the vapor molal condensate and the liquid temperature, the comparisons on the liquid composition will be made for these two runs. Fig. 7.29 presents the comparison of liquid mole fractions for seven liquid components in Run 7. The agreements between the model and the experimental results are excellent for all the seven components. Acrylamide is not shown in the figure because it is assumed to be completely converted into acrylamide sulfate. Another component, diethyl ether was totally vaporized and not detectable in the liquid phase.

Fig. 7.30 is a similar presentation for Run 9, which is considered to be the worst case for matching the experimental and theoretical values of total vapor molal quantity. But it is amazing how well the model predicts the experimental liquid compositions for even Run 9. The agreements between the calculated and the experimental mole fractions of each component in the liquid phase are excellent, except of the ethyl acrylate. This may be

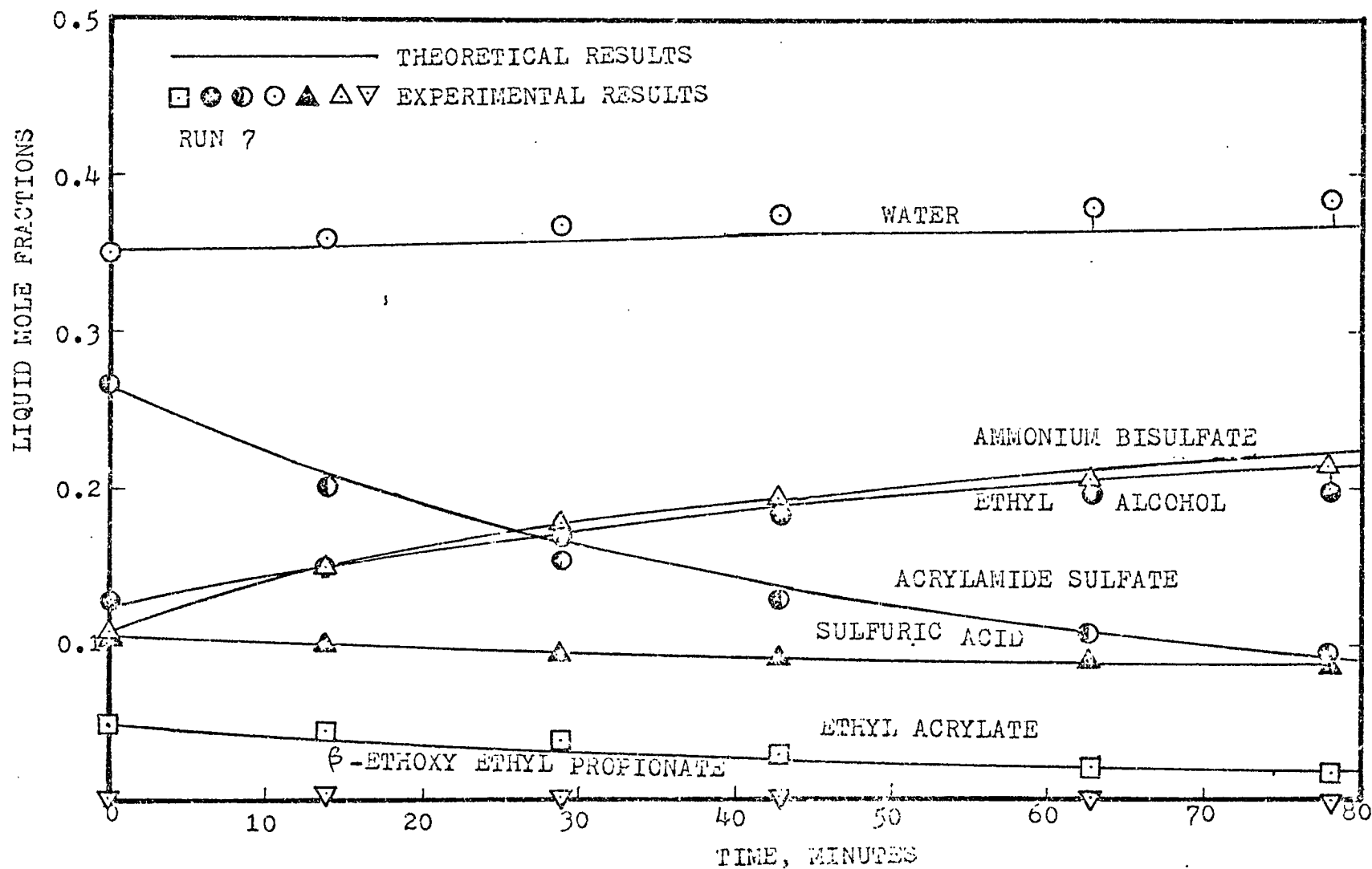


Fig. 7.29 Comparison of Liquid Mole Fractions, Run 7

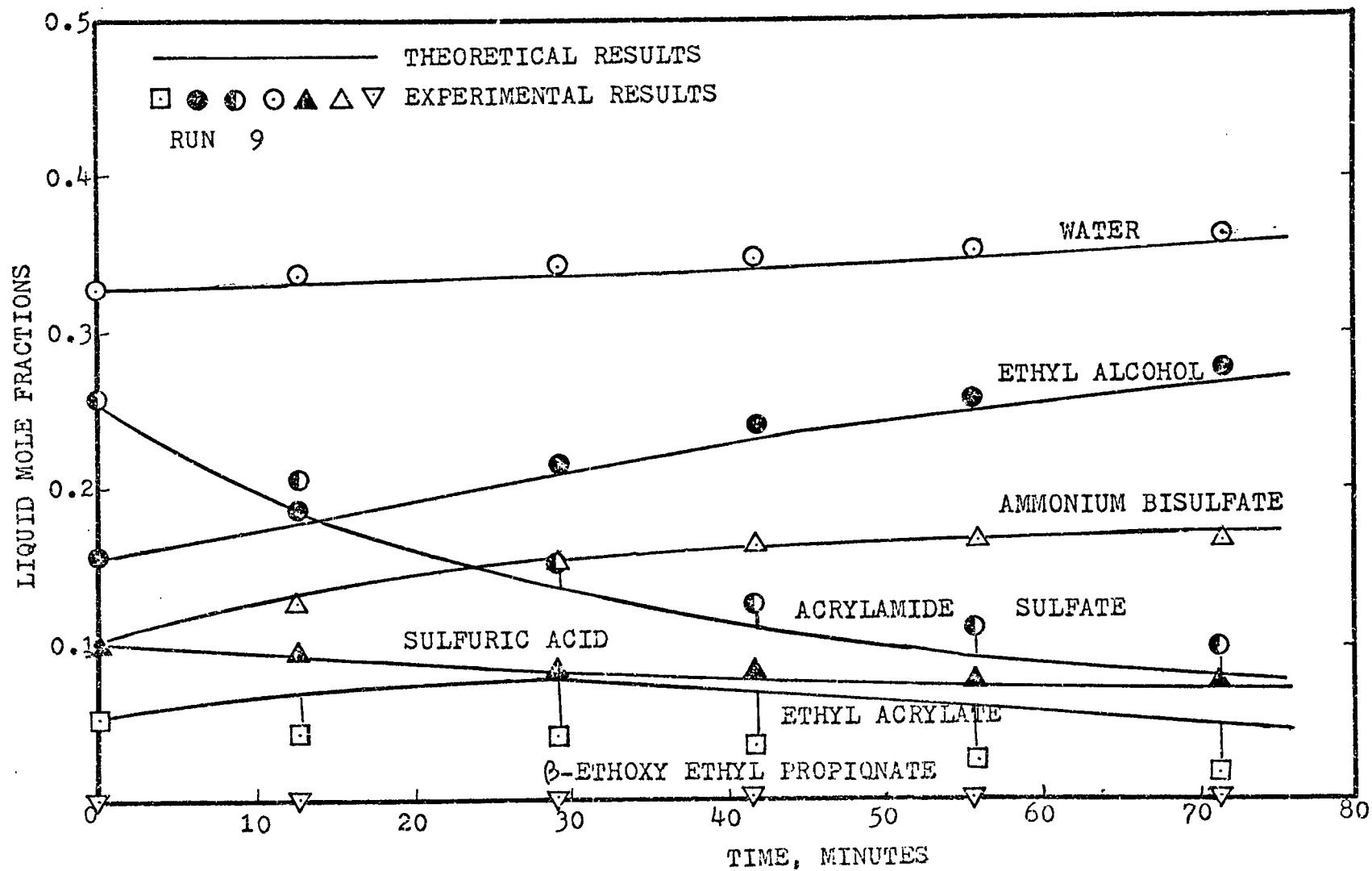


Fig. 7.30 Comparison of Liquid Mole Fractions, Run 9

due to an under estimation of liquid activity coefficient of ethyl acrylate at low temperatures. A better correlation of multicomponent "chemical" vapor-liquid equilibrium data is needed. In fact, until the present study, there was no "chemical" vapor-liquid equilibrium correlation available on the sound thermodynamic basis. The present approach of using the Wilson-type equation, as presented earlier, is the first attempt for such a correlation.

Chapter 8 Conclusions

The following conclusions have been drawn from this study:

1 A general and theoretical model for unsteady state distillation accompanied by chemical reaction is proposed. The model is a general model since it can be reduced to represent all the four basic cases of distillation operation. With substitution of proper limiting values to certain terms of the equations, the proposed general mathematical model yields the theoretical equations for

- (a) Marek Model for Steady-State Distillation with Chemical Reaction
- (b) Holland Model for Unsteady-State Distillation without Chemical Reaction
- (c) Thiele-Geddes Model for Steady State Distillation without Chemical Reaction

2 The model contains 18 simultaneous differential equations. Even for a simpler system of nonisothermal system of unsteady-state distillation without chemical reaction, Holland's numerical solution of such equations requires that at least four values must be initially assumed. However, the numerical solution proposed in

this study requires only one assumed initial value, i.e., the outlet vapor flow rate. The proposed procedure is based on the Runge-Kutta method and the solution converges very rapidly.

3 In order to verify the proposed theoretical model, the experiments were conducted to determine the system responses of a semibatch (therefore unsteady-state) distillation accompanied by chemical reaction. The chemical reactions involved are esterification between acrylamide sulfate and ethyl alcohol to produce ethyl acrylate, and the associated side and competitive reactions. The experimental apparatus and procedures developed were sound because the reproducible results were obtained. It is concluded that the apparatus and the procedures can be readily adopted for other distillation systems with different reactions.

4 The experimental results compare very satisfactorily with the theoretical predictions by the mathematical model. The quantitative predictions of the accumulated total vapor condensate by the model agree with the experimental values, with the average error of 7.9 % for all the nine experimental runs. The maximum deviation was observed for Run 9 which is 19.5 %.

5 The agreement between the experimental and the calculated values for the vapor condensate of ethyl acrylate,

the reaction product, is very satisfactory. So is the similar comparison for ethyl alcohol, one of the major reactants. The excellent agreements imply that not only the mathematical model is theoretically sound but also the correlations for the reaction rates and for the vapor-liquid equilibrium are good.

6 The liquid temperature calculated by the model deviates from the experimental values with an average deviation of 1.2°C for the entire experiments. It is noted that the magnitude of 1.2°C temperature deviation is too small to yield any significant error in predicting the accumulated vapor molal condensates.

7 Another proof of the soundness of the theoretical model is that the calculated liquid compositions of each component agree excellently with the measured values by the chromatograph.

8 The attempt by the Wilson-type equation, which was made to correlate the "chemical" vapor-liquid equilibrium data, is found to be satisfactory. The proposed method is more useful for computer calculations than that employed by Hirata and Komatsu, who correlated "chemical" vapor-liquid equilibrium data by discrete equations.

2 The mass transfer effects on chemical reactions were correlated by the film theory and the Arrhenius-type equation. The activation energy in the Arrhenius equation is found to be uniform for the three reactions involved in the system. The frequency factor is successfully correlated by a general function of the three operating parameters, initial and surrounding temperature, volatil reactant feed rate, and vapor fraction in the total feed. The major advantage of the general function is to express the three operating parameters as separated variables. Therefore, their individual effects on the frequency factor can be evaluated. It is found that the frequency factor is most sensitive to initial and surrounding temperature and least affected by volatile reactant feed rate. If the initial and surrounding temperature is increased from 106 °C to 115 °C, the frequency factor will be reduced by a factor of 2.65. This implies that the reaction occurs mostly in the liquid film due to a high reaction rate at a high temperature. If the vapor fraction in the total feed is reduced from 0.85 to zero, the frequency factor will be increased by a factor of 1.48. This implies that the film reaction is reduced to the minimum by introducing a totally liquid feed stream. The volatile reactant feed rate mostly contributes to increasing the

concentration of the volatile reactant, ethyl alcohol in the liquid holdup. Its effect on the frequency factor is then small.

10 With the above sound general correlations for the "chemical" vapor-liquid equilibrium and the chemical reaction rate expressions, the system characteristics are then investigated by the appropriate parametric studies using the theoretical model. The increase of heat of reaction promotes the product yield as well as the liquid temperature increase. If the system is operated adiabatically, it can reach very rapidly to high liquid temperature of 135°C at which the decomposition of acrylamide sulfate takes place. Since the tendency is particularly apparent if the feed contains a larger fraction of vapor, the proportion of liquid in the feed may be increased to avoid the undesirable decomposition. In a case with a large proportion of vapor in the feed, the liquid temperature is initially high. But as the reaction time progresses, the liquid composition moves toward the higher content of volatile materials, resulting in the lowering of the liquid temperature. The product yield does not increase proportionately with the vapor content in the feed.

11 The effects of chemical reactions on distillation

behavior are very complex. At this time, no simple and general methods are available to predict these effects. Heat of reaction, particular if it is significantly large, certainly affects the distillation. For example, the esterification encountered in the present system has the heat of reaction of -19.2 Kcal/g-mole. The heat released by the reaction is fairly large and directly influences the vapor-liquid equilibrium and thus the distillation performance.

12 A chemical reaction within a given distillation system affects directly its vapor-liquid equilibrium, then, in turn, the distillation performance. More specifically, the value of liquid activity coefficient of the same compound differs depending on whether the system is in physical equilibrium or accompanied by chemical reaction. Thus, it is concluded that a chemical reaction affects distillation behavior mainly by changing the value of liquid activity coefficient or by supplying the latent heat of vaporization.

13 The present model of a single-tray distillation accompanied by chemical reaction can be used in the future as a building block for a more complicated multiple-tray distillation problem. This is recommended as a follow-up to the present study.

NOMENCLATURE

A_i	: Total molal quantities of component i in both vapor and liquid phases
a_i	: Inside heat transfer area
C_b	: Concentration of reactant A in liquid bulk
C_i	: Concentration for component i, g-mole/l
\bar{C}_p	: Average or molal heat capacity
C_p	: Liquid heat capacity at temperature T, cal/g-°C
C_T	: Concentration measured from a overall liquid sample
\mathcal{D}	: Diffusivity of liquid through liquid
E_o	: Activation energy, cal/g-mole
E_{o1}	: Activation energy for the rate constant k_1
E_1^o	: Vaporization tray efficient defined by Holland
F	: Total feed rate
F_i	: Feed rate for component i
f_1^{OL}	: Standard-state fugacity, i.e., fugacity of pure liquid i at temperature T adjusted to the reference pressure, P^r
H_F	: heat of formation
h_F	: Liquid enthalpy for total feed at the exit temperature of the preheater

H_{IN}	: Inlet vapor enthalpy
h_{IN}	: Inlet liquid enthalpy
H_{OUT}	: Outlet vapor enthalpy
h_{OUT}	: Outlet liquid enthalpy
$-\Delta H_{R,j}$: Heat of reaction of reaction j
h_S	: Enthalpy of hold up on the tray (assuming negligible vapor holdup)
K_o	: Frequency factor
K_{o1}	: Frequency factor for the rate constant k_1
K_i	: y_i/x_i =vapor-liquid equilibrium ratios
k_i	: Rate constant for reaction i
$K_{s,i}$: Frequency factor for reaction i and run number s
L_i	: Molal liquid quantity for component i
L_{IN}	: Total liquid inlet molal quantity
L_{OUT}	: Total liquid outlet molal quantity
M	: $\sum_{i=1}^n M_i$ =Total molal holdup on the tray
M_i	: Molal quantity of component i in the liquid hold up
n	: Number of components
n_j	: Number of data points for an experimental run
n_r	: Number of reactions

n_s	: Number of experimental runs
n_T	: Total vapor molal condensate
P	: Product or total pressure
P_i^o	: Saturated vapor pressure of pure liquid i at temperature T
Q	: Heat transfer rate across the wall of the reaction-distillation tray
Q_L	: Net heat transfer rate from the system to the surrounding
R_i	: Net rate of component i generated and/or consumed by reaction
R_j	: Rate of reaction for reaction j
Δt	: Integration step size, or measured time interval
T	: Absolute temperature, $^{\circ}\text{K}$ or liquid temperature in the reaction-distillation tray in $^{\circ}\text{C}$
t	: Temperature in $^{\circ}\text{C}$, or time in minutes
T_o	: Oil bath temperature or initial and surrounding temperature
T_1	: Temperature of glycerine before absorbing ethyl alcohol solution
T_2	: Temperature of glycerine at the end of a measuring period
t_i	: Independent variable
T_m	: Melting point in degree Kelvin
t_n	: Time at the end of n th integration step

- U_i : Overall heat transfer coefficient in terms of inside heat transfer area
 v : Total volume of liquid holdup
 v_a : Aerated water volume
 V_i : Molal vapor quantity for component i
 \bar{V}_i^L : Partial molal volume of i in the solution at temperature T
 V_i^L : Molar liquid volume of pure i at temperature T
 V_{IN} : Total vapor inlet molal quantity
 V_{OUT} : Total vapor outlet molal quantity
 $V_{OUT,z}$: Outlet vapor flow rate at the previous time of the z th integration step
 $V_{z+1}^{(1)}$: Initially assumed V_{OUT} at the elapsed time of the $(z+1)$ th integration step
 W_o : Amount of water in the reaction-distillation tray at the beginning of measurement
 W_c : Amount of water vapor condensate collected at the end of measurement
 x_i : Liquid mole fraction
 y_i : Vapor mole fraction
 $y_i(t_i)$: True solution of a dependent variable
 γ_i : Activity coefficient of component i in the liquid mixture

η	: Mass transfer correction factor on the intrinsic rate expression
δ	: Film thickness
λ	: Heat of vaporization
λ_f	: Heat of fusion at melting point
λ_{H_2O}	: Heat of vaporization of water
γ_i^o	: Fugacity coefficient of component i in the liquid phase
ϕ_i	: Vapor fugacity coefficient of component i in the vapor mixture
ϕ_i^o	: Fugacity coefficient of pure saturated vapor i at temperature T and pressure P_i^o
ψ	: Relative ratio of vapor to total feed
σ	: $(1-\psi)/\mu$
σ^2	: Variance
ϵ	: Volumetric ratio of aerated water to clear water
μ	: Multiplier for the implicit method
ω	: Acentric factor
ρ	: Water density at 100 °C
ρ_i	: Liquid density for component i at the temperature of the reacting liquid mixture
ξ	: T_o , F or ψ

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Appendix A Basic Physical and Chemical Data

As mentioned in Chapter 1, a good quantitative evaluation of the theoretical model can be made only if all the values of system parameters are accurately obtained from existing experimental data, or predicted from reliable correlation methods. In a reaction-distillation system, the system parameters include those for material balance calculations such as vapor-liquid equilibrium ratios and reaction rates, as well as those for energy balance calculations such as liquid and vapor enthalpies, heats of reaction and heat transfer rate across the system boundary.

Since some of these parameters are determined and/or calculated on the bases of more fundamental physical and chemical data, the latters must be very accurate too. The fundamental physical and chemical data used in this study include the following twelve items.

- (1) Normal Boiling Point (NBP)
- (2) Critical Temperature (T_c)
- (3) Critical Pressure (P_c)
- (4) Liquid Density (ρ)
- (5) Vapor Pressure (p^0)
- (6) Acentric Factor (ω)

- (7) Liquid Enthalpy (h)
- (8) Vapor Enthalpy (H)
- (9) Heat of Formation (H_f) .
- (10) Heat of Reaction (ΔH_R)
- (11) Fugacity Coefficient of Pure Liquid (ν^0)
- (12) Fugacity Coefficient of Pure Vapor (ϕ^0)

This Appendix presents and discusses the sources of experimental data for the above physical and chemical properties as well as the methods used for estimating the values if experimental data are not available. The discussions are followed by tables summarizing the final data, both experimental and predicted, for the compounds encountered in the study.

A.1 Normal Boiling Point (NBP)

Estimated NBP

1. β -Ethoxy-ethyl propionate

FORMULA: $C_2H_5OC_2H_4COOC_2H_5$

METHOD: Three methods may be used for estimating the normal boiling point according to the compilation of Gold and Ogle (20). They are the Burnop Rule, the Watson Method, and the Atomic Number correlation. The last one is the best method with an absolute average error of only 3.38 % for 90 organic compounds. However, it can be used only for specific homologous series such as ketones, aldehydes, etc. Since the ester group is not included in this correlation, the next best method, Burnop Rule is then adopted here. The Burnop Rule has an absolute average error of 28.47 % for 255 organic compounds. Any other chemical and physical properties derived from this boiling point must be used with care. Since β -ethoxy-ethyl propionate is trace in the system, any errors induced from this approximation should have little effects on predicting the system behavior. The Burnop Rule states that

$$W = M \log_{10} T_B + 8\sqrt{M} \quad (A-1)$$

where

W = atomic contribution

M = molecular weight

T_B = normal boiling point in $^{\circ}\text{K}$

ESTIMATION DETAILS:

Atom	Atomic Contribution	No. of Atoms	Subtotal Contribution
C	23.2	7	162.4
H	10.9	14	152.6
O	51.0	3	153.0
Total Atomic Contribution			468.0
Double Bond Contribution			16.1

W = Total Contribution 484.1

M = 146.2

Then, solve Equation (A-1) for T_B

$$484.1 = 146.2 \log_{10} T_B + 8\sqrt{146.2}$$

$$T_B = 446.2 \text{ } ^{\circ}\text{K} = 173.0 \text{ } ^{\circ}\text{C}$$

2. Acrylamide

FORMULA : $\text{CH}_2\text{CHCOONH}_2$

METHOD : The molten acrylamide (M.P. $84.5 \text{ } ^{\circ}\text{C}$) poly-

merizes vigorously and exothermally before it reaches the normal boiling point. However it becomes very stable when it forms a molecular complex, acrylamide sulfate, with sulfuric acid at a temperature well above its melting point. Therefore, many thermophysical properties of acrylamide and acrylamide sulfate are estimated on an assumption that they have same thermophysical properties of compounds with similar molecular structure. The following comparison method is then used for estimating the normal boiling point of acrylamide.

ESTIMATION DETAILS:

Comparison of Amide Group

Compound	Formula	NBP, °C	Ref.
Ethyl amide	CH_3CONH_2	222	(52)
Butyl amide	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CONH}_2$	216	(52)
$\text{Propyl amide } (\text{CH}_3\text{CH}_2\text{CONH}_2) \approx \frac{222 + 216}{2} = 219^\circ\text{C}$			

Comparison between Double Bond and Single Bond

Ethyl Propionate	$\text{CH}_3\text{CH}_2\text{COOC}_2\text{H}_5$	99.1 °C
Ethyl Acrylate	$\text{CH}_2\text{CHCOOC}_2\text{H}_5$	100.1 °C
Double Bond Contribution		+1.0 °C

pseuo-NBP of acrylamide $\cong 219 + 1 = 220$ °C

The experimental and the calculated values of NBP for the compounds are summarized in Table A.1.

Table A.1 Normal Boiling Points

<u>No.</u>	<u>Component</u>	<u>NBP, °C</u>	<u>Ref.</u>
1	Ethyl Alcohol	78.4	(52)
2	Ethyl Acrylate	100.1	(17)
3	Water	100.0	(52)
4	Diethyl Ether	34.6	(52)
5	β -Ethoxy-ethyl Propionate	173	(Est.).
6	Acrylamide Sulfate	Not in use	-
7	Sulfuric Acid	340.0	(52)
8	Ammonium Bisulfate	490.0	(52)
9	Acrylamide	220	(Est.)

A.2 Critical Temperature (T_c)Estimated T_c 1. β -Ethoxy-ethyl propionateFORMULA : $C_2H_5OC_2H_4COOC_2H_5$

METHOD : The Lydersen method is generally recommended for estimating critical temperatures of organic compounds (18, 52). The absolute average error by the method is 5.14 % on the basis of 216 organic compounds. This method is adopted here. The Lydersen method (43) states that

$$T_c = T_B / \theta \quad (A-2)$$

and

$$\theta = 0.567 + \sum \Delta t - (\sum \Delta t)^2 \quad (A-3)$$

where

 Δt = group contribution

ESTIMATION DETAILS :

Atomic Group	Group Contribution, Δt	No. of Group	Subtotal Contribution
$-CH_2$	0.02	4	0.08
$-CH_3$	0.02	2	0.04
$-O-$	0.021	1	0.021

-COO-	0.047	1	<u>0.047</u>
			0.188

$$\theta = 0.567 + 0.188 - (0.188)^2 = 0.7197$$

$$T_c = 446.2/0.7197 = 620.0 \text{ K} = 346.8 \text{ }^\circ\text{C}$$

2. Acrylamide

FORMULA : $\text{CH}_2\text{CHCOONH}_2$

METHOD : The Lydersen method is also adopted here.

ESTIMATION DETAILS:

Atomic Group	Group Contribution, Δt	No. of Groups	Subtotal Contribution
$\text{CH}_2=$	0.018	1	0.018
$=\text{CH}-$	0.0	1	0.0
$-\text{C}=\text{O}$	0.040	1	0.04
$-\text{NH}_2$	0.031	1	<u>0.031</u>
			0.089

$$\theta = 0.567 + 0.039 - (0.089)^2 = 0.648$$

$$T_c = (220 + 273.2)/0.648 = 760.8 \text{ }^\circ\text{K} = 487.6 \text{ }^\circ\text{C}$$

Table A.2 Critical Temperature

<u>No.</u>	<u>Compound</u>	<u>T_c, °C</u>	<u>Ref.</u>
1	Ethanol	243.1	(15)
2	Ethyl Acrylate	288.0	(17)
3	Water	374.1	(49)
4	Diethyl Ethyl	193.8	(16)
5	β -Ethoxy-Ethyl Propionate	346.8	(Est.)
9	Acrylamide	487.6	(Est.)

A.3 Critical Pressure (P_c)Estimated P_c 1. β -Ethoxy-ethyl PropionateFORMULA : $C_2H_5OC_2H_4COOC_2H_5$

METHOD : The Lydersen method is also recommended for estimating critical pressures of organic compounds(52). It has an absolute average error of 3.7 % for 182 compounds. The working equation is given as follows (44)

$$P_c = \frac{M}{(0.34 + \Delta p)^2} \quad (A-4)$$

where

M = molecular weight

 Δp = atomic group contribution

ESTIMATION DETAILS :

Atomic Group	Group Contribution, Δp	NO. of Groups	Subtotal Contribution
$-CH_2, -CH_3$	0.227	6	1.362
$-COO-$	0.47	1	0.470
$-O-$	0.16	1	<u>0.16</u>
			1.992

$$P_c = \frac{146}{(0.34 + 1.992)^2} = 26.9 \text{ atm.}$$

2. AcrylamideFORMULA : $\text{CH}_2\text{CHCOONH}_2$

METHOD : The Lydersen method given by Equation (A-4)
is also used.

ESTIMATION DETAILS

Atomic Group	Group Contribution	No. of Groups	Subtotal Contribution
$\text{CH}_2=$	0.198	1	0.198
$=\text{CH}-$	0.198	1	0.198
$-\text{C}=\text{O}$	0.290	1	0.290
$-\text{NH}_2$	0.095	1	0.095
			<hr/> 0.781

$$P_c = \frac{71.08}{(0.34 + 0.781)^2} = 56.6 \text{ atm.}$$

Table A.3 Critical Pressures

No.	Component	P_c , Atm	Ref.
1	Ethyl Alcohol	62.9	(15)
2	Ethyl Acrylate	36.3	(17)
3	Water	218.2	(49)
4	Diethyl Ether	35.5	(16)
5	β -Ethoxy-ethyl	26.9	(Est.)
9	Acrylamide	56.6	(Est.)

A.4 Liquid Density (ρ) :Estimated ρ 1. β -Ethoxy-ethyl PropionateFORMULA : $C_2H_5OC_2H_4COOC_2H_5$

METHOD : There are ten methods available for estimating liquid density (19). The first Guggenheim method is considered to be the most suitable for the compounds dealt in this system considering both accuracy and availability of the basic data required. The working equation can be represented by

$$\rho_r = 1 + 1.75(1 - T_r)^{1/3} + 0.75(1 - T_r) \quad (A-5)$$

where

T_r = reduced temperature

$\rho_r = \rho V_c =$ reduced density

V_c = critical volume

The critical volume is estimated by the Lyderson method as shown below.

Atomic Group	Group Contribution, ΔV	No. of Groups	Subtotal Contributions
$-\text{CH}_2, -\text{CH}_3$	55	6	330
$-\text{COO}-$	80	1	80
$-\text{O}-$	20	1	20
			<hr/> 430

$$V_c = \Sigma (\Delta V) = 430 \text{ c.c./g-mole} = 2.94 \text{ c.c./g.}$$

$$\rho_c = 1/V_c = 0.34 \text{ g/c.c.}$$

The critical temperature T_c can be obtained from Appendix A. 2. Then for any given temperature a corresponding liquid density can be calculated by Equation (A-5).

2. Acrylamide

FORMULA : $\text{CH}_2\text{CHCONH}_2$

METHOD : The First Guggenheim method, or Equation (A-5), is used. The required critical volume of acrylamide is estimated as follows.

Atomic Group	Group Contribution,	No. of Groups	Subtotal contribution
$\text{CH}_2=, \text{CH}=$	45	2	90
C=O	60	1	60
$-\text{NH}_2$	28	1	28
			<hr/> 178

$$V_c = 178 \text{ c.c./g-mole} = 2.505 \text{ c.c./g.}$$

$$\rho_c = 0.399 \text{ g/c.c.}$$

3. Acrylamide Sulfate

FORMULA : $\text{CH}_2\text{CHC}(\text{OH})\text{NH}_2\text{HSO}_4$

METHOD : Assume that the liquid molar volume of this molecular complex is approximately equal to the sum of the liquid molar volumes of its two pure constituents. Then

$$\frac{1}{\bar{\rho}_6} \cong \frac{1}{\bar{\rho}_6} + \frac{1}{\bar{\rho}_7} \quad (\text{A-5})$$

where

$\bar{\rho}_i$ = liquid molar density for component i

$1/\bar{\rho}$ = liquid molar volume

4. Ammonium Bisulfate

FORMULA : NH_4HSO_4

METHOD : Ammonium bisulfate is a dissolved solid in the liquid solution. Its molar volume may be assumed equal to the average molar volume of ammonium sulfate, $(\text{NH}_4)_2\text{SO}_4$, and sulfuric acid, H_2SO_4 . Then,

$$\frac{1}{\bar{\rho}_8} = \left[\frac{1}{\bar{\rho}_{(\text{NH}_4)_2\text{SO}_4}} + \frac{1}{\bar{\rho}_7} \right] / 2$$

At a low operating pressure, liquid density is only a function of temperature. The densities obtained from either the literature or Equation (A-5) are then fitted as a function of temperature according to the following polynomial equation.

$$\rho_i = a_{i,1} + a_{i,2}T + a_{i,3}T^2 \quad (\text{A-6})$$

The program POLYFIT given in Appendix C.6 can be used for data regression to obtain the coefficients of Equation (A-6). These determined coefficients for the nine components in this system are summarized in TABLE A.4.

Table A.4 Liquid Densities

$$\rho_i = a_{i,1} + a_{i,2}T + a_{i,3}T^2$$

where

ρ = liquid density, g/ml

T = temperature, °C

i	Compound	$a_{i,1}$	$a_{i,2} \times 10^3$	$a_{i,3} \times 10^5$	Data Sources
1	Ethyl Alcohol	0.79800	-0.75060	-0.16369	(15)
2	Ethyl Acrylate	0.93971	-0.94345	-0.16369	(17)
3	Water	0.10067	-0.25200	-0.22973	(52)
4	Diethyl Ether	0.73271	-0.88333	-0.32738	(16)
5	β -Ethoxy-ethyl Propionate	0.97266	-0.87446	-0.014881	(Est.)
6	Acrylamide Sulfate	1.4734	-0.95768	+0.0031945	(Est.)
7	Sulfuric Acid	1.8511	-0.99000	-	(52)
8	Ammonium Bisulfate	1.8141	-2.7500	-	(Est.)
9	Acrylamide	1.1452	-0.76236	-0.38601	(Est.)

A.5 Vapor Pressure (p^0)Estimated p^0 1. β -Ethoxy-ethyl PropionateFORMULA : $C_2H_5OC_2H_4COOC_2H_5$

METHOD : The Riedel correlation is a suitable method among the "reduced" correlations (24) for estimating vapor pressure, considering both accuracy and availability of correlating parameters. There are four different forms of the Riedel Correlation. The third form is most suitable for the compound being studied and thus presented here as follows.

$$\log_{10} p_r^0 = -\Phi(T_r) - (\alpha_c - 7) \psi(T_r) \quad (A-7)$$

$$\Phi(T_r) = 0.118 \phi(T_r) - 7 \log T_r \quad (A-8)$$

$$\psi(T_r) = 0.0364 \phi(T_r) - \log T_r \quad (A-9)$$

$$\phi(T_r) = 36/T_r + 42 \log T_r - 35 - T_r^6 \quad (A-10)$$

$$\alpha_c = 0.9076 \left[1 + \frac{T_{B,r} \ln P_c}{1 - T_{B,r}} \right] \quad (A-11)$$

where

$$p_r^0 = p^0/p_c$$

p° = vapor pressure

$$T_r = T/T_c$$

The required critical temperature (T_c) and critical pressure (p_c) are obtained in the previous sections.

The vapor pressure data obtained from either the literature or the above Riedel method can be correlated by the following Antoine equation

$$\log_{10} p^{\circ} = A - \frac{C}{B + T} \quad (A-12)$$

where

p° = vapor pressure, mm H_g

T = temperature, °C

A, B, C = Antoine constants

The Antoine constants for the five volatile components in the system are obtained and given in Table A.5.

Table A.5 Antoine Constants for Vapor Pressure

No.	Component	A	B	C	Ref.
1	Ethanol	8.1629	1623.2	228.98	(26)
2	Ethyl Acrylate	6.9773	1283.1	212.19	(17)
3	Water	7.96681	1668.2	228.0	(26)
4	Diethyl Ether	6.89227	1051.3	227.43	(26)
5	β-Ethoxy-ethyl Propionate	8.3190	2691.9	313.38	(Est.)

A.6 Acentric Factor (ω):

The acentric factor is defined as

$$\omega = -1 - (\log P_r)_{T_r = 0.7} \quad (\text{A-13})$$

It is a factor to account for the degree of departure of a real fluid from a simple fluid. It is used in this study for estimating fugacity coefficient of a pure vapor by the Prausnitz general correlation (53). The acentric factors of ethyl alcohol, water and diethyl ether are given by the Prausnitz compilation (53) while those of ethyl acrylate and β -ethoxy-ethyl propionate can be calculated from Equation (A-13) utilizing the vapor pressure data estimated in Section A.5. Table A.6 is a list of the acentric factors for the five volatile components.

Table A.6 Acentric Factor

No.	Component	Acentric Factor	Ref.
1	Ethanol	0.637	(53)
2	Ethyl Acrylate	0.329	(Est.)
3	Water	0.344	(53)
4	Diethyl Ether	0.283	(53)
5	β -Ethoxy-ethyl Propionate	0.557	(Est.)

A.7 Liquid Enthalpy (h)

Liquid enthalpy is only dependent on temperature at low pressure and can be calculated from liquid heat capacity by

$$h = \int_{T_d}^T C_p dT \quad (A-14)$$

where

C_p = liquid heat capacity

T_d = datum temperature

h = liquid enthalpy

If liquid heat capacity is expressed by a polynomial equation,

$$C_p = a_1 + a_2 T + a_3 T^2 \quad (A-15)$$

and the datum temperature is chosen as 0°C, the liquid enthalpy can be obtained readily by integration of Equation (A-14):

$$h = a_1 T + a_2 T^2/2 + a_3 T^3/3 \quad (A-16)$$

Therefore, only liquid heat capacities are required for obtaining liquid enthalpies. The liquid heat capacities are estimated for the compounds for which measured data are not available.

Estimated Liquid Heat Capacity, C_p

1. β -Ethoxy-ethyl propionate

FORMULA: $C_2H_5OC_2H_4COOC_2H_5$

METHOD: The heat capacities of organic liquids at 20 °C may be simply evaluated with relatively good accuracy (5 and 16 per cent average and maximum errors) with the additive-contribution method of Johnson and Huang (39). The working equations can be expressed by

$$\bar{C}_{p,20^{\circ}C} = \Sigma \text{Atomic Group Contributions} \quad (k-17)$$

where

$$\bar{C}_{p,20^{\circ}C} = \text{molar heat capacity at } 20^{\circ}C$$

Heat capacities calculated in this manner at 20 °C may be used to calculate the constant b of the following Chow and Bright general correlation; (10, 23)

$$\bar{C}_p \omega^{2.8} = bM$$

Once the constant b is determined, the equation can be used for calculating a heat capacity at any temperature. Since the system is operated at atmospheric pressure and the reduced temperature encountered in this study is less than 0.65, the following Watson expansion factor is used (52)

$$\omega = 0.1745 - 0.0838 T_r$$

The following working equation is obtained by combining the above two equations.

$$\bar{C}_p (0.1745 - 0.0838 T_r)^{2.8} = bM \quad (A-18)$$

ESTIMATION DETAILS :

For \bar{C}_p , 20 °C

Atomic Group	Group Contribution	No. of Group	Subtotal Contribution
CH ₃	9.9	2	19.8
-CH ₂	6.3	4	25.2
-COO-	14.5	1	14.5
-O-	8.4	1	8.4
			<hr/> 67.9

$$\bar{C}_p, 20^\circ\text{C} = 67.9 \text{ Cal/g-mole-}^\circ\text{C} \quad (\text{Molal Basis})$$

$$\text{Molecular Weight} = 146.2$$

$$C_p, 20^\circ\text{C} = \frac{67.9}{146.2} = 0.464 \text{ Cal/g-}^\circ\text{C} \quad (\text{Mass Basis})$$

Determination of b using $C_p, 20^\circ\text{C}$

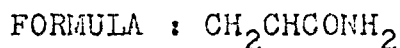
$$0.464 (0.1745 - 0.0838 \times \frac{20 + 273.2}{346.8 + 273.2})^{2.8} = b$$

$$b = 0.007893$$

For C_p at Other Temperatures

$$C_p = 126.69(0.1745 - 0.0838 T_r)^{2.8}$$

2. Acrylamide



METHOD :The Johnson-Huang method given by Equation (A-17) and the Watson expansion factor method given by Equation (A-18) are also adopted here.

ESTIMATION DETAILS :

For \bar{C}_p , 20 °C

Atomic Group	Group contribution	No. of Groups	Subtotal Contribution
CH ₂ =	6.3	1	6.3
=CH-	5.4	1	5.4
C=O	14.7	1	14.7
-NH ₂	15.2	1	15.2
			$\bar{C}_p = 41.6$

Molecular Weight = 71.06

$$C_{p, 20\text{ °C}} = \frac{41.6}{71.06} = 0.5854 \text{ Cal/g-°C}$$

For C_p at Other Temperature

$$0.5854 \left(0.1745 - 0.0838 \times \frac{20 + 273.2}{487.6 + 273.2} \right)^{2.8} = b$$

$$b = 0.007253$$

$$C_p = 137.88 \left(0.1745 - 0.00838 T_r \right)^{2.8}$$

3. Acrylamide Sulfate :

FORMULA : CH₂CHC(OH)NH₂HSO₄

METHOD: The enthalpy of acrylamide sulfate is equal to the sum of the enthalpies of its two constituent compounds, acrylamide and sulfuric according to the assumption made in Chapter 7. Its molal heat capacity can then be readily determined, by definition, from the following equation.

$$\bar{c}_{p,6} = \left(\frac{M_7}{M_6} \bar{c}_{p,7} + \frac{M_9}{M_6} \bar{c}_{p,9} \right) \quad (\text{A-19})$$

where M stands for molecular weight.

4. Ammonium Bisulfate

FORMULA: NH_4HSO_4

METHOD: The method used for acrylamide sulfate as stated above is also used here. Accordingly, the heat capacity of ammonium bisulfate can be expressed in terms of those of sulfuric acid and ammonium sulfate as follows.

$$\bar{c}_{p,8} = \frac{1}{2} \left[\frac{M_7}{M_8} \bar{c}_{p,7} + \frac{M_{(\text{NH}_4)_2\text{SO}_4}}{M_8} \bar{c}_{p,(\text{NH}_4)_2\text{SO}_4} \right] \quad (\text{A-20})$$

Liquid heat capacities obtained from the literature or estimated by the above mentioned methods are then fitted to Equation (A-15) by the computer program POLYFIT given in Appendix C.6. The fitted coefficients are listed in Table A.7.

Table A.7 Liquid Enthalpies and Heat Capacities

$$C_p = a_1 + a_2T + a_3T^2 + a_4T^3$$

$$h = a_1T + a_2T^2/2 + a_3T^3/3 + a_4T^4/4$$

$$C_p = \text{cal/g-}^\circ\text{C} ; h = \text{cal/g} ; T = ^\circ\text{C}$$

<u>Component Name</u>	<u>a_1</u>	<u>$a_2 \times 10^3$</u>	<u>$a_3 \times 10^5$</u>	<u>$a_4 \times 10^7$</u>	<u>Ref.</u>
Ethyl Alcohol	0.53150	2.2012	0.72024	-	(15)
Ethyl Acrylate	0.45560	0.48312	0.17086	-	(17)
Water	1.0060	-0.31738	0.34230	-	(52)
Diethyl Ether	0.53002	0.97143	1.10120	-	(16)
β -Ethoxy-ethyl Propionate	0.44220	1.0364	0.26786	-	(Est.)
Acrylamide Sulfate	0.51106	-2.6872	2.5080	-0.46642	(Est.)
Sulfuric Acid	0.47483	-5.4866	4.1811	-0.81692	(52)
Ammonium Bisulfate (Solid)	0.42665	-2.3368	1.7822	-0.34821	(Est.)
Acrylamide	0.56106	1.1766	0.19881	-0.017361	(Est.)

A.8 Vapor Enthalpy (H)

A vapor mixture at atmospheric pressure may be treated as an ideal gas without a significant error. Two methods are used to obtain vapor enthalpies for the five volatile compounds. The first method uses the following equation to calculate vapor enthalpy.

$$H = \lambda_0 + \int_0^T C_{p_v} dT \quad (A-21)$$

where

H = vapor enthalpy at temperature T °C

λ_0 = heat of vaporization at 0 °C

C_{p_v} = vapor heat capacity

This method is applied for the first four volatile compounds. The data for λ at 0 °C and C_{p_v} for these four compounds are available in the literature.

For the least volatile compound, β -Ethoxy-ethyl propionate, none of the above data are available. It is then more convenient to obtain its vapor enthalpy from the previously estimated liquid enthalpy plus heat of vaporization for a given temperature. Thus,

$$H = \lambda_T + h \quad (A-22)$$

where

λ_T = heat of vaporization at temperature T

Since vapor pressure of β -ethoxy-ethyl propionate in the system is always less than atmospheric pressure, the vapor enthalpy obtained from the above equation may be treated as an ideal gas enthalpy.

Estimated Heat of Vaporization, λ

FORMULA: $C_2H_5OC_2H_4COOC_2H_5$

METHOD: There are four methods which may be used to estimate heat of vaporization at the normal boiling point (21). The Giacalone correlation is most suitable for this compound, considering both accuracy and availability of correlating parameters. His method is presented here as follows.

$$B = \frac{R T_B T_c \ln P_c}{(T_c - T_B)M} \quad (A-23)$$

The above equation has average and maximum errors of about 3 and 10 per cent, respectively.

For heat of vaporization at other temperatures, the Watson temperature correlation can be employed and is expressed as follows:

$$\lambda_T = \lambda_B \left(\frac{1 - T_r}{1 - T_{B,r}} \right)^{0.38} \quad (\text{A-24})$$

where

λ_T = heat of vaporization at temperature T

$$T_{B,r} = T_B / T_c$$

The average absolute error of Equation (A-24) is 4.7 % for 247 organic compounds.

ESTIMATION DETAILS:

From TABLE A.1, $T_{B,5} = 173^\circ\text{C} = 446.2^\circ\text{K}$

From TABLE A.2, $T_{c,5} = 346.8^\circ\text{C} = 620^\circ\text{K}$

$$T_{B,r} = \frac{446.2}{620} = 0.7197$$

From TABLE A.3, $P_c = 26.9 \text{ atm}$

From Equation (A-23)

$$\begin{aligned} \lambda_B &= \frac{1.937 \times 446.2 \times 620 \times \ln 26.9}{(620 - 446.2) \times 146.2} \\ &= 71.2 \text{ cal/g} \end{aligned}$$

From Equation (A-24)

$$\begin{aligned} \lambda_T &= 71.2 \left(\frac{1 - T_r}{1 - 0.7197} \right)^{0.38} \\ \text{or } \lambda_T &= 115.42 (1 - T_r)^{0.38} \end{aligned}$$

From Equation (A-22)

$$H_5 = \lambda_{T,5} + h_5$$

or

$$H_5 = 115.42 (1 - T_r)^{0.38} + h_5 \quad (\text{A-25})$$

The vapor enthalpy of β -ethoxy-ethyl propionate can now be calculated from Equation (A-25) as a function of temperature (or reduced temperature).

The vapor enthalpy calculated from either Equation (A-21) or Equation (A-25) is then fitted into a polynomial equation again by the program POLYFIT given in Appendix C.6. The fitted coefficients and the data sources for the five volatile compounds are listed in Table A.8.

Table A.8 Vapor Enthalpies at 1 Atm.

$$H = a_1 + a_2T + a_3T^2 + \dots$$

T = temperature, °C

H = ideal gas enthalpy, cal/g

Component	a_1	a_2	$a_3 \times 10^5$	$a_4 \times 10^7$	Ref.
Ethanol	227.0	0.3630	33.978		(15)
Ethyl Acrylate	96.0	0.2387	67.20	-0.132	(16)
water	597.6	0.4200	0.102		(52)
Diethyl Ether	90.0	0.3450	0.375		(16)
β -Ethoxy-ethyl Propionate	79.7	0.3695	- 6.211	8.929	(Est.)

A.9 Heat of Formation (H_f)

The heats of formation presented in this section are all evaluated at normal reference temperature, 25 °C. They are needed for calculating heat of reaction by Hess' rule in the next section.

Estimated H_f

1. Ethyl Acrylate

FORMULA: $\text{CH}_2\text{CHCOOC}_2\text{H}_5$

METHOD: The heat of formation of ethyl acrylate in the liquid state is estimated by two steps. The first step is to estimate its heat of formation in the ideal gas state, namely H_f^O , by the method of Andersen, Beyer and Watson as mentioned in Chapter 7. To reduce error to a minimum, a largest molecule of "close size and structure", ethyl propionate, is used as base group. The second step is to estimate its heat of vaporization by Equations (A-23) and (A-24) following the procedures gives in Section A.8. Then, its heat of formation in the liquid state, namely H_f^L , can be readily calculated.

ESTIMATION DETAILS

(1) $H_{f,2}^O$ (Ideal gas heat of formation):

	Kcal/g-mole	Ref.
Base Group		
Ethyl Propionate		
$CH_3CH_2COOC_2H_5$	-112.36	(52)
Double Bond Contribution	<u>+30.0</u>	
$CH_2CHCOOC_2H_5$	-82.36	
(2) λ_2	<u>-) 10.1</u>	
(3) $H_{f,2}^L$	-92.46	

2. β -Ethoxy-ethyl propionate

FORMULA: $C_2H_5OC_2H_4COOC_2H_5$

METHOD: The same method used for ethyl acrylate
is employed.

ESTIMATION DETAILS:

(1) $H_{f,5}^O$

	Kcal/g-mole	Ref.
Base Group		
Ethyl Propionate		
$CH_3CH_2COOC_2H_5$	-112.36	(52)
Contribution of Secondary CH_3 to $CH_3CH_2CH_2COOC_2H_5$	-5.2	
Contribution of Substitution of CH_3 by $-OH$ to		

$\text{HOCH}_2\text{CH}_2\text{COOC}_2\text{H}_5$	-32.7
Contribution of Substitution of H in OH group by CH_3 to	
$\text{CH}_3\text{OCH}_2\text{CH}_2\text{COOC}_2\text{H}_5$	+9.5
Contribution of Secondary CH_3 to $\text{C}_2\text{H}_5\text{OC}_2\text{H}_4\text{COOC}_2\text{H}_5$	
	<u>-7.0</u>
	-147.76
(2) λ_5	<u>-) 13.05</u>
(3) $H_{f,5}^L$	-160.81

3. Ammonium Bisulfate

FORMULA: NH_4HSO_4

METHOD: Heat of formation of solid ammonium bisulfate is assumed equal to the average heat of formation of solid sulfuric acid and ammonium sulfate. It is defined as $H_{f,8}^S$.

ESTIMATION DETAILS:

	Kcal/g-mole	Ref.
$H_{f,7}^L$	-193.69	(52)
$\lambda_{\text{fusion},7}$	<u>-) 2.55</u>	(58)
$H_{f,7}^S$	-196.24	
$H_{f,(NH_4)_2SO_4}^S$	<u>-281.74</u>	(52)

$$H_{f,8}^S = [(-196.24) + (-281.74)]/2$$

$$= -238.99 \text{ Kcal/g-mole}$$

4. Acrylamide:

FORMULA: $\text{CH}_2\text{CHCONH}_2$

METHOD: The method used for ethyl acrylate
is employed.

ESTIMATION DETAILS:

(1) $H_{f,9}^O$

Kcal/g-mole Ref.

Base Group

Formamide, HCONH_2 -49.5 (52)Contribution of Primary CH_3 Substitution to CH_3CONH_2 -9.0Contribution of Secondary CH_3 Substitution to $\text{CH}_3\text{CH}_2\text{CONH}_2$ -5.0

Contribution of Double Bond

to $\text{CH}_2\text{CHCONH}_2$ +30.0

-33.5

(2) λ_9 -) -13.1(3) $H_{f,9}^L$

-46.6

Experimentally Determined H_f

5. Acrylamide Sulfate:

FORMULA: $\text{CH}_2\text{CHC}(\text{OH})\text{NH}_2\text{HSO}$

METHOD: Acrylamide sulfate is a molecular complex.

Its heat of formation can not be estimated

by any available correlation methods. Therefore, it must be determined from the experimental heat of reaction data between sulfuric acid and acrylamide and their heats of formation by Equation (7-3) as discussed in Chapter 7.

$$H_{f,6}^L = H_{f,7}^L + H_{f,9}^L + \Delta H_R \quad (7-3)$$

From Section 5.4.5 of Chapter 5,

$$\Delta H_R = -5.62 \text{ Kcal/g-mole}$$

From Perrys' Handbook (52),

$$H_{f,7}^L = -193.69 \text{ Kcal/g-mole}$$

From the previous section,

$$H_{f,9}^L = -46.6 \text{ Kcal/g-mole}$$

Then, the heat of formation of acrylamide sulfate can be readily calculated by Equation (7-3).

$$\begin{aligned} H_{f,6}^L &= (-193.69) + (-46.6) + (-5.62) \\ &= -245.91 \text{ Kcal/g-mole.} \end{aligned}$$

Table A.9 Heats of Formation

No.	Component	Phase	Kcal/g-mole	Ref.
1	Ethyl Alcohol	L	-66.35	(52)
2	Ethyl Acrylate	L	-92.46	(Est.)
3	Water	L	-68.32	(52)
4	Diethyl Ether	L	-65.2	(52)
5	β -Ethoxy-Ethyl Propionate	L	-160.81	(Est.)
6	Acrylamide Sulfate	L	-245.91	(Exp.)
7	Sulfuric Acid	L	-193.69	(52)
8	Ammonium Bisulfate	S	-238.99	(Est.)
9	Acrylamide	L	-46.6	(Est.)

A.10 Heat of Reaction, (ΔH_R)

The heats of reaction for the three reactions encountered in this study are determined by Equation (7-4) through (7-6), using the data listed in Table A.9. The details of calculation are given below.

1. ΔH_{R_1} for Reaction 1, Esterification:

From TABLE A.9

$$H_{f,1}^L = -66.35$$

$$H_{f,2}^L = -92.46$$

$$H_{f,6}^L = -245.91$$

$$H_{f,8}^S = -238.99$$

Substituting the above data into Equation (7-4) gives

$$\begin{aligned} \Delta H_{R_1} &= H_{f,2}^L + H_{f,8}^S - H_{f,6}^L - H_{f,1}^L & (7-4) \\ &= (-92.46) + (-238.99) - (-245.91) - (-66.35) \\ &= -19.19 = -19.2 \text{ Kcal/g-mole} \end{aligned}$$

2. ΔH_{R_2} for Reaction 2, Dehydration:

From Table A.9.

$$H_{f,1}^L = -66.35$$

$$H_{f,3}^L = -68.32$$

$$H_{f,4}^L = -65.2$$

The heat of reaction for Dehydration can now be readily calculated from Equation (7-5):

$$\begin{aligned}\Delta H_{R_2} &= H_{f,3}^L + H_{f,4}^L - 2H_{f,1}^L & (7-5) \\ &= (-68.32) + (-65.2) - 2(-66.35) \\ &= -0.82 \text{ Kcal/g-mole}\end{aligned}$$

3. ΔH_{R_3} for Reaction 3, Successive Reaction

From TABLE A.9.

$$H_{f,1}^L = -66.35$$

$$H_{f,5}^L = -160.81$$

$$H_{f,6}^L = -245.91$$

$$H_{f,8}^S = -238.99$$

Then, the heat of reaction of Successive Reaction can be determined from the above four heats of formation by Equation (7-6) as follows.

$$\begin{aligned}\Delta H_{R_3} &= H_{f,5}^L + H_{f,8}^S - H_{f,6}^L - 2H_{f,1}^L & (7-6) \\ &= (-160.81) + (-238.99) - (-245.91) - 2(-66.35) \\ &= -21.19 \approx -21.2 \text{ Kcal/g-mole}\end{aligned}$$

Table A.10 Heats of Reaction

Reaction No.	Reaction	Equation	Heat of Reaction Kcal/g-mole
1	Esterification	(4-2)	-19.2
2	Dehydration	(4-3)	- 0.82
3	Successive Reaction	(4-4)	-21.2
4	Equilibrium Reaction (Complex Formation)	(4-1)	- 5.62

Appendix A.11 Fugacity Coefficients of Pure Liquid (ρ)

Table 11 Constants of Equation (2-6) for Determining Fugacity Coefficients of Pure Liquid

Constant	<u>Grayson-Streed Correlation</u>			<u>Chao-Seader Correlation</u>		
	<u>Hydrogen</u>	<u>Methane</u>	<u>Simple Fluid</u>	<u>Hydrogen</u>	<u>Methane</u>	<u>Simple Fluid</u>
A ₀	1.50709	1.36822	2.05135	1.96718	2.43840	5.75748
A ₁	2.74283	-1.54831	-2.10899	1.02972	-2.24550	-3.01761
A ₂	-0.02110	0.	0.	-0.054009	-0.34084	-4.98500
A ₃	0.00011	0.02889	-0.19396	0.0005288	0.00212	2.02299
A ₄	0.	-0.01076	0.02282	0.	-0.00223	0.
A ₅	0.008585	0.1.486	0.08852	0.008585	0.10486	0.08427
A ₆	0.	-0.02529	0.	0.	-0.03691	0.26667
A ₇	0.	0.	-0.00872	0.	0.	-0.31138
A ₈	0.	0.	-0.00353	0.	0.	-0.02655
A ₉	0.	0.	0.00203	0.	0.	0.02883

A.12 Fugacity Coefficient of Pure Vapor (ϕ^0)

Fugacity coefficient of pure vapor is estimated by Prausnitz's three-parameter general correlation (53). The correlating equations are:

$$\log \phi_i^0 = \log \phi_i^{(0)} + \omega_i \log \phi_i^{(1)}$$

$$\log \phi_i^{(0)} = ((0.57335/T_r - 3.0756)/T_r - 5.6086)/T_r - 3.5021$$

and

$$\log \phi_i^{(1)} = ((((((((((0.012089/T_r - 0.015172)/T_r - 0.068604)/T_r + 0.024365)/T_r + 0.14937)/T_r + 0.18927)/T_r - 0.12147)/T_r - 0.10666)/T_r - 1.1662)/T_r + 0.12666)/T_r + 0.31661)/T_r + 4.3539)/T_r - 3.7694$$

where

$$T_r = \frac{T}{T_c} = \text{reduced temperature}$$

$$\omega_i = \text{acentric factor}$$

The required critical temperature T_c and acentric factor can be obtained from Section A.2 and A.6, respectively.

Appendix B Calibration

The five calibration curves and one calibration table are included in this appendix. The methods of calibration and the respective data sources are described in Chapter 5. The calibration curves and table are listed as follows:

Fig. B.1 Calibration Curve for Helium Flow Rate

Fig. B.2 Calibration Curve for the Flow Rate of
86 Wt % Aqueous Ethyl Alcohol Solution

Fig. B.3 Calibration Curve for Weight Ratios of
Volatile Components to 1-Propanol in
the Gas Chromatography

Fig. B.4 Interrelations among Volume of Liquid
Holdup, Inside Wall Surface Area, Liquid
Height on the Reaction-Distillation Tray

Fig. B.5 Calibration Curves for Vapor Weight
Fraction in Feed Stream as a Function of
Feed Rate

TABLE B.1 Calibration Table for Iron-Constantan
Thermocouples

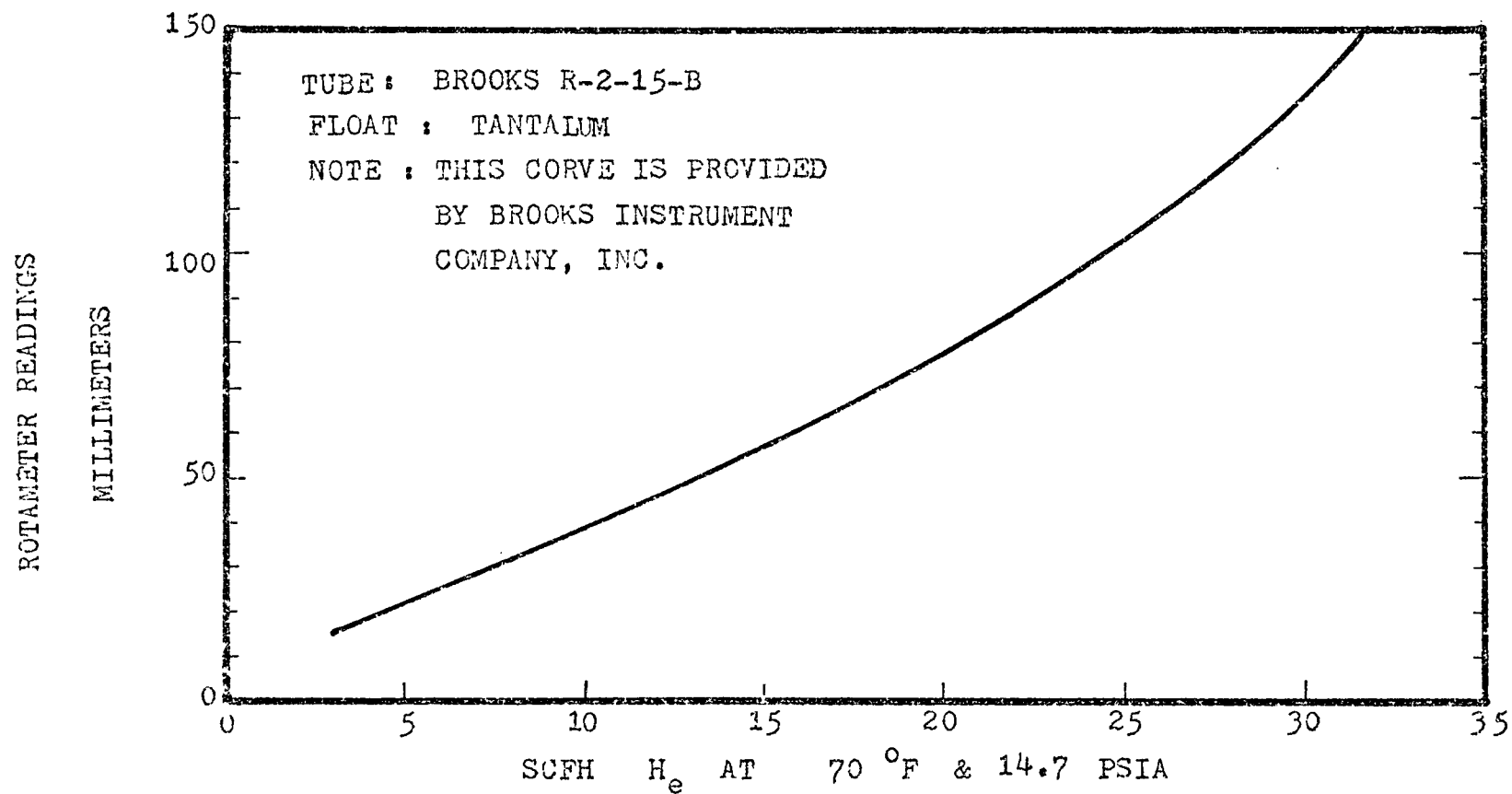


Fig. B.1 Calibration Curve For Helium Flow Rate

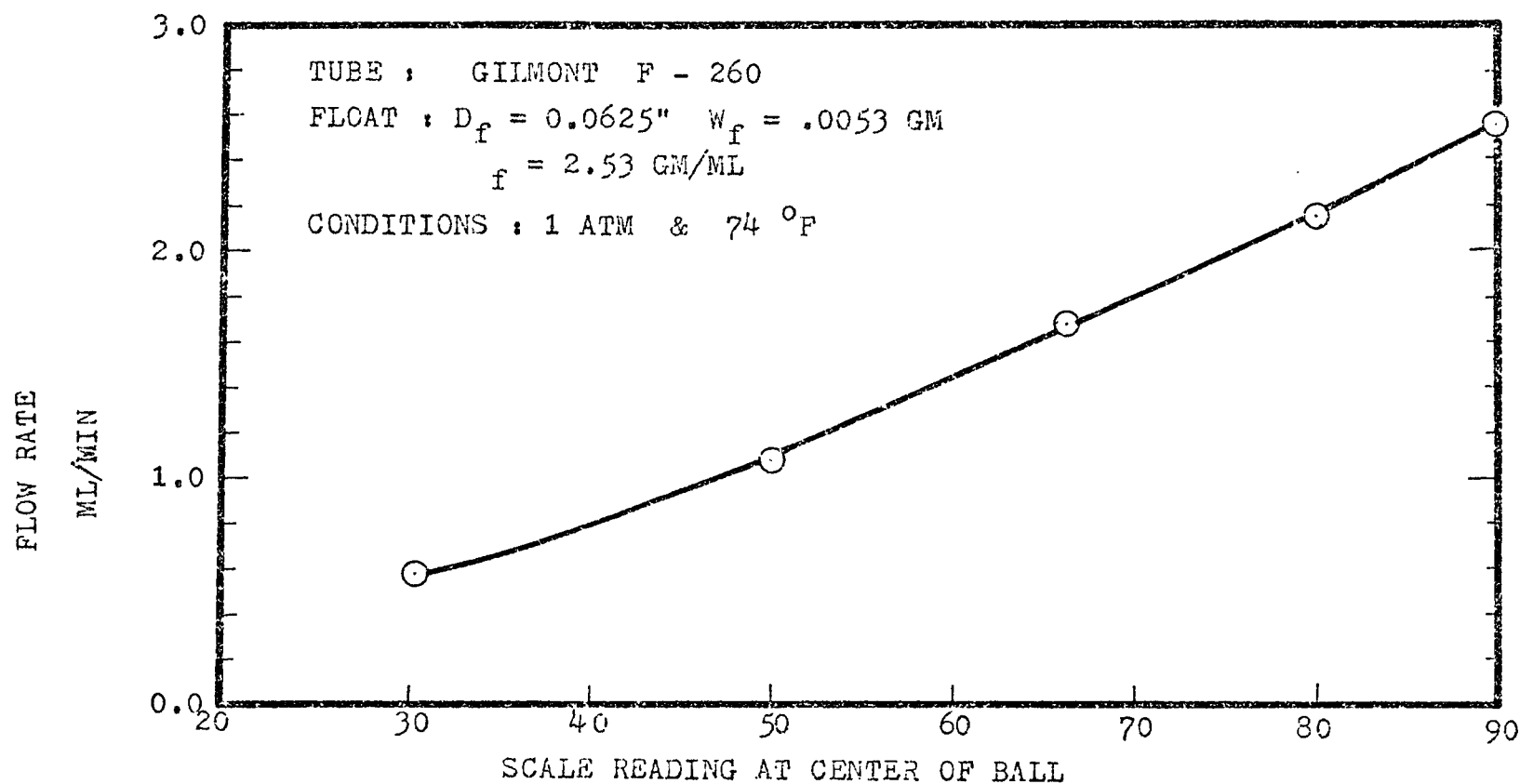


Fig. B. 2. Calibration Curve for the Flow Rate
of 86 Wt % Aqueous Ethyl Alcohol Solution

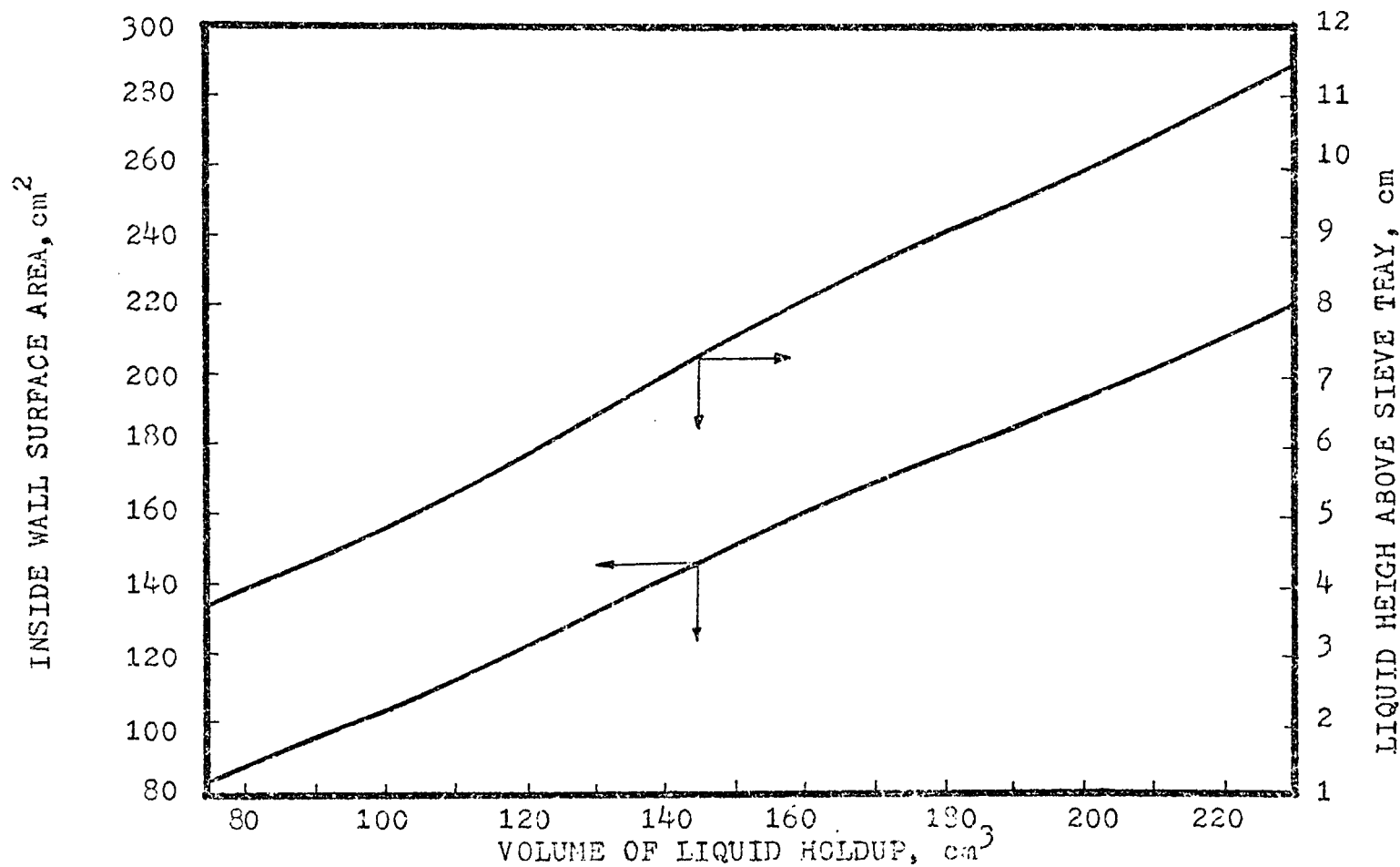


Fig. B.3 Interrelations Among Volume of Liquid Holdup, Inside Wall Surface Area, liquid Height on the Reaction-Distillation Tray

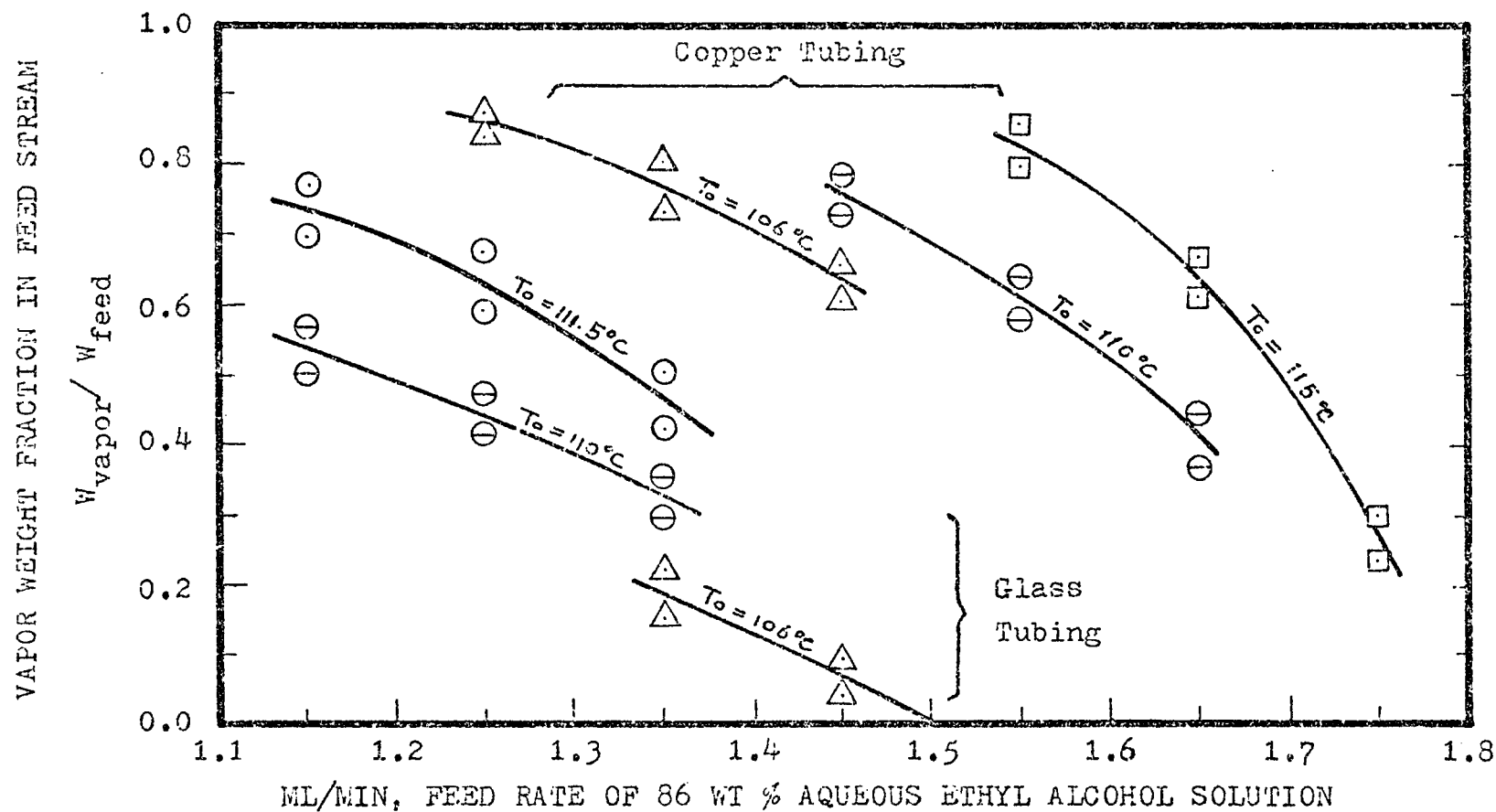


Fig. B.4 Calibration Curves for Vapor Weight Fraction in Feed Stream As a Function of Feed Rate

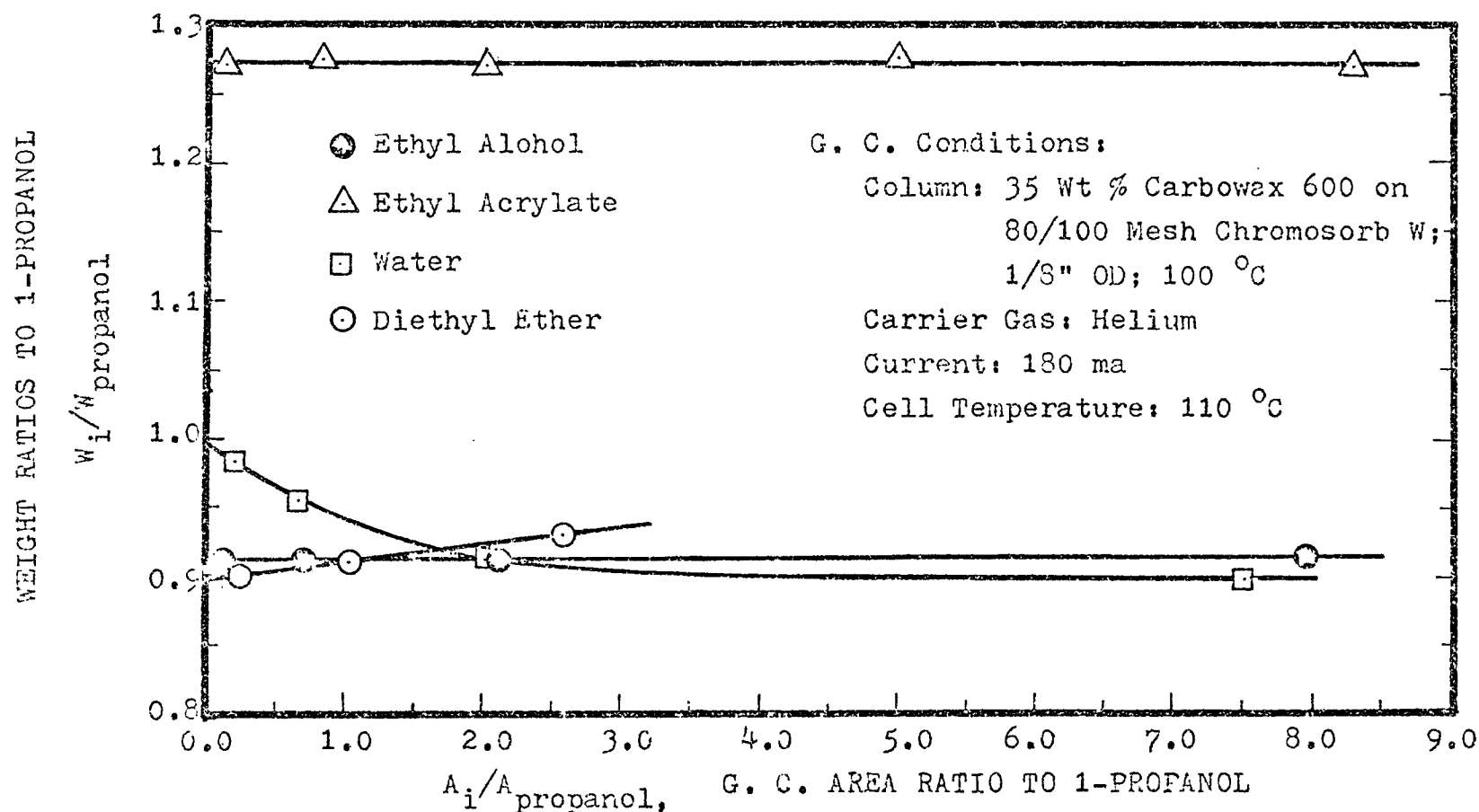


Fig. B.5 Calibration Curve for Weight Ratios of Volatile Components to 1-Propanol in the Gas Chromatography

CALIBRATION TABLES
 FOR THERMOCOUPLES (Continued)
 IRON-CONSTANTAN THERMOCOUPLES
 (MODIFIED 1913)

(Electromotive Force in Absolute Millivolts. Temperatures in Degrees C
(Int. 1943). Reference Junctions at 0° C.)

	0	1	2	3	4	5	6	7	8	9
-180	-7.66	-7.69	-7.71	-7.73	-7.74	-7.78	-7.81	-7.85	-7.90	-7.95
-183	-7.50	-7.43	-7.45	-7.49	-7.51	-7.54	-7.58	-7.59	-7.61	-7.63
-187	-7.12	-7.15	-7.18	-7.21	-7.24	-7.27	-7.30	-7.32	-7.35	-7.38
-190	-6.82	-6.85	-6.88	-6.91	-6.94	-6.97	-7.00	-7.02	-7.05	-7.08
-193	-6.53	-6.53	-6.56	-6.59	-6.63	-6.66	-6.69	-6.72	-6.76	-6.78
-195	-6.16	-6.19	-5.22	-6.26	-6.29	-6.33	-6.36	-6.40	-6.43	-6.47
-198	-5.80	-5.84	-5.87	-5.91	-5.94	-5.98	-6.01	-6.05	-6.08	-6.12
-199	-5.42	-5.45	-5.50	-5.54	-5.55	-5.58	-5.59	-5.59	-5.59	-5.59
-199	-5.03	-5.07	-5.11	-5.15	-5.19	-5.23	-5.27	-5.31	-5.35	-5.38
-100	-4.63	-4.67	-4.71	-4.75	-4.79	-4.83	-4.87	-4.91	-4.95	-4.99
-95	-4.21	-4.25	-4.30	-4.34	-4.38	-4.42	-4.45	-4.50	-4.55	-4.59
-90	-3.78	-3.82	-3.87	-3.91	-3.95	-4.00	-4.04	-4.08	-4.13	-4.17
-85	-3.34	-3.38	-3.43	-3.47	-3.52	-3.56	-3.60	-3.65	-3.69	-3.73
-80	-2.89	-2.94	-2.98	-3.03	-3.07	-3.12	-3.16	-3.21	-3.25	-3.29
-75	-2.43	-2.45	-2.52	-2.57	-2.62	-2.66	-2.71	-2.75	-2.80	-2.84
-70	-1.96	-2.01	-2.05	-2.10	-2.15	-2.20	-2.24	-2.29	-2.34	-2.38
-65	-1.49	-1.53	-1.58	-1.63	-1.67	-1.72	-1.77	-1.82	-1.87	-1.91
-60	-1.00	-1.04	-1.08	-1.13	-1.17	-1.22	-1.26	-1.31	-1.36	-1.40
-55	-0.52	-0.55	-0.60	-0.65	-0.70	-0.75	-0.80	-0.85	-0.90	-0.94
(-10)	0.00	-0.05	-0.10	-0.15	-0.20	-0.25	-0.30	-0.35	-0.40	-0.44
(+10)	0.60	0.65	0.70	0.75	0.80	0.85	0.90	0.95	1.00	1.04
10	0.50	0.56	0.61	0.66	0.71	0.76	0.81	0.86	0.91	0.95
20	1.02	1.07	1.12	1.17	1.22	1.28	1.33	1.38	1.43	1.47
30	1.54	1.59	1.64	1.69	1.74	1.80	1.85	1.90	1.95	2.00
40	2.06	2.11	2.16	2.22	2.27	2.32	2.37	2.42	2.47	2.52
50	2.58	2.64	2.69	2.74	2.80	2.85	2.90	2.96	3.01	3.06
60	3.11	3.17	3.22	3.27	3.33	3.38	3.43	3.49	3.54	3.59
70	3.65	3.70	3.76	3.81	3.86	3.92	3.97	4.02	4.08	4.13
80	4.19	4.24	4.29	4.35	4.40	4.46	4.51	4.56	4.62	4.67
90	4.73	4.78	4.83	4.89	4.94	5.00	5.05	5.10	5.16	5.21
100	5.27	5.32	5.38	5.43	5.48	5.54	5.59	5.65	5.70	5.75
110	5.81	5.86	5.92	5.97	6.03	6.08	6.14	6.19	6.25	6.30
120	6.36	6.41	6.46	6.52	6.58	6.63	6.68	6.74	6.79	6.85
130	6.90	6.95	7.01	7.07	7.12	7.18	7.23	7.29	7.34	7.39
140	7.45	7.51	7.56	7.62	7.67	7.73	7.78	7.84	7.89	7.95
150	8.00	8.06	8.12	8.17	8.23	8.28	8.34	8.39	8.45	8.50
160	8.56	8.61	8.67	8.72	8.78	8.84	8.89	8.95	9.00	9.06
170	9.11	9.17	9.22	9.28	9.33	9.39	9.44	9.50	9.56	9.61
180	9.67	9.72	9.78	9.83	9.89	9.95	10.00	10.06	10.11	10.17
190	10.22	10.26	10.34	10.39	10.45	10.51	10.57	10.61	10.67	10.72
200	10.78	10.84	10.89	10.95	11.00	11.06	11.12	11.17	11.23	11.29
210	11.34	11.39	11.45	11.50	11.56	11.62	11.67	11.73	11.78	11.83
220	11.89	11.95	12.00	12.06	12.12	12.17	12.23	12.28	12.34	12.39
230	12.45	12.50	12.56	12.62	12.67	12.73	12.78	12.84	12.89	12.95
240	13.01	13.06	13.12	13.17	13.23	13.28	13.34	13.40	13.45	13.51
250	13.56	13.62	13.67	13.73	13.78	13.84	13.89	13.95	14.00	14.06
260	14.12	14.17	14.23	14.28	14.34	14.39	14.45	14.50	14.56	14.61
270	14.67	14.72	14.78	14.83	14.89	14.94	15.00	15.05	15.11	15.17
280	15.22	15.28	15.33	15.39	15.44	15.50	15.55	15.61	15.66	15.72
290	15.77	15.83	15.88	15.94	16.00	16.05	16.11	16.16	16.22	16.27
300	16.33	16.38	16.44	16.49	16.55	16.60	16.66	16.71	16.77	16.82
310	16.88	16.93	16.99	17.04	17.10	17.15	17.21	17.26	17.32	17.37
320	17.43	17.48	17.54	17.60	17.65	17.71	17.76	17.81	17.87	17.92
330	17.97	18.03	18.08	18.14	18.20	18.26	18.32	18.37	18.43	18.48
340	18.54	18.59	18.65	18.71	18.76	18.81	18.87	18.92	18.98	19.03
350	19.09	19.15	19.21	19.27	19.32	19.37	19.43	19.48	19.53	19.59

TABLE B.1 Calibration Table for Iron-Constantan Thermocouples

Appendix C Computer Programs

C.1 Program LABDATA: For treating the laboratory data
of semibatch distillation accompanied by
chemical reactions

C.1.1 Program List

C.1.2 Input Data

C.1.3 Results

C.2 Program MODEL: For solving the mathematical model
of semibatch distillation accompanied by
chemical reactions

C.2.1 Program List

C.2.2 Input Data

C.2.3 Results

C.3 Program CHEMACT: For correlating liquid activity
coefficients under the effect of chemical
reactions

C.3.1 Program List

C.3.2 Input Data

C.3.3 Results

C.4 Program RXNRATE: For calculating activation energy
and frequency factor for reaction rate con-
stant

C.4.1 Program List

C.4.2 Input Data

C.4.3 Results

C.5 Program BSOLFIT: For fitting data into nonlinear
equation by the BSOLVE technique

C.5.1 Program List

C.6 Program POLYFIT: For fitting data into polynomial
equation by the Gauss elimination method

C.6.1 Program List

```

PROGRAM LABDATA(INPUT,OUTPUT,TAPE8=INPUT,TAPE5,TAPE7,TAPE6=OUTPUT)
REAL NT,MW
COMMON CC(6),JJJ,YPN(10)
DIMENSION A(9,5),ACVS(5,5),VG(10,5),XP(10,5),GAMMA(10,5),CH(5,5),
IRK(10,5),D(10,9),XX(10,9),YY(10,5),RR(10,4),YPR(10,9),CS(10,5),
ZEK(10,5)
DIMENSION AP(5),BP(5),CP(5),MV(9),YF(9),XL(10),XV(10),
INT(10),PG(10),T(10),YI(5),XVC(10),X(10),RS(10),DJ(9),Q(10),YSA(10),
2,Q(10),Q3(10),VC(10),WT(10),WI(5),DELV(10),V(10),TLAG(10),VY(10)
3,XSUM(10),SYPR(10),PFRR(20),STDEV(20),NAME(5),YS(9)
4,EK1(10),EK2(10),EK3(10),RTINV(10),TC(5),OMEGA(5)
DATA NAME/10HALCOHOL,10HACRYLATE,10HWATER,
+10HEXER,10HPROPIONATE/
READ(7,10) JSET
READ(7,10) M,MW,MV
READ(7,14) ((A(K,J),J=1,M),K=1,MM)
READ(7,11) (MW(K),K=1,MM)
READ(7,11) (TC(I),I=1,MV)
READ(7,11) (OMEGA(I),I=1,MV)
READ(7,14) ((ACVS(J,K),K=1,M),J=1,MV)
READ(7,16) (AP(J),BP(J),CP(J),J=1,MV)
READ(7,11) XΓ
READ(7,11) (YF(J),J=1,MM)
RC=82.05
55 REWIND 5
READ(8,10) JSTOP,MU
MUJ=MU+1
10 FORMAT(8I5)
11 FORMAT(8F10.0)
12 FORMAT(5E16.5)
14 FORMAT(5E14.5)
15 FORMAT(5F10.0)
16 FORMAT(3F10.0)
02 FORMAT(6F10.0)
00 FORMAT(1H1,///1X,8HPUN NO.,I2)
1 READ(5,10) N1,ISET
READ(5,11) FEED,H2SO4,AMIDE,PT,TI,H2O,YI1,RHOA,FRACTI
N=N1-2
READ(5,11) (XL(I),I=1,N1)
READ(5,11) (XV(I),I=1,N1)
READ(5,11) (NT(I),I=1,N1)
READ(5,202) ((VG(I,J),J=1,MV),PG(I),I=1,N1)
READ(5,15) ((XP(I,J),J=1,MV),I=1,N)
READ(5,11) (T(I),I=1,N)

```

DETERMINATION OF INSTANTANEOUS VAPOR QUANTITIES AND TIME LAGS

```

JJJ=1
YI(1)=YI1
YI(3)=1.-YI(1)
YI(2)=0.
YI(4)=0.
YI(5)=0.
DO 206 I=3,N1
II=I-2

```



```

XVC(II)=XV(I)-XL(3)
06 X(II)=XL(I)-XL(3)
IF(ISFT.EQ.8) GO TO 84
DO 229 J=1,N1
RS(I)=0.
DO 229 J=1,MV
R=VG(I,J)/PG(I)
CVS=ACVS(J,1)
DO 205 K=2,M
05 CVS=CVS+ACVS(J,K)*R**(K-1)
RA=PR*CVS
RS(I)=RS(I)+RA
RN(I,J)=RA*NT(I)
29 CONTINUE
DO 208 I=1,N1
DO 208 J=1,MV
08 RN(I,J)=RN(I,J)/RS(I)
DO 210 I=2,N1
II=I-1
NT(I)=NT(I)+NT(II)
DO 210 J=1,MV
10 RN(I,J)=RN(I,J)+RN(II,J)
GO TO 85
84 DO 86 I=1,N1
DO 86 J=1,MV
86 RN(I,J)=VG(I,J)
85 DO 211 I=1,N
DO 211 K=1,MM
D(I,K)=A(K,1)
DO 211 J=2,M
11 D(I,K)=D(I,K)+A(K,J)*T(I)**(J-1)
DO 212 K=1,MM
DI(K)=0.
DO 212 J=1,M
12 DI(K)=DI(K)+A(K,J)*TI**(J-1)
V0=H2O/DI(3)+AMIDE/DI(6)+H2SO4/DI(7)
H2OM=H2O/MW(3)
H2SO4=H2SO4/MW(7)
AMIDE=AMIDE/71.06
W0=H2OM+H2SO4+AMIDE
DO 213 I=1,N
J=1+2
Q(I)=FEED*XL(J)
Q(I)=Q(I)*RHOA
Q1(I)=Q(I)*YI1
Q3(I)=Q(I)*(1.-YI1)
V0N=V0+Q1(I)/D(I,1)+Q3(I)/D(I,3)-RN(J,1)/D(I,1)-RN(J,2)/D(I,2)-
1 RN(J,3)/D(I,3)-RN(J,4)/D(I,4)-RN(J,5)/D(I,5)
13 VC(I)=323.1-V0N
DO 216 J=1,MV
DO 231 K=1,N
31 VY(K)=VN(K+2,J)
YS(J)=YF(J)/10.
CALL LSTSOR(N,MU,XVC,VY,XF,YS(J),PERR(J),STDEV(J))
DO 216 K=1,N

```

```

16 YPR(K,J)=YPN(K)/MW(J)
DO 219 K=1,N
TNR=YPR(K,1)
DO 290 J=2,MV
90 TNR=TNR+YPR(K,J)
VP=TNR*RC*(T(K)+273.16)/(PT/760.)
TLAG(K)=VC(K)/VR+250./(2170.+VR)
19 XVC(K)=XVC(K)-TLAG(K)
DO 220 J=1,MV
DO 234 K=1,N
34 VY(K)=PN(K+2,J)
L=V+J
CALL LSTSQP(N,MU,XVC,VY,XF,YS(J),PEPR(L),STDEV(L))
DO 220 JL=1,MU1
20 CH(J,JL)=CC(JL)
DO 221 I=1,N
DO 221 J=1,MV
YY(I,J)=CH(J,1)
DO 222 JL=2,MU1
22 YY(I,J)=YY(I,J)+CH(J,JL)*X(I)**(JL-1)
IF(YY(I,J).LT.0.) YY(I,J)=0.
21 CONTINUE

```

DETERMINATION OF INSTANTANEOUS LIQUID QUANTITIES

```

DO 88 I=1,N
XP(I,1)=XP(I,1)*0.913
XP(I,2)=XP(I,2)*1.274
WI(1)=Q1(I)-YY(I,1)
WJ(2)=-YY(I,2)
WJ(3)=Q3(I)-YY(I,3)
WI(4)=-YY(I,4)
WJ(5)=-YY(I,5)
DELV(I)=0.
DO 35 K=1,MV
35 DELV(I)=DELV(I)+WI(K)/D(I,K)
V(I)=V0+DELV(I)
C1=1.+(0.4602*XP(I,2)+0.626*XP(I,5))/XP(I,1)
C2=WJ(1)-0.4602*YY(I,2)-1.244*YY(I,4)-0.626*YY(I,5)
XX(I,1)=C2/C1
XX(I,2)=XP(I,2)*XX(I,1)/XP(I,1)
XX(I,4)=XP(I,4)*XX(I,1)/XP(I,1)
XX(I,5)=XP(I,5)*XX(I,1)/XP(I,1)
XX(I,3)=WI(3)+H2O+0.2432*YY(I,4)
88 CONTINUE
DO 72 I=1,N
DO 72 K=1,MV
XX(I,K)=XX(I,K)/MW(K)
72 YY(I,K)=YY(I,K)/MW(K)
DO 73 I=1,N
ACR=XX(I,2)+YY(I,2)+XX(I,5)+YY(I,5)
XX(I,6)=AMIDE-ACR
XX(I,7)=H2SO4-AMIDE
XX(I,8)=ACR
73 CONTINUE

```

```

DO 80 I=1,N
WT(I)=0.
DO 80 J=1,MV
DO 37 I=1,N
DO 37 K=1,MV
CS(I,K)=XX(I,K)+YY(I,K)

```

DETERMINATION OF INSTANTANEOUS REACTION RATES

```

DO 61 J=2,MV
JM=J-1
IF(J.EQ.3) GO TO 61
IF(J.GT.3) JM=J-2
LL=L+JM
CALL LSTSQR(N,MU,X,CS(1,J),XF,YF(J),PEPR(LL),STDEV(LL))
DO 64 J=1,N
PP(I,JM)=YPR(I)
61 CONTINUE
DO 471 I=1,N1
DO 471 J=1,MV
71 RM(I,J)=RN(I,J)/WM(J)
DO 434 I=1,N
RK1(J)=RR(1,1)*V(I)/XX(I,1)/XY(I,6)
RK2(1)=RR(1,2)*V(I)/(XX(I,1))**2
RK3(1)=RR(1,3)*(V(I)/XX(I,1))**2/XX(I,6)
RTINV(I)=219.53/(T(I)+273.16)
34 YSA(I)=YY(I,1)+YY(I,2)+YY(I,3)+YY(I,4)+YY(I,5)
IF(IPS.EQ.1) GO TO 696
WRITE(6,500) ISET
WRITE(6,131)
31 FORMAT(/1X,12HDEFINITIONS-)
WRITE(6,112)
12 FORMAT( 3X,*REAL TIME IS COUNTED FROM THE MOMENT ALCOHOL IS FIRST
1 MIXED WITH ACRYLAMIDE SULFATE*/3X,*ADJUSTED TIME IS COUNTED FROM
2THE MOMENT STUDIES FOR DISTILLATION ACCOMPANIED BY CHEMICAL REACTI
3ONS BEGIN*/3X,*ADJUSTED TIME MUST BEGIN RIGHT OR SLIGHTLY AFTER TH
4E REACTING LIQUID MIXTURE BECOMES BOILING*/1X,*INITIAL CONDITIONS
5 FOR THE REAL TIME*/)
WRITE(6,113) TI,V0,W0,AMIDE,H2SO4,H2OM
13 FORMAT(2X,5HTEMP=,F7.2,2H C,3X,4HVOL=,F7.2,3H ML,3X,8HTOT LIQ=,
1F7.4,4H MOL,3X,6HAMIDE=,F6.3,4H MOL,3X,6HH2SO4=,F6.3,4H MOL,3X,
26HWATER=,F6.3,4H MOL)
WRITE(6,114) FEED,YI(1),YI(3),FRACTI
14 FORMAT(/1X,15HFEED CONDITIONS//2X,5HRATE=,F6.4,7H ML/MIN,4X,8HALCO
1HOL=,F6.4,12H WT FRACTION,4X,6HWATER=,F6.4,12H WT FRACTION,4X,
21HVAPOR FRACTION=,F6.4)
WRITE(6,1011)
11 FORMAT(/1X,*MIXTURE QUANTITIES AND REACTION RATES VS ADJUSTED TIM
1E*)
WRITE(6,115)
15 FORMAT(/4X,4HTIME,4X,8HTIME LAG,8X,4HTEMP,5X,7H LIQ VOL,5X,
+7H LIQ MOL,5X,7HVAP MOL,4X,6HACP RATE,4X,8HPROR RATE)
WRITE(6,144) (X(I),TLAG(I),T(I),V(I),WT(I),YSA(I),(RR(I,J),
+J=1,3),I=1,N)

```

```

44 FORMAT(F8.2,F12.5,2F12.2,2F12.5,3F12.7)
   WRITE(6,1033)
33 FORMAT(/ /1X,*INSTANTANEOUS LIQUID MOLAR QUANTITIES VS ADJUSTED TIME*)
   WRITE(6,103)
03 FORMAT(/4X,4HTIME,5X,7HALCOHOL,4X,8HACRYLATE,7X,5HWATER,7X,5HETHER
+ ,2X,10HPPROPIONATE,5X,7HCOMPLEX,7X,5HH2SO4,5X,7H4HSO4)
   WRITE(6,104) (X(I),(XX(I,K),K=1,MM),I=1,N)
04 FORMAT(F8.2,8F12.6)
   WRITE(6,320)
20 FORMAT(/ /1X,*ACCUMULATED VAPOR MOLAR QUANTITIES VS ADJUSTED TIME*)
   WRITE(6,340)
40 FORMAT(/4X,4HTIME,5X,7HALCOHOL,4X,8HACRYLATE,7X,5HWATER,7X,
+ 5HETHER,2X,10HPPROPIONATE)
43 FORMAT(/4X,4HTIME,5X,7HALCOHOL,4X,8HACRYLATE,7X,5HWATER,7X,
+ 5HETHER,2X,10HPPROPIONATE,7X,5HVRATE)
   WRITE(6,310) (X(I),(YY(I,K),K=1,MV),I=1,N)
10 FORMAT(F8.2,5F12.6)
12 FORMAT(F8.2,6F12.6)
   WRITE(6,505) ISET
05 FORMAT(1H1, / /1X,3HRUN NO. ,12,12H (CONTINUED))
   WRITE(6,390)
90 FORMAT(/ /1X,*INSTANTANEOUS TOTAL MOLAR QUANTITIES VS ADJUSTED TIME
+ *,16X,*REACTION RATE CONSTANTS*)
   WRITE(6,342)
42 FORMAT(/4X,4HTIME,5X,7HALCOHOL,4X,8HACRYLATE,7X,5HWATER,7X,
+ 5HETHER,2X,10HPPROPIONATE,2X,10H1000/2.3RT,2X,10HACR RCONST,2X,
+ 10HPROP RCONST,2X,10HPRO RCONST)
   WRITE(6,105) (X(I),(CS(I,K),K=1,MV),RTINV(I),RK1(I),RK2(I),RK3(I),
+ I=1,N)
05 FORMAT(F8.2,9F12.6)
   WRITE(6,324)
24 FORMAT(/ /1X,*ACCUMULATED VAPOR QUANTITIES VS REAL TIME*)
   WRITE(6,340)
   WRITE(6,310) (XV(I),(RN(I,K),K=1,MV),I=1,N1)
96 L1=LL+1
   L2=LL+2
   JJJ=2
   CALL LSTSOR(N,MU,X,T,XF,YF(1),PERR(L1),STDEV(L1))
   DO 40 I=1,N
     XSUM(I)=0.
     DO 40 J=1,MM
040 XSUM(I)=XSUM(I)+XX(I,J)
     CALL LSTSOR(N,MU,X,XSUM,XF,YF(1),PERR(L2),STDEV(L2))
     T01L=TJ
     DO 43 J=1,N
       DO 43 J=1,MV
         YPR(I,J)=CH(J,2)
         IF(MU1.LT.3) GO TO 43
         DO 29 K=3,MU1
29 YPR(I,J)=YPR(I,J)+FLOAT(K-1)*CH(J,K)*X(I)**(K-2)
         IF(YPR(I,J).LT.0.) YPR(I,J)=0.
43 CONTINUE

```

DETERMINATION OF INSTANTANEOUS VAPOR-LIQUID EQUILIBRIA

```

DO 41 I=1,N
DO 41 J=1,MM
41 XX(I,J)=XX(I,J)/XSUM(I)
DO 44 I=1,N
SYPR(J)=0.
DO 44 J=1,MV
YPR(I,J)=YPR(I,J)/MP(J)
44 SYPP(I)=SYPR(I)+YPR(I,J)
PT=PI/760.
DO 45 I=1,N
DO 45 J=1,MV
YY(I,J)=YPR(I,J)/SYPR(I)
PS=10.**(AP(J)-BP(J)/(CP(J)+T(I)))/760.
IF(J.EQ.4) GO TO 58
IF(XX(I,J)-0.00001) 58,58,59
58 EK(I,J)=100.
GAMMA(I,J)=100.
GO TO 45
59 EK(I,J)=YY(I,J)/XX(I,J)
TP=(T(I)+273.16)/(TC(J)+273.16)
PHIS0=((0.57335/TR-3.0766)/TR+5.6086)/TR-3.5021
PHIS1(((((((0.012089/TR-0.015172)/TR-0.068604)/TR+0.024365)/
1TP+0.14937)/TR+0.18927)/TP-0.12147)/TR-0.10666)/TR-1.1662)/TP+
20.12666)/TR+0.31661)/TR+4.3539)/TR-3.7694
PHIS=10.**(PHIS0+OMEGA(J)*PHIS1)
GAMMA(I,J)=PT*EK(I,J)/PS/PHIS
45 CONTINUE
WRITE(6,350)
50 FORMAT(/ /1X,*INSTANTANEOUS LIQUID MOLE FRACTION VS ADJUSTED TIME*)
WRITE(6,103)
WRITE(6,104) (X(I),(XX(I,K),K=1,MM),I=1,N)
WRITE(6,360)
60 FORMAT(/ /1X,*INSTANTANEOUS VAPOR MOLE FRACTIONS AND TOTAL VAPOR FL
LOW RATE VS ADJUSTED TIME*)
WRITE(6,343)
WRITE(6,312) (X(I),(YY(I,K),K=1,MV),SYPR(I),I=1,N)
WRITE(6,505) ISET
WRITE(6,370)
70 FORMAT(/ /1X,*INSTANTANEOUS EQUILIBRIUM CONSTANTS VS ADJUSTED TIME*)
1)
WRITE(6,340)
WRITE(6,314) (X(I),(EK(I,K),K=1,3),EK(I,5),I=1,N)
14 FORMAT(F6.2,3F12.6,12X,F12.6)
WRITE(6,370)
70 FORMAT(/ /1X,*INSTANTANEOUS LIQUID ACTIVITY COEFFICIENT VS ADJUSTED
1 TIME*)
WRITE(6,340)
WRITE(6,314) (X(I),(GAMMA(I,K),K=1,3),GAMMA(I,5),I=1,N)
WRITE(6,404) MJ
04 FORMAT(/ /1X,*SUMMARY OF ERRORS FOR CURVE FITS--*,I2,* DEGREE P
10LYNOMIALS*)
WRITE(6,406)
06 FORMAT(/ /1X,*VAPOR FLOW RATES*)
WRITE(6,407)

```

```
07 FORMAT(21X,*VAPOR RATE VS VAPOR *,10X,*VAPOR RATE VS LIQUID *  
+721X,*ADJUSTED TIME BEFORE*,10X,*ADJUSTED TIME AFTER *,/  
+11X,2(10X,*TIME LAG CORRECTION *))  
WRITE(6,408)  
08 FORMAT(11X,2(10X,20H-----))  
WRITE(6,410)  
10 FORMAT(14X,2(4X,11HABS PCT ERR,3X,12HSTANDARD DEV)/)  
DO 419 I=1,MV  
IX=I+5  
14 WRITE(6,411) NAME(I),PERR(I),STDEV(I),PERR(IX),STDEV(IX)  
11 FORMAT(2X,A10,2X,4E15.5)  
WRITE(6,412)  
12 FORMAT(/71X,*REACTION RATE* /22X,8HACR RATE,7X,8HRROR RATE,7X,  
+8HPRD RATE)  
WRITE(6,414) (PERR(I),I=11,13)  
14 FORMAT(/3X,12HABS PCT ERR ,3E15.5)  
WRITE(6,416) (STDEV(I),I=11,13)  
16 FORMAT(3X,12HSTANDARD DEV,3E15.5)  
IF (ISFT-JSFT) 1,999,999  
99 IF (JSTOP-2) 555,9999,9999  
99 STOP  
END
```

```
SUBROUTINE LSTSOR(N,K,XA,YA,XF,YF,PEPR,STDEV)
DIMENSION XA(1),YA(1),YCAL(10),XSUM(10),A(6,6)
COMMON CA(6),JJJ,YPN(10)
DO 10 I=1,N
XA(I)=XA(I)*XF
10 YA(I)=YA(I)*YF
CA(1)=0.
DO 12 J=1,N
12 CA(1)=CA(1)+YA(J)
XSUM(1)=N
K1=K+1
DO 14 I=2,K1
CA(I)=0.
DO 14 J=1,N
14 CA(I)=CA(I)+YA(J)*(XA(J))**(I-1)
KK=2*K+1
DO 16 I=2,KK
XSUM(I)=0.
DO 16 J=1,N
16 XSUM(I)=XSUM(I)+XA(J)**(I-1)
DO 18 I=1,K1
DO 18 J=1,K1
L=I+J-1
18 A(I,J)=XSUM(L)
DO 20 I=1,K1
DO 24 J=1,K1
DET=A(J,I)
CA(J)=CA(J)/A(J,I)
DO 24 L=1,K1
24 A(J,L)=A(J,L)/DET
DO 20 J=1,K1
IF(J.EQ.I) GO TO 20
CA(J)=CA(J)-CA(I)
DO 26 L=1,K1
26 A(J,L)=A(J,L)-A(I,L)
20 CONTINUE
DO 28 I=1,K1
28 CA(I)=CA(I)/A(I,I)
CA(1)=CA(1)/YF
DO 30 I=2,K1
30 CA(1)=CA(1)/YF*XF**(I-1)
DO 32 I=1,N
XA(I)=XA(I)/XF
YA(I)=YA(I)/YF
YCAL(I)=CA(1)
DO 32 J=2,K1
32 YCAL(I)=YCAL(I)+CA(J)*XA(I)**(J-1)
DO 34 I=1,N
YPN(I)=CA(2)
IF(K1.LT.3) GO TO 34
DO 36 J=3,K1
36 YPN(I)=YPN(I)+FLOAT(J-1)*CA(J)*XA(I)**(J-2)
GO TO (38,34),JJJ
38 IF(YPN(I).LT.0.) YPN(I)=0.
34 CONTINUE
```

```
PEPR=0.  
STDEV=0.  
NM=N  
DO 42 I=1,N  
  DELY=YCAL(I)-YA(I)  
  IF (ABS(YA(I))*YF-.001) 44,46,46  
44 NM=NM-1  
  GO TO 42  
46 PEPR=PEPR+ABS(DELY/YA(I))  
  STDEV=STDEV+DELY*DELY  
42 CONTINUE  
STDEV=SQRT(STDEV/FLOAT(NM-1))  
PEPR=PEPR/FLOAT(NM)*100.  
RETURN  
END
```


5	8	5						
.79800E+00	-0.75060E-03	-0.16369E-05						
.93971E+00	-0.94345E-03	-0.16369E-05						
.10067E+01	-0.25200E-03	-0.22973E-05						
.73271E+00	-0.88333E-03	-0.32738E-05						
.97206E+00	-0.87446E-03	-0.14881E-06						
.14734E+01	-0.95768E-03	0.31945E-07						
.14511E+01	-0.99000E-03							
.18141E+01	-0.27900E-02							
.07	100.11	18.016	74.08	147.2	169.14	98.08	115.05	
1	288.	374.1	193.8	346.8				
7	0.329	0.344	0.283	0.557				
.91300E+00								
.12740E+01								
.10045E+01	-0.75617E-01	0.15432E-01						
.89730E+00	0.10910E-01							
.10000E+01								
29	1623.2	228.98						
73	1283.1	212.19						
681	1668.2	228.0						
227	1051.3	227.43						
46	1795.2	211.67						
	1.0	10.0	100.	100.	1.0	1.9	1.0	

	1						378
		125.2	71.9	762.0	115.0	11.0	0.86
		20.2	31.0	43.57	57.95	74.92	88.0
		132.35					103.52
		20.67	31.58	44.17	58.33	75.43	88.58
7		133.33					104.33
		12.712	16.3283	18.6803	19.997	24.6075	19.027
58		10.1350					22.6547
		90.	224.	1.	0.	928.	
		1500.	162.	40.	14.	480.	
		1692.	230.	52.	72.	928.	
		2480.	260.	92.	142.	920.	
		2382.	420.	100.	204.	896.	
		1080.	234.	92.	234.	736.	
		856.	542.	112.	310.	1432.	
		326.	384.	84.	212.	816.	
		208.	544.	92.	176.	928.	
		200.	650.	86.	163.	1216.	
		30.			0.		
		14.			4.		
		18.			5.		
		13.			7.		
		6.			5.		
		4.5			4.		
		4.			4.		
		3.			4.		
41		123.16	120.83	118.47	116.99	115.65	114.93
0	2						114.42
6		126.2	70.83	765.	115.	12.51	0.86
							0.825
		20.17	30.53	42.	52.	64.92	78.83
1		115.1					90.25
		20.75	31.47	42.67	52.88	65.58	79.5
72		115.4					90.83
1		13.3230	15.5898	17.5507	12.7885	18.3210	21.1943
190		19.9357					16.7985
		184.	534.	10.	0.	4672.	
		448.	60.	6.	2.	120.	
		424.	58.	16.	10.	168.	
		344.	38.	14.	26.	176.	
		430.	96.	16.	64.	288.	
		672.	122.	32.	60.	368.	
		544.	286.	32.	94.	568.	
		318.	180.	18.	70.	448.	
		264.	236.	14.	58.	400.	
		25.	268.	6.	50.	480.	
		26.			3.		
		25.			3.		
		30.			4.		
		21.			3.		
		22.			5.		
		22.			6.		
		17.			4.		
		8.			3.		
57		120.65	118.26	114.07	111.28	110.2	109.6
							108.2

	3						379
	125.1	73.02	768.	111.5	13.3	.86	.826
	18.67	31.47	40.67	51.62	75.	85.62	99.08
13	124.08						
	14.72	33.17	41.33	52.03	70.67	86.12	99.7
3	125.08						
	1.9055	12.2569	11.0025	13.4326	24.2902	20.7939	18.2722
7	20.1344						
	164.	0.	3.	.0	403.		
	16.	2.	2.	0.	20.		
	112.	11.	4.	2.	52.		
	136.	26.	7.	12.	72.		
	76.	20.	4.	4.	52.		
	200.	38.	16.	18.	60.		
	144.	48.	5.	20.	96.		
	44.	34.	4.	12.	40.		
	76.	50.	8.	28.	116.		
	112.	114.	12.	55.	192.		
	60.			.0			
	44.			6.			
	36.			8.			
	28.			8.			
	22.			16.			
	32.			14.			
	22.			14.			
	10.			6.			
13	116.26	115.8	114.45	112.9	109.	107.9	107.
4							
5	122.3	69.89	760.2	111.5	12.1	.86	.826
	15.17	25.08	36.	59.	73.33	85.17	98.67
5							
	16.	25.83	36.83	60.42	74.42	87.	100.
7							
	1.5267	12.0440	15.7124	31.5077	19.4365	19.0522	18.556
25							
	32.	30.	40.	0.	100.		
	76.	25.	3.	.0	104.		
	372.	25.	4.	6.	152.		
	188.	30.	18.	10.	76.		
	1320.	194.	90.	132.	720.		
	129.	44.	16.	28.	116.		
	84.	48.	19.	12.5	102.		
	44.	50.	22.	20.	140.		
	246.	230.	40.	54.	512.		
	32.						
	21.			3.5			
	6.5			3.5			
	7.5			5.5			
	5.			4.			
	4.			4.			
	4.5			5.			
6	117.91	115.12	113.6	112.51	111.6	111.52	

5	123.	72.7	764.5	111.5	12.1	.86	.826
5	14.	31.75	45.67	61.33	74.75	90.68	102.14
5	19.75	32.25	46.33	62.08	75.5	91.	102.87
5	1.7921	11.6142	16.2350	17.8692	16.5196	16.1718	15.2768
5	72.	200.	2.		195.		
5	100.	12.	4.	.0	44.		
5	248.	33.	6.	.0	124.		
5	508.	50.	20.	8.	208.		
5	549.	60.	26.	36.	230.		
5	320.	70.	18.	40.	188.		
5	247.	54.	20.	40.	184.		
5	168.	68.	14.	30.	128.		
5	248.	188.	30.	80.	264.		
5	60.			4.			
5	57.			12.			
5	42.			18.			
5	38.			27.			
5	36.			24.			
5	26.			16.			
5	28.			14.			
5	116.8	115.47	114.16	113.07	112.71	111.63	
6	120.25	72.22	762.	110.	12.87	.86	.826
5	20.5	37.17	49.17	63.67	80.	98.17	111.
5	21.67	37.75	50.33	64.67	87.58	98.58	111.58
5	4.5771	18.1065	12.2995	15.6062	23.8542	13.0677	13.2782
5	128.	920.	2.	.0	7360.		
5	124.	.0	2.	0.	120.		
5	312.	32.	4.	6.	96.		
5	364.	40.	16.	14.	156.		
5	1024.	123.	10.	22.	448.		
5	235.	38.	14.	14.	132.		
5	128.	40.	10.	12.	184.		
5	220.	112.	14.	14.	320.		
5	48.	28.	6.	14.	128.		
5	38.			2.			
5	42.			4.			
5	24.			6.			
5	32.			15.			
5	12.			5.			
5	8.			5.			
5	4.			4.			
5	116.81	115.	112.7	110.5	109.	107.3	

7	125.7	71.2	760.	110.	13.6	.86	.826
	10.43	30.5	44.22	59.52	73.55	93.58	108.82
	20.17	31.1	44.83	60.17	74.03	91.72	109.22
03	6.2839	13.921	18.4603	20.4970	18.543	23.6981	23.3788
	40.	16.	2.	.0	80.		
	1056.	176.	48.	8.	608.		
	1984.	266.	40.	36.	752.		
	2048.	244.	72.	95.	704.		
	1600.	138.	64.	121.	704.		
	1568.	408.	84.	180.	1104.		
	1200.	586.	80.	94.	976.		
	400.	266.	44.	37.	448.		
	464.	600.	56.	124.	1072.		
	40.			3.5			
	30.			6.0			
	55.			9.0			
	20.			3.5			
	24.			5.5			
	28.			6.			
	12.			4.5			
7	118.92	116.32	114.07	111.74	110.71	110.02	
8	125.8	71.08	752.3	106.	11.4	0.86	0.826
	20.	30.	41.	50.	60.1	71.	104.
	20.35	30.35	41.35	50.35	60.45	71.35	104.35
85	2.7333	12.5778	24.9192	36.4829	47.6515	61.4556	77.5095
2	.03	.0	.004	.0	1.		
809	2.28	.0	.096	.0	1.		
	7.33	.44	.271	.032	1.		
	21.63	1.03	.692	0.3248	1.		
	31.246	2.05	.945	.72	1.		
	33.32	3.55	1.289	1.12	1.		
	40.24	4.8	1.83	1.68	1.		
	45.04	7.75	2.452	2.89	1.		
	56.62	10.29	2.752	3.91	1.0		
	87.			2.			
	47.			5.			
	52.			9.			
	51.			10.			
	61.			12.			
	31.			9.5			
	23.			0.			
71	114.04	113.42	111.97	110.8	109.36	107.39	

4						382
	126.8	71.5	768.0	106.	12.1	.86
	20.45	33.47	46.12	62.75	75.23	89.38
7	20.98	34.08	46.98	63.33	76.03	90.
7						105.7
2	1.5737	14.1775	16.1748	18.1824	12.5872	15.3696
54						19.1200
	300.	400.	2.	.0	1280.	
	180.	58.	5.	.0	272.	
	568.	60.	12.	4.	204.	
	288.	20.	6.	16.	128.	
	1344.	152.	44.	31.	528.	
	480.	80.	16.	60.	384.	
	1120.	231.	44.	70.	928.	
	544.	152.	26.	100.	496.	
	302.	120.	13.	84.	384.	
	62.			2.		
	48.			6.		
	54.			8.		
	42.			10.		
	40.			12.		
	24.			7.		
	13.			6.		
	105.47	105.	102.6	100.38	98.	97.

C.1.3 Results from Program LABDATA

Each run contains three pages of computer outputs to represent the treated experimental data. The major work of this program is to convert measured temperature, feed rate, total vapor condensate and analytical results from Gas Chromatography into vapor and liquid molal quantities, reaction rate and all associated quantities. The items shown on the computer printouts are explained as follows.

Page 1 -

1. INITIAL CONDITIONS FOR THE REAL TIME

TEMP = initial and surrounding temperature, °C

VOL = clear liquid volume, milliliters

TOT LIQ = initial total liquid molal quantity

AMIDE = initial molal quantity of acrylamide

H₂SO₄ = initial molal quantity of sulfuric acid

H₂O = initial molar quantity of water

2. FEED CONDITIONS

RATE = feed rate of aqueous ethyl alcohol solution

ALCOHOL = weight fraction of ethyl alcohol

WATER = weight fraction of water

VAPOR FRACTION = vapor to feed ratio by weight

3. MIXTURE QUANTITIES AND REACTION RATES VS ADJUSTED TIME

TIME = adjusted time as defined in the computer
printouts

TIME LAG = time lag for vapor condensate from its
leaving liquid surface to vapor sample
bottle

= vapor travelling time, minutes

TEMP = instantaneous liquid temperature

LIQ VOL = instantaneous clear liquid volume, ml

VAP MOL = accumulated total vapor condensate, g-moles

ACR RATE = reaction rate of esterification, g-moles
/min.-ml

ROR RATE = reaction rate of dehydration, g-moles
/min.-ml

4. INSTANTANEOUS LIQUID MOLAL QUANTITIES VS ADJUSTED TIME

All the terms are well defined

5. ACCUMULATED VAPOR MOLAL QUANTITIES VS ADJUSTED TIME

All the terms are well defined

Page 2 -

1. INSTANTANEOUS TOTAL MOLAL QUANTITIES VS ADJUSTED TIME ... REACTION RATE CONSTANTS

$$1000/2.3 \text{ RT} = \frac{1000}{(2.3)(1.987)(\text{temperature in } ^\circ\text{K})}$$

ACR RCONST = rate constant of esterification,
ml/g-mole-min.

ROR RCONST = rate constant of dehydration,
ml/g-mole-min.

PRO RCONST = rate constant of successive reaction,
(ml/g-mole)²/min.

2. ACCUMULATED VAPOR QUANTITIES VS REAL TIME

All the quantities are in g-moles.

3. INSTANTANEOUS LIQUID MOLE FRACTION VS ADJUSTED TIME

All the terms are well defined

4. INSTANTANEOUS VAPOR MOLE FRACTIONS AND TOTAL VAPOR FLOW RATE VS ADJUSTED TIME

V RATE = total vapor flow rate, g-moles/min.

Page3 -

1. INSTANTANEOUS EQUILIBRIUM CONSTANTS VS ADJUSTED TIME

All the terms are well defined.

2. INSTANTANEOUS LIQUID ACTIVITY COEFFICIENT VS ADJUST TIME

All the terms are well defined.

3. SUMMARY OF ERRORS FOR CURVES FITS-3 DEGREE POLYNOMIALS

In order to calculate vapor flow rate and reaction rate, all the instantaneous molal quantities are fitted with respect to time into third order

polynomial equations. The errors for each set of data fit are represented by absolute average percentage error and standard deviation.

DEFINITIONS-

REAL TIME IS COUNTED FROM THE MOMENT ALCOHOL IS FIRST MIXED WITH ACRYLAMIDE SULFATE

ADJUSTED TIME IS COUNTED FROM THE MOMENT STUDIES FOR DISTILLATION ACCOMPANIED BY CHEMICAL REACTIONS BEGIN

ADJUSTED TIME MUST BEGIN RIGHT OR SLIGHTLY AFTER THE REACTING LIQUID MIXTURE BECOMES BOILING

INITIAL CONDITIONS FOR THE REAL TIME

TEMP= 115.00 C VOL= 136.40 ML TOT_LIQ= 2.8989 MOL AMIDE= 1.012 MOL H2SO4= 1.277 MOL WATER= .611 MOL

FEED CONDITIONS

RATE=1.5600 ML/MIN ALCOHOL= .8600 WT FRACTION WATER= .1400 WT FRACTION VAPOR FRACTION= .8200

MIXTURE QUANTITIES AND REACTION RATES VS ADJUSTED TIME

TIME	TIME LAG	TEMP	LIQ VOL	LIQ MOL	VAP MOL	ACR RATE	ROP RATE	PPD RATE
0.00	.33651	125.41	156.03	2.50867	.43191	.0091911	.0004011	.0009354
12.57	.31394	123.16	155.23	2.45009	.70411	.0077392	.0003765	.0008345
26.95	.29213	120.83	154.10	2.78919	1.04793	.0062251	.0003495	.0007109
43.92	.27416	118.47	152.47	2.90723	1.49586	.0044439	.0003194	.0005528
57.00	.26329	116.99	151.00	2.97113	1.87056	.0035763	.0002975	.0004244
72.52	.25108	115.65	149.01	3.01878	2.34641	.0024800	.0002729	.0002614
88.02	.24249	114.93	146.75	3.03711	2.85341	.0015700	.0002500	.0000885
101.35	.23617	114.82	144.60	3.03171	3.31313	.0009350	.0002315	0.0000000

INSTANTANEOUS LIQUID MOLAR QUANTITIES VS. ADJUSTED TIME

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE	COMPLEX	H2SO4	NH4HSO4
0.00	.341391	.092631	.798134	0.000000	0.000000	.686895	.264688	.324926
12.57	.343766	.088969	.880844	0.000000	.009999	.559089	.264688	.452732
26.95	.473730	.072049	.956222	0.000000	.010684	.454814	.264688	.557007
43.92	.542430	.051457	1.022043	0.000000	.014791	.384927	.264688	.657894
57.00	.585555	.035252	1.058135	0.000000	.015682	.296765	.264688	.715056
72.52	.610177	.030400	1.087264	0.000000	.014425	.236773	.264688	.775048
88.02	.621146	.022793	1.104494	0.000000	.012157	.201737	.264688	.810084
101.35	.620249	.013277	1.112224	0.000000	.009450	.191874	.264688	.819947

ACCUMULATED VAPOR MOLAR QUANTITIES VS ADJUSTED TIME

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE
0.00	.065494	.229716	.128481	.005636	.002580
12.57	.163300	.346500	.176524	.010522	.007174
26.95	.307560	.460830	.250353	.015740	.013444
43.92	.522672	.570165	.360130	.021413	.021481
57.00	.721949	.636540	.459044	.025446	.027582
72.52	.996576	.696160	.589745	.029871	.034062
88.02	1.312596	.736098	.731770	.033921	.029026
101.35	1.618057	.755680	.860724	.037128	.041540

INSTANTANEOUS TOTAL MOLAR QUANTITIES VS ADJUSTED TIME

REACTION RATE CONSTANTS

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE	1000/P.3FT	ACR RCONST	ROP RCONST	PRO RCONST
0.00	.406885	.322346	.926615	.005636	.002580	.548285	6.115397	.537017	284.445787
12.57	.557065	.435559	1.057367	.010522	.017173	.551398	5.455291	.376892	231.970560
26.95	.781289	.532879	1.206576	.015740	.024128	.554659	4.452343	.239982	165.403652
43.92	1.045102	.621622	1.382173	.021413	.036272	.558001	3.694273	.165514	123.638654
57.00	1.307504	.671792	1.517179	.025446	.043264	.560118	3.107630	.131008	95.100421
72.52	1.606753	.726560	1.677009	.029870	.048487	.562048	2.557874	.104227	65.848840
88.02	1.933742	.758891	1.836264	.033921	.051194	.563091	1.838687	.095075	24.491023
101.35	2.238305	.768957	1.972948	.037128	.050990	.563251	1.136122	.086999	0.000000

ACCUMULATED VAPOR QUANTITIES VS REAL TIME

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE
10.42	.000871	.000786	.008424	.000008	0.000000
20.67	.029806	.103254	.055763	.002612	.000511
31.58	.082646	.222863	.125736	.006113	.003228
44.17	.151397	.359876	.178842	.010284	.006834
58.33	.275130	.475847	.265572	.014924	.012136
75.43	.544612	.563017	.346469	.022002	.022219
88.58	.742138	.603901	.456903	.027099	.030122
104.33	.948358	.727777	.600697	.028550	.032556
119.67	1.316864	.740595	.741867	.033952	.038412
133.33	1.644258	.749462	.863598	.037585	.042269

INSTANTANEOUS LIQUID MOLE FRACTION VS ADJUSTED TIME

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE	COMPLEX	H2SO4	NH4HSO4
0.00	.136085	.036924	.318151	0.000000	0.000000	.273809	.105509	.129521
12.57	.148586	.033572	.332383	0.000000	.003773	.210970	.099879	.170837
26.95	.169845	.025832	.342831	0.000000	.003830	.163063	.094898	.199702
43.92	.186580	.017700	.351552	0.000000	.005088	.121740	.091045	.226296
57.00	.197081	.011865	.356139	0.000000	.005279	.099883	.089087	.240668
72.52	.202127	.010070	.360167	0.000000	.004779	.078434	.087681	.256742
88.02	.204519	.007505	.363666	0.000000	.004006	.064424	.087151	.266729
101.35	.204587	.004379	.366864	0.000000	.003117	.063289	.087307	.270457

INSTANTANEOUS VAPOR MOLE FRACTIONS AND TOTAL VAPOR FLOW RATE VS ADJUSTED TIME

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE	VSATE
0.00	.327526	.483575	.153760	.019501	.015638	.020570
12.57	.388459	.380955	.196230	.016566	.017789	.022724
26.95	.448285	.288852	.230533	.013938	.018391	.025074
43.92	.509850	.204355	.267043	.011535	.017217	.027689
57.00	.552810	.152084	.269823	.010054	.015230	.024588
72.52	.600392	.100786	.278337	.008607	.011878	.031700
88.02	.645467	.058487	.281021	.007420	.007604	.033536
101.35	.683008	.027708	.279453	.006562	.003269	.035272

INSTANTANEOUS EQUILIBRIUM CONSTANTS VS ADJUSTED TIME

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE
0.00	2.406778	13.096401	.483291		100.000000
12.57	2.614374	11.347407	.590374		4.714859
26.95	2.639383	11.142162	.672439		4.801321
43.42	2.732613	11.545717	.731167		3.384020
57.00	2.804980	12.818165	.757634		2.885521
72.52	2.970368	10.008112	.772799		2.485679
88.02	3.156028	7.793407	.772744		1.898136
101.35	3.338467	6.327256	.761735		1.048690

INSTANTANEOUS LIQUID ACTIVITY COEFFICIENT VS ADJUSTED TIME

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE
0.00	.572884	7.741847	.220218		100.000000
12.57	.650509	7.072706	.287840		22.527482
26.95	.707950	7.369938	.352011		24.957217
43.42	.740950	8.060908	.411793		19.183815
57.00	.834713	9.283515	.446980		17.284738
72.52	.917300	7.495861	.475687		15.659167
88.02	.994412	5.944233	.486695		12.288375
101.35	1.055140	4.839434	.481451		6.817560

SUMMARY OF ERRORS FOR CURVE FITS-- 3 DEGREE POLYNOMIALS

VAPOR FLOW RATES

	VAPOR RATE VS VAPOR ADJUSTED TIME BEFORE TIME LAG CORRECTION		VAPOR RATE VS LIQUID ADJUSTED TIME AFTER TIME LAG CORRECTION	
	ABS PCT ERR	STANDARD DEV	ABS PCT ERR	STANDARD DEV
ALCOHOL	.74251E+01	.17214E+01	.74209E+01	.17216E+01
ACRYLATE	.28588E+01	.19276E+01	.28572E+01	.19272E+01
WATER	.20909E+01	.16428E+00	.20909E+01	.16428E+00
ETHER	.36816E+01	.68164E-01	.36815E+01	.68179E-01
PROPIONATE	.68655E+01	.19567E+00	.68590E+01	.19565E+00

REACTION RATE

	ACR RATE	ROP RATE	PRO RATE
ABS PCT ERR	.54590E+00	.61763E-10	.77444E+01
STANDARD DEV	.35369E-02	.94537E-14	.12087E-02

DEFINITIONS

REAL TIME IS COUNTED FROM THE MOMENT ALCOHOL IS FIRST MIXED WITH ACRYLAMIDE SULFATE

ADJUSTED TIME IS COUNTED FROM THE MOMENT STUDIES FOR DISTILLATION ACCOMPANIED BY CHEMICAL REACTIONS BEGIN

ADJUSTED TIME MUST BEGIN RIGHT OR SLIGHTLY AFTER THE REACTING LIQUID MIXTURE BECOMES BOILING

INITIAL CONDITIONS FOR THE REAL TIME

TEMP= 115.00 C VOL= 137.79 ML TOT LIQ= 2.9779 MOL AMIDE= .997 MOL H2SO4= 1.287 MOL WATER= .694 MOL

FEED CONDITIONS

RATE=1.7360 ML/MIN ALCOHOL= .8600 WT FRACTION WATER= .1400 WT FRACTION VAPOR FRACTION= .3400

MIXTURE QUANTITIES AND REACTION RATES VS ADJUSTED TIME

TIME	TIME LAG	TEMP	LIQ VOL	LIQ MOL	VAP MOL	ACP RATE	ROP RATE	PRO RATE
0.00	.36473	123.57	163.16	2.69542	.43814	.0110038	.0003453	.0004965
11.47	.30729	120.65	165.64	2.88715	.67444	.0084700	.0003406	.0004792
21.47	.27710	118.26	167.19	3.02478	.91176	.0065471	.0002956	.0004587
34.39	.25193	114.07	168.24	3.16339	1.25896	.0044575	.0002413	.0004248
48.30	.23365	111.28	168.51	3.26183	1.68037	.0027051	.0001475	.0003749
59.72	.22080	110.20	168.18	3.31017	2.06041	.0016521	.0001470	.0003339
71.57	.21026	109.60	167.38	3.33317	2.48461	.0009269	.0001046	.0002802
84.57	.20176	108.80	166.04	3.32466	2.98193	.0005620	.0000705	.0002133

INSTANTANEOUS LIQUID MOLAR QUANTITIES VS ADJUSTED TIME

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE	COMPLEX	H2SO4	NH4HSO4
0.00	.418144	.079233	.907816	0.000000	.003525	.691470	.289941	.305243
11.47	.539163	.076599	.979780	0.000000	.004907	.571331	.289941	.425432
21.47	.625784	.067728	1.039740	0.000000	.004821	.496493	.289941	.500360
34.39	.700527	.062887	1.109335	0.000000	.003874	.419473	.289941	.577291
48.30	.745840	.053766	1.168896	0.000000	.006523	.343091	.289941	.633763
59.72	.764178	.050448	1.201497	0.000000	.007345	.329050	.289941	.667714
71.57	.743602	.031523	1.215729	0.000000	.005609	.321762	.289941	.675001
84.57	.801698	.027095	1.203739	0.000000	.005424	.301971	.289941	.694792

ACCUMULATED VAPOR MOLAR QUANTITIES VS ADJUSTED TIME

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE
0.00	.077872	.221134	.132248	.005487	.001401
11.47	.128494	.337102	.192310	.009704	.006825
21.47	.224105	.416746	.246959	.012883	.011066
34.39	.407286	.494522	.324794	.016347	.016008
48.30	.564365	.552638	.423208	.019323	.020836
59.72	.908496	.585356	.519766	.021231	.024565
71.57	1.184909	.609520	.639089	.022742	.028349
84.57	1.498659	.629715	.797096	.023901	.032658

INSTANTANEOUS TOTAL MOLAR QUANTITIES VS ADJUSTED TIME REACTION RATE CONSTANTS

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE	1030/2.3RT	ACR RCONST	POP RCONST	PRO RCONST
0.00	.496016	.300367	1.040064	.005487	.004926	.550828	6.204472	.368875	109.333212
11.47	.667657	.413700	1.172090	.009704	.011732	.554912	4.555648	.194115	79.207877
21.47	.849891	.484473	1.286699	.012883	.015887	.558301	3.523689	.126206	65.962112
34.39	1.107873	.557409	1.434129	.016347	.019881	.564342	2.551791	.082701	58.398748
48.30	1.410306	.606404	1.592104	.019323	.027359	.568437	1.683497	.056788	53.254167
59.72	1.673674	.635804	1.721263	.021231	.031910	.570039	1.104975	.042350	49.144958
71.57	1.978511	.641043	1.854818	.022742	.033959	.572932	.607569	.028853	38.740586
84.57	2.300357	.656810	2.000835	.023901	.037982	.572128	.385424	.018201	30.290933

ACCUMULATED VAPOR QUANTITIES VS REAL TIME

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE
8.42	.000390	.000390	.004918	.000020	0.000000
20.75	.023310	.110290	.067226	.001422	.000262
31.47	.074030	.225371	.134530	.005560	.001711
42.67	.144555	.347082	.192520	.010279	.006622
52.88	.230191	.414259	.256692	.012650	.011959
65.58	.338109	.502991	.325628	.016656	.016188
79.50	.495403	.547552	.424778	.019182	.020299
90.43	.626868	.584769	.514514	.021189	.024672
102.72	1.175853	.616747	.656354	.023092	.029092
115.80	1.516462	.627885	.799442	.023815	.032470

INSTANTANEOUS LIQUID MOLE FRACTION VS ADJUSTED TIME

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE	COMPLEX	H2SO4	NH4HSO4
0.00	.155131	.029396	.336799	0.000000	.001308	.256535	.107568	.113263
11.47	.186746	.026531	.330359	0.000000	.001700	.197887	.100425	.147354
21.47	.206886	.022391	.343741	0.000000	.001594	.154112	.095855	.165420
34.39	.221467	.019880	.350680	0.000000	.001224	.132602	.091655	.182491
48.30	.228688	.016483	.358356	0.000000	.002000	.111287	.084889	.194297
59.72	.230857	.015240	.362971	0.000000	.002219	.099406	.087591	.201716
71.57	.238092	.009457	.364737	0.000000	.001683	.096533	.086987	.202510
84.57	.241137	.008150	.362064	0.000000	.001631	.090928	.087209	.208951

INSTANTANEOUS VAPOR MOLE FRACTIONS AND TOTAL VAPOR FLOW RATE VS ADJUSTED TIME

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE	VPATE
0.00	.073627	.602457	.276336	.020954	.020625	.018265
11.47	.326916	.399653	.238195	.015271	.019955	.022203
21.47	.466248	.280844	.225067	.011761	.016081	.025136
34.39	.575859	.176912	.226076	.008446	.012708	.025567
48.30	.634784	.105932	.242984	.005864	.010436	.031975
59.72	.650886	.069472	.265088	.004258	.009297	.034549
71.57	.644147	.047011	.297279	.002934	.008629	.027009
84.57	.614364	.036529	.338951	.001786	.008371	.030450

INSTANTANEOUS EQUILIBRIUM CONSTANTS VS ADJUSTED TIME

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPRIONATE
0.00	.474614	20.494866	.820478		20.360884
11.47	1.750596	15.063729	.701899		11.747123
21.47	2.253640	12.542729	.654759		10.090117
34.39	2.600199	8.899127	.644679		10.377958
48.30	2.775768	6.426532	.678053		5.218424
59.72	2.819428	4.558454	.733083		4.190292
71.57	2.705449	4.970885	.815051		5.127869
84.57	2.547782	4.482202	.936163		5.130888

INSTANTANEOUS LIQUID ACTIVITY COEFFICIENT VS ADJUSTED TIME

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPRIONATE
0.00	.118923	12.700462	.396653		96.242627
11.47	.473668	10.010804	.370928		61.705617
21.47	.650301	8.837005	.372649		57.874358
34.39	.842615	6.964917	.419021		69.696302
48.30	.974029	5.404909	.482425		39.027828
59.72	1.020822	3.943735	.540394		32.690141
71.57	.996868	4.369082	.612827		40.959718
84.57	.961095	4.023956	.722797		42.300270

SUMMARY OF ERRORS FOR CURVE FITS-- 3 DEGREE POLYNOMIALS

VAPOR FLOW RATES

	VAPOR RATE VS VAPOR ADJUSTED TIME BEFORE TIME LAG CORRECTION		VAPOR RATE VS LIQUID ADJUSTED TIME AFTER TIME LAG CORRECTION	
	ABS PCT ERR	STANDARD DEV	ABS PCT ERR	STANDARD DEV
ALCOHOL	.36128E+01	.74618E+00	.36242E+01	.74678E+00
ACRYLATE	.11062E+01	.57696E+00	.11044E+01	.57630E+00
WATER	.11357E+01	.11894E+00	.11350E+01	.11885E+00
ETHER	.19165E+01	.21964E-01	.19150E+01	.21955E-01
PROPRIONATE	.22727E+01	.67296E-01	.22765E+01	.67224E-01

REACTION RATE

	ACP RATE	ROR RATE	PRO RATE
ABS PCT ERR	.34654E+00	.29924E-10	.38257E+01
STANDARD DEV	.28744E-02	.40696E-14	.79992E-03

DEFINITIONS-
 REAL TIME IS COUNTED FROM THE MOMENT ALCOHOL IS FIRST MIXED WITH ACRYLAMIDE SULFATE
 ADJUSTED TIME IS COUNTED FROM THE MOMENT STUDIES FOR DISTILLATION ACCOMPANIED BY CHEMICAL REACTIONS BEGIN
 ADJUSTED TIME MUST BEGIN RIGHT OR SLIGHTLY AFTER THE REACTING LIQUID MIXTURE BECOMES BOILING

INITIAL CONDITIONS FOR THE REAL TIME

TEMP= 111.50 C VOL= 139.28 ML TOT LIG= 3.0413 MOL AMIDE= 1.028 MOL H2SO4= 1.275 MOL WATER= .739 MOL

FEED CONDITIONS

RATE=1.4960 ML/MIN ALCOHOL= .8600 WT FRACTION WATER= .1400 WT FRACTION VAPOR FRACTION= .6900

MIXTURE QUANTITIES AND REACTION RATES VS ADJUSTED TIME

TIME	TIME LAG	TEMP	LIG VOL	LIG MOL	VAP MOL	ACR RATE	RDR RATE	PRD RATE
0.00	.31740	118.03	177.70	2.85516	.18560	.0079597	.0005198	.0009599
9.20	.30304	116.86	178.45	2.95539	.37584	.0073100	.0004585	.0008584
20.15	.28670	115.80	179.12	3.06550	.61664	.0064973	.0004139	.0007474
43.53	.25366	114.45	179.51	3.24588	1.18650	.0046192	.0003213	.0005468
54.15	.24847	112.90	179.06	3.29513	1.47199	.0037018	.0002899	.0004719
67.61	.23772	109.00	177.80	3.35040	1.85923	.0024812	.0002598	.0003917
78.66	.22931	107.90	176.34	3.36160	2.19929	.0014310	.0002431	.0003381
92.61	.21991	107.00	173.75	3.35584	2.65842	.0000429	.0002324	.0002851

INSTANTANEOUS LIQUID MOLAR QUANTITIES VS ADJUSTED TIME

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE	COMPLEX	H2SO4	VA4HSO4
0.00	.453074	.127607	.998985	0.000000	0.000000	.803898	.247907	.223685
9.20	.531154	.105688	1.035362	0.000000	.007693	.736378	.247907	.291204
20.15	.607408	.096177	1.075016	0.000000	.011409	.654469	.247907	.373113
43.53	.698055	.112065	1.143177	0.000000	.017092	.478812	.247907	.548771
54.15	.765118	.064340	1.165199	0.000000	.024979	.462789	.247907	.564793
67.61	.807387	.067996	1.193651	0.000000	.015280	.409366	.247907	.519217
78.66	.812631	.057826	1.190009	0.000000	.019644	.276950	.247907	.650632
92.61	.840097	.041498	1.185464	0.000000	.013292	.362201	.247907	.665381

ACCUMULATED VAPOR MOLAR QUANTITIES VS ADJUSTED TIME

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE
0.00	.040952	.095009	.044999	.003563	.001069
9.20	.088402	.174360	.101507	.008105	.003463
20.15	.166360	.258968	.171824	.012930	.006559
43.53	.408731	.405176	.336699	.021461	.014438
54.15	.551925	.456713	.419895	.024701	.018761
67.61	.762125	.509268	.524379	.028389	.025073
78.66	.958065	.542110	.636901	.031161	.031053
92.61	1.234659	.570818	.778703	.034464	.039773

INSTANTANEOUS TOTAL MOLAR QUANTITIES VS ADJUSTED TIME

REACTION RATE CONSTANTS

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE	1000/2.3RT	ACP RCONST	ROR RCONST	PRO RCONST
0.00	.494036	.222616	1.043984	.003563	.001069	.558529	3.883491	.449959	183.695450
9.20	.619557	.280048	1.136869	.008105	.011157	.560305	3.335145	.296311	131.573279
20.15	.773768	.355145	1.246840	.012930	.017969	.561932	2.927528	.200952	99.306952
43.53	1.106786	.517240	1.479877	.021461	.031530	.563788	2.450834	.118364	75.513160
54.15	1.317043	.521053	1.585094	.024701	.043740	.566052	1.871959	.088687	55.851030
67.61	1.559511	.577263	1.718031	.028389	.040953	.571829	1.334752	.070867	46.402944
78.66	1.776696	.599936	1.826910	.031161	.050697	.573479	.817713	.063975	41.515732
92.61	2.074755	.612316	1.964168	.034464	.053065	.574937	.024518	.057216	33.791561

ACCUMULATED VAPOR QUANTITIES VS REAL TIME

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE
9.53	.000886	.000365	0.000000	.000006	0.000000
19.72	.008869	.013546	.006369	.001402	0.000000
33.17	.050131	.106285	.045667	.004557	.000884
41.33	.084532	.181393	.106994	.008241	.004422
52.03	.169669	.255590	.190257	.011962	.005506
70.67	.354856	.379463	.289094	.021424	.012458
86.12	.555942	.462474	.406227	.024170	.018613
99.70	.765405	.508800	.554768	.028183	.025357
110.83	.968229	.541296	.645665	.031441	.031748
125.08	1.251094	.573084	.781854	.034585	.040081

INSTANTANEOUS LIQUID MOLE FRACTION VS ADJUSTED TIME

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE	COMPLEX	H2SO4	NH4HSO4
0.00	.158686	.044693	.349888	0.000000	0.000000	.281560	.086828	.078344
9.20	.179724	.035761	.350330	0.000000	.002503	.249165	.083883	.099533
20.15	.198143	.031374	.350682	0.000000	.003722	.213495	.080870	.121714
43.53	.215059	.034525	.352193	0.000000	.005266	.147514	.076376	.169067
54.15	.232197	.019526	.353613	0.000000	.007581	.140447	.075234	.171403
67.61	.240982	.020295	.353286	0.000000	.004740	.122194	.073993	.184520
78.66	.243524	.017202	.354001	0.000000	.005844	.112134	.073747	.193549
92.61	.250339	.012366	.353254	0.000000	.003961	.107932	.073873	.198276

INSTANTANEOUS VAPOR MOLE FRACTIONS AND TOTAL VAPOR FLOW RATE VS ADJUSTED TIME

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE	VRATE
0.00	.211401	.449951	.300241	.025865	.012543	.020096
9.20	.244906	.386082	.294314	.022027	.012671	.021266
20.15	.359572	.318885	.290249	.018213	.013082	.022725
43.53	.480328	.202528	.290091	.012322	.014570	.024075
54.15	.521051	.159893	.292965	.010467	.015625	.027701
67.61	.562299	.113438	.294578	.008703	.016982	.029856
78.66	.588824	.080815	.304505	.007669	.018186	.031704
92.61	.614368	.045728	.313304	.006806	.019793	.034139

---INSTANTANEOUS EQUILIBRIUM CONSTANTS VS ADJUSTED TIME

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE
0.00	1.332195	10.067497	.858105		100.000000
9.20	1.585241	10.796173	.840105		4.867270
20.15	1.814707	10.164017	.827669		3.514819
43.53	2.233751	5.866098	.823671		2.785815
54.15	2.244002	8.188772	.828490		2.061158
67.61	2.333366	5.589537	.845146		3.562810
78.66	2.417925	4.698043	.860182		3.112401
92.61	2.454146	3.597911	.886907		4.997329

---INSTANTANEOUS LIQUID ACTIVITY COEFFICIENT VS ADJUSTED TIME

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE
0.00	.388344	7.151463	.493838		100.000000
9.20	.477158	7.906254	.501590		29.528718
20.15	.562475	7.643653	.511031		22.190802
43.53	.718973	4.564728	.530947		18.512042
54.15	.754643	6.629886	.561389		14.534421
67.61	.878473	5.011072	.650748		29.419428
78.66	.940394	4.337141	.687029		26.698382
92.61	.980432	3.497370	.730055		44.439047

SUMMARY OF EPROPS FOR CURVE FITS-- 3 DEGREE POLYNOMIALS

VAPOR FLOW RATES

VAPOR RATE VS VAPOR		VAPOR RATE VS LIQUID	
ADJUSTED TIME BEFORE		ADJUSTED TIME AFTER	
TIME LAG CORRECTION		TIME LAG CORRECTION	
ABS	PCT EPR	ABS	PCT FPR
STANDARD DEV		STANDARD DEV	
ALCOHOL	.19743E+01	.13948E+00	.19663E+01
ACRYLATE	.88415E+00	.30889E+00	.88595E+00
WATER	.52502E+01	.22978E+00	.52555E+01
ETHER	.32748E+01	.54435E-01	.32695E+01
PROPIONATE	.10888E+02	.66102E-01	.10894E+02

REACTION RATE	ACR RATE	ROR RATE	PRO RATE
ABS PCT FPR	.19472E+01	.56018E-11	.11497E+02
STANDARD DEV	.11912E-01	.13729E-14	.25980E-02

DEFINITIONS-

REAL TIME IS COUNTED FROM THE MOMENT ALCOHOL IS FIRST MIXED WITH ACRYLAMIDE SULFATE

ADJUSTED TIME IS COUNTED FROM THE MOMENT STUDIES FOR DISTILLATION ACCOMPANIED BY CHEMICAL REACTIONS BEGIN

ADJUSTED TIME MUST BEGIN RIGHT OR SLIGHTLY AFTER THE REACTING LIQUID MIXTURE BECOMES BOILING

INITIAL CONDITIONS FOR THE REAL TIME

TEMP= 111.50 C VOL= 134.12 ML TOT LIQ= 2.9021 MOL AMIDE= .984 MOL H2SO4= 1.247 MOL WATER= .672 MOL

FEED CONDITIONS

RATE=1.5575 ML/MIN ALCOHOL= .8600 WT FRACTION WATER= .1400 WT FRACTION VAPOR FRACTION= .6000

MIXTURE QUANTITIES AND REACTION RATES VS ADJUSTED TIME

TIME	TIME LAG	TEMP	LIQ VOL	LIQ MOL	VAP MOL	ACR RATE	POP RATE	PRO RATE
0.00	.39015	119.46	162.22	2.57020	.20084	.0061780	.0004171	.0010704
10.92	.33825	117.91	163.63	2.72996	.40048	.0070556	.0005505	.0008797
33.92	.27643	115.12	164.00	2.96764	.93052	.0049540	.0007024	.0005384
48.25	.25689	113.60	162.82	3.05593	1.32204	.0036244	.0007085	.0003674
60.09	.24959	112.51	161.28	3.10544	1.67284	.0024951	.0006622	.0002501
73.59	.24267	111.60	159.08	3.13755	2.09571	.0021646	.0005528	.0001429
94.67	.23769	111.52	155.23	3.15287	2.78662	.0011128	.0002612	.0000322

INSTANTANEOUS LIQUID MOLAR QUANTITIES VS ADJUSTED TIME

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE	COMPLEX	H2SO4	NH4HSO4
0.00	.334454	.114545	.874261	0.000000	0.000000	.765238	.263406	.218297
10.92	.432274	.097155	.944945	0.000000	.008644	.661446	.263406	.322090
33.92	.608889	.046633	1.051775	0.000000	.013404	.520201	.263406	.463334
48.25	.660244	.036341	1.098181	0.000000	.014227	.443993	.263406	.539542
60.09	.690632	.026556	1.129973	0.000000	.011341	.401689	.263406	.581846
73.59	.696956	.019630	1.163549	0.000000	.010479	.362435	.263406	.621100
94.67	.675530	.011759	1.221661	0.000000	.006975	.329136	.263406	.654399

ACCUMULATED VAPOR MOLAR QUANTITIES VS ADJUSTED TIME

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE
0.00	.043488	.103202	.050849	.002756	.000551
10.92	.061462	.212367	.094654	.008075	.003923
33.92	.271900	.389578	.232504	.022820	.013719
48.25	.460502	.468490	.339548	.033011	.020485
60.09	.653435	.518189	.434285	.041171	.025760
73.59	.911339	.560185	.543939	.049440	.030807
94.67	1.387268	.600594	.705406	.058279	.035070

INSTANTANEOUS TOTAL MOLAR QUANTITIES VS ADJUSTED TIME

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE	1000/2.3PT	ACP RCONST	POP RCONST	PRO RCONST
0.00	.377942	.217746	.925110	.002756	.000551	.556594	5.183416	.504865	329.080896
10.92	.513736	.309522	1.039599	.008075	.012567	.554800	4.037874	.482101	190.564686
33.92	.880789	.435211	1.284279	.022820	.027123	.562815	2.564954	.310718	75.082952
48.25	1.120746	.504831	1.437730	.033011	.034711	.565027	2.124201	.264539	50.319350
60.09	1.344058	.544745	1.564257	.041171	.037102	.566524	1.741216	.223913	33.948931
73.59	1.608295	.579814	1.707489	.049440	.041285	.567964	1.363215	.181038	20.542881
94.67	2.062798	.612353	1.927068	.058279	.042045	.568083	.776923	.088866	5.164531

ACCUMULATED VAPOR QUANTITIES VS REAL TIME

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE
6.33	.000209	.000043	.000172	.000051	0.000000
16.00	.005353	.010086	.014398	.000429	0.000000
25.83	.036399	.108936	.043155	.001441	.000851
36.83	.092534	.213138	.114016	.010964	.003810
60.42	.278531	.400115	.232105	.023116	.013791
74.42	.466585	.470924	.335134	.031490	.021996
87.00	.683681	.524731	.459603	.042572	.026076
100.00	.940598	.561588	.553327	.051777	.030761
120.17	1.389036	.601308	.704872	.057690	.035233

INSTANTANEOUS LIQUID MOLE FRACTION VS ADJUSTED TIME

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE	COMPLEX	H2SO4	NH4HSO4
0.00	.130128	.044566	.340153	0.000000	0.000000	.297735	.102485	.084934
10.92	.158345	.035589	.346139	0.000000	.003166	.242291	.096487	.117983
33.92	.205176	.015714	.354414	0.000000	.004517	.175291	.088759	.156129
48.25	.216053	.011892	.359360	0.000000	.004655	.145289	.086195	.176555
60.09	.222394	.008552	.363868	0.000000	.003652	.129350	.084821	.187363
73.59	.222133	.006256	.370845	0.000000	.003340	.115515	.083953	.197457
94.67	.213582	.003718	.386251	0.000000	.002205	.104063	.083281	.206900

INSTANTANEOUS VAPOR MOLE FRACTIONS AND TOTAL VAPOR FLOW RATE VS ADJUSTED TIME

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE	VRATE
0.00	.111688	.652675	.195075	.025202	.015359	.016549
10.92	.254629	.461841	.237986	.027596	.017947	.019450
33.92	.439399	.243310	.271966	.027167	.018158	.025857
48.25	.520135	.165969	.272959	.024708	.016229	.028676
60.09	.578347	.120007	.266191	.021707	.013747	.030506
73.59	.640503	.080937	.251325	.017252	.009983	.032043
94.67	.737349	.039688	.213178	.007852	.001932	.033269

INSTANTANEOUS EQUILIBRIUM CONSTANTS VS ADJUSTED TIME

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE
0.00	.858299	14.644999	.573493		100.000000
10.92	1.608071	12.977234	.687546		5.667993
33.92	2.141572	15.483791	.767369		4.019980
44.25	2.407443	13.956431	.759569		3.486104
60.09	2.600552	14.033328	.731559		3.764228
73.59	2.883416	12.936922	.677707		2.989037
94.67	2.452308	10.674622	.551916		.876106

INSTANTANEOUS LIQUID ACTIVITY COEFFICIENT VS ADJUSTED TIME

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE
0.00	.238250	9.955608	.312451		100.000000
10.92	.465524	9.164696	.393138		32.728981
33.92	.669612	11.725458	.479252		25.777024
44.25	.785617	10.985626	.498073		23.687233
60.09	.875349	11.360064	.496914		26.672315
73.59	.996222	10.722373	.474171		21.939458
94.67	1.195526	8.865763	.387168		6.450625

SUMMARY OF ERRORS FOR CURVE FITS-- 3 DEGREE POLYNOMIALS

VAPOR FLOW RATES

	VAPOR RATE VS VAPOR ADJUSTED TIME BEFORE TIME LAG CORRECTION		VAPOR RATE VS LIQUID ADJUSTED TIME AFTER TIME LAG CORRECTION	
	ABS PCT ERR	STANDARD DEV	ABS PCT ERR	STANDARD DEV
ALCOHOL	.58561E+01	.38122E+00	.54705E+01	.38275E+00
ACRYLATE	.72442E+00	.23701E+00	.73157E+00	.23913E+00
WATER	.64925E+01	.19697E+00	.64969E+01	.19725E+00
ETHER	.19997E+02	.12560E+00	.19978E+02	.12573E+00
PROPIONATE	.62723E+01	.82926E-01	.62269E+01	.82791E-01

REACTION RATE

	ACP RATE	ROR RATE	PRO RATE
ABS PCT ERR	.69592E+00	.26933E-10	.14526E+02
STANDARD DEV	.33847E-02	.32037E-14	.70547E-03

DEFINITIONS-

REAL TIME IS COUNTED FROM THE MOMENT ALCOHOL IS FIRST MIXED WITH ACRYLAMIDE SULFATE

ADJUSTED TIME IS COUNTED FROM THE MOMENT STUDIES FOR DISTILLATION ACCOMPANIED BY CHEMICAL REACTIONS BEGIN

ADJUSTED TIME MUST BEGIN RIGHT OR SLIGHTLY AFTER THE REACTING LIQUID MIXTURE BECOMES BOILING

INITIAL CONDITIONS FOR THE REAL TIME

TEMP= 111.50 C VOL= 136.58 ML TOT LIQ= 2.9488 MOL AMIDE= 1.023 MOL H2SO4= 1.254 MOL WATER= .672 MOL

FEED CONDITIONS

RATE=1.1920 ML/MIN ALCOHOL= .8600 WT FRACTION WATER= .1400 WT FRACTION VAPOR FRACTION= .7000

MIXTURE QUANTITIES AND REACTION RATES VS ADJUSTED TIME

TIME	TIME LAG	TEMP	LIQ VOL	LIQ MOL	VAP MOL	ACR RATE	ROR RATE	PRO RATE
0.00	.40039	118.86	163.44	2.54249	.20576	.0074508	.0003143	.0005439
13.92	.38780	116.80	162.13	2.66646	.43731	.0067901	.0003284	.0006431
29.58	.36622	115.47	160.48	2.78431	.71600	.0059267	.0003408	.0006188
43.00	.34756	114.16	158.86	2.86420	.97571	.0050951	.0003485	.0005214
58.93	.31920	113.07	156.66	2.93416	1.31613	.0039981	.0003542	.0003141
70.39	.30196	112.71	154.85	2.95943	1.58695	.0031351	.0003560	.0001034
84.17	.27967	111.63	152.36	2.95826	1.94616	.0020157	.0003555	0.0000000

INSTANTANEOUS LIQUID MOLAR QUANTITIES VS ADJUSTED TIME

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE	COMPLEX	H2SO4	NH4HSO4
0.00	.315402	.110475	.858602	0.000000	.003932	.807022	.230999	.216057
13.92	.402017	.084569	.916297	0.000000	.009504	.702784	.230999	.320295
29.58	.459412	.072886	.981261	0.000000	.016675	.586569	.230999	.435410
43.00	.502658	.056786	1.029140	0.000000	.021539	.510004	.230999	.513071
58.93	.541373	.053031	1.066809	0.000000	.018873	.429264	.230999	.593815
70.39	.566802	.047795	1.075054	0.000000	.015701	.385568	.230999	.537421
84.17	.599982	.036945	1.057389	0.000000	.009861	.350718	.230999	.572361

ACCUMULATED VAPOR MOLAR QUANTITIES VS ADJUSTED TIME

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE
0.00	.042997	.101651	.058527	.002580	0.000000
13.92	.092218	.224980	.111813	.007057	.001242
29.58	.184940	.341679	.171910	.012301	.005171
43.00	.292696	.424707	.231337	.016929	.010039
58.93	.450535	.504927	.321153	.022531	.016985
70.39	.581760	.551544	.404661	.026602	.022382
84.17	.756434	.596659	.532664	.031508	.028886

INSTANTANEOUS TOTAL MOLAR QUANTITIES VS ADJUSTED TIME

REACTION RATE CONSTANTS

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE	1000/2.3RT	ACR RCONST	ROR RCONST	PRO RCONST
0.00	.358399	.212125	.917129	.002580	.003932	.557446	4.790561	.515384	194.292051
13.92	.494235	.309549	1.028110	.007057	.010746	.560391	3.896484	.329416	148.826391
29.58	.644351	.414564	1.153171	.012301	.021846	.562309	3.528941	.259113	128.702825
43.00	.745353	.481493	1.260477	.016929	.031577	.564210	3.157412	.219122	102.114462
58.93	.991909	.557957	1.387962	.022531	.035857	.565803	2.695157	.189330	61.266917
70.39	1.144563	.599339	1.479715	.026602	.038083	.566331	2.220847	.171582	20.005447
84.17	1.356416	.633614	1.590053	.031508	.038747	.567920	1.459408	.150479	0.000000

ACCUMULATED VAPOR QUANTITIES VS REAL TIME

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE
12.00	.001647	.000164	.001875	.000004	0.000000
19.75	.006821	.014009	.009013	.000532	0.000000
32.25	.042550	.102915	.059862	.002580	0.000000
46.33	.095521	.226343	.112172	.007211	.001038
62.08	.185043	.344054	.166497	.012429	.005084
75.50	.299106	.430226	.246946	.017048	.010835
91.00	.446362	.499533	.311953	.022397	.016826
102.87	.590624	.556752	.409805	.026941	.022281
116.67	.761662	.597285	.538259	.031614	.029260

INSTANTANEOUS LIQUID MOLE FRACTION VS ADJUSTED TIME

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE	COMPLEX	H2SO4	W444504
0.00	.124053	.043451	.337701	0.000000	.001546	.317414	.090856	.084979
13.92	.150768	.031716	.343637	0.000000	.003564	.263564	.086631	.120120
29.58	.165000	.026177	.352425	0.000000	.005989	.210705	.082965	.156739
43.00	.175497	.019826	.359311	0.000000	.007520	.178063	.080650	.179132
58.93	.184507	.018074	.363582	0.000000	.006432	.146299	.078727	.202340
70.39	.191524	.016150	.363264	0.000000	.005305	.130315	.078055	.215384
84.17	.202816	.012489	.357437	0.000000	.003333	.119556	.078086	.227283

INSTANTANEOUS VAPOR MOLE FRACTIONS AND TOTAL VAPOR FLOW RATE VS ADJUSTED TIME

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE	VPATE
0.00	.143823	.588697	.247190	.019351	.000934	.016242
13.92	.274619	.477809	.218038	.019189	.010345	.017113
29.58	.392271	.363567	.218606	.018353	.017099	.018562
43.00	.441974	.279186	.241660	.017250	.019931	.020202
58.93	.479140	.196938	.287852	.015657	.020413	.022524
70.39	.487631	.149597	.329060	.014422	.019290	.024684
84.17	.482606	.104479	.383197	.012922	.016796	.027515

INSTANTANEOUS EQUILIBRIUM CONSTANTS VS ADJUSTED TIME

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE
0.00	1.159375	13.548407	.731978		.606599
13.92	1.821469	15.065425	.634501		2.902283
29.54	2.316791	13.892467	.620291		2.855147
43.00	2.519416	14.081701	.672563		2.650350
58.93	2.596467	10.896523	.791713		3.173578
70.39	2.546057	9.263032	.905842		3.635923
84.17	2.379522	8.365910	1.072069		5.038790

INSTANTANEOUS LIQUID ACTIVITY COEFFICIENT VS ADJUSTED TIME

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE
0.00	.328424	9.399434	.408603		3.400628
13.92	.546666	10.998891	.377821		17.566760
29.54	.721418	10.486772	.385265		18.168955
43.00	.813514	10.988620	.435599		17.726560
58.93	.865135	8.743643	.531095		22.131471
70.39	.856947	7.502088	.614777		25.709717
84.17	.826063	6.967612	.753598		37.150524

SUMMARY OF ERRORS FOR CURVE FITS-- 3 DEGREE POLYNOMIALS

VAPOR FLOW RATES

	VAPOR RATE VS VAPOR ADJUSTED TIME BEFORE TIME LAG CORRECTION		VAPOR RATE VS LIQUID ADJUSTED TIME AFTER TIME LAG CORRECTION	
	A9S PCT ERR	STANDARD DEV	A9S PCT ERR	STANDARD DEV
ALCOHOL	.11105E+01	.13477E+00	.11104E+01	.13522E+00
ACRYLATE	.47916E+00	.30090E+00	.47948E+00	.30140E+00
WATER	.21878E+01	.13226E+00	.21899E+01	.13237E+00
ETHER	.53435E+00	.75281E-02	.53494E+00	.75485E-02
PROPIONATE	.61829E+01	.53082E-01	.61953E+01	.53152E-01

REACTION RATE

	ACR RATE	ROP RATE	PRO RATE
A9S PCT ERR	.36429E+00	.40862E-11	.54306E+01
STANDARD DEV	.22064E-02	.62004E-15	.10615E-02

DEFINITIONS-

REAL TIME IS COUNTED FROM THE MOMENT ALCOHOL IS FIRST MIXED WITH ACRYLAMIDE SULFATE

ADJUSTED TIME IS COUNTED FROM THE MOMENT STUDIES FOR DISTILLATION ACCOMPANIED BY CHEMICAL REACTIONS BEGIN

ADJUSTED TIME MUST BEGIN RIGHT OR SLIGHTLY AFTER THE REACTING LIQUID MIXTURE BECOMES BOILING

INITIAL CONDITIONS FOR THE REAL TIME

TEMP= 110.00 C VOL= 135.33 ML TOT LIQ= 2.9567 MOL AMIDE= 1.016 MOL H2SO4= 1.226 MOL WATER= .714 MOL

FEED CONDITIONS

RATE=1.1470 ML/MIN ALCOHOL= .8600 WT FRACTION WATER= .1400 WT FRACTION VAPOF FRACTION= .5500

MIXTURE QUANTITIES AND REACTION RATES VS ADJUSTED TIME

TIME	TIME LAG	TEMP	LIQ VOL	LIQ MOL	VAP MOL	ACP RATE	ROP RATE	PRO RATE
0.00	.50110	118.34	155.63	2.53738	.33001	.0078523	.0001328	.0004537
12.00	.43924	116.81	156.62	2.66625	.49735	.0067068	.0001999	.0003878
26.50	.39469	115.00	156.35	2.78901	.73224	.0054160	.0002534	.0003067
42.83	.36419	112.70	156.84	2.89165	1.03401	.0040847	.0002778	.0002137
61.00	.34041	110.60	152.72	2.97023	1.40811	.0027557	.0002601	.0001079
73.83	.32955	109.00	151.54	3.00751	1.69169	.0019139	.0002191	.0000319
82.83	.32371	107.80	151.13	3.02567	1.69817	.0013712	.0001764	0.0000000

INSTANTANEOUS LIQUID MOLAR QUANTITIES VS ADJUSTED TIME

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE	COMPLEX	H2SO4	NH4HSO4
0.00	.316017	.087630	.905228	0.000000	.002462	.738085	.209716	.278239
12.00	.371656	.106635	.956507	0.000000	.005421	.622450	.209716	.393875
26.50	.473099	.067512	1.013355	0.000000	.009010	.553574	.209716	.462750
42.83	.541035	.044471	1.068971	0.000000	.011128	.472781	.209716	.543544
61.00	.576829	.038991	1.117961	0.000000	.010407	.391801	.209716	.624523
73.83	.604628	.025460	1.142885	0.000000	.008494	.356000	.209716	.650324
82.83	.619532	.017603	1.154973	0.000000	.007518	.357531	.209716	.658793

ACCUMULATED VAPOR MOLAR QUANTITIES VS ADJUSTED TIME

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE
0.00	.053337	.186560	.085659	.002866	.001587
12.00	.085902	.278835	.124745	.004882	.002982
26.50	.159836	.381292	.177973	.008205	.004937
42.83	.286495	.480489	.246972	.012594	.007456
61.00	.478724	.564518	.336712	.017552	.010607
73.83	.645328	.603345	.409345	.020651	.013024
82.83	.776748	.618870	.465307	.022439	.014802

INSTANTANEOUS TOTAL MOLAR QUANTITIES VS ADJUSTED TIME REACTION RATE CONSTANTS

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE	1000/2.3RT	ACP RCONST	ROP RCONST	PO RCONST
0.00	.369354	.274190	.990487	.002866	.004049	.558186	5.239388	.206990	149.102136
12.00	.457557	.385471	1.081251	.004882	.008404	.560376	4.540611	.226622	110.627838
26.50	.632934	.448804	1.191327	.008205	.013947	.562989	3.233272	.177024	60.517403
42.83	.827531	.524960	1.315943	.012544	.018584	.566345	2.472651	.146932	37.021753
61.00	1.055553	.603509	1.454673	.017552	.021015	.569444	1.862121	.119353	19.310559
73.83	1.249554	.628805	1.552231	.020651	.021519	.571829	1.310639	.090839	5.467848
82.83	1.396279	.636473	1.620280	.022439	.022320	.573630	.935544	.069456	0.000000

ACCUMULATED VAPOR QUANTITIES VS REAL TIME

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE
12.00	.001959	.000649	.020261	.000010	0.000000
21.57	.011225	.041640	.020261	.000639	0.000000
37.75	.052258	.188479	.084701	.002432	.001527
50.33	.090058	.280491	.128191	.006286	.003397
64.67	.166377	.388649	.184000	.007292	.004637
87.58	.348120	.516161	.272120	.014501	.008675
98.59	.483620	.565883	.339131	.018200	.011163
111.58	.653502	.602489	.418783	.020419	.012407
120.67	.778792	.620029	.462906	.022507	.015138

INSTANTANEOUS LIQUID MOLE FRACTION VS ADJUSTED TIME

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE	COMPLEX	H2SO4	NH4HSO4
0.00	.124545	.034536	.356757	0.000000	.000970	.290885	.082651	.109656
12.00	.139392	.039994	.358745	0.000000	.002033	.233454	.078655	.147726
26.50	.169629	.024706	.363338	0.000000	.003230	.195484	.075193	.165919
42.83	.187103	.015379	.369676	0.000000	.003843	.163499	.072525	.187970
61.00	.194204	.013127	.376389	0.000000	.003504	.131909	.070606	.210261
73.83	.201039	.008465	.380011	0.000000	.002824	.121696	.069731	.216234
82.83	.204759	.005818	.381725	0.000000	.002485	.114166	.069312	.217735

INSTANTANEOUS VAPOR MOLE FRACTIONS AND TOTAL VAPOR FLOW RATE VS ADJUSTED TIME

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE	VPATE
0.00	.125017	.615850	.240426	.010344	.008363	.012841
12.00	.253763	.495779	.228821	.013314	.008522	.015011
26.50	.367486	.383498	.226070	.014620	.008325	.017333
42.83	.466320	.278594	.232505	.014204	.008377	.019555
61.00	.557661	.173408	.248379	.012075	.008477	.021537
73.83	.616373	.100978	.264391	.009685	.008572	.022626
82.83	.656363	.049443	.277950	.007592	.008552	.023236

INSTANTANEOUS EQUILIBRIUM CONSTANTS VS ADJUSTED TIME

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE
0.00	1.003789	17.832358	.673920		8.618434
12.00	1.820499	12.396219	.637438		4.092732
26.50	2.166405	15.842925	.622203		2.577275
42.83	2.492315	18.115154	.624944		2.176690
61.00	2.871528	13.202869	.659900		2.419276
73.83	2.065931	11.929258	.695746		3.035036
82.83	2.205543	9.498370	.728142		3.482004

INSTANTANEOUS LIQUID ACTIVITY COEFFICIENT VS ADJUSTED TIME

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE
0.00	.287887	12.489878	.381096		49.095677
12.00	.544438	9.018323	.378447		24.681977
26.50	.691263	12.062405	.391005		16.640789
42.83	.836354	14.627174	.425594		15.347020
61.00	1.023632	11.264723	.478208		18.507329
73.83	1.145254	10.610250	.531528		24.726810
82.83	1.240659	7.805106	.578956		29.753977

SUMMARY OF ERRORS FOR CURVE FITS-- 3 DEGREE POLYNOMIALS

VAPOR FLOW RATES

	VAPOR RATE VS VAPOR ADJUSTED TIME BEFORE TIME LAG CORRECTION		VAPOR RATE VS LIQUID ADJUSTED TIME AFTER TIME LAG CORRECTION	
	ABS PCT ERR	STANDARD DEV	ABS PCT ERR	STANDARD DEV
ALCOHOL	.14075E+01	.21654E+00	.14003E+01	.21522E+00
ACRYLATE	.52735E+00	.23232E+00	.52732E+00	.23231E+00
WATER	.15599E+01	.99241E-01	.15530E+01	.98960E-01
ETHER	.83624E+01	.55828E-01	.83574E+01	.55844E-01
PROPIONATE	.51183E+01	.62226E-01	.51188E+01	.62225E-01

REACTION RATE

	ACP RATE	ROR RATE	PRO RATE
ABS PCT ERR	.18273E+01	.21163E-10	.25175E+01
STANDARD DEV	.96334E-02	.17879E-14	.35547E-03

DEFINITIONS-

REAL TIME IS COUNTED FROM THE MOMENT ALCOHOL IS FIRST MIXED WITH ACRYLAMIDE SULFATE

ADJUSTED TIME IS COUNTED FROM THE MOMENT STUDIES FOR DISTILLATION ACCOMPANIED BY CHEMICAL REACTIONS BEGIN

ADJUSTED TIME MUST BEGIN RIGHT OR SLIGHTLY AFTER THE REACTING LIQUID MIXTURE BECOMES BOILING

INITIAL CONDITIONS FOR THE REAL TIME

TEMP= 110.00 C VOL= 139.48 ML TOT LIO= 3.0385 MOL AMIDE= 1.002 MOL H2SO4= 1.282 MOL WATER= .755 MOL

FEED CONDITIONS

RATE=1.4650 ML/MIN ALCOHOL=.8600 WT FRACTION WATER=.1400 WT FRACTION VAPOR FRACTION=.7500

MIXTURE QUANTITIES AND REACTION RATES VS ADJUSTED TIME

TIME	TIME LAG	TEMP	LIQ VOL	LIQ MOL	VAP MOL	ACP RATE	ROP RATE	PRO RATE
0.00	.38533	120.77	164.84	2.68972	.31693	.0108451	.0003246	.0007003
13.72	.33159	118.92	164.69	2.84613	.56286	.0041809	.0003110	.0004697
29.02	.29520	116.32	163.91	3.01500	.90635	.0056545	.0002948	.0002755
43.05	.27364	114.07	162.74	3.10892	1.25871	.0037499	.0002790	.0001559
63.08	.25212	111.74	160.49	3.18355	1.82166	.0017141	.0002549	.0000821
78.32	.24579	110.71	158.43	3.20410	2.28722	.0007035	.0002353	.0001022
92.00	.24133	110.03	156.41	3.20261	2.72522	.0001926	.0002169	.0001764

INSTANTANEOUS LIQUID MOLAR QUANTITIES VS ADJUSTED TIME

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE	COMPLEX	H2SO4	NH4HSO4
0.00	.334808	.126927	.941537	0.000000	.004840	.714460	.279637	.287510
13.72	.422734	.121689	1.030110	0.000000	.009994	.573783	.279637	.428187
29.02	.505509	.110893	1.107308	0.000000	.009687	.462739	.279637	.539231
43.05	.565284	.093077	1.160252	0.000000	.008695	.397207	.279637	.604763
63.08	.622177	.061863	1.210338	0.000000	.007568	.346256	.279637	.655714
78.32	.629404	.055204	1.231570	0.000000	.006315	.313149	.279637	.688621
92.00	.647887	.027133	1.240556	0.000000	.005432	.316703	.279637	.685267

ACCUMULATED VAPOR MOLAR QUANTITIES VS ADJUSTED TIME

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE
0.00	.052611	.154978	.104365	.004213	.000766
13.72	.1115609	.291300	.149169	.008574	.005204
29.02	.254014	.409025	.220479	.013209	.009626
43.05	.434991	.489787	.303491	.017235	.013204
63.08	.765690	.568737	.447106	.022584	.017546
78.32	1.060674	.607037	.572919	.026320	.020264
92.00	1.347434	.630415	.695666	.029414	.022237

INSTANTANEOUS TOTAL MOLAR QUANTITIES VS ADJUSTED TIME

REACTION RATE CONSTANTS

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE	1000/2.3PT	ACR PCNST	ROR PCNST	PRO PCNST
0.00	.347419	.281905	1.045902	.004213	.005606	.554743	7.473510	.477376	237.587783
13.72	.538343	.412989	1.179279	.008574	.015198	.557361	5.554533	.286589	124.230146
29.02	.759523	.519919	1.327787	.013209	.019313	.561081	3.962153	.189064	62.601479
43.05	1.000276	.582864	1.463743	.017235	.021899	.564342	2.717880	.142067	32.538518
63.08	1.387867	.630600	1.657444	.022584	.025114	.567758	1.276942	.105662	15.770849
78.32	1.690978	.662242	1.804489	.026320	.026579	.569281	.565487	.094112	20.675628
92.00	1.995320	.657549	1.936222	.029414	.027719	.570292	.146776	.080817	32.463331

ACCUMULATED VAPOR QUANTITIES VS REAL TIME

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE
10.17	.001483	.001904	.002741	.000076	0.000000
20.17	.014684	.050558	.037152	.002182	.000197
31.10	.051304	.158555	.099023	.004256	.001243
44.83	.121852	.290344	.166147	.008672	.004506
60.17	.256607	.413963	.212199	.013383	.009497
74.03	.434631	.491764	.298613	.017354	.014245
91.72	.724619	.560067	.438953	.021692	.017121
109.22	1.064545	.608075	.573331	.026725	.019491
122.92	1.350567	.630645	.696426	.029319	.022711

INSTANTANEOUS LIQUID MOLE FRACTION VS ADJUSTED TIME

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE	COMPLEX	H2SO4	NH4HSO4
0.00	.124477	.047190	.350050	0.000000	.001799	.265526	.103965	.106892
13.72	.147493	.042458	.359407	0.000000	.003487	.200194	.097566	.149395
29.02	.167664	.036780	.367266	0.000000	.003213	.153479	.092748	.178849
43.05	.181827	.029939	.373202	0.000000	.002797	.127764	.089947	.194525
63.08	.195435	.019432	.380185	0.000000	.002377	.108764	.087838	.205469
78.32	.196437	.017229	.384373	0.000000	.001971	.097734	.087275	.214981
92.00	.202299	.008472	.387357	0.000000	.001696	.098889	.087315	.213971

INSTANTANEOUS VAPOR MOLE FRACTIONS AND TOTAL VAPOR FLOW RATE VS ADJUSTED TIME

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE	VPATE
0.00	.137404	.668520	.154039	.019553	.020484	.016602
13.72	.336969	.436807	.195623	.015398	.015203	.020196
29.02	.471112	.279628	.225386	.012436	.011439	.023702
43.05	.549331	.186598	.244488	.010546	.009038	.024452
63.08	.617513	.103055	.264246	.008608	.006577	.024508
78.32	.646774	.064816	.275752	.007494	.005164	.031401
92.00	.660808	.043946	.284479	.006660	.004107	.032564

INSTANTANEOUS EQUILIBRIUM CONSTANTS VS ADJUSTED TIME

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE
0.00	1.103850	14.166686	.440047		11.384082
13.72	2.284647	10.288065	.544294		4.359934
29.02	2.809848	7.602615	.613686		3.560288
43.05	3.021174	6.232686	.655109		3.231348
63.08	3.159688	5.303341	.695047		2.766787
78.32	3.242526	3.761963	.717408		2.620042
92.00	3.266486	5.187101	.734409		2.421406

INSTANTANEOUS LIQUID ACTIVITY COEFFICIENT VS ADJUSTED TIME

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE
0.00	.295776	9.325998	.230178		59.148271
13.72	.643320	7.085057	.301482		24.244372
29.02	.849518	5.884450	.368830		21.812203
43.05	.972637	4.845140	.423018		21.559256
63.08	1.087000	4.378397	.483960		20.192701
78.32	1.166897	3.190405	.516647		19.904729
92.00	1.180794	4.478259	.540854		18.892585

SUMMARY OF ERRORS FOR CURVE FITS-- 3 DEGREE POLYNOMIALS

VAPOR FLOW RATES

VAPOR RATE VS VAPOR
ADJUSTED TIME BEFORE
TIME LAG CORRECTION

VAPOR RATE VS LIQUID
ADJUSTED TIME AFTER
TIME LAG CORRECTION

ABS PCT ERR STANDARD DEV

ABS PCT ERR STANDARD DEV

ALCOHOL	.12521E+01	.12020E+00	.12588E+01	.12064E+00
ACRYLATE	.45871E+00	.20424E+00	.46287E+00	.20602E+00
WATER	.35090E+01	.16424E+00	.35073E+01	.16421E+00
ETHER	.72623E+00	.16156E-01	.72394E+00	.16166E-01
PROPIONATE	.93279E+01	.97693E-01	.93213E+01	.97768E-01

REACTION RATE

ACR RATE

PRR RATE

PRN RATE

ABS PCT ERR	.47792E+00	.22122E-10	.35950E+01
STANDARD DEV	.42623E-02	.25639E-14	.65219E-03

DEFINITIONS--

REAL TIME IS COUNTED FROM THE MOMENT ALCOHOL IS FIRST MIXED WITH ACRYLAMIDE SULFATE

ADJUSTED TIME IS COUNTED FROM THE MOMENT STUDIES FOR DISTILLATION ACCOMPANIED BY CHEMICAL REACTIONS BEGIN

ADJUSTED TIME MUST BEGIN RIGHT OR SLIGHTLY AFTER THE REACTING LIQUID MIXTURE BECOMES BOILING

INITIAL CONDITIONS FOR THE REAL TIME

TEMP= 106.00 C VOL= 135.79 ML TOT LIQ= 2.9157 MOL AMIDE= 1.000 MOL H2SO4= 1.283 MOL WATER= .633 MOL

FEED CONDITIONS

RATE=1.2600 ML/MIN ALCOHOL= .8600 WT FRACTION WATER= .1400 WT FRACTION VAPOF FRACTION= .8500

MIXTURE QUANTITIES AND REACTION RATES VS ADJUSTED TIME

TIME	TIME LAG	TEMP	LIQ VOL	LIQ MOL	VAP MOL	ACR RATE	ROP RATE	PPD RATE
0.00	.32041	115.71	165.86	2.60603	.13304	.0113640	.0005178	.0008334
11.00	.33115	114.94	162.45	2.67167	.36118	.0089632	.0005030	.0006770
20.00	.33742	113.42	160.51	2.72651	.54801	.0072277	.0004835	.0005621
30.10	.32587	111.97	159.09	2.78835	.75957	.0055255	.0004539	.0004472
41.00	.32467	110.80	158.20	2.85241	.99225	.0039795	.0004125	.0003399
74.00	.30058	109.36	156.58	2.99505	1.74887	.0011410	.0002284	.0001201
94.00	.27778	107.39	153.80	3.02653	2.26675	.0007686	.0000738	.0000640

INSTANTANEOUS LIQUID MOLAR QUANTITIES VS ADJUSTED TIME

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE	COMPLEX	H2SO4	NH4HSO4
0.00	.306817	.146505	.868283	0.000000	.001798	.765755	.282345	.234527
11.00	.343980	.140294	.896803	0.000000	.007967	.646201	.282345	.354081
20.00	.371572	.139790	.920947	0.000000	.011579	.561576	.282345	.438705
30.10	.415431	.128352	.948506	0.000000	.013435	.495279	.282345	.505003
41.00	.468476	.108905	.978326	0.000000	.012679	.448703	.282345	.551578
74.00	.556059	.079636	1.063697	0.000000	.013028	.354136	.282345	.545145
94.00	.574021	.055052	1.107164	0.000000	.007667	.339607	.282345	.560674

ACCUMULATED VAPOR MOLAR QUANTITIES VS ADJUSTED TIME

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE
0.00	.032781	.086224	.010575	.003458	0.000000
11.00	.069637	.203103	.076641	.009082	.002716
20.00	.117422	.282273	.129731	.013526	.005063
30.10	.189486	.355490	.188597	.018267	.007726
41.00	.288598	.418341	.251662	.022997	.010653
74.00	.533411	.533411	.444003	.033817	.020071
94.00	1.066539	.571581	.565364	.036893	.026374

INSTANTANEOUS TOTAL MOLAR QUANTITIES VS ADJUSTED TIME

REACTION RATE CONSTANTS

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE	1000/2.3RT	ACR RCONST	ROP RCONST	PRO RCONST
0.00	.339598	.232729	.878857	.003458	.001798	.561962	8.022461	.912363	318.042323
11.00	.413617	.343397	.973445	.009082	.010583	.563077	6.550538	.690576	233.657496
20.00	.488994	.422062	1.050677	.013526	.016643	.565290	5.554615	.562133	186.775121
30.10	.604417	.483842	1.137103	.018267	.021161	.567419	4.272268	.418370	132.418361
41.00	.757473	.527246	1.229989	.022997	.024332	.569148	2.992279	.296841	86.221852
74.00	1.277323	.613047	1.507700	.033817	.033098	.571290	.907246	.115681	26.895555
94.00	1.640560	.626634	1.672528	.036893	.034040	.574248	.606430	.034436	13.529227

ACCUMULATED VAPOR QUANTITIES VS REAL TIME

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE
10.35	0.000000	.000300	0.000000	.000054	0.000000
20.35	.007779	.022775	0.000000	.001296	0.000000
30.35	.030536	.073219	.024423	.003658	.000217
41.35	.071496	.216062	.057171	.009341	.002207
50.35	.124031	.312117	.114343	.012756	.004891
60.45	.184176	.332834	.204263	.017400	.007609
71.35	.286629	.401958	.266430	.024703	.011413
104.35	.721133	.549795	.430173	.033099	.019633
124.35	1.066855	.565578	.571159	.037149	.026562

INSTANTANEOUS LIQUID MOLE FRACTION VS ADJUSTED TIME

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE	COMPLEX	H2SO4	NH4HSO4
0.00	.117734	.056218	.333182	0.000000	.000690	.293840	.108343	.089994
11.00	.128751	.052512	.325671	0.000000	.002982	.241871	.105641	.132532
20.00	.136281	.051270	.337774	0.000000	.004247	.205969	.103555	.160903
30.10	.148988	.046032	.340167	0.000000	.004818	.177624	.101259	.181112
41.00	.164379	.038180	.342982	0.000000	.004796	.157307	.098985	.193372
74.00	.185660	.026589	.355152	0.000000	.004350	.118241	.094271	.215738
94.00	.189663	.018190	.365820	0.000000	.002533	.112210	.093290	.218294

INSTANTANEOUS VAPOR MOLE FRACTIONS AND TOTAL VAPOR FLOW RATE VS ADJUSTED TIME

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE	VRATE
0.00	.108359	.562378	.291927	.024874	.012461	.020818
11.00	.214022	.462486	.286680	.024269	.012542	.020725
20.00	.296696	.385996	.281503	.023226	.012579	.020819
30.10	.383109	.307888	.274908	.021505	.012589	.021104
41.00	.466584	.234688	.267090	.019074	.012563	.021627
74.00	.643972	.092620	.241814	.009298	.012296	.024569
94.00	.696453	.061438	.227365	.002698	.012045	.027345

INSTANTANEOUS EQUILIBRIUM CONSTANTS VS ADJUSTED TIME

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE
0.00	.920376	10.003577	.876179		18.062202
11.00	1.662297	8.807304	.854051		4.205774
20.00	2.177082	7.528618	.833406		2.961955
30.10	2.571410	6.688641	.808154		2.612850
41.00	2.838474	6.146886	.778730		2.619725
74.00	3.468564	3.483385	.680875		2.826705
94.00	3.672055	3.377594	.621523		4.755141

INSTANTANEOUS LIQUID ACTIVITY COEFFICIENT VS ADJUSTED TIME

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE
0.00	.280142	7.385919	.531441		112.084661
11.00	.514950	6.630366	.530887		26.871026
20.00	.706657	5.891575	.543959		20.054576
30.10	.869891	5.433614	.552856		18.702359
41.00	.993190	5.148026	.553490		19.631486
74.00	1.265704	3.030003	.507455		22.415134
94.00	1.420355	3.096449	.494632		40.778548

SUMMARY OF ERRORS FOR CURVE FITS-- 3 DEGREE POLYNOMIALS

VAPOR FLOW RATES

	VAPOR RATE VS VAPOR ADJUSTED TIME BEFORE TIME LAG CORRECTION		VAPOR RATE VS LIQUID ADJUSTED TIME AFTER TIME LAG CORRECTION	
	ABS PCT ERR	STANDARD DEV	ABS PCT ERR	STANDARD DEV
ALCOHOL	.27859E+01	.18279E+00	.27951E+01	.18352E+00
ACRYLATE	.69388E+01	.19659E+01	.69543E+01	.19691E+01
WATER	.17297E+02	.28444E+00	.17293E+02	.28414E+00
ETHER	.40866E+01	.67215E-01	.40844E+01	.67187E-01
PROPIONATE	.28319E+02	.66729E-01	.28315E+02	.66666E-01

REACTION RATE

	ACR RATE	WOR RATE	PRO RATE
ABS PCT ERR	.56876E+00	.13097E-10	.45928E+01
STANDARD DEV	.34811E-02	.18169E-14	.58349E-03

DEFINITIONS-

REAL TIME IS COUNTED FROM THE MOMENT ALCOHOL IS FIRST MIXED WITH ACRYLAMIDE SULFATE

ADJUSTED TIME IS COUNTED FROM THE MOMENT STUDIES FOR DISTILLATION ACCOMPANIED BY CHEMICAL REACTIONS BEGIN

ADJUSTED TIME MUST BEGIN RIGHT OR SLIGHTLY AFTER THE REACTING LIQUID MIXTURE BECOMES BOILING

INITIAL CONDITIONS FOR THE REAL TIME

TEMP= 106.00 C VOL= 137.40 ML TOT LIO= 2.9706 MOL AMIDE= 1.006 MOL H2SO4= 1.293 MOL WATER= .672 MOL

FEED CONDITIONS

RATE=1.5060 ML/MIN ALCOHOL= .8600 WT FRACTION WATER= .1400 WT FRACTION VAPOR FRACTION=0.0000

MIXTURE QUANTITIES AND REACTION RATES VS ADJUSTED TIME

TIME	TIME LAG	TEMP	LIO VOL	LIO MOL	VAP MOL	ACR RATE	ROR RATE	PRD RATE
0.00	.36350	110.80	175.50	2.82511	.23682	.0093422	.0001945	.0007131
12.65	.36854	108.47	177.56	3.01435	.45510	.0074428	.0001962	.0005449
29.28	.35107	105.00	182.40	3.26903	.74331	.0052282	.0001913	.0003696
41.76	.32505	102.60	186.57	3.44269	.97179	.0037770	.0001823	.0002722
55.91	.29320	100.38	190.72	3.62123	1.25561	.0023501	.0001656	.0001972
71.66	.25972	98.00	193.22	3.77762	1.61729	.0010350	.0001422	.0001580
85.50	.23223	97.00	192.39	3.85737	1.98822	.0001169	.0001147	.0001621

INSTANTANEOUS LIQUID MOLAR QUANTITIES VS ADJUSTED TIME

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE	COMPLEX	H2SO4	NH4HSO4
0.00	.447400	.153557	.928691	0.000000	.002644	.726725	.286630	.279467
12.65	.566378	.129316	1.017205	0.000000	.008629	.624482	.286630	.377710
29.28	.705045	.134339	1.125164	0.000000	.010624	.501271	.286630	.504921
41.76	.812174	.121693	1.200533	0.000000	.015467	.438390	.286630	.567802
55.91	.938382	.094154	1.280798	0.000000	.015079	.400958	.286630	.605233
71.66	1.046370	.063993	1.364470	0.000000	.009964	.375283	.286630	.630909
85.50	1.087870	.034400	1.433800	0.000000	.008475	.357070	.286630	.649122

ACCUMULATED VAPOR MOLAR QUANTITIES VS ADJUSTED TIME

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE
0.00	.042065	.122646	.058983	.002506	.000520
12.65	.105128	.236620	.105227	.004982	.003144
29.28	.213879	.353777	.161258	.008216	.006180
41.76	.321735	.422006	.208864	.010552	.008636
55.91	.479726	.483978	.267858	.013028	.012022
71.66	.705995	.539847	.338876	.015469	.017055
85.50	.959602	.583211	.405116	.017253	.023036

INSTANTANEOUS TOTAL MOLAR QUANTITIES VS ADJUSTED TIME

REACTION RATE CONSTANTS

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE	1000/P.3BT	ACP RCONST	POP RCONST	PRO RCONST
0.00	.489465	.276203	.997674	.002506	.003264	.569148	5.042564	.170498	150.980198
12.65	.671506	.365437	1.122432	.004282	.011773	.572523	3.712546	.109595	85.204897
29.28	.918064	.484117	1.286422	.008216	.014804	.577477	2.694102	.070193	49.337590
41.76	1.133909	.543699	1.400397	.010552	.024103	.581568	1.979104	.051568	32.759578
55.91	1.417108	.578133	1.548656	.013028	.027101	.585024	1.191266	.036083	20.312852
71.66	1.752365	.603890	1.703346	.015469	.027019	.588776	.509263	.025039	14.352836
85.50	2.047472	.617610	1.838916	.017253	.031512	.590366	.057911	.018646	14.194684

ACCUMULATED VAPOR QUANTITIES VS REAL TIME

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE
10.58	.000969	.000526	.002371	.000003	0.000000
20.98	.005621	.010911	.018612	.000312	0.000000
34.08	.042995	.123901	.069817	.002585	.000425
48.98	.108219	.242161	.105388	.004932	.003932
63.33	.215989	.358572	.165533	.008563	.005365
76.03	.324968	.418987	.208487	.010480	.009347
90.00	.444081	.483934	.266631	.012910	.011564
105.70	.710700	.545782	.343568	.015726	.017533
119.67	.969184	.592641	.406322	.017236	.023106

INSTANTANEOUS LIQUID MOLE FRACTION VS ADJUSTED TIME

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE	COMPLEX	H2SO4	NH4HSO4
0.00	.158365	.054354	.328727	0.000000	.000936	.257237	.101458	.098922
12.65	.187894	.042900	.337454	0.000000	.002453	.204497	.045089	.125304
29.28	.215752	.041107	.344294	0.000000	.003251	.153386	.087707	.154503
41.76	.235913	.035348	.348720	0.000000	.004493	.127339	.083258	.164930
55.91	.259133	.026001	.353591	0.000000	.004164	.110724	.079153	.167135
71.66	.276992	.016940	.361198	0.000000	.002638	.099344	.075876	.157012
85.50	.282024	.008918	.371704	0.000000	.002197	.092568	.074307	.158281

INSTANTANEOUS VAPOR MOLE FRACTIONS AND TOTAL VAPOR FLOW RATE VS ADJUSTED TIME

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE	VRATE
0.00	.256241	.569956	.150324	.011113	.012366	.017498
12.65	.324555	.472570	.180520	.011452	.010904	.017132
29.28	.431104	.342794	.204863	.010785	.010452	.017735
41.76	.511169	.258089	.209975	.009598	.011170	.017997
55.91	.591078	.184240	.204079	.007833	.012770	.021258
71.66	.660217	.131179	.187832	.005723	.015049	.024844
85.50	.703588	.105852	.169444	.003969	.017137	.027900

INSTANTANEOUS EQUILIBRIUM CONSTANTS VS ADJUSTED TIME

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE
0.00	1.618940	10.485959	.457291		13.211312
12.65	1.727329	11.015550	.534046		3.809114
29.28	1.949145	8.339049	.595023		3.214966
41.76	2.166771	7.301326	.602131		2.486212
55.91	2.240982	7.085987	.576498		3.066831
71.66	2.343526	7.743656	.520025		5.705781
85.50	2.494774	11.870681	.455857		7.799560

INSTANTANEOUS LIQUID ACTIVITY COEFFICIENT VS ADJUSTED TIME

TIME	ALCOHOL	ACRYLATE	WATER	ETHER	PROPIONATE
0.00	.577972	8.965281	.331807		101.067998
12.65	.660554	10.015710	.419218		31.941891
29.28	.847008	8.327176	.524044		30.996186
41.76	.980823	7.790925	.575737		26.451568
55.91	1.117008	8.048561	.595911		35.794925
71.66	1.259316	9.416235	.583968		73.665102
85.50	1.361432	14.859862	.530410		109.109495

SUMMARY OF ERRORS FOR CURVE FITS-- 3 DEGREE POLYNOMIALS

VAPOR FLOW RATES

VAPOR RATE VS VAPOR
ADJUSTED TIME BEFORE
TIME LAG CORRECTION

VAPOR RATE VS LIQUID
ADJUSTED TIME AFTER
TIME LAG CORRECTION

ABS PCT ERR STANDARD DEV

ABS PCT ERR STANDARD DEV

ALCOHOL	.23766E+00	.37398E-01	.23460E+00	.37240E-01
ACRYLATE	.75909E+00	.34893E+00	.76465E+00	.35049E+00
WATER	.95458E+00	.43843E-01	.95577E+00	.43882E-01
ETHER	.17590E+01	.14147E-01	.17593E+01	.14157E-01
PROPIONATE	.15305E+02	.90230E-01	.15327E+02	.90247E-01

REACTION RATE

ACP RATE

ROR RATE

PRO RATE

ABS PCT ERR	.12291E+01	.18497E-10	.50102E+01
STANDARD DEV	.64117E-02	.12533E-14	.13240E-02

```

PROGRAM MODEL(INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
COMMON MM,MV,M,NN,VF,V,Y(5),YIN(5),RMW(9),X(18),X1(18),XLAMDA(5,5)
1,HINT,HOUTOT,HLOSS,HRXN,HDXDTM,CPMOTDT
COMMON /BLOCK1/ ARHO(9,5),ACPL(9,5),AHVO(5,5),TIN,RC,ARK1,E01,
1APK2,E02,ARK3,E03,DHR1,DHR2,DHR3,QUALE,U0,FEEDP
COMMON /BLOCK2/ AP(5),BP(5),CP(5),TC(5),PT,SUMY,DY,RMT,OMEGA(5)
COMMON /BLOCK3/ RM(18),TIME,TIME1,DTIME,VN
DIMENSION RP(9),IDEN(9),RMO(18),YO(5)

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```

X(1) --- X(9) LIQUID MOLE FRACTIONS
RM(1) --- RM(9) LIQUID MOLAR QUANTITIES
RM(10)=TEMPERATURE
RM(11)=LIQUID TOTAL MOLAR QUANTITY
RM(12)=CLEAR LIQUID VOLUME
RM(13) --- RM(17) ACCUMULATED VAPOR MOLAR QUANTITIES
RM(18)=ACCUMULATED VAPOR TOTAL MOLAR QUANTITY
Y(1) --- Y(5) EQUILIBRIUM VAPOR MOLE FRACTIONS
V=INSTANTANEOUS MOLAR EVAPORATION RATE

```

```

READ(5,24) MM,MV,M,NN
READ(5,12) ((ARHO(I,J),J=1,M),I=1,MM)
READ(5,12) ((ACPL(I,J),J=1,M),I=1,MM)
READ(5,12) ((AHVO(I,J),J=1,M),I=1,MV)
READ(5,11) (RMW(I),I=1,MM)
READ(5,11) (TC(I),I=1,MV)
READ(5,11) (OMEGA(I),I=1,MV)
READ(5,14) (AP(I),BP(I),CP(I),I=1,MV)
READ(5,11) E01,E02,E03,PC
READ(5,27) ((XLAMDA(I,J),J=1,5),I=1,5)
27 FORMAT(5F10.0)
READ(5,87) (IDEN(I),I=1,MM)
DO 16 J=1,MM
DO 16 J=1,M
ARHO(I,J)=ARHO(I,J)*1000./PMW(I)
ACPL(I,J)=ACPL(I,J)*RMW(I)
16 CONTINUE
DO 28 I=1,MV
DO 28 J=1,M
28 AHVO(I,J)=AHVO(I,J)*RMW(I)
30 READ(5,24) ISET
READ(5,11) TIN,FEEDV,RHOIN,PT,V
READ(5,11) (PY(I),I=1,NN)
READ(5,11) (Y(I),I=1,MV)
READ(5,11) (YIN(I),I=1,MV)
DO 15 J=1,MV
15 YIN(I)=YIN(I)*FEEDV*RHOIN/RMW(I)
FEEDP=YIN(1)+YIN(3)
YIN(1)=YIN(1)/FEEDP
YIN(3)=1.-YIN(1)
PT=PT/760.
DO 44 I=1,NN
44 RMO(I)=RM(I)
DO 443 I=1,MV
43 YO(I)=Y(I)
V0=V

```

```

11 FORMAT(8F10.0)
12 FORMAT(5E14.5)
14 FORMAT(3F10.0)
24 FORMAT(4I5)
87 FORMAT(9A6)
002 READ(5,11) DHR1,DHR2,DHR3,U0,QUALE
    READ(5,11) DTIME,ATIME,TSLT,DVN,EPS
    WRITE(6,129) ISET
129 FORMAT(1H1,2X,7HRUN NO.,I3)
    WRITE(6,144) QUALE,DTIME,U0,DHR1
144 FORMAT(/2X,21HINLET VAPOR FRACTION=,F5.2,5X,22HINTEGRATION STEP-SI
    IZE=,F7.2,8H MINUTES//2X,3HUU=,F5.2,14H CAL/CM2-MIN-C,5X,5HDHR1=,
    IF8.1,10H CAL/G MOL/)
    ARK1=2.303*(18.19607-0.57106*ALOG10(TIN-104.))-0.13054*ALOG10(
    1QUALE+0.044739)-0.50106*ALOG10(0.9112+FEEDV))
    ARK2=2.303*(24.3061-1.1396*ALOG10(TIN-103.22)+0.13061*ALOG10(
    1QUALE+0.01))-0.25786*ALOG10(FEEDV-0.66092))
    ARK3=2.303*(26.72173-0.88507*ALOG10(TIN-104.))-0.39986*ALOG10(
    1QUALE+1.8434)-0.16398*ALOG10(6.7684+FEEDV))
    RMS=RM(2)+RM(5)+RM(14)+RM(17)
    JJ=0
    TIME1=0.
    SUMY=1.
    RMT=0.
    DO 25 J=1,MM
25 RMT=RMT+RM(J)
    DO 26 I=1,MM
26 X(I)=RM(I)/RMT
    WRITE(6,100)
100 FORMAT(/1X,41HINITIAL CONDITIONS BASED ON ADJUSTED TIME/)
    DO 70 I=1,MM
70 RP(I)=Y(I)
    RP(6)=V
    RP(7)=SUMY
    RP(8)=0.
    RP(9)=0.
    DO 88 I=1,MM
    JP=I+9
88 WRITE(6,101) I,X(I),I,RP(I),JP,RP(JP),IDEN(I),RP(I)
101 FORMAT(3X,2HX(,I2,2H)=,F9.5,6X,3HRM(,I2,2H)=,F9.5,6X,3HRM(,I2,
    12H)=,F11.5,6X,A6,F11.5)
72 VPRFV=-0.1
    ITER=0
    VN=V+DVN
540 ITER=ITER+1
    IF(ITER.GE.20) GO TO 18
    CALL RUNOUT
    IF(ARK(DY)-EPS) 18,18,20
20 IF(VPRFV) 600,600,615
600 SUMYP=SUMY
    VPRFV=VN
    IF(DY) 605,18,610
605 VN=0.75*VN
    DY1=DY
    GO TO 540

```

```

10 VN=VN*1.25
   DY)=DY
   GO TO 540
15 IF(DY#0(1) 626.18,600
26 IF(ABS((VN-VPREV)/VN).LT,.1E-05) GO TO 18
   SLOPE=(SUMY-SUMYP)/(VN-VPREV)
   VPREV=VN
   SUMYP=SUMY
   VN=VN-DY/SLOPE
   GO TO 540
18 TIME1=TIME
   V=VN
   DO 51 J=1,N
51 RM(J)=X1(J)
   RTM=TIME1/ATIME
   IRTM=RTM
   RTM=RTM-FLOAT(1-RTM)
   IF(ABS(RTM)-0.01) 789,789,788
89 WRITE(6,102) TIME1,ITER
02 FORMAT(///1X,5HTIME=,F8.2,8H MINUTES,15X,21HNUMBER OF ITERATIONS=,
1I3/)
   DO 186 I=1,MV
186 RP(I)=Y(I)
   RP(6)=V
   RP(7)=SUMY
   RP(8)=DY1
   RP(9)=DY
   DO 89 I=1,NM
   JP=I+9
89 WRITE(6,101) I,X(I),I,RP(I),JP,RP(JP),IDFN(I),RP(I)
   WRITE(6,104) HINT,HOUTOT,HLOSS,HPXN,HDXDTM,CPMDTDT
04 FORMAT(3X,6HHINT =,F9.3,3X,6HHOUTO=,F9.3,3X,6HFLOSS=,F9.3,3X,
16HHPXNS=,F9.3,3X,6HMDMDT=,F9.3,3X,6HMDMDT=,F9.3)
88 IF(TIME1-TSET) 72,72,999
99 READ(5,24) IREP
   GO TO (30,32,999),IREP
32 DO 434 I=1,NM
34 RM(I)=P40(I)
   DO 433 I=1,MV
33 Y(I)=Y0(I)
   V=V0
   GO TO 1002
98 STOP
END

```



```
SUBROUTINE RUNKUT
COMMON MM,MV,M,NN,VF,V,Y(5),YIN(5),RMW(9),Y(18),X1(18),XLAMDA(5,5)
COMMON /BLOCK3/ RM(18),TIME,TIME1,DTIME,VN
COMMON /BLOCK4/ FF(18)
DIMENSION G1(18),G2(18),G3(18),G4(18)
DO 10 J=1,NN
0 X1(1)=RM(1)
VF=V
TIME=TIME1
CALL FUNC
DO 12 J=1,NN
G1(1)=DTIME*FF(1)
2 X1(1)=RM(1)+G1(1)/2.
VF=(V+VN)/2.
TIME=TIME1+DTIME/2.
CALL YVALUE
CALL FUNC
DO 14 J=1,NN
G2(1)=DTIME*FF(1)
4 X1(1)=RM(1)+G2(1)/2.
CALL YVALUE
CALL FUNC
DO 16 J=1,NN
G3(1)=DTIME*FF(1)
6 X1(1)=RM(1)+G3(1)/2.
VF=VN
TIME=TIME+DTIME/2.
CALL YVALUE
CALL FUNC
DO 18 J=1,NN
G4(1)=DTIME*FF(1)
8 X1(1)=RM(1)+(G1(1)+2.*G2(1)+2.*G3(1)+G4(1))/6.
CALL YVALUE
RETURN
END
```

SUBROUTINE YVALUE

```

COMMON MM,MV,X,NN,VF,V,Y(5),YIN(5),PMW(9),X(18),X1(18),XLAMDA(5,5)
COMMON /BLOCK1/ ARHO(9,5),ACPL(9,5),AHV0(5,5),TIN,PC,ARK1,E01,
1ARK2,E02,ARK3,E03,DHR1,DHR2,DHR3,QUALE,U0,FEEDR
COMMON /BLOCK2/ AP(5),BP(5),CP(5),TC(5),PT,SUMY,DY,RMT,OMEGA(5)
COMMON /BLOCK3/ RM(13),TIME,TIME1,DTIME,VN
COMMON /BLOCK4/ FF(18)
DIMENSION XG(5),GAMMA(5),SUM(5)

```

CALCULATE LIQUID MOLE FRACTIONS

```

RMT=0.
DO 10 I=1,MM
10 RMT=RMT+X1(I)
DO 11 J=1,MV
11 X(I)=X1(I)/RMT

```

CALCULATE VAPOR MOLE FRACTIONS

```

TK=X1(10)+273.16
XG(1)=X(1)
XG(2)=X(2)
XG(3)=X(3)
XG(4)=X(5)
XG(5)=1.-XG(1)-XG(2)-XG(3)-XG(4)
DO 42 I=1,5
SUM(I)=0.
DO 42 J=1,5
42 SUM(I)=SUM(I)+XG(J)*XLAMDA(I,J)
DO 44 I=1,4
SUMT=0.
DO 46 K=1,5
46 SUMT=SUMT+XG(K)*XLAMDA(K,I)/SUM(I)
44 GAMMA(I)=EXP(1.-ALOG(SUM(I))-SUMT)
GAMMA(5)=GAMMA(4)
DO 31 I=1,MV
IF(I,FO,4) GO TO 31
PS=10.**((AP(I)-BP(I))/(CP(I)+X1(10)))/760.
TR=TK/(TC(I)+273.16)
PHIS0=((0.57335/TR-3.0766)/TR+5.6086)/TR-3.5021
PHIS1=(((((0.012089/TR-0.015172)/TR-0.068604)/TR+0.024365)/
1TR+0.14937)/TR+0.18927)/TR-0.12147)/TR-0.10666)/TR-1.1662)/TR+
20.12666)/TR+0.31661)/TR+4.3539)/TR-3.7694
PHIS=10.**((PHIS0+OMEGA(I)*PHIS1)
Y(I)=GAMMA(I)*PS*PHIS*X(I)/PT
31 CONTINUE
RATE2=EXP(ARK2-E02/PC/TK)*X1(1)**2/X1(12)
Y(4)=RATE2/VF
SUMY=0.
DO 12 I=1,MV
12 SUMY=SUMY+Y(I)
DY=SUMY-1.
RETURN
END

```

```

SUBROUTINE FUNC
COMMON MM,MV,M,NN,VF,V,Y(5),YIN(5),RMW(9),X(18),X1(18),XLAMDA(5,5)
1 HINT,HOUTOT,HLOSS,HRXN,HDXDTM,CPMDTDT
COMMON /BLOCK1/ ARHO(9,5),ACPL(9,5),AHV0(5,5),TIN,RC,ARK1,E01,
1 ARK2,E02,ARK3,E03,DHR1,DHR2,DHF3,QUALE,U0,FEEDR
COMMON /BLOCK4/ FF(18)
DIMENSION CPL(9),HL(9),HLIN(9),HIN(5),HVIN(5),HV(5),RHO(9)
DO 15 I=1,MM
RHO(I)=ARHO(I,1)
CPL(I)=ACPL(I,1)
HL(I)=ACPL(I,1)*X1(10)
HLIN(I)=ACPL(I,1)*TIN
DO 15 J=2,M
RHO(I)=RHO(I)+ARHO(I,J)*X1(10)**(J-1)
CPL(I)=CPL(I)+ACPL(I,J)*X1(10)**(J-1)
HL(I)=HL(I)+ACPL(I,J)*X1(10)**J/FLOAT(J)
15 HLIN(I)=HLIN(I)+ACPL(I,J)*TIN**J/FLOAT(J)
DO 16 I=1,MV
HV(I)=AHV0(I,1)
HVIN(I)=AHV0(I,1)
DO 16 J=2,M
HV(I)=HV(I)+AHV0(I,J)*X1(10)**(J-1)
16 HVIN(I)=HVIN(I)+AHV0(I,J)*TIN**J/FLOAT(J)
DO 18 I=1,MV
18 HIN(I)=HLIN(I)*(1.-QUALE)+HVIN(I)*QUALE
TK=X1(10)+273.16
RATE1=EXP( ARK1 -E01/RC/TK)*X1(1)*X1(6)/X1(12)
RATE2=EXP( ARK2 -E02/RC/TK)*X1(1)**2/X1(12)
RATE3=EXP( ARK3 -E03/RC/TK)*X1(1)**2*X1(6)/X1(12)**2
FF(1)=YIN(1)*FEEDR-Y(1)*VF-RATE1-2.*(RATE2+RATE3)
FF(2)=-Y(2)*VF+RATE1
FF(3)=YIN(3)*FEEDR-Y(3)*VF+RATE2
FF(4)=0.
FF(5)=-Y(5)*VF+RATE3
FF(12)=0.
DO 125 J=1,5
26 FF(12)=FF(12)+(FEEDR*YIN(J)-VF*Y(J))/RHO(J)
XS=X1(2)+X1(5)+X1(14)+X1(17)
FF(6)=-RATE1-RATE3
FF(7)=0.
FF(8)=RATE1+RATE3
FF(9)=0.
RMXCP=0.
HDXDTM=0.
HINT=0.
HOUTOT=0.
DO 20 J=1,M
RMXCP=RMXCP+X1(J)*CPL(J)
HDXDTM=HDXDTM+HL(J)*FF(J)
DO 22 J=1,MV
HINT=HINT+HIN(J)*FEEDR*YIN(J)
2 HOUTOT=HOUTOT+HV(J)*Y(J)*VF
VS=X1(12)*1.06*1000.
TIL=TIN
IF(VS-150.) 50,50,51

```

```
50 UA=U0*AF(VS)
   GO TO 65
51 IF(VS-172.4) 52,52,53
52 XR=1.3750+(VS-150.)/89.6
   US1=1./(1./U0+16.4*ALOG(XR/1.125))
   UA=U0*150.4+US1*(AF(VS)-150.4)
   GO TO 65
53 IF(VS-187.4) 54,54,55
54 UA=U0*150.4+(AF(VS)-172.4)/(1./U0+4.74)+22.4/(1./U0+4.)
   GO TO 65
55 IF(VS-212.2) 56,56,57
56 XR=1.6750-(VS-187.4)/91.6
   US3=1./(1./U0+4.+16.4*ALOG(XR/1.125))
   UA=U0*150.4+22.4/(1./U0+2.)+10.9/(1./U0+2.37)+(AF(VS)-183.2)*US3
   GO TO 65
57 UA=U0*150.4+22.4/(1./U0+4.)+10.9/(1./U0+4.74)+29./(1./U0+4.84)+
   1U0*(AF(VS)-212.2)
65 HLOSS=UA*(X1(10)-TOIL)
   HRXN=DHR1*RATE1+DHR2*RATE2+DHR3*RATE3
   FF(10)=(HINT-HOUTOT-HLOSS+HRXN-HDXDTM)/RMXCP
   CPMDDTDT=FF(10)*RMXCP
   FF(11)=0.
   DO 26 J=1,MM
26 FF(11)=FF(11)+FF(J)
   DO 27 J=13,17
   JJ=J-12
27 FF(J)=Y(JJ)*VF
   FF(18)=VF
   RETURN
END
```

FUNCTION AF(VS)

AF=48.844-0.12787*VS+0.011009*VS**2-0.49516E-04*VS**3+0.79715E-07
1*VS**4

RETURN

END

5	18	74.08	147.2	169.14	98.08	115.05
795.00E+00	-0.75000E-03	-0.16369E-05				
-397.1E+00	-0.94345E-03	-0.16369E-05				
10057E+01	-0.25200E-03	-0.22973E-05				
73271E+00	-0.88333E-03	-0.32738E-05				
7266E+00	-0.87445E-03	-0.14881E-06				
14734E+01	-0.95765E-03	0.31945E-07				
18511E+01	-0.99000E-03					
18141E+01	-0.27500E-02					
11452E+01	-0.76236E-03	-0.38601E-06				
53150E+00	0.22012E-02	0.72024E-05				
45560E+00	0.48312E-03	0.17086E-05				
10060E+01	-0.31738E-03	0.34230E-05				
53002E+00	0.47143E-03	0.11012E-04				
44220E+00	0.10364E-02	0.26786E-05				
51106E+00	-0.26872E-02	0.25080E-04	-0.46642E-07			
47483E+00	-0.54866E-02	0.41811E-04	-0.81692E-07			
42665E+00	-0.23368E-02	0.17822E-04	-0.34821E-07			
56106E+00	0.11766E-02	0.19881E-05	0.17361E-08			
22700E+03	0.36300E+00	0.33978E-03				
55000E+02	0.23869E+00	0.67200E-03	-0.13211E-07			
59760E+03	0.42000E+00	0.10200E-05				
90000E+02	0.34500E+00	0.37500E-05				
79598E+02	0.36948E+00	-0.62110E-04	0.89290E-06			
07	100.11	18.016	74.08	147.2	169.14	98.08
288.	374.1	193.8	352.8			
0.329	0.344	0.283	0.288			
9	1623.2	228.93				
3	1283.1	212.19				
81	1868.2	228.0				
27	1651.3	227.43				
6	1795.2	211.67				
.	47970.	52880.	1.987			
	0.070872	0.	0.	0.67696		
5	1.0	0.	0.27093	0.		
7	9.1069	1.	10.873	6.0193		
	0.	0.026937	1.	0.		
3	0.	3.9135	6.9154	1.		
= Y(2) = Y(3) = Y(4) = Y(5) = VPATE = SUMY = DY1 = DY =						
	1.56	0.826	762.	0.02057		
91	.092631	.795134	0.	0.	.686395	.264688
	125.41	2.50857	.15603	.065494	.229716	.128481
	.43191					.005536
25	.483575	.15376	.019501	.015638		
	0.	0.14	0.	0.		
.	820.	21200.	0.16	0.82		
4.	83.	0.008	0.0001			
	1.735	.826	765.	.018865		
44	.079233	.907816	.0	.003525	.69147	.289941
	123.57	2.69542	.16316	.077872	.221134	.132248
01	.43814					.005457
7	.802457	.275336	.020954	.026625		
	0.	0.14	0.	0.		
.	820.	21200.	0.16	.34		
4.	87.	0.008	0.0001			

	1.496	.826	768.	.020096			
76	.127607	.499955	.0	.0	.803898	.247907	.223495
	118.03	2.85516	.1777	.040962	.095009	.044999	.003553
69	.1856						
01	.449451	.300241	.025865	.012543			
	0.	0.14	0.	0.			
	820.	21200.	0.16	.69			
	4.	95.	0.008	0.0001			
	1.5575	.826	760.2	.016549			
54	.114545	.874251	.0	.0	.765238	.263406	.218297
	119.46	2.5702	.16222	.043488	.103020	.050849	.002756
51	.20024						
88	.652675	.195075	.025202	.015359			
	0.	0.14	0.	0.			
	820.	21200.	0.16	.60			
	4.	95.	0.008	0.0001			
	1.192	.826	764.5	.016242			
02	.110475	.858602	.0	.003932	.807022	.230999	.216037
	118.86	2.54249	.16344	.042997	.101651	.058527	.00255
	0.20576						
23	.588697	.24714	.019351	.000938			
	0.	0.14	0.	0.			
	820.	21200.	0.16	.70			
	4.	87.	0.008	0.0001			
	1.147	.826	762.	.012841			
017	.08763	.905228	0.	.002462	.738085	.209716	.278239
	118.34	2.53738	.15563	.053337	.18656	.085659	.002555
8.7	.33001						
017	.61585	.240426	.010344	.008363			
	0.	0.14	0.	0.			
	820.	21200.	0.16	.55			
	4.	83.	0.008	0.0001			
	1.465	.826	760.	.016602			
08	.126927	.941537	.0	.00484	.71446	.279537	.28751
	120.77	2.68972	.16484	.052611	.154978	.104355	.004213
766	.31693						
04	.66552	.154039	.019553	.020484			
	0.	0.14	0.	0.			
	820.	21200.	0.16	.76			
	4.	91.	0.008	0.0001			
	1.26	.826	752.3	.020818			
17	.146505	.868283	.0	.001798	.765755	.282345	.234527
	115.71	2.60603	.16586	.032781	.086224	.010575	.003459
	.13304						
859	.562375	.291927	.024874	.012461			
	0.	0.14	0.	0.			
	820.	21200.	0.16	.85			
	4.	95.	0.008	0.0001			

4	1.506	.826	763.5	.017498			
4	.153557	.928691	.0	.002644	.726725	.28663	.279467
2	110.8	2.82511	.1755	.042055	.122646	.068983	.002506
241	.23682						
	.569456	.150324	.011113	.012366			
	0.	0.14	0.	0.			
0.	820.	21200.	0.0000001	0.			
3	4.	83.	0.012	0.0001			

C.2.3 Results form Program MODEL

Each integration step contains forty two instantaneous quantities. They are defined as follows.

X(1) to X(9) = liquid mole fractions for components
1 to 9

RM(1) to RM(9) = liquid molal quantities for components
1 to 9

RM(10) = liquid temperature

RM(11) = total liquid molal quantity

RM(12) = clear liquid volume

RM(13) to RM(17) = accumulated vapor molal condensate
for components 1 to 5

RM(18) = accumulated total vapor condensate, g-moles

Y(1) to Y(5) = vapor mole fractions for components
1 to 5

V RATE = vapor flow rate, g-moles/min.

SUMY = calculated total vapor mole fraction

DY1 = deviation in total vapor mole fraction right
before the last iteration

DY = deviation in total vapor mole fraction after the
last iteration

HINT = total feed enthalpy, cal/min.

HOUTO = total outlet vapor enthalpy, cal/min.

HLOSS = convection heat loss across the reactor wall,
cal/min.

HRXNS = total heat generated by chemical reactions,
cal/min.

$$\text{HDMDT} = h_s \frac{dM}{dt} \text{ shown in Equation (4-132)}$$

$$\text{MDHDT} = M \frac{dH}{dt} = MC_p \frac{dT}{dt} \text{ shown in Equation (4-132)}$$

INITIAL CONDITIONS BASED ON ADJUSTED TIME

X(1)= .13608	RM(1)= .34139	RM(10)= 125.41000	Y(1)= .32753
X(2)= .03692	RM(2)= .09263	RM(11)= 2.50867	Y(2)= .48358
X(3)= .31815	RM(3)= .79813	RM(12)= .15603	Y(3)= .15376
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .06549	Y(4)= .01950
X(5)= 0.00000	RM(5)= 0.00000	RM(14)= .22972	Y(5)= .01564
X(6)= .27381	RM(6)= .68689	RM(15)= .12848	VRATE= .02057
X(7)= .10551	RM(7)= .26469	RM(16)= .00564	SUMY= 1.00000
X(8)= .12952	RM(8)= .32493	RM(17)= .00258	DY1= 0.00000
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= .43191	DY= 0.00000

TIME= 4.00 MINUTES

NUMBER OF ITERATIONS= 14

X(1)= .14050	RM(1)= .35184	RM(10)= 123.77776	Y(1)= .27726
X(2)= .02703	RM(2)= .06768	RM(11)= 2.50424	Y(2)= .42760
X(3)= .32161	RM(3)= .80540	RM(12)= .15174	Y(3)= .25411
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .10173	Y(4)= .03285
X(5)= .00112	RM(5)= .00280	RM(14)= .29397	Y(5)= .00812
X(6)= .25721	RM(6)= .64411	RM(15)= .16290	VRATE= .01181
X(7)= .10570	RM(7)= .26469	RM(16)= .00780	SUMY= .99993
X(8)= .14684	RM(8)= .36771	RM(17)= .00326	DY1= -.00022
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= .56753	DY= -.00007

HINT= 363.406

HOUTO= 153.116

HLOSS= 223.095

HRXNS= 193.661

HMDT= 41.044

MDHDT= 139.812

TIME= 8.00 MINUTES

NUMBER OF ITERATIONS= 11

X(1)= .14512	RM(1)= .36686	RM(10)= 124.27339	Y(1)= .30667
X(2)= .02406	RM(2)= .06082	RM(11)= 2.52793	Y(2)= .39319
X(3)= .32342	RM(3)= .81858	RM(12)= .15017	Y(3)= .26540
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .13403	Y(4)= .02176
X(5)= .00204	RM(5)= .00515	RM(14)= .33911	Y(5)= .01294
X(6)= .23825	RM(6)= .60227	RM(15)= .19151	VRATE= .02112
X(7)= .10471	RM(7)= .26469	RM(16)= .00970	SUMY= .99995
X(8)= .16201	RM(8)= .40955	RM(17)= .00448	DY1= -.00017
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= .67565	DY= -.00005

HINT= 363.406

HOUTO= 272.650

HLOSS= 232.275

HRXNS= 203.662

HMDT= -.857

MDHDT= 63.000

TIME= 12.00 MINUTES

NUMBER OF ITERATIONS= 10

X(1)= .14829	RM(1)= .37782	RM(10)= 124.33357	Y(1)= .32699
X(2)= .02201	RM(2)= .05608	RM(11)= 2.54783	Y(2)= .36475
X(3)= .32585	RM(3)= .83021	RM(12)= .14852	Y(3)= .27182
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .16921	Y(4)= .02038
X(5)= .00283	RM(5)= .00721	RM(14)= .34190	Y(5)= .01602
X(6)= .21999	RM(6)= .56049	RM(15)= .22188	VRATE= .02441
X(7)= .10389	RM(7)= .26469	RM(16)= .01172	SUMY= .99996
X(8)= .17714	RM(8)= .45133	RM(17)= .00514	DY1= -.00014
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= .78121	DY= -.00001

X(1)= .15125	RM(1)= .38848	PM(10)= 124.19370	Y(1)= .34464
X(2)= .02059	RM(2)= .05288	PM(11)= 2.56844	Y(2)= .34113
X(3)= .32767	RM(3)= .84160	PM(12)= .14708	Y(3)= .27622
X(4)= 0.00000	RM(4)= 0.00000	PM(13)= .20760	Y(4)= .01997
X(5)= .00349	RM(5)= .00897	PM(14)= .42150	Y(5)= .01902
X(6)= .20261	RM(6)= .52040	PM(15)= .25259	VRATE= .02603
X(7)= .10305	RM(7)= .26469	PM(16)= .01392	SUMY= .99997
X(8)= .19133	RM(8)= .49142	PM(17)= .00807	OY1= -.00012
X(9)= 0.00000	RM(9)= 0.00000	PM(18)= .90075	OY= -.00003
HINT= 363.406	HOUTO= 334.243	HLOSS= 228.511	HRXNS= 191.936
			HDMOT= -18.423
			MDHDT= 10.871

TIME= 20.00 MINUTES

NUMBER OF ITERATIONS= 8

X(1)= .15446	RM(1)= .40013	PM(10)= 123.90115	Y(1)= .36179
X(2)= .01947	RM(2)= .05044	PM(11)= 2.59055	Y(2)= .31947
X(3)= .32929	RM(3)= .85303	PM(12)= .14589	Y(3)= .27934
X(4)= 0.00000	RM(4)= 0.00000	PM(13)= .24672	Y(4)= .02000
X(5)= .00403	RM(5)= .01044	PM(14)= .45807	Y(5)= .01931
X(6)= .18634	RM(6)= .48272	PM(15)= .28331	VRATE= .02657
X(7)= .10217	RM(7)= .26469	PM(16)= .01619	SUMY= .99991
X(8)= .20424	RM(8)= .52910	PM(17)= .01015	OY1= -.00030
X(9)= 0.00000	RM(9)= 0.00000	PM(18)= 1.01095	OY= -.00009
HINT= 363.406	HOUTO= 340.447	HLOSS= 220.981	HRXNS= 179.747
			HDMOT= -18.023
			MDHDT= -.152

TIME= 24.00 MINUTES

NUMBER OF ITERATIONS= 9

X(1)= .15809	RM(1)= .41330	PM(10)= 123.50342	Y(1)= .37950
X(2)= .01848	RM(2)= .04832	PM(11)= 2.61440	Y(2)= .29837
X(3)= .33072	RM(3)= .86463	PM(12)= .14495	Y(3)= .28175
X(4)= 0.00000	RM(4)= 0.00000	PM(13)= .28720	Y(4)= .02013
X(5)= .00445	RM(5)= .01163	PM(14)= .49179	Y(5)= .02012
X(6)= .17127	RM(6)= .44777	PM(15)= .31390	VRATE= .02668
X(7)= .10124	RM(7)= .26469	PM(16)= .01849	SUMY= .99996
X(8)= .21575	RM(8)= .56405	PM(17)= .01231	OY1= -.00013
X(9)= 0.00000	RM(9)= 0.00000	PM(18)= 1.11963	OY= -.00004
HINT= 363.406	HOUTO= 341.920	HLOSS= 210.756	HRXNS= 166.300
			HDMOT= -15.599
			MDHDT= -6.472

TIME= 28.00 MINUTES

NUMBER OF ITERATIONS= 9

X(1)= .16214	RM(1)= .42799	PM(10)= 123.02986	Y(1)= .39825
X(2)= .01753	RM(2)= .04628	PM(11)= 2.63967	Y(2)= .27726
X(3)= .33199	RM(3)= .87635	PM(12)= .14424	Y(3)= .29365
X(4)= 0.00000	RM(4)= 0.00000	PM(13)= .32921	Y(4)= .02021
X(5)= .00475	RM(5)= .01254	PM(14)= .52284	Y(5)= .02059
X(6)= .15747	RM(6)= .41566	PM(15)= .34438	VRATE= .02652
X(7)= .10027	RM(7)= .26469	PM(16)= .02080	SUMY= .99997
X(8)= .22545	RM(8)= .59617	PM(17)= .01451	OY1= -.00012
X(9)= 0.00000	RM(9)= 0.00000	PM(18)= 1.22714	OY= -.00003
HINT= 363.406	HOUTO= 339.524	HLOSS= 198.923	HRXNS= 152.637
			HDMOT= -12.469
			MDHDT= -9.935

X(4) = 0.00000	RM(4) = 0.00000	PM(13) = .37206	Y(4) = .02017
X(5) = .00495	RM(5) = .01320	PM(14) = .55140	Y(5) = .02080
X(6) = .14490	RM(6) = .38629	PM(15) = .37483	VRATE = .02658
X(7) = .00929	RM(7) = .26469	PM(16) = .02311	SUMY = .99997
X(8) = .23464	RM(8) = .62553	PM(17) = .01673	DY1 = -.00011
X(9) = 0.00000	RM(9) = 0.00000	PM(18) = 1.33389	DY = -.00003
HINT = 363.406	HOUTO = 338.142	HLOSS = 186.006	HRXNS = 139.416
			HOMDT = -9.446
			MDHDT = -11.880

TIME= 36.00 MINUTES NUMBER OF ITERATIONS= 9

X(1) = .17111	RM(1) = .46074	PM(10) = 121.95713	Y(1) = .43722
X(2) = .01562	RM(2) = .04205	PM(11) = 2.69269	Y(2) = .23550
X(3) = .33415	RM(3) = .89076	PM(12) = .14335	Y(3) = .28647
X(4) = 0.00000	RM(4) = 0.00000	PM(13) = .41869	Y(4) = .01999
X(5) = .00506	RM(5) = .01363	PM(14) = .57764	Y(5) = .02080
X(6) = .13353	RM(6) = .35954	PM(15) = .40536	VRATE = .02661
X(7) = .09830	RM(7) = .26469	PM(16) = .02540	SUMY = .99997
X(8) = .24224	RM(8) = .65228	PM(17) = .01896	DY1 = -.00011
X(9) = 0.00000	RM(9) = 0.00000	PM(18) = 1.44039	DY = -.00003
HINT = 363.406	HOUTO = 337.674	HLOSS = 172.472	HRXNS = 126.974
			HOMDT = -5.838
			MDHDT = -12.927

TIME= 40.00 MINUTES NUMBER OF ITERATIONS= 7

X(1) = .17579	RM(1) = .47806	PM(10) = 121.39382	Y(1) = .45655
X(2) = .01465	RM(2) = .03984	PM(11) = 2.71946	Y(2) = .21545
X(3) = .33507	RM(3) = .91121	PM(12) = .14311	Y(3) = .28749
X(4) = 0.00000	RM(4) = 0.00000	PM(13) = .46661	Y(4) = .01955
X(5) = .00509	RM(5) = .01383	PM(14) = .60176	Y(5) = .02064
X(6) = .12327	RM(6) = .33521	PM(15) = .43606	VRATE = .02674
X(7) = .09733	RM(7) = .26469	PM(16) = .02767	SUMY = .99990
X(8) = .24087	RM(8) = .67661	PM(17) = .02118	DY1 = -.00074
X(9) = 0.00000	RM(9) = 0.00000	PM(18) = 1.54710	DY = -.00010
HINT = 363.406	HOUTO = 338.566	HLOSS = 158.674	HRXNS = 115.470
			HOMDT = -4.807
			MDHDT = -13.557

TIME= 44.00 MINUTES NUMBER OF ITERATIONS= 7

X(1) = .19046	RM(1) = .49552	PM(10) = 120.83349	Y(1) = .47559
X(2) = .01369	RM(2) = .03760	PM(11) = 2.74586	Y(2) = .19638
X(3) = .33592	RM(3) = .92237	PM(12) = .14205	Y(3) = .28833
X(4) = 0.00000	RM(4) = 0.00000	PM(13) = .51485	Y(4) = .01924
X(5) = .00504	RM(5) = .01385	PM(14) = .62349	Y(5) = .02035
X(6) = .11493	RM(6) = .31310	PM(15) = .46704	VRATE = .02593
X(7) = .09640	RM(7) = .26469	PM(16) = .02991	SUMY = .99996
X(8) = .25446	RM(8) = .69872	PM(17) = .02338	DY1 = -.00071
X(9) = 0.00000	RM(9) = 0.00000	PM(18) = 1.65440	DY = -.00010
HINT = 363.406	HOUTO = 340.123	HLOSS = 144.926	HRXNS = 104.981
			HOMDT = -3.143
			MDHDT = -13.520

TIME= 48.00 MINUTES NUMBER OF ITERATIONS= 7

X(1) = .18504	RM(1) = .51282	PM(10) = 120.24454	Y(1) = .49365
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X(6)= .10572	RM(6)= .29300	RM(15)= .49836	VRATE= .02718
X(7)= .09550	RM(7)= .26469	RM(16)= .03211	SUMY= .99991
X(8)= .25936	RM(8)= .71883	RM(17)= .02957	DY1= -.00069
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= 1.76260	DY= -.00009
HINT = 363.406	HOUTO= 342.633	HLOSS= 131.484	HRXNS= 95.519
			HMDT= -1.938
			MDMDT= -13.255

TIME= 52.00 MINUTES NUMBER OF ITERATIONS= 7

X(1)= .18943	RM(1)= .52968	RM(10)= 119.75587	Y(1)= .51051
X(2)= .01186	RM(2)= .03317	RM(11)= 2.79626	Y(2)= .16207
X(3)= .33742	RM(3)= .94351	RM(12)= .14282	Y(3)= .28956
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .62469	Y(4)= .01822
X(5)= .00475	RM(5)= .01338	RM(14)= .66285	Y(5)= .01945
X(6)= .89823	RM(6)= .27469	RM(15)= .53008	VRATE= .02749
X(7)= .09466	RM(7)= .26469	RM(16)= .03428	SUMY= .99991
X(8)= .26361	RM(8)= .73713	RM(17)= .02773	DY1= -.00065
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= 1.87194	DY= -.00009
HINT = 363.406	HOUTO= 345.822	HLOSS= 118.503	HRXNS= 87.031
			HMDT= -1.098
			MDMDT= -12.790

TIME= 56.00 MINUTES NUMBER OF ITERATIONS= 7

X(1)= .19360	RM(1)= .54591	RM(10)= 119.25193	Y(1)= .52633
X(2)= .01161	RM(2)= .03105	RM(11)= 2.81941	Y(2)= .14703
X(3)= .33811	RM(3)= .95339	RM(12)= .14280	Y(3)= .29001
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .58232	Y(4)= .01767
X(5)= .00459	RM(5)= .01294	RM(14)= .67998	Y(5)= .01688
X(6)= .09149	RM(6)= .25799	RM(15)= .56223	VRATE= .02794
X(7)= .09387	RM(7)= .26469	RM(16)= .03640	SUMY= .99492
X(8)= .26723	RM(8)= .75383	RM(17)= .02986	DY1= -.00065
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= 1.98260	DY= -.00006
HINT = 363.406	HOUTO= 349.466	HLOSS= 106.115	HRXNS= 79.453
			HMDT= -.547
			MDMDT= -12.174

TIME= 60.00 MINUTES NUMBER OF ITERATIONS= 7

X(1)= .19752	RM(1)= .56136	RM(10)= 118.77650	Y(1)= .54074
X(2)= .01021	RM(2)= .02903	RM(11)= 2.84209	Y(2)= .13344
X(3)= .33876	RM(3)= .96278	RM(12)= .14279	Y(3)= .29039
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .74238	Y(4)= .01712
X(5)= .00437	RM(5)= .01241	RM(14)= .69572	Y(5)= .01823
X(6)= .08540	RM(6)= .24273	RM(15)= .59485	VRATE= .02820
X(7)= .09313	RM(7)= .26469	RM(16)= .03849	SUMY= .98902
X(8)= .27061	RM(8)= .76909	RM(17)= .03194	DY1= -.00053
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= 2.09457	DY= -.00003
HINT = 363.406	HOUTO= 353.374	HLOSS= 94.411	HRXNS= 72.710
			HMDT= -.215
			MDMDT= -11.453

TIME= 64.00 MINUTES NUMBER OF ITERATIONS= 7

X(1)= .20116	RM(1)= .57503	RM(10)= 118.33204	Y(1)= .55386
X(2)= .00947	RM(2)= .02712	RM(11)= 2.86302	Y(2)= .12123
X(3)= .33734	RM(3)= .97156	RM(12)= .14279	Y(3)= .28072

RM(9)= 0.00000 RM(10)= 2.20820 RM(11)= 2.88259 RM(12)= 1.4278 RM(13)= .86945 RM(14)= .72353 RM(15)= .66148 RM(16)= .04256 RM(17)= .03595 RM(18)= 2.32320
HINT = 363.406 HOUTO= 357.390 HLOSS= 83.445 HRXNS= 56.717 HDMDT= -.045 MDMDT= -10.667

TIME= 68.00 MINUTES NUMBER OF ITERATIONS= 7

X(1)= .20453 RM(1)= .58957 RM(10)= 117.91938 Y(1)= .56571
X(2)= .00879 RM(2)= .02534 RM(11)= 2.88259 Y(2)= .11034
X(3)= .33499 RM(3)= .98004 RM(12)= .14278 Y(3)= .29102
X(4)= 0.00000 RM(4)= 0.00000 RM(13)= .86945 Y(4)= .01608
X(5)= .00386 RM(5)= .01112 RM(14)= .72353 Y(5)= .01678
X(6)= .07489 RM(6)= .21588 RM(15)= .66148 VRATE= .02843
X(7)= .09182 RM(7)= .26469 RM(16)= .04256 SUMY= .99992
X(8)= .27612 RM(8)= .79594 RM(17)= .03595 DY1= -.00061
X(9)= 0.00000 RM(9)= 0.00000 RM(18)= 2.32320 DY= -.00008
HINT = 363.406 HOUTO= 361.391 HLOSS= 73.246 HRXNS= 61.394 HDMDT= .012 MDMDT= -9.849

TIME= 72.00 MINUTES NUMBER OF ITERATIONS= 7

X(1)= .20762 RM(1)= .60227 RM(10)= 117.53842 Y(1)= .57637
X(2)= .00816 RM(2)= .02368 RM(11)= 2.90082 Y(2)= .10055
X(3)= .34057 RM(3)= .98793 RM(12)= .14277 Y(3)= .29130
X(4)= 0.00000 RM(4)= 0.00000 RM(13)= .93623 Y(4)= .01561
X(5)= .00359 RM(5)= .01042 RM(14)= .73583 Y(5)= .01599
X(6)= .07033 RM(6)= .20403 RM(15)= .69548 VRATE= .02929
X(7)= .09125 RM(7)= .26469 RM(16)= .04454 SUMY= .99992
X(8)= .27647 RM(8)= .80780 RM(17)= .03787 DY1= -.00060
X(9)= 0.00000 RM(9)= 0.00000 RM(18)= 2.43965 DY= -.00008
HINT = 363.406 HOUTO= 365.283 HLOSS= 63.615 HRXNS= 56.662 HDMDT= -.005 MDMDT= -9.025

TIME= 76.00 MINUTES NUMBER OF ITERATIONS= 7

X(1)= .21045 RM(1)= .61403 RM(10)= 117.18836 Y(1)= .58594
X(2)= .00749 RM(2)= .02216 RM(11)= 2.91775 Y(2)= .09205
X(3)= .34114 RM(3)= .99535 RM(12)= .14274 Y(3)= .29159
X(4)= 0.00000 RM(4)= 0.00000 RM(13)= 1.00499 Y(4)= .01518
X(5)= .00332 RM(5)= .00969 RM(14)= .74720 Y(5)= .01517
X(6)= .06617 RM(6)= .19307 RM(15)= .72993 VRATE= .02962
X(7)= .09072 RM(7)= .26469 RM(16)= .04648 SUMY= .99993
X(8)= .28061 RM(8)= .81875 RM(17)= .03971 DY1= -.00059
X(9)= 0.00000 RM(9)= 0.00000 RM(18)= 2.55747 DY= -.00007
HINT = 363.406 HOUTO= 368.999 HLOSS= 55.138 HRXNS= 52.447 HDMDT= -.067 MDMDT= -9.217

TIME= 80.00 MINUTES NUMBER OF ITERATIONS= 7

X(1)= .21302 RM(1)= .62488 RM(10)= 116.86783 Y(1)= .59451
X(2)= .00708 RM(2)= .02075 RM(11)= 2.93344 Y(2)= .08443
X(3)= .34169 RM(3)= 1.00232 RM(12)= .14271 Y(3)= .29188
X(4)= 0.00000 RM(4)= 0.00000 RM(13)= 1.07560 Y(4)= .01479
X(5)= .00306 RM(5)= .00896 RM(14)= .75713 Y(5)= .01433
X(6)= .06235 RM(6)= .18291 RM(15)= .76479 VRATE= .02984
X(7)= .09000 RM(7)= .26469 RM(16)= .04648 SUMY= .99993
X(8)= .28000 RM(8)= .81875 RM(17)= .03971 DY1= -.00059
X(9)= 0.00000 RM(9)= 0.00000 RM(18)= 2.55747 DY= -.00007

TIME= 84.00 MINUTES NUMBER OF ITERATIONS= 7

X(1)= .21536	RM(1)= .63487	RM(10)= 116.57510	Y(1)= .60214
X(2)= .00640	RM(2)= .01947	RM(11)= 2.94796	Y(2)= .07767
X(3)= .34223	RM(3)= 1.00887	RM(12)= .14266	Y(3)= .29217
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= 1.14792	Y(4)= .01443
X(5)= .00280	RM(5)= .00824	RM(14)= .76750	Y(5)= .01347
X(6)= .05494	RM(6)= .17346	RM(15)= .80005	VPATE= .03024
X(7)= .08979	RM(7)= .26469	RM(16)= .05029	SUMY= .99993
X(8)= .24439	RM(8)= .83836	RM(17)= .04314	DY1= -.00058
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= 2.79698	DY= -.00007
HINT = 363.406	HOUTO= 375.753	HLOSS= 39.915	HRXNS= 45.313
			HMDT= -.243
			MDHDT= -6.706

TIME= 88.00 MINUTES NUMBER OF ITERATIONS= 7

X(1)= .21748	RM(1)= .64403	RM(10)= 116.30820	Y(1)= .60906
X(2)= .00617	RM(2)= .01829	RM(11)= 2.96141	Y(2)= .07166
X(3)= .34275	RM(3)= 1.01502	RM(12)= .14261	Y(3)= .292+8
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= 1.22181	Y(4)= .01411
X(5)= .00255	RM(5)= .00755	RM(14)= .77659	Y(5)= .01262
X(6)= .05560	RM(6)= .16466	RM(15)= .83548	VPATE= .03051
X(7)= .08436	RM(7)= .26469	RM(16)= .05215	SUMY= .99993
X(8)= .24607	RM(8)= .84716	RM(17)= .04473	DY1= -.00057
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= 2.91850	DY= -.00007
HINT = 363.406	HOUTO= 378.756	HLOSS= 33.285	HRXNS= 42.284
			HMDT= -.330
			MDHDT= -6.021

TIME= 92.00 MINUTES NUMBER OF ITERATIONS= 7

X(1)= .21939	RM(1)= .65244	RM(10)= 116.06507	Y(1)= .61524
X(2)= .00578	RM(2)= .01720	RM(11)= 2.97385	Y(2)= .06631
X(3)= .34326	RM(3)= 1.02080	RM(12)= .14255	Y(3)= .29279
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= 1.29714	Y(4)= .01382
X(5)= .00232	RM(5)= .00689	RM(14)= .78507	Y(5)= .01177
X(6)= .05260	RM(6)= .15644	RM(15)= .87166	VPATE= .03077
X(7)= .08901	RM(7)= .26469	RM(16)= .05399	SUMY= .99993
X(8)= .24744	RM(8)= .85538	RM(17)= .04623	DY1= -.00057
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= 3.04107	DY= -.00007
HINT = 363.406	HOUTO= 381.509	HLOSS= 27.245	HRXNS= 39.550
			HMDT= -.408
			MDHDT= -5.390

TIME= 96.00 MINUTES NUMBER OF ITERATIONS= 7

X(1)= .22113	RM(1)= .66014	RM(10)= 115.84359	Y(1)= .62078
X(2)= .00543	RM(2)= .01621	RM(11)= 2.98536	Y(2)= .06154
X(3)= .34376	RM(3)= 1.02624	RM(12)= .14248	Y(3)= .29311
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= 1.37380	Y(4)= .01356
X(5)= .00210	RM(5)= .00626	RM(14)= .79298	Y(5)= .01093
X(6)= .04982	RM(6)= .14873	RM(15)= .80797	VPATE= .03100
X(7)= .08866	RM(7)= .26469	RM(16)= .05541	SUMY= .99993
X(8)= .24911	RM(8)= .86309	RM(17)= .04763	DY1= -.00056
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= 3.16461	DY= -.00007
HINT = 363.406	HOUTO= 384.521	HLOSS= 21.746	HRXNS= 37.075
			HMDT= -.472
			MDHDT= -4.412

INITIAL CONDITIONS BASED ON ADJUSTED TIME

X(1)= .15513	RM(1)= .41814	PM(10)= 123.57000	Y(1)= .07353
X(2)= .02940	RM(2)= .07923	PM(11)= 2.69542	Y(2)= .60246
X(3)= .33680	RM(3)= .90782	PM(12)= .16316	Y(3)= .27634
X(4)= 0.00000	RM(4)= 0.00000	PM(13)= .07787	Y(4)= .02095
X(5)= .00131	RM(5)= .00353	PM(14)= .22113	Y(5)= .02653
X(6)= .25653	RM(6)= .69147	PM(15)= .13225	VPATE= .01887
X(7)= .10757	RM(7)= .28494	PM(16)= .00549	SUMY= 1.00000
X(8)= .11326	RM(8)= .30529	PM(17)= .00140	DY1= 0.00000
X(9)= 0.00000	RM(9)= 0.00000	PM(18)= .43414	DY= 0.00000

TIME= 4.00 MINUTES

NUMBER OF ITERATIONS= 15

X(1)= .16050	RM(1)= .43708	PM(10)= 119.92464	Y(1)= .36267
X(2)= .02672	RM(2)= .07277	PM(11)= 2.72328	Y(2)= .33104
X(3)= .33926	RM(3)= .92118	PM(12)= .16196	Y(3)= .26504
X(4)= 0.00000	RM(4)= 0.00000	PM(13)= .12061	Y(4)= .03015
X(5)= .00204	RM(5)= .00555	PM(14)= .26387	Y(5)= .01107
X(6)= .23940	RM(6)= .65194	PM(15)= .16477	VPATE= .00874
X(7)= .10647	RM(7)= .28994	PM(16)= .00721	SUMY= .94997
X(8)= .12662	RM(8)= .34482	PM(17)= .00264	DY1= -.00012
X(9)= 0.00000	RM(9)= 0.00000	PM(18)= .55717	DY= -.00003

HINT = 238.498 HOUTO= 111.969 HLOSS= 141.862 HRXNS= 165.534 HDMDT= 71.723 HMDHT= 79.478

TIME= 8.00 MINUTES

NUMBER OF ITERATIONS= 9

X(1)= .17017	RM(1)= .47384	PM(10)= 118.95119	Y(1)= .39977
X(2)= .02645	RM(2)= .07366	PM(11)= 2.78445	Y(2)= .30658
X(3)= .33977	RM(3)= .94329	PM(12)= .16342	Y(3)= .26655
X(4)= 0.00000	RM(4)= 0.00000	PM(13)= .15451	Y(4)= .01448
X(5)= .00250	RM(5)= .00696	PM(14)= .29214	Y(5)= .01257
X(6)= .22277	RM(6)= .62030	PM(15)= .18832	VPATE= .01820
X(7)= .10413	RM(7)= .28994	PM(16)= .00836	SUMY= .94994
X(8)= .13520	RM(8)= .37646	PM(17)= .00370	DY1= -.00035
X(9)= 0.00000	RM(9)= 0.00000	PM(18)= .64517	DY= -.00006

HINT = 238.498 HOUTO= 231.157 HLOSS= 113.277 HRXNS= 147.825 HDMDT= 34.791 HMDHT= 7.047

TIME= 12.00 MINUTES

NUMBER OF ITERATIONS= 8

X(1)= .17924	RM(1)= .50881	PM(10)= 117.82029	Y(1)= .43166
X(2)= .02528	RM(2)= .07176	PM(11)= 2.93474	Y(2)= .27730
X(3)= .33942	RM(3)= .96354	PM(12)= .16451	Y(3)= .26608
X(4)= 0.00000	RM(4)= 0.00000	PM(13)= .19438	Y(4)= .01163
X(5)= .00279	RM(5)= .00792	PM(14)= .31948	Y(5)= .01320
X(6)= .20844	RM(6)= .59226	PM(15)= .21350	VPATE= .02171
X(7)= .10214	RM(7)= .28994	PM(16)= .00942	SUMY= .94945
X(8)= .14249	RM(8)= .40450	PM(17)= .00494	DY1= -.00035
X(9)= 0.00000	RM(9)= 0.00000	PM(18)= .70000	DY= .00000

TIME= 16.00 MINUTES

NUMBER OF ITERATIONS= 8

X(1)= .18774	RM(1)= .54237	RM(10)= 116.80199	Y(1)= .46124
X(2)= .02378	RM(2)= .06869	RM(11)= 2.88897	Y(2)= .24934
X(3)= .34014	RM(3)= .98266	RM(12)= .16545	Y(3)= .26587
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .23495	Y(4)= .01012
X(5)= .00245	RM(5)= .00855	RM(14)= .34600	Y(5)= .01340
X(6)= .19635	RM(6)= .56726	RM(15)= .24013	VRATE= .02401
X(7)= .10036	RM(7)= .28994	RM(16)= .01048	SUMY= .99997
X(8)= .14867	RM(8)= .42950	RM(17)= .00627	DY1= -.00018
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= .83940	DY= -.00003

HINT = 238.498 HOUTO= 302.514 HLOSS= 54.406 HRXNS= 117.478 HQMDT= 15.874 MDHDT= -17.918

TIME= 20.00 MINUTES

NUMBER OF ITERATIONS= 6

X(1)= .19551	RM(1)= .57384	RM(10)= 115.89477	Y(1)= .48793
X(2)= .02217	RM(2)= .06506	RM(11)= 2.93516	Y(2)= .22366
X(3)= .34091	RM(3)= 1.00063	RM(12)= .16624	Y(3)= .26584
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .28831	Y(4)= .00913
X(5)= .00304	RM(5)= .00892	RM(14)= .37043	Y(5)= .01335
X(6)= .18558	RM(6)= .54470	RM(15)= .26769	VRATE= .02566
X(7)= .09478	RM(7)= .28994	RM(16)= .01149	SUMY= .99991
X(8)= .15402	RM(8)= .45206	RM(17)= .00766	DY1= -.00105
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= .94277	DY= -.00009

HINT = 238.498 HOUTO= 322.327 HLOSS= 29.720 HRXNS= 106.411 HQMDT= 12.907 MDHDT= -20.045

TIME= 24.00 MINUTES

NUMBER OF ITERATIONS= 7

X(1)= .20251	RM(1)= .60297	RM(10)= 115.09325	Y(1)= .51168
X(2)= .02057	RM(2)= .06125	RM(11)= 2.97754	Y(2)= .20076
X(3)= .34173	RM(3)= 1.01751	RM(12)= .16691	Y(3)= .26597
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .34225	Y(4)= .00841
X(5)= .00306	RM(5)= .00910	RM(14)= .39318	Y(5)= .01314
X(6)= .17403	RM(6)= .52415	RM(15)= .29630	VRATE= .02695
X(7)= .09739	RM(7)= .28994	RM(16)= .01247	SUMY= .99996
X(8)= .15873	RM(8)= .47262	RM(17)= .00909	DY1= -.00044
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= 1.05010	DY= -.00004

HINT = 238.498 HOUTO= 337.546 HLOSS= 7.840 HRXNS= 97.216 HQMDT= 10.237 MDHDT= -19.909

TIME= 28.00 MINUTES

NUMBER OF ITERATIONS= 7

X(1)= .20875	RM(1)= .62964	RM(10)= 114.38270	Y(1)= .53250
X(2)= .01906	RM(2)= .05749	RM(11)= 3.01630	Y(2)= .18061
X(3)= .34259	RM(3)= 1.03335	RM(12)= .16747	Y(3)= .26619
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .40053	Y(4)= .00745
X(5)= .00302	RM(5)= .00912	RM(14)= .41434	Y(5)= .01282
X(6)= .16752	RM(6)= .50528	RM(15)= .32593	VRATE= .02300
X(7)= .09612	RM(7)= .28994	RM(16)= .01343	SUMY= .99996
X(8)= .16294	RM(8)= .49148	RM(17)= .01053	DY1= -.00042
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= 1.16116	DY= -.00004

HINT = 238.498 HOUTO= 349.971 HLOSS= 11.599 HRXNS= 89.449 HQMDT= 8.278 MDHDT= -14.704

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X(3)= .34348	PM(3)= 1.04820	RM(12)= .16793	Y(3)= .26648
X(4)= 0.00000	PM(4)= 0.00000	RM(13)= .44284	Y(4)= .00738
X(5)= .00296	PM(5)= .00903	RM(14)= .43399	Y(5)= .01243
X(6)= .15986	PM(6)= .48785	RM(15)= .35551	VRATE= .02892
X(7)= .09501	PM(7)= .28994	RM(16)= .01435	SUMY= .99996
X(8)= .16676	PM(8)= .50891	RM(17)= .01198	DY1= -.00041
X(9)= 0.00000	PM(9)= 0.00000	RM(18)= 1.27566	DY= -.00004

HINT = 238.498 HOUTO= 360.603 HLOSS= -28.861 HRYNS= 82.821 HDMDT= 6.716 MDHDT= -17.139

TIME= 36.00 MINUTES NUMBER OF ITERATIONS= 7

X(1)= .21912	PM(1)= .67579	RM(10)= 113.19515	Y(1)= .56632
X(2)= .01640	PM(2)= .05057	RM(11)= 3.08408	Y(2)= .14782
X(3)= .34440	PM(3)= 1.06216	RM(12)= .16831	Y(3)= .25683
X(4)= 0.00000	PM(4)= 0.00000	RM(13)= .52885	Y(4)= .00700
X(5)= .00287	PM(5)= .00885	RM(14)= .45227	Y(5)= .01199
X(6)= .15293	PM(6)= .47165	RM(15)= .38797	VRATE= .02972
X(7)= .09401	PM(7)= .28994	RM(16)= .01525	SUMY= .99996
X(8)= .17027	PM(8)= .52511	RM(17)= .01342	DY1= -.00040
X(9)= 0.00000	PM(9)= 0.00000	RM(18)= 1.39331	DY= -.00004

HINT = 238.498 HOUTO= 369.883 HLOSS= -44.202 HRYNS= 77.110 HDMDT= 5.419 MDHDT= -15.492

TIME= 40.00 MINUTES NUMBER OF ITERATIONS= 7

X(1)= .22338	PM(1)= .69554	RM(10)= 112.69940	Y(1)= .57988
X(2)= .01526	PM(2)= .04752	RM(11)= 3.11365	Y(2)= .13465
X(3)= .34534	PM(3)= 1.07528	RM(12)= .16860	Y(3)= .26723
X(4)= 0.00000	PM(4)= 0.00000	RM(13)= .59822	Y(4)= .00667
X(5)= .00276	PM(5)= .00861	RM(14)= .46928	Y(5)= .01152
X(6)= .14662	PM(6)= .45651	RM(15)= .42024	VRATE= .03042
X(7)= .09312	PM(7)= .28994	RM(16)= .01613	SUMY= .99996
X(8)= .17351	PM(8)= .54025	RM(17)= .01484	DY1= -.00040
X(9)= 0.00000	PM(9)= 0.00000	RM(18)= 1.51382	DY= -.00004

HINT = 238.498 HOUTO= 378.069 HLOSS= -57.847 HRYNS= 72.147 HDMDT= 4.316 MDHDT= -13.893

TIME= 44.00 MINUTES NUMBER OF ITERATIONS= 7

X(1)= .22711	PM(1)= .71329	RM(10)= 112.25833	Y(1)= .59188
X(2)= .01425	PM(2)= .04474	RM(11)= 3.14069	Y(2)= .12325
X(3)= .34531	PM(3)= 1.08764	RM(12)= .16883	Y(3)= .25757
X(4)= 0.00000	PM(4)= 0.00000	RM(13)= .67063	Y(4)= .00539
X(5)= .00265	PM(5)= .00832	RM(14)= .48516	Y(5)= .01104
X(6)= .14043	PM(6)= .44231	RM(15)= .45326	VRATE= .03105
X(7)= .09232	PM(7)= .28994	RM(16)= .01699	SUMY= .99996
X(8)= .17454	PM(8)= .55446	RM(17)= .01624	DY1= -.00040
X(9)= 0.00000	PM(9)= 0.00000	RM(18)= 1.63692	DY= -.00004

HINT = 238.498 HOUTO= 385.329 HLOSS= -69.997 HRYNS= 67.801 HDMDT= 3.368 MDHDT= -12.401

TIME= 48.00 MINUTES NUMBER OF ITERATIONS= 7

X(6) = .13550	RM(6) = .42892	PM(15) = .48596	VRATE = .03152
X(7) = .09160	RM(7) = .28994	PM(16) = .01784	SIMY = .99796
X(8) = .17939	RM(8) = .56784	PM(17) = .01759	DY1 = -.00040
X(9) = 0.00000	RM(9) = 0.00000	PM(18) = 1.76235	DY = -.00004

HINT = 238.498 HOUTO = 391.785 HLOSS = -80.828 HRXNS = 63.967 HQMDT = 2.547 MDHDT = -11.038

TIME = 52.00 MINUTES NUMBER OF ITERATIONS = 7

X(1) = .23321	RM(1) = .74351	PM(10) = 111.51398	Y(1) = .61040
X(2) = .01254	RM(2) = .03999	PM(11) = 3.18817	Y(2) = .10493
X(3) = .34826	RM(3) = 1.11030	PM(12) = .16911	Y(3) = .26464
X(4) = 0.00000	RM(4) = 0.00000	PM(13) = .82337	Y(4) = .00594
X(5) = .00240	RM(5) = .00766	PM(14) = .51394	Y(5) = .01005
X(6) = .13056	RM(6) = .41626	PM(15) = .52129	VRATE = .03212
X(7) = .09034	RM(7) = .28994	PM(16) = .01866	SIMY = .99995
X(8) = .18208	RM(8) = .58050	PM(17) = .01891	DY1 = -.00039
X(9) = 0.00000	RM(9) = 0.00000	PM(18) = 1.89987	DY = -.00004

HINT = 238.498 HOUTO = 397.533 HLOSS = -90.499 HRXNS = 60.562 HQMDT = 1.836 MDHDT = -9.810

TIME = 56.00 MINUTES NUMBER OF ITERATIONS = 7

X(1) = .23569	RM(1) = .75634	PM(10) = 111.19958	Y(1) = .61796
X(2) = .01183	RM(2) = .03797	PM(11) = 3.20904	Y(2) = .09750
X(3) = .34924	RM(3) = 1.12072	PM(12) = .16917	Y(3) = .26917
X(4) = 0.00000	RM(4) = 0.00000	PM(13) = .90317	Y(4) = .00575
X(5) = .00228	RM(5) = .00731	PM(14) = .52705	Y(5) = .00954
X(6) = .12597	RM(6) = .40425	PM(15) = .55620	VRATE = .03257
X(7) = .09035	RM(7) = .28994	PM(16) = .01947	SIMY = .99996
X(8) = .18464	RM(8) = .59251	PM(17) = .02018	DY1 = -.00039
X(9) = 0.00000	RM(9) = 0.00000	PM(18) = 2.01928	DY = -.00004

HINT = 238.498 HOUTO = 402.655 HLOSS = -99.147 HRXNS = 57.518 HQMDT = 1.221 MDHDT = -8.713

TIME = 60.00 MINUTES NUMBER OF ITERATIONS = 7

X(1) = .23785	RM(1) = .76785	PM(10) = 110.91744	Y(1) = .62452
X(2) = .01120	RM(2) = .03615	PM(11) = 3.22826	Y(2) = .09102
X(3) = .35022	RM(3) = 1.13060	PM(12) = .16920	Y(3) = .26973
X(4) = 0.00000	RM(4) = 0.00000	PM(13) = .98493	Y(4) = .00560
X(5) = .00216	RM(5) = .00697	PM(14) = .53942	Y(5) = .00911
X(6) = .12168	RM(6) = .39282	PM(15) = .59163	VRATE = .03297
X(7) = .08981	RM(7) = .28994	PM(16) = .02027	SIMY = .99995
X(8) = .18708	RM(8) = .60394	PM(17) = .02141	DY1 = -.00039
X(9) = 0.00000	RM(9) = 0.00000	PM(18) = 2.15038	DY = -.00004

HINT = 238.498 HOUTO = 407.220 HLOSS = -106.896 HRXNS = 54.780 HQMDT = .690 MDHDT = -7.737

TIME = 64.00 MINUTES NUMBER OF ITERATIONS = 7

X(1) = .23974	RM(1) = .77819	PM(10) = 110.66356	Y(1) = .63023
X(2) = .01063	RM(2) = .03450	PM(11) = 3.24601	Y(2) = .08533
X(3) = .35120	RM(3) = 1.13298	PM(12) = .16912	Y(3) = .27030

X(9)= .000000 RM(9)= 0.000000 RM(10)= 110.43449 Y(1)= .53523
 HINT= 238.498 HOUT= 411.290 FLOSS= -113.853 HRXNS= 52.302 HDMDT= .235 WDMDT= -6.872

TIME= 68.00 MINUTES NUMBER OF ITERATIONS= 7

X(1)= .24138 RM(1)= .78750 RM(10)= 110.43449 Y(1)= .53523
 X(2)= .01012 RM(2)= .03302 RM(11)= 3.26242 Y(2)= .08030
 X(3)= .35216 RM(3)= 1.14891 RM(12)= .14915 Y(3)= .27086
 X(4)= 0.00000 RM(4)= 0.00000 RM(13)= 1.15355 Y(4)= .00533
 X(5)= .00193 RM(5)= .00629 RM(14)= .56224 Y(5)= .00822
 X(6)= .11387 RM(6)= .37149 RM(15)= .66392 VPATE= .03365
 X(7)= .08897 RM(7)= .28994 RM(16)= .02183 SUMY= .99996
 X(8)= .19165 RM(8)= .62527 RM(17)= .02372 DY1= -.00039
 X(9)= 0.00000 RM(9)= 0.00000 RM(18)= 2.41596 DY= -.00004
 HINT= 238.498 HOUT= 414.921 FLOSS= -120.114 HRXNS= 50.048 HDMDT= -.154 WDMDT= -6.107

TIME= 72.00 MINUTES NUMBER OF ITERATIONS= 7

X(1)= .24282 RM(1)= .79589 RM(10)= 110.22716 Y(1)= .63962
 X(2)= .00966 RM(2)= .03167 RM(11)= 3.27765 Y(2)= .07585
 X(3)= .35312 RM(3)= 1.15742 RM(12)= .16909 Y(3)= .27148
 X(4)= 0.00000 RM(4)= 0.00000 RM(13)= 1.24005 Y(4)= .00522
 X(5)= .00182 RM(5)= .00597 RM(14)= .57281 Y(5)= .00780
 X(6)= .11029 RM(6)= .36150 RM(15)= .70070 VPATE= .03394
 X(7)= .08546 RM(7)= .28994 RM(16)= .02260 SUMY= .99996
 X(8)= .19382 RM(8)= .63526 RM(17)= .02491 DY1= -.00039
 X(9)= 0.00000 RM(9)= 0.00000 RM(18)= 2.55214 DY= -.00004
 HINT= 238.498 HOUT= 418.163 FLOSS= -125.763 HRXNS= 47.985 HDMDT= -.485 WDMDT= -5.432

TIME= 76.00 MINUTES NUMBER OF ITERATIONS= 7

X(1)= .24408 RM(1)= .80347 RM(10)= 110.03894 Y(1)= .64348
 X(2)= .00925 RM(2)= .03044 RM(11)= 3.29182 Y(2)= .07188
 X(3)= .35407 RM(3)= 1.16553 RM(12)= .16900 Y(3)= .27208
 X(4)= 0.00000 RM(4)= 0.00000 RM(13)= 1.32781 Y(4)= .00512
 X(5)= .00172 RM(5)= .00567 RM(14)= .58290 Y(5)= .00740
 X(6)= .10690 RM(6)= .35191 RM(15)= .73785 VPATE= .03420
 X(7)= .08808 RM(7)= .28994 RM(16)= .02336 SUMY= .99996
 X(8)= .19590 RM(8)= .64485 RM(17)= .02585 DY1= -.00039
 X(9)= 0.00000 RM(9)= 0.00000 RM(18)= 2.69841 DY= -.00004
 HINT= 238.498 HOUT= 421.061 FLOSS= -130.874 HRXNS= 46.088 HDMDT= -.764 WDMDT= -4.836

TIME= 80.00 MINUTES NUMBER OF ITERATIONS= 7

X(1)= .24518 RM(1)= .81033 RM(10)= 109.86751 Y(1)= .64691
 X(2)= .00887 RM(2)= .02932 RM(11)= 3.30503 Y(2)= .06831
 X(3)= .35500 RM(3)= 1.17329 RM(12)= .16889 Y(3)= .27269
 X(4)= 0.00000 RM(4)= 0.00000 RM(13)= 1.41670 Y(4)= .00503
 X(5)= .00153 RM(5)= .00538 RM(14)= .59254 Y(5)= .00703

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TIME= 64.00 MINUTES

NUMBER OF ITERATIONS= 7

X(1)= .24615	RM(1)= .81656	PM(10)= -109.71084	Y(1)= .64995
X(2)= .00852	RM(2)= .02828	PM(11)= 3.31738	Y(2)= .06510
X(3)= .35592	RM(3)= 1.18072	PM(12)= .16477	Y(3)= .27330
X(4)= 0.00000	RM(4)= 0.00000	PM(13)= -1.50550	Y(4)= .00495
X(5)= .00154	RM(5)= .00511	PM(14)= .60177	Y(5)= .00567
X(6)= .10062	RM(6)= .33381	PM(15)= .81320	VPATE= .03464
X(7)= .08740	RM(7)= .28994	PM(16)= .02485	SUMPY= .99995
Y(8)= .19484	RM(8)= .66295	RM(17)= .02779	DY1= -.00039
X(8)= 0.00000	RM(9)= 0.00000	PM(18)= 2.95379	DY= -.00004
HINT= -238.498	HOUTO= 425.978	HLOSS= -139.733	HMAXNS= -42.708
		HMDT= -1.193	MDHDT= -3.846

TIME= 88.00 MINUTES

NUMBER OF ITERATIONS= 7

X(-1)= .24489	RM(-1)= .82224	PM(10)= -109.55718	Y(1)= .65265
X(2)= .00821	RM(2)= .02732	PM(11)= 3.32896	Y(2)= .06218
X(3)= .35442	RM(3)= 1.18783	PM(12)= .16854	Y(3)= .27390
X(-4)= 0.00000	RM(-4)= 0.00000	PM(13)= -1.59743	Y(4)= .00488
X(5)= .00146	RM(5)= .00486	PM(14)= .61063	Y(5)= .00534
X(6)= .09770	RM(6)= .32525	PM(15)= .85134	VPATE= .03482
X(-7)= .08710	RM(7)= .28994	PM(16)= .02559	SUMPY= .99996
X(8)= .20172	RM(8)= .67151	PM(17)= .02970	DY1= -.00039
X(9)= 0.00000	RM(9)= 0.00000	PM(18)= 3.10272	DY= -.00004
HINT = -238.498	HOUTO= 428.066	HLOSS= -143.587	HMAXNS= -41.192
		HMDT= -1.353	MDHDT= -3.436

INITIAL CONDITIONS BASED ON ADJUSTED TIME

X(1)= .15869	RM(1)= .45307	RM(10)= 118.03000	Y(1)= .21140
X(2)= .04469	RM(2)= .12761	RM(11)= 2.85516	Y(2)= .44945
X(3)= .34989	RM(3)= .99899	RM(12)= .17770	Y(3)= .30024
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .04096	Y(4)= .02587
X(5)= 0.00000	RM(5)= 0.00000	RM(14)= .09501	Y(5)= .01254
X(6)= .28156	RM(6)= .80390	RM(15)= .04500	VPATE= .02010
X(7)= .08683	RM(7)= .24791	RM(16)= .00356	SUMY= 1.00000
Y(8)= .07834	RM(8)= .22368	RM(17)= .00107	DY1= 0.00000
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= .18560	DY= 0.00000

TIME= 4.00 MINUTES

NUMBER OF ITERATIONS= 10

X(1)= .16240	RM(1)= .46524	RM(10)= 116.80649	Y(1)= .36391
X(2)= .03984	RM(2)= .11414	RM(11)= 2.86480	Y(2)= .35588
X(3)= .35181	RM(3)= 1.00787	RM(12)= .17550	Y(3)= .25953
Y(4)= 0.00000	RM(4)= 0.00000	RM(13)= .08328	Y(4)= .01645
X(5)= .06072	RM(5)= .00205	RM(14)= .13909	Y(5)= .00415
X(6)= .26911	RM(6)= .77094	RM(15)= .07576	VPATE= .01790
X(7)= .08654	RM(7)= .24791	RM(16)= .00493	SUMY= .99994
X(8)= .08959	RM(8)= .25665	RM(17)= .00137	DY1= -.00030
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= .30365	DY= -.00006

HINT = 307.274 HOUTO= 226.257 HLOSS= 148.900 HRXNS= 151.757 HMDT= 16.372 MCHDT= 67.502

TIME= 8.00 MINUTES

NUMBER OF ITERATIONS= 9

X(1)= .16687	RM(1)= .48161	RM(10)= 116.59798	Y(1)= .38435
X(2)= .03672	RM(2)= .10598	RM(11)= 2.88617	Y(2)= .33213
X(3)= .35321	RM(3)= 1.01941	RM(12)= .17434	Y(3)= .26332
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .12358	Y(4)= .01351
X(5)= .00127	RM(5)= .00367	RM(14)= .17594	Y(5)= .00656
X(6)= .25640	RM(6)= .74002	RM(15)= .10395	VPATE= .02275
X(7)= .08589	RM(7)= .24791	RM(16)= .00521	SUMY= .99997
X(8)= .09964	RM(8)= .28757	RM(17)= .00197	DY1= -.00011
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= .41068	DY= -.00003

HINT = 307.274 HOUTO= 287.068 HLOSS= 141.295 HRXNS= 147.913 HMDT= -1.913 MCHDT= 28.737

TIME= 12.00 MINUTES

NUMBER OF ITERATIONS= 8

X(1)= .17085	RM(1)= .49652	RM(10)= 116.35449	Y(1)= .40235
X(2)= .03402	RM(2)= .09887	RM(11)= 2.90524	Y(2)= .31033
X(3)= .35452	RM(3)= 1.03033	RM(12)= .17321	Y(3)= .26623
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .16537	Y(4)= .01259
X(5)= .00173	RM(5)= .00503	RM(14)= .21074	Y(5)= .00835
X(6)= .24435	RM(6)= .71014	RM(15)= .13260	VPATE= .02512
X(7)= .08530	RM(7)= .24791	RM(16)= .00755	SUMY= .99995
X(8)= .10922	RM(8)= .31744	RM(17)= .00280	DY1= -.00027

X(1)=	.17445	RM(1)=	.51036	RM(10)=	-116.10323	Y(1)=	.41859
X(2)=	.03171	RM(2)=	.09277	RM(11)=	2.92562	Y(2)=	.29069
X(3)=	.35575	RM(3)=	1.04080	RM(12)=	.17216	Y(3)=	.26885
X(4)=	0.00000	RM(4)=	0.00000	RM(13)=	.21124	Y(4)=	.01227
X(5)=	.00212	RM(5)=	.00620	RM(14)=	.24348	Y(5)=	.00956
X(6)=	.23289	RM(6)=	.68134	RM(15)=	.16142	VRATE=	.02632
X(7)=	.00474	RM(7)=	.24791	RM(16)=	.00892	SUMY=	.99997
X(8)=	.11835	RM(8)=	.34624	RM(17)=	.00379	DY1=	-.00015
X(9)=	0.00000	RM(9)=	0.00000	RM(18)=	.62760	DY=	-.00003

HINT = 307.274 HOUTO = 330.963 HLOSS = 126.098 H2XNS = 138.164 HDMOT = -12.928 MDMOT = 1.310

TIME= 20.00 MINUTES

NUMBER OF ITERATIONS= 7

X(1)=	.17776	RM(1)=	.52342	RM(10)=	-115.84633	Y(1)=	.43339
X(2)=	.02972	RM(2)=	.08750	RM(11)=	2.94452	Y(2)=	.27295
X(3)=	.35690	RM(3)=	1.05090	RM(12)=	.17118	Y(3)=	.27098
X(4)=	0.00000	RM(4)=	0.00000	RM(13)=	.25808	Y(4)=	.01217
X(5)=	.00244	RM(5)=	.00720	RM(14)=	.27434	Y(5)=	.01044
X(6)=	.22199	RM(6)=	.65365	RM(15)=	.19143	VRATE=	.02694
X(7)=	.08419	RM(7)=	.24791	RM(16)=	.01032	SUMY=	.99995
X(8)=	.12609	RM(8)=	.37393	RM(17)=	.00490	DY1=	-.00050
X(9)=	0.00000	RM(9)=	0.00000	RM(18)=	.73097	DY=	-.00005

HINT = 307.274 HOUTO = 338.295 HLOSS = 118.686 H2XNS = 132.851 HDMOT = -13.785 MDMOT = -3.070

TIME= 24.00 MINUTES

NUMBER OF ITERATIONS= 7

X(1)=	.18086	RM(1)=	.53590	RM(10)=	-115.58641	Y(1)=	.44705
X(2)=	.02798	RM(2)=	.08291	RM(11)=	2.96305	Y(2)=	.25687
X(3)=	.35797	RM(3)=	1.06069	RM(12)=	.17028	Y(3)=	.27280
X(4)=	0.00000	RM(4)=	0.00000	RM(13)=	.30663	Y(4)=	.01215
X(5)=	.00272	RM(5)=	.00805	RM(14)=	.30345	Y(5)=	.01107
X(6)=	.21164	RM(6)=	.62709	RM(15)=	.22137	VRATE=	.02728
X(7)=	.08367	RM(7)=	.24791	RM(16)=	.01173	SUMY=	.99995
X(8)=	.13516	RM(8)=	.40050	RM(17)=	.00609	DY1=	-.00047
X(9)=	0.00000	RM(9)=	0.00000	RM(18)=	.84676	DY=	-.00005

HINT = 307.274 HOUTO = 342.172 HLOSS = 111.331 H2XNS = 127.407 HDMOT = -13.605 MDMOT = -5.217

TIME= 28.00 MINUTES

NUMBER OF ITERATIONS= 7

X(1)=	.18380	RM(1)=	.54794	RM(10)=	-115.32404	Y(1)=	.45974
X(2)=	.02644	RM(2)=	.07883	RM(11)=	2.98125	Y(2)=	.24216
X(3)=	.35898	RM(3)=	1.07020	RM(12)=	.16945	Y(3)=	.27436
X(4)=	0.00000	RM(4)=	0.00000	RM(13)=	.35679	Y(4)=	.01215
X(5)=	.00295	RM(5)=	.00878	RM(14)=	.33097	Y(5)=	.01153
X(6)=	.20181	RM(6)=	.60166	RM(15)=	.25159	VRATE=	.02749
X(7)=	.08316	RM(7)=	.24791	RM(16)=	.01316	SUMY=	.99995
X(8)=	.14287	RM(8)=	.42592	RM(17)=	.00734	DY1=	-.00046
X(9)=	0.00000	RM(9)=	0.00000	RM(18)=	.95595	DY=	-.00005

HINT = 307.274 HOUTO = 344.394 HLOSS = 104.005 H2XNS = 121.926 HDMOT = -12.962 MDMOT = -6.237

X(1)= .35492	RM(3)= 1.07946	RM(12)= .15858	Y(3)= .27572
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .40848	Y(4)= .01214
X(5)= .00313	RM(5)= .00930	RM(14)= .35703	Y(5)= .01186
X(6)= .19251	RM(6)= .57736	RM(15)= .28209	VRATE= .02754
X(7)= .08266	RM(7)= .24791	RM(16)= .01460	SUMY= .99995
X(8)= .15012	RM(8)= .45022	RM(17)= .00854	DY1= -.00045
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= 1.06752	DY= -.00005
HINT = 307.274	HOUT0= 345.890	HLOSS= 96.721	HRXNS= 115.490
			HDMOT= -12.151
			MDHDT= -6.696

TIME= 36.00 MINUTES NUMBER OF ITERATIONS= 7

X(1)= .18929	RM(1)= .57102	RM(10)= 114.79423	Y(1)= .48282
X(2)= .02380	RM(2)= .07180	RM(11)= 3.01669	Y(2)= .21604
X(3)= .36082	RM(3)= 1.08846	RM(12)= .16798	Y(3)= .27691
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .46165	Y(4)= .01211
X(5)= .00328	RM(5)= .00990	RM(14)= .38173	Y(5)= .01208
X(6)= .18370	RM(6)= .55418	RM(15)= .31283	VRATE= .02777
X(7)= .08218	RM(7)= .24791	RM(16)= .01604	SUMY= .99995
X(8)= .15693	RM(8)= .47341	RM(17)= .00998	DY1= -.00045
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= 1.17849	DY= -.00005
HINT = 307.274	HOUT0= 347.106	HLOSS= 89.506	HRXNS= 111.165
			HDMOT= -11.309
			MDHDT= -6.864

TIME= 40.00 MINUTES NUMBER OF ITERATIONS= 7

X(1)= .19188	RM(1)= .58214	RM(10)= 114.53804	Y(1)= .49339
X(2)= .02264	RM(2)= .06470	RM(11)= 3.03388	Y(2)= .20432
X(3)= .36166	RM(3)= 1.09723	RM(12)= .16733	Y(3)= .27796
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .51623	Y(4)= .01207
X(5)= .00340	RM(5)= .01031	RM(14)= .40517	Y(5)= .01221
X(6)= .17537	RM(6)= .53207	RM(15)= .34382	VRATE= .02789
X(7)= .08171	RM(7)= .24791	RM(16)= .01748	SUMY= .99995
X(8)= .16333	RM(8)= .49552	RM(17)= .01134	DY1= -.00045
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= 1.28989	DY= -.00005
HINT = 307.274	HOUT0= 348.250	HLOSS= 82.392	HRXNS= 105.997
			HDMOT= -10.499
			MDHDT= -6.872

TIME= 44.00 MINUTES NUMBER OF ITERATIONS= 7

X(1)= .19438	RM(1)= .59300	RM(10)= 114.28168	Y(1)= .50340
X(2)= .02157	RM(2)= .06580	RM(11)= 3.05069	Y(2)= .19337
X(3)= .36246	RM(3)= 1.10576	RM(12)= .16672	Y(3)= .27890
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .57218	Y(4)= .01201
X(5)= .00349	RM(5)= .01064	RM(14)= .42744	Y(5)= .01222
X(6)= .16750	RM(6)= .51099	RM(15)= .37504	VRATE= .02802
X(7)= .08126	RM(7)= .24791	RM(16)= .01893	SUMY= .99995
X(8)= .16934	RM(8)= .51659	RM(17)= .01271	DY1= -.00045
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= 1.40174	DY= -.00005
HINT = 307.274	HOUT0= 349.416	HLOSS= 75.413	HRXNS= 101.021
			HDMOT= -9.744
			MDHDT= -5.785

TIME= 48.00 MINUTES NUMBER OF ITERATIONS= 7

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X(6)= .16006	PM(6)= .49092	RM(15)= .46640	VPATE= .02814
X(7)= .04083	PM(7)= .24791	RM(16)= .02037	SIMY= .99995
X(8)= .17498	PM(8)= .53666	RM(17)= .01410	DY1= -.00045
X(9)= 0.00000	PM(9)= 0.00000	RM(18)= 1.51408	DY= -.00005
HINT = 307.274	HOUT0= 350.638	HLOSS= 60.598	HMXNS= 96.257
			HOMDT= -9.066
			MOHDT= -5.639

TIME= 52.00 MINUTES NUMBER OF ITERATIONS= 7

X(1)= .19912	PM(1)= .61389	RM(10)= 113.78532	Y(1)= .52186
X(2)= .01962	PM(2)= .06049	RM(11)= 3.08303	Y(2)= .17345
X(3)= .36396	PM(3)= 1.12210	RM(12)= .16562	Y(3)= .28054
X(4)= 0.00000	PM(4)= 0.00000	RM(13)= .68807	Y(4)= .01195
X(5)= .00359	PM(5)= .01136	RM(14)= .46876	Y(5)= .01225
X(6)= .15303	PM(6)= .47180	RM(15)= .43820	VPATE= .02827
X(7)= .08041	PM(7)= .24791	RM(16)= .02181	SIMY= .99995
X(8)= .18027	PM(8)= .55579	RM(17)= .01549	DY1= -.00044
X(9)= 0.00000	PM(9)= 0.00000	RM(18)= 1.62692	DY= -.00005
HINT = 307.274	HOUT0= 351.922	HLOSS= 61.971	HMXNS= 91.715
			HOMDT= -8.451
			MOHDT= -6.452

TIME= 56.00 MINUTES NUMBER OF ITERATIONS= 7

X(1)= .20136	PM(1)= .62391	RM(10)= 113.54721	Y(1)= .53037
X(2)= .01973	PM(2)= .05804	RM(11)= 3.09452	Y(2)= .16439
X(3)= .36466	PM(3)= 1.12992	RM(12)= .16512	Y(3)= .28127
X(4)= 0.00000	PM(4)= 0.00000	RM(13)= .74793	Y(4)= .01176
X(5)= .00360	PM(5)= .01116	RM(14)= .44793	Y(5)= .01217
X(6)= .14638	PM(6)= .45358	RM(15)= .47013	VPATE= .02841
X(7)= .08001	PM(7)= .24791	RM(16)= .02324	SIMY= .99995
X(8)= .18525	PM(8)= .57401	RM(17)= .01688	DY1= -.00044
X(9)= 0.00000	PM(9)= 0.00000	RM(18)= 1.74028	DY= -.00005
HINT = 307.274	HOUT0= 353.262	HLOSS= 55.551	HMXNS= 87.401
			HOMDT= -7.901
			MOHDT= -6.236

TIME= 60.00 MINUTES NUMBER OF ITERATIONS= 7

X(1)= .20351	PM(1)= .63363	RM(10)= 113.31671	Y(1)= .53842
X(2)= .01789	PM(2)= .05570	RM(11)= 3.11353	Y(2)= .15586
X(3)= .36534	PM(3)= 1.13750	RM(12)= .16465	Y(3)= .28194
X(4)= 0.00000	PM(4)= 0.00000	RM(13)= .80902	Y(4)= .01156
X(5)= .00360	PM(5)= .01121	RM(14)= .50620	Y(5)= .01206
X(6)= .14010	PM(6)= .43621	RM(15)= .50229	VPATE= .02854
X(7)= .07962	PM(7)= .24791	RM(16)= .02467	SIMY= .99995
X(8)= .18994	PM(8)= .59137	RM(17)= .01826	DY1= -.00044
X(9)= 0.00000	PM(9)= 0.00000	RM(18)= 1.85419	DY= -.00005
HINT = 307.274	HOUT0= 354.645	HLOSS= 49.353	HMXNS= 83.313
			HOMDT= -7.409
			MOHDT= -6.001

TIME= 64.00 MINUTES NUMBER OF ITERATIONS= 7

X(1)= .20557	PM(1)= .64303	RM(10)= 113.09427	Y(1)= .54604
X(2)= .01710	PM(2)= .05348	RM(11)= 3.12805	Y(2)= .14785
X(3)= .36599	PM(3)= 1.14484	RM(12)= .16420	Y(3)= .28258

HINT = 307.274 HOUT0= 356.058 HLOSS= 43.385 HRXNS= 79.446 HDMDT= -5.970 MDHDT= -5.753
 TIME= 68.00 MINUTES NUMBER OF ITERATIONS= 7
 X(1)= .20754 RM(1)= .65212 RM(10)= 112.88017 Y(1)= .55323
 X(2)= .01534 RM(2)= .05135 RM(11)= 3.14205 Y(2)= .14032
 X(3)= .36562 RM(3)= 1.15195 RM(12)= .16378 Y(3)= .28318
 X(4)= 0.00000 RM(4)= 0.00000 RM(13)= .93475 Y(4)= .01146
 X(5)= .00355 RM(5)= .01115 RM(14)= .54020 Y(5)= .01176
 X(6)= .12454 RM(6)= .40387 RM(15)= .56731 VPATE= .02882
 X(7)= .07890 RM(7)= .24791 RM(16)= .02752 SUMY= .99995
 X(8)= .19850 RM(8)= .62371 RM(17)= .02100 DY1= -.00044
 X(9)= 0.00000 RM(9)= 0.00000 RM(18)= 2.08366 DY= -.00005
 HINT = 307.274 HOUT0= 357.485 HLOSS= 37.455 HRXNS= 75.792 HDMDT= -6.578 MDHDT= -5.497

TIME= 72.00 MINUTES NUMBER OF ITERATIONS= 7
 X(1)= .20943 RM(1)= .66088 RM(10)= 112.67455 Y(1)= .56001
 X(2)= .01563 RM(2)= .04933 RM(11)= 3.15558 Y(2)= .13324
 X(3)= .36723 RM(3)= 1.15882 RM(12)= .16337 Y(3)= .28376
 X(4)= 0.00000 RM(4)= 0.00000 RM(13)= .99930 Y(4)= .01136
 X(5)= .00350 RM(5)= .01106 RM(14)= .55604 Y(5)= .01158
 X(6)= .12321 RM(6)= .38981 RM(15)= .60016 VPATE= .02846
 X(7)= .07856 RM(7)= .24791 RM(16)= .02893 SUMY= .99995
 X(8)= .20243 RM(8)= .63877 RM(17)= .02236 DY1= -.00044
 X(9)= 0.00000 RM(9)= 0.00000 RM(18)= 2.19922 DY= -.00005
 HINT = 307.274 HOUT0= 358.914 HLOSS= 32.164 HRXNS= 72.342 HDMDT= -6.226 MDHDT= -5.237

TIME= 76.00 MINUTES NUMBER OF ITERATIONS= 7
 X(1)= .21123 RM(1)= .66931 RM(10)= 112.47746 Y(1)= .56641
 X(2)= .01496 RM(2)= .04739 RM(11)= 3.16859 Y(2)= .12650
 X(3)= .36782 RM(3)= 1.16547 RM(12)= .16298 Y(3)= .28431
 X(4)= 0.00000 RM(4)= 0.00000 RM(13)= 1.05493 Y(4)= .01126
 X(5)= .00345 RM(5)= .01092 RM(14)= .57115 Y(5)= .01138
 X(6)= .11817 RM(6)= .37443 RM(15)= .63323 VPATE= .02910
 X(7)= .07824 RM(7)= .24791 RM(16)= .03034 SUMY= .99995
 X(8)= .20613 RM(8)= .65315 RM(17)= .02369 DY1= -.00044
 X(9)= 0.00000 RM(9)= 0.00000 RM(18)= 2.31533 DY= -.00005
 HINT = 307.274 HOUT0= 360.333 HLOSS= 26.912 HRXNS= 69.086 HDMDT= -5.909 MDHDT= -4.976

TIME= 80.00 MINUTES NUMBER OF ITERATIONS= 7
 X(1)= .21295 RM(1)= .67742 RM(10)= 112.28882 Y(1)= .57244
 X(2)= .01432 RM(2)= .04555 RM(11)= 3.18111 Y(2)= .12035
 X(3)= .36839 RM(3)= 1.17190 RM(12)= .16261 Y(3)= .28484
 X(4)= 0.00000 RM(4)= 0.00000 RM(13)= 1.13159 Y(4)= .01116
 X(5)= .00338 RM(5)= .01076 RM(14)= .59567 Y(5)= .01117
 X(6)= .11339 RM(6)= .36069 RM(15)= .64562 VPATE= .02923
 X(7)= .07791 RM(7)= .24791 RM(16)= .03175 SUMY= .99995
 X(8)= .20461 RM(8)= .65315 RM(17)= .02369 DY1= -.00044
 X(9)= 0.00000 RM(9)= 0.00000 RM(18)= 2.31533 DY= -.00005

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TIME= 84.00 MINUTES NUMBER OF ITERATIONS= 7

X(1)= .21458	RM(1)= .68515	RM(10)= 112.11045	Y(1)= .57811
X(2)= .01371	RM(2)= .04378	RM(11)= 3.19307	Y(2)= .11444
X(3)= .36895	RM(3)= 1.17808	RM(12)= .16224	Y(3)= .28536
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= 1.19929	Y(4)= .01106
X(5)= .00331	RM(5)= .01056	RM(14)= .59937	Y(5)= .01094
X(6)= .10845	RM(6)= .34756	RM(15)= .70005	VRATE= .02937
X(7)= .07764	RM(7)= .24791	RM(16)= .03314	SIMY= .99995
X(8)= .21297	RM(8)= .68002	RM(17)= .02631	DY1= -.00044
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= 2.54925	DY= -.00005
HINT= 307.274	HOUTO= 363.159	HLOSS= 16.910	HRXNS= 63.125
			HOMDT= -5.378
			MDHDT= -4.243

TIME= 88.00 MINUTES NUMBER OF ITERATIONS= 7

X(1)= .21512	RM(1)= .69259	RM(10)= 111.93934	Y(1)= .58344
X(2)= .01314	RM(2)= .04209	RM(11)= 3.20458	Y(2)= .10897
X(3)= .36949	RM(3)= 1.18406	RM(12)= .16189	Y(3)= .28586
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= 1.26792	Y(4)= .01097
X(5)= .00323	RM(5)= .01035	RM(14)= .61255	Y(5)= .01071
X(6)= .10454	RM(6)= .33500	RM(15)= .73377	VRATE= .02949
X(7)= .07735	RM(7)= .24791	RM(16)= .03454	SIMY= .99995
X(8)= .21512	RM(8)= .69258	RM(17)= .02759	DY1= -.00044
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= 2.66701	DY= -.00005
HINT= 307.274	HOUTO= 364.479	HLOSS= 12.451	HRXNS= 60.394
			HOMDT= -5.136
			MDHDT= -4.126

TIME= 92.00 MINUTES NUMBER OF ITERATIONS= 7

X(1)= .21760	RM(1)= .69972	RM(10)= 111.77548	Y(1)= .58847
X(2)= .01259	RM(2)= .04049	RM(11)= 3.21555	Y(2)= .10380
X(3)= .37001	RM(3)= 1.18984	RM(12)= .16155	Y(3)= .28634
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= 1.33744	Y(4)= .01088
X(5)= .00314	RM(5)= .01011	RM(14)= .62515	Y(5)= .01047
X(6)= .10044	RM(6)= .32299	RM(15)= .76769	VRATE= .02951
X(7)= .07709	RM(7)= .24791	RM(16)= .03592	SIMY= .99995
X(8)= .21911	RM(8)= .70459	RM(17)= .02885	DY1= -.00044
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= 2.78523	DY= -.00005
HINT= 307.274	HOUTO= 365.737	HLOSS= 8.186	HRXNS= 57.810
			HOMDT= -4.907
			MDHDT= -3.932

TIME= 96.00 MINUTES NUMBER OF ITERATIONS= 7

X(1)= .21900	RM(1)= .70657	RM(10)= 111.61877	Y(1)= .59321
X(2)= .01208	RM(2)= .03896	RM(11)= 3.22630	Y(2)= .09804
X(3)= .37052	RM(3)= 1.19542	RM(12)= .16122	Y(3)= .28680
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= 1.40781	Y(4)= .01079
X(5)= .00305	RM(5)= .00986	RM(14)= .63720	Y(5)= .01021
X(6)= .09655	RM(6)= .31148	RM(15)= .80180	VRATE= .02975
X(7)= .07684	RM(7)= .24791	RM(16)= .03731	SIMY= .99995
X(8)= .22194	RM(8)= .71610	RM(17)= .03008	DY1= -.00044
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= 2.90093	DY= -.00005
HINT= 307.274	HOUTO= 366.941	HLOSS= 4.112	HRXNS= 55.265
			HOMDT= -4.654
			MDHDT= -3.723

X(1)=	.13013	RM(1)=	.33445	RM(10)=	119.46000	Y(1)=	.11159
X(2)=	.04457	RM(2)=	.11455	RM(11)=	2.57020	Y(2)=	.65267
X(3)=	.34615	RM(3)=	.87426	RM(12)=	.16222	Y(3)=	.19508
X(4)=	0.00000	RM(4)=	0.00000	RM(13)=	.04349	Y(4)=	.02520
X(5)=	0.00000	RM(5)=	0.00000	RM(14)=	.10302	Y(5)=	.01535
X(6)=	.24773	RM(6)=	.76524	RM(15)=	.05085	VRATE=	.01655
X(7)=	.10249	RM(7)=	.26341	RM(16)=	.00276	SUMY=	1.00000
X(8)=	.08493	RM(8)=	.21430	RM(17)=	.00055	OY1=	0.00000
X(9)=	0.00000	RM(9)=	0.00000	RM(18)=	.20054	OY=	0.00000

NUMBER OF ITERATIONS= 3

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X( 1)= .14147 RM( 1)= .37238 PM(10)= 119.49185 Y(1)= .28442
X( 2)= .04299 RM( 2)= .11315 PM(11)= 2.63221 Y(2)= .44866
X( 3)= .34100 RM( 3)= .89760 PM(12)= .16347 Y(3)= .24993
X( 4)= 0.00000 RM( 4)= 0.00000 PM(13)= .05267 Y(4)= .01190
X( 5)= .00042 RM( 5)= .00215 PM(14)= .13643 Y(5)= .09505
X( 6)= .27766 RM( 6)= .73086 PM(15)= .06861 VRATE= .02507
X( 7)= .16007 RM( 7)= .26341 PM(16)= .00388 SUMY= .99996
X( 8)= .04599 RM( 8)= .25267 PM(17)= .00077 DY1= .00622
X( 9)= 0.00000 RM( 9)= 0.00000 PM(18)= .27285 DY= -.00004
HINT = 291.812 HOUTO= 318.817 HLOSS= 213.198 HMXNS= 168.903 HMDT= -15.228 MMDT= -56.072

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NUMBER OF ITERATIONS= 7

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X( 1) = .15073      RM( 1) = .40355      RM(10) = 119.60892      Y(1) = .31877
X( 2) = .03474      RM( 2) = .10640      RM(11) = 2.67734      Y(2) = .40725
X( 3) = .34223      RM( 3) = .91654      RM(12) = .16351      Y(3) = .25309
X( 4) = 0.00000      RM( 4) = 0.00000      RM(13) = .08945      Y(4) = .01291
X( 5) = .00147      RM( 5) = .00394      RM(14) = .17410      Y(5) = .00807
X( 6) = .26053      RM( 6) = .69755      RM(15) = .09085      VRATE = .02341
X( 7) = .04438      RM( 7) = .26341      RM(16) = .00514      SUMY = .99997
X( 8) = .10442      RM( 8) = .28599      RM(17) = .00137      DY1 = -.00022
X( 9) = 0.00000      RM( 9) = 0.00000      RM(18) = .36119      DY = -.00003
HINT = 201.812      HOUT0 = 302.589      HLOSS = 191.067      HRYNS = 154.960      HMDOT = -7.098      YMDOT = -35.785

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NUMBER OF ITERATIONS= 7

X(1) =	.15914	RM(1) =	.43279	RM(10) =	117.92740	Y(1) =	.35075
X(2) =	.03675	RM(2) =	.09993	RM(11) =	2.71953	Y(2) =	.37023
X(3) =	.34361	RM(3) =	.93445	RM(12) =	.16350	Y(3) =	.25597
X(4) =	0.00000	RM(4) =	0.00000	RM(13) =	.12023	Y(4) =	.01304
X(5) =	.00199	RM(5) =	.00542	RM(14) =	.26454	Y(5) =	.20496
X(6) =	.24499	RM(6) =	.66626	RM(15) =	.11415	VRATE =	.02377
X(7) =	.04545	RM(7) =	.26341	RM(16) =	.00649	SIMV =	.99996
X(8) =	.11647	RM(8) =	.31727	RM(17) =	.00221	DM =	.00034
X(9) =	.00000	RM(9) =	0.00000	RM(18) =	.05257	DM =	.00000

TIME= 10.00 MINUTES

X(1)= .16679	RM(1)= .46016	RM(10)= 117.11975	Y(1)= .38020
X(2)= .03400	RM(2)= .09379	RM(11)= 2.75891	Y(2)= .33706
X(3)= .34484	RM(3)= .95139	RM(12)= .16344	Y(3)= .25852
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .15487	Y(4)= .01299
X(5)= .00240	RM(5)= .00663	RM(14)= .24281	Y(5)= .01119
X(6)= .23086	RM(6)= .63691	RM(15)= .13845	VRATE= .02414
X(7)= .09547	RM(7)= .26341	RM(16)= .00782	SUMY= .99995
X(8)= .12564	RM(8)= .34662	RM(17)= .00321	DY1= -.00039
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= .54679	DY= -.00004

HINT = 291.812 HOUTO= 305.245 HLOSS= 151.684 HRXNS= 139.913 HDMDT= -3.173 MDHDT= -22.031

TIME= 20.00 MINUTES

NUMBER OF ITERATIONS= 7

X(1)= .17374	RM(1)= .48575	RM(10)= 116.47030	Y(1)= .40709
X(2)= .03149	RM(2)= .08803	RM(11)= 2.79577	Y(2)= .30733
X(3)= .34604	RM(3)= .96744	RM(12)= .16336	Y(3)= .26074
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .19319	Y(4)= .01280
X(5)= .00272	RM(5)= .00762	RM(14)= .27396	Y(5)= .01198
X(6)= .21797	RM(6)= .60940	RM(15)= .16364	VRATE= .02462
X(7)= .09422	RM(7)= .26341	RM(16)= .00917	SUMY= .99995
X(8)= .13382	RM(8)= .37414	RM(17)= .00435	DY1= -.00041
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= .64360	DY= -.00005

HINT = 291.812 HOUTO= 310.511 HLOSS= 134.343 HRXNS= 131.179 HDMDT= -2.690 MDHDT= -19.172

TIME= 24.00 MINUTES

NUMBER OF ITERATIONS= 7

X(1)= .18007	RM(1)= .50967	RM(10)= 115.87025	Y(1)= .43152
X(2)= .02921	RM(2)= .08267	RM(11)= 2.82035	Y(2)= .28073
X(3)= .34719	RM(3)= .98266	RM(12)= .16327	Y(3)= .26266
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .23501	Y(4)= .01256
X(5)= .00297	RM(5)= .00841	RM(14)= .30310	Y(5)= .01248
X(6)= .20620	RM(6)= .58360	RM(15)= .18967	VRATE= .02513
X(7)= .09306	RM(7)= .26341	RM(16)= .01052	SUMY= .99995
X(8)= .14130	RM(8)= .39993	RM(17)= .00557	DY1= -.00043
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= .74279	DY= -.00005

HINT = 291.812 HOUTO= 316.184 HLOSS= 118.314 HRXNS= 123.005 HDMDT= -2.455 MDHDT= -17.226

TIME= 28.00 MINUTES

NUMBER OF ITERATIONS= 7

X(1)= .18543	RM(1)= .53201	RM(10)= 115.31383	Y(1)= .45363
X(2)= .02714	RM(2)= .07771	RM(11)= 2.86282	Y(2)= .25095
X(3)= .34830	RM(3)= .99713	RM(12)= .16317	Y(3)= .26332
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .28010	Y(4)= .01228
X(5)= .00316	RM(5)= .00904	RM(14)= .33034	Y(5)= .01277
X(6)= .19541	RM(6)= .55941	RM(15)= .21645	VRATE= .02563
X(7)= .09201	RM(7)= .26341	RM(16)= .01186	SUMY= .99995
X(8)= .14815	RM(8)= .42412	RM(17)= .00685	DY1= -.00043
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= .84418	DY= -.00005

HINT = 291.812 HOUTO= 321.794 HLOSS= 103.451 HRXNS= 115.390 HDMDT= -2.321 MDHDT= -15.723

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X(1)= .000000	RM(1)= 1.000000	RM(10)= .32429	Y(1)= .01199
X(2)= .00329	RM(2)= .00452	RM(11)= .35580	Y(2)= .01290
X(3)= .18550	RM(3)= .53671	RM(12)= .24394	VRATE= .02611
X(4)= .09104	RM(4)= .26341	RM(13)= .01321	SUMPY= .99995
X(5)= .15443	RM(5)= .44682	RM(14)= .00819	DY1= -.00044
X(6)= 0.00000	RM(6)= 0.00000	RM(15)= .94752	DY= -.00005

HINT = 291.812 HOUTO= 327.186 HLOSS= 89.651 HRXNS= 108.329 HDMDT= -2.239 MDHDT= -14.457

---TIME= 36.00 MINUTES--- NUMBER OF ITERATIONS= 7

X(1)= .19586	RM(1)= .57231	RM(10)= 114.31694	Y(1)= .49158
X(2)= .02358	RM(2)= .06891	RM(11)= 2.92201	Y(2)= .21671
X(3)= .35044	RM(3)= 1.02398	RM(12)= .16294	Y(3)= .26704
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .37936	Y(4)= .01170
X(5)= .00338	RM(5)= .00987	RM(14)= .37463	Y(5)= .01292
X(6)= .17638	RM(6)= .51539	RM(15)= .27202	VRATE= .02657
X(7)= .09015	RM(7)= .26341	RM(16)= .01454	SUMPY= .99995
X(8)= .16021	RM(8)= .46814	RM(17)= .00955	DY1= -.00044
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= 1.05297	DY= -.00005

HINT = 291.812 HOUTO= 332.315 HLOSS= 76.832 HRXNS= 101.807 HDMDT= -2.193 MDHDT= -13.333

---TIME= 40.00 MINUTES--- NUMBER OF ITERATIONS= 7

X(1)= .20022	RM(1)= .59044	RM(10)= 113.87093	Y(1)= .50776
X(2)= .02285	RM(2)= .06503	RM(11)= 2.94497	Y(2)= .14975
X(3)= .35146	RM(3)= 1.03645	RM(12)= .16282	Y(3)= .25818
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .43314	Y(4)= .01141
X(5)= .00343	RM(5)= .01011	RM(14)= .40194	Y(5)= .01245
X(6)= .16797	RM(6)= .49534	RM(15)= .30083	VRATE= .02701
X(7)= .08932	RM(7)= .26341	RM(16)= .01587	SUMPY= .99995
X(8)= .16555	RM(8)= .48820	RM(17)= .01094	DY1= -.00044
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= 1.16013	DY= -.00005

HINT = 291.812 HOUTO= 337.173 HLOSS= 64.927 HRXNS= 95.800 HDMDT= -2.178 MDHDT= -12.309

---TIME= 44.00 MINUTES--- NUMBER OF ITERATIONS= 7

X(1)= .20419	RM(1)= .60732	RM(10)= 113.45583	Y(1)= .52232
X(2)= .02066	RM(2)= .06146	RM(11)= 2.97431	Y(2)= .18458
X(3)= .35246	RM(3)= 1.04834	RM(12)= .16269	Y(3)= .26920
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .48244	Y(4)= .01113
X(5)= .00345	RM(5)= .01025	RM(14)= .42285	Y(5)= .01272
X(6)= .16019	RM(6)= .47645	RM(15)= .33016	VRATE= .02742
X(7)= .08856	RM(7)= .26341	RM(16)= .01718	SUMPY= .99995
X(8)= .17049	RM(8)= .50708	RM(17)= .01234	DY1= -.00044
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= 1.26898	DY= -.00005

HINT = 291.812 HOUTO= 341.759 HLOSS= 53.877 HRXNS= 90.277 HDMDT= -2.188 MDHDT= -11.359

---TIME= 48.00 MINUTES--- NUMBER OF ITERATIONS= 7

X(1)= .20770	RM(1)= .62226	RM(10)= 113.07681	Y(1)= .53941
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X(7)=	.08785	RM(7)=	.26341	RM(16)=	.01848	SUMY=	.94096
X(8)=	.17508	RM(8)=	.52490	RM(17)=	.01374	DY1=	-.00043
X(9)=	0.00000	RM(9)=	0.00000	RM(18)=	1.37955	DY=	-.00004
HINT =	291.812	HOUT0=	346.916	HLOSS=	43.076	HRXNS=	85.233
						HQMDT=	-2.458
						MDHDT=	-10.489

TIME= 52.00 MINUTES NUMBER OF ITERATIONS= 7

X(1)=	.21107	RM(1)=	.63747	RM(10)=	112.72363	Y(1)=	.54715
X(2)=	.01825	RM(2)=	.05512	RM(11)=	3.02023	Y(2)=	.15443
X(3)=	.35441	RM(3)=	1.07041	RM(12)=	.16238	Y(3)=	.27105
X(4)=	0.00000	RM(4)=	0.00000	RM(13)=	.60909	Y(4)=	.01051
X(5)=	.00341	RM(5)=	.01029	RM(14)=	.46101	Y(5)=	.01232
X(6)=	.14528	RM(6)=	.44179	RM(15)=	.39048	VRATE=	.02821
X(7)=	.08721	RM(7)=	.26341	RM(16)=	.01977	SUMY=	.99996
X(8)=	.17937	RM(8)=	.54174	RM(17)=	.01514	DY1=	-.00043
X(9)=	0.00000	RM(9)=	0.00000	RM(18)=	1.49166	DY=	-.00004
HINT =	291.812	HOUT0=	350.636	HLOSS=	33.812	HRXNS=	80.602
						HQMDT=	-2.404
						MDHDT=	-9.629

TIME= 56.00 MINUTES NUMBER OF ITERATIONS= 7

X(1)=	.21406	RM(1)=	.65098	RM(10)=	112.39481	Y(1)=	.55771
X(2)=	.01721	RM(2)=	.05233	RM(11)=	3.04117	Y(2)=	.14793
X(3)=	.35536	RM(3)=	1.08070	RM(12)=	.16222	Y(3)=	.27187
X(4)=	0.00000	RM(4)=	0.00000	RM(13)=	.67201	Y(4)=	.01038
X(5)=	.00336	RM(5)=	.01022	RM(14)=	.47842	Y(5)=	.01205
X(6)=	.14003	RM(6)=	.42585	RM(15)=	.42137	VRATE=	.02853
X(7)=	.08661	RM(7)=	.26341	RM(16)=	.02105	SUMY=	.99995
X(8)=	.18338	RM(8)=	.55768	RM(17)=	.01653	DY1=	-.00044
X(9)=	0.00000	RM(9)=	0.00000	RM(18)=	1.60511	DY=	-.00005
HINT =	291.812	HOUT0=	354.204	HLOSS=	25.189	HRXNS=	76.331
						HQMDT=	-2.390
						MDHDT=	-8.859

TIME= 60.00 MINUTES NUMBER OF ITERATIONS= 7

X(1)=	.21678	RM(1)=	.66355	RM(10)=	112.08892	Y(1)=	.56723
X(2)=	.01626	RM(2)=	.04977	RM(11)=	3.06090	Y(2)=	.14813
X(3)=	.35628	RM(3)=	1.09055	RM(12)=	.16205	Y(3)=	.27254
X(4)=	0.00000	RM(4)=	0.00000	RM(13)=	.73619	Y(4)=	.01015
X(5)=	.00330	RM(5)=	.01009	RM(14)=	.49485	Y(5)=	.01179
X(6)=	.13419	RM(6)=	.41075	RM(15)=	.45259	VRATE=	.02444
X(7)=	.08606	RM(7)=	.26341	RM(16)=	.02231	SUMY=	.99995
X(8)=	.18713	RM(8)=	.57279	RM(17)=	.01790	DY1=	-.00044
X(9)=	0.00000	RM(9)=	0.00000	RM(18)=	1.71084	DY=	-.00005
HINT =	291.812	HOUT0=	357.596	HLOSS=	17.171	HRXNS=	72.393
						HQMDT=	-2.401
						MDHDT=	-8.160

TIME= 64.00 MINUTES NUMBER OF ITERATIONS= 7

X(1)=	.21927	RM(1)=	.67525	RM(10)=	111.80446	Y(1)=	.57593
X(2)=	.01540	RM(2)=	.04741	RM(11)=	3.07940	Y(2)=	.12930
X(3)=	.35719	RM(3)=	1.09996	RM(12)=	.16188	Y(3)=	.27137
X(4)=	0.00000	RM(4)=	0.00000	RM(13)=	.80370	Y(4)=	.01055

TIME= 60.00 MINUTES NUMBER OF ITERATIONS= 7
X(1)= .22155 RM(1)= .68614 RM(10)= 111.53998 Y(1)= .58359
X(2)= .01460 RM(2)= .04523 RM(11)= 3.09701 Y(2)= .12133
X(3)= .35868 RM(3)= 1.10898 RM(12)= .16170 Y(3)= .27407
X(4)= 0.00000 RM(4)= 0.00000 RM(13)= .87140 Y(4)= .00977
X(5)= .00314 RM(5)= .00972 RM(14)= .52504 Y(5)= .01110
X(6)= .12359 RM(6)= .38277 RM(15)= .51655 VRATE= .02439
X(7)= .08505 RM(7)= .26341 RM(16)= .02480 SUMY= .99995
X(8)= .19398 RM(8)= .60076 RM(17)= .02058 DY1= -.00044
X(9)= 0.00000 RM(9)= 0.00000 RM(18)= 1.95279 DY= -.00005
HINT = 291.812 HOUTO= 360.794 HLOSS= 9.718 HRXNS= 68.760 HMDT= -2.426 MDHDT= -7.515

TIME= 72.00 MINUTES NUMBER OF ITERATIONS= 7
X(1)= .22363 RM(1)= .69627 RM(10)= 111.29407 Y(1)= .59062
X(2)= .01388 RM(2)= .04322 RM(11)= 3.11353 Y(2)= .11411
X(3)= .35295 RM(3)= 1.11761 RM(12)= .16152 Y(3)= .27475
X(4)= 0.00000 RM(4)= 0.00000 RM(13)= .94099 Y(4)= .00959
X(5)= .00305 RM(5)= .00949 RM(14)= .53896 Y(5)= .01087
X(6)= .11877 RM(6)= .36979 RM(15)= .54905 VRATE= .02955
X(7)= .08460 RM(7)= .26341 RM(16)= .02603 SUMY= .99995
X(8)= .19712 RM(8)= .61374 RM(17)= .02189 DY1= -.00043
X(9)= 0.00000 RM(9)= 0.00000 RM(18)= 2.07088 DY= -.00005
HINT = 291.812 HOUTO= 366.601 HLOSS= -3.638 HRXNS= 62.299 HMDT= -2.490 MDHDT= -6.361

TIME= 76.00 MINUTES NUMBER OF ITERATIONS= 7
X(1)= .22553 RM(1)= .70570 RM(10)= 111.06538 Y(1)= .59700
X(2)= .01321 RM(2)= .04135 RM(11)= 3.12911 Y(2)= .10756
X(3)= .35981 RM(3)= 1.12588 RM(12)= .16133 Y(3)= .27541
X(4)= 0.00000 RM(4)= 0.00000 RM(13)= 1.01196 Y(4)= .00943
X(5)= .00295 RM(5)= .00924 RM(14)= .55218 Y(5)= .01055
X(6)= .11422 RM(6)= .35742 RM(15)= .58190 VRATE= .02988
X(7)= .08418 RM(7)= .26341 RM(16)= .02725 SUMY= .99995
X(8)= .20009 RM(8)= .62612 RM(17)= .02317 DY1= -.00043
X(9)= 0.00000 RM(9)= 0.00000 RM(18)= 2.18995 DY= -.00005
HINT = 291.812 HOUTO= 369.218 HLOSS= -9.614 HRXNS= 59.423 HMDT= -2.521 MDHDT= -5.848

TIME= 80.00 MINUTES NUMBER OF ITERATIONS= 7
X(1)= .22727 RM(1)= .71449 RM(10)= 110.85259 Y(1)= .60280
X(2)= .01260 RM(2)= .03961 RM(11)= 3.14382 Y(2)= .10150
X(3)= .36045 RM(3)= 1.13380 RM(12)= .16113 Y(3)= .27506
X(4)= 0.00000 RM(4)= 0.00000 RM(13)= 1.08429 Y(4)= .00920
X(5)= .00285 RM(5)= .00897 RM(14)= .56474 Y(5)= .01023
X(6)= .10583 RM(6)= .34561 RM(15)= .61508 VRATE= .03011
X(7)= .08261 RM(7)= .26341 RM(16)= .02285 SUMY= .99995
X(8)= .20000 RM(8)= .62612 RM(17)= .02317 DY1= -.00043
X(9)= 0.00000 RM(9)= 0.00000 RM(18)= 2.18995 DY= -.00005
HINT = 291.812 HOUTO= 372.812 HLOSS= -14.614 HRXNS= 56.423 HMDT= -2.521 MDHDT= -5.848

TIME= 84.00 MINUTES

NUMBER OF ITERATIONS= 7

X(1)= .22846	PM(1)= .72268	PM(10)= 110.65445	Y(1)= .60804
X(2)= .01203	PM(2)= .03799	PM(11)= 3.15771	Y(2)= .09615
X(3)= .36147	PM(3)= 1.14141	PM(12)= .16093	Y(3)= .27659
X(4)= 0.00000	PM(4)= 0.00000	PM(13)= 1.15763	Y(4)= .00914
X(5)= .00275	PM(5)= .00869	PM(14)= .57671	Y(5)= .00990
X(6)= .10587	PM(6)= .33432	PM(15)= .64858	VPATE= .03031
X(7)= .08342	PM(7)= .26341	PM(16)= .02965	SUMY= .99996
X(8)= .20560	PM(8)= .64921	PM(17)= .02564	DY1= -.00043
X(9)= 0.00000	PM(9)= 0.00000	PM(18)= 2.43077	DY= -.00004

HINT = 291.812 HOUTO= 373.918 HLOSS= -20.335 HRXNS= 54.267 HMDT= -2.569 MMDT= -4.936

TIME= 88.00 MINUTES

NUMBER OF ITERATIONS= 7

X(1)= .23032	PM(1)= .73031	PM(10)= 110.46981	Y(1)= .61289
X(2)= .01151	PM(2)= .03548	PM(11)= 3.17084	Y(2)= .09117
X(3)= .36227	PM(3)= 1.14870	PM(12)= .16073	Y(3)= .27731
X(4)= 0.00000	PM(4)= 0.00000	PM(13)= 1.23215	Y(4)= .00901
X(5)= .00265	PM(5)= .00841	PM(14)= .58812	Y(5)= .00957
X(6)= .10203	PM(6)= .32352	PM(15)= .68237	VPATE= .03050
X(7)= .08307	PM(7)= .26341	PM(16)= .03083	SUMY= .99995
X(8)= .20815	PM(8)= .66001	PM(17)= .02583	DY1= -.00043
X(9)= 0.00000	PM(9)= 0.00000	PM(18)= 2.55240	DY= -.00004

HINT = 291.812 HOUTO= 376.019 HLOSS= -25.142 HRXNS= 51.950 HMDT= -2.583 MMDT= -4.532

TIME= 92.00 MINUTES

NUMBER OF ITERATIONS= 7

X(1)= .23166	PM(1)= .73744	PM(10)= 110.29756	Y(1)= .61730
X(2)= .01102	PM(2)= .03507	PM(11)= 3.18327	Y(2)= .08660
X(3)= .36306	PM(3)= 1.15571	PM(12)= .16052	Y(3)= .27792
X(4)= 0.00000	PM(4)= 0.00000	PM(13)= 1.30769	Y(4)= .00889
X(5)= .00255	PM(5)= .00811	PM(14)= .59901	Y(5)= .00924
X(6)= .09838	PM(6)= .31317	PM(15)= .71645	VPATE= .03058
X(7)= .08275	PM(7)= .26341	PM(16)= .03201	SUMY= .99995
X(8)= .21059	PM(8)= .67036	PM(17)= .02798	DY1= -.00043
X(9)= 0.00000	PM(9)= 0.00000	PM(18)= 2.67477	DY= -.00004

HINT = 291.812 HOUTO= 377.968 HLOSS= -29.620 HRXNS= 49.785 HMDT= -2.590 MMDT= -4.161

TIME= 96.00 MINUTES

NUMBER OF ITERATIONS= 7

X(1)= .23299	PM(1)= .74410	PM(10)= 110.13669	Y(1)= .62134
X(2)= .01056	PM(2)= .03375	PM(11)= 3.19505	Y(2)= .08239
X(3)= .36383	PM(3)= 1.16244	PM(12)= .16031	Y(3)= .27453
X(4)= 0.00000	PM(4)= 0.00000	PM(13)= 1.36417	Y(4)= .00878
X(5)= .00245	PM(5)= .00782	PM(14)= .60943	Y(5)= .00892
X(6)= .09491	PM(6)= .30325	PM(15)= .75078	VPATE= .03085
X(7)= .08244	PM(7)= .26341	PM(16)= .02318	SUMY= .99996
X(8)= .21292	PM(8)= .68028	PM(17)= .02810	DY1= -.00043
X(9)= 0.00000	PM(9)= 0.00000	PM(18)= 2.74782	DY= -.00004

INITIAL CONDITIONS BASED ON ADJUSTED TIME

X(1)= .12405	RM(1)= .31540	RM(10)= 118.86000	Y(1)= .14382
X(2)= .04345	RM(2)= .11048	RM(11)= 2.54249	Y(2)= .58870
X(3)= .33770	RM(3)= .85860	RM(12)= .16344	Y(3)= .24719
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .04300	Y(4)= .01935
X(5)= .00155	RM(5)= .00393	RM(14)= .10165	Y(5)= .00094
X(6)= .31741	RM(6)= .80702	RM(15)= .05853	VRATE= .01624
X(7)= .09086	RM(7)= .23100	RM(16)= .00258	SUMY= 1.00000
X(8)= .08498	RM(8)= .21606	RM(17)= 0.00000	DY1= 0.00000
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= .20576	DY= 0.00000

TIME= 4.00 MINUTES NUMBER OF ITERATIONS= 5

X(1)= .13045	RM(1)= .33880	RM(10)= 120.17700	Y(1)= .24374
X(2)= .04611	RM(2)= .11975	RM(11)= 2.59720	Y(2)= .49005
X(3)= .33845	RM(3)= .87903	RM(12)= .16485	Y(3)= .23951
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .05411	Y(4)= .01625
X(5)= .00214	RM(5)= .00555	RM(14)= .12508	Y(5)= .01040
X(6)= .24734	RM(6)= .77225	RM(15)= .06980	VRATE= .01958
X(7)= .08894	RM(7)= .23100	RM(16)= .00386	SUMY= .99995
X(8)= .09658	RM(8)= .25082	RM(17)= .00044	DY1= .00660
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= .25405	DY= -.00005

TIME= 4.00 MINUTES HOUTO= 247.356 HLOSS= 221.510 HRXNS= 176.671 HOMDT= -20.164 MDHDT= -24.809

TIME= 8.00 MINUTES NUMBER OF ITERATIONS= 6

X(1)= .13435	RM(1)= .35288	RM(10)= 119.63731	Y(1)= .25882
X(2)= .04532	RM(2)= .11903	RM(11)= 2.62648	Y(2)= .47069
X(3)= .34018	RM(3)= .89347	RM(12)= .16417	Y(3)= .24127
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .07236	Y(4)= .01724
X(5)= .00268	RM(5)= .00703	RM(14)= .15987	Y(5)= .01190
X(6)= .28014	RM(6)= .73589	RM(15)= .08722	VRATE= .01843
X(7)= .08795	RM(7)= .23100	RM(16)= .00522	SUMY= .99992
X(8)= .10934	RM(8)= .28719	RM(17)= .00126	DY1= -.00056
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= .32650	DY= -.00008

TIME= 8.00 MINUTES HOUTO= 236.619 HLOSS= 216.616 HRXNS= 173.056 HOMDT= -15.501 MDHDT= -17.455

TIME= 12.00 MINUTES NUMBER OF ITERATIONS= 8

X(1)= .13854	RM(1)= .36791	RM(10)= 119.14126	Y(1)= .27513
X(2)= .04427	RM(2)= .11757	RM(11)= 2.65557	Y(2)= .45093
X(3)= .34181	RM(3)= .90770	RM(12)= .16355	Y(3)= .24343
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .09184	Y(4)= .01751
X(5)= .00313	RM(5)= .00831	RM(14)= .19339	Y(5)= .01297
X(6)= .26421	RM(6)= .70164	RM(15)= .10488	VRATE= .01836
X(7)= .08699	RM(7)= .23100	RM(16)= .00558	SUMY= .99994
X(8)= .12105	RM(8)= .32144	RM(17)= .00217	DY1= -.00013
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= .39231	DY= -.00002

TIME= 16.00 MINUTES NUMBER OF ITERATIONS= 6

X(1)= .14285	PM(1)= .38343	PM(10)= 118.67109	Y(1)= .29207
X(2)= .04300	PM(2)= .11540	PM(11)= 2.68393	Y(2)= .43083
X(3)= .34337	PM(3)= .92158	PM(12)= .16294	Y(3)= .24574
X(4)= 0.00000	PM(4)= 0.00000	PM(13)= .11278	Y(4)= .01759
X(5)= .00351	PM(5)= .00943	PM(14)= .22582	Y(5)= .01375
X(6)= .24936	PM(6)= .66927	PM(15)= .12289	VRATE= .01852
X(7)= .08607	PM(7)= .23100	PM(16)= .00797	SUMY= .99998
X(8)= .13183	PM(8)= .35381	PM(17)= .00316	DY1= -.00014
X(9)= 0.00000	PM(9)= 0.00000	PM(18)= .47272	DY= -.00002

HINT = 247.222 HOUTO= 236.324 HLOSS= 190.549 HRXNS= 154.383 HDMDT= -12.084 MDHDT= -13.184

TIME= 20.00 MINUTES NUMBER OF ITERATIONS= 6

X(1)= .14720	PM(1)= .39907	PM(10)= 118.23973	Y(1)= .30933
X(2)= .04152	PM(2)= .11255	PM(11)= 2.71112	Y(2)= .41057
X(3)= .34489	PM(3)= .93500	PM(12)= .16232	Y(3)= .24821
X(4)= 0.00000	PM(4)= 0.00000	PM(13)= .13535	Y(4)= .01737
X(5)= .00384	PM(5)= .01041	PM(14)= .25728	Y(5)= .01433
X(6)= .23555	PM(6)= .63862	PM(15)= .14138	VRATE= .01904
X(7)= .08520	PM(7)= .23100	PM(16)= .00936	SUMY= .99991
X(8)= .14181	PM(8)= .38446	PM(17)= .00422	DY1= -.00075
X(9)= 0.00000	PM(9)= 0.00000	PM(18)= .54749	DY= -.00009

HINT = 247.222 HOUTO= 242.596 HLOSS= 176.111 HRXNS= 146.433 HDMDT= -12.668 MDHDT= -12.383

TIME= 24.00 MINUTES NUMBER OF ITERATIONS= 8

X(1)= .15145	PM(1)= .41450	PM(10)= 117.83454	Y(1)= .32643
X(2)= .03988	PM(2)= .10915	PM(11)= 2.73688	Y(2)= .39059
X(3)= .34634	PM(3)= .94788	PM(12)= .16168	Y(3)= .25059
X(4)= 0.00000	PM(4)= 0.00000	PM(13)= .15969	Y(4)= .01750
X(5)= .00412	PM(5)= .01126	PM(14)= .28784	Y(5)= .01476
X(6)= .22270	PM(6)= .60950	PM(15)= .16044	VRATE= .01920
X(7)= .08440	PM(7)= .23100	PM(16)= .01079	SUMY= .99998
X(8)= .15111	PM(8)= .41358	PM(17)= .00533	DY1= -.00013
X(9)= 0.00000	PM(9)= 0.00000	PM(18)= .62373	DY= -.00002

HINT = 247.222 HOUTO= 244.160 HLOSS= 165.284 HRXNS= 139.158 HDMDT= -11.702 MDHDT= -11.361

TIME= 28.00 MINUTES NUMBER OF ITERATIONS= 8

X(1)= .15563	PM(1)= .42981	PM(10)= 117.44398	Y(1)= .34329
X(2)= .03821	PM(2)= .10554	PM(11)= 2.76180	Y(2)= .37685
X(3)= .34773	PM(3)= .96037	PM(12)= .16105	Y(3)= .25207
X(4)= 0.00000	PM(4)= 0.00000	PM(13)= .18562	Y(4)= .01758
X(5)= .00435	PM(5)= .01201	PM(14)= .31722	Y(5)= .01508
X(6)= .21067	PM(6)= .58182	PM(15)= .17491	VRATE= .01940
X(7)= .08364	PM(7)= .23100	PM(16)= .01220	SUMY= .99998
X(8)= .15277	PM(8)= .44126	PM(17)= .00549	DY1= -.00013
X(9)= 0.00000	PM(9)= 0.00000	PM(18)= .70947	DY= -.00002

HINT = 247.222 HOUTO= 246.195 HLOSS= 150.942 HRXNS= 132.282 HDMDT= -12.035 MDHDT= -10.696

X(4)= .000000	RM(4)= 0.00000	RM(12)= .18043	Y(4)= .01753
X(5)= .00454	RM(5)= .01266	RM(13)= .21316	Y(5)= .01530
X(6)= .19940	RM(6)= .55552	RM(14)= .34542	VRATE= .01951
X(7)= .08292	RM(7)= .23100	RM(15)= .19978	SUMY= .99998
X(8)= .16783	RM(8)= .46756	RM(16)= .01370	DY1= -.00013
X(9)= 0.00000	RM(9)= 0.00000	RM(17)= .00758	DY= -.00002
HINT = 247.222	HOUTO= 248.399	HLOSS= 145.016	HRXNS= 125.743
			HOMDT= -10.264
			MDHDT= -10.185

TIME= 36.00 MINUTES

NUMBER OF ITERATIONS= 8

X(1)= .16366	RM(1)= .45976	RM(10)= 116.70797	Y(1)= .37595
X(2)= .03488	RM(2)= .09799	RM(11)= 2.80924	Y(2)= .33338
X(3)= .35034	RM(3)= .98420	RM(12)= .15987	Y(3)= .25755
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .24228	Y(4)= .01755
X(5)= .00470	RM(5)= .01322	RM(14)= .37245	Y(5)= .01545
X(6)= .18885	RM(6)= .53053	RM(15)= .22005	VRATE= .01982
X(7)= .08223	RM(7)= .23100	RM(16)= .01518	SUMY= .99998
X(8)= .17533	RM(8)= .49255	RM(17)= .00839	DY1= -.00013
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= .85774	DY= -.00002
HINT = 247.222	HOUTO= 250.608	HLOSS= 135.495	HRXNS= 119.520
			HOMDT= -9.632
			MDHDT= -9.729

TIME= 40.00 MINUTES

NUMBER OF ITERATIONS= 8

X(1)= .16749	RM(1)= .47430	RM(10)= 116.36123	Y(1)= .39159
X(2)= .03325	RM(2)= .09416	RM(11)= 2.83178	Y(2)= .31557
X(3)= .35156	RM(3)= .99555	RM(12)= .15932	Y(3)= .25933
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .27299	Y(4)= .01755
X(5)= .00483	RM(5)= .01369	RM(14)= .39832	Y(5)= .01553
X(6)= .17596	RM(6)= .50678	RM(15)= .24071	VRATE= .02003
X(7)= .08157	RM(7)= .23100	RM(16)= .01669	SUMY= .99998
X(8)= .18232	RM(8)= .51630	RM(17)= .01013	DY1= -.00013
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= .93744	DY= -.00002
HINT = 247.222	HOUTO= 252.782	HLOSS= 126.366	HRXNS= 113.597
			HOMDT= -9.029
			MDHDT= -9.300

TIME= 44.00 MINUTES

NUMBER OF ITERATIONS= 8

X(1)= .17119	RM(1)= .48851	RM(10)= 116.02799	Y(1)= .40670
X(2)= .03146	RM(2)= .09035	RM(11)= 2.85356	Y(2)= .29849
X(3)= .35273	RM(3)= 1.00654	RM(12)= .15879	Y(3)= .26150
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .30525	Y(4)= .01754
X(5)= .00493	RM(5)= .01408	RM(14)= .42305	Y(5)= .01556
X(6)= .16969	RM(6)= .48422	RM(15)= .26174	VRATE= .02023
X(7)= .08095	RM(7)= .23100	RM(16)= .01820	SUMY= .99998
X(8)= .18884	RM(8)= .53386	RM(17)= .01139	DY1= -.00012
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= 1.01797	DY= -.00002
HINT = 247.222	HOUTO= 254.912	HLOSS= 117.615	HRXNS= 107.959
			HOMDT= -8.455
			MDHDT= -8.891

TIME= 48.00 MINUTES

NUMBER OF ITERATIONS= 8

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X(7)= .08036	RM(7)= .23100	RM(16)= .01473	SUMY= .99998
Y(8)= .19492	RM(9)= .56030	RM(17)= .01266	DY1= -.00012
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= 1.09930	DY= -.00002
HINT = 247.222	HOUT0= 257.001	HLOSS= 109.228	HMXNS= 102.597
			HOMDT= -7.910
			MOHDT= -8.499

TIME= 52.00 MINUTES NUMBER OF ITERATIONS= 8

X(1)= .17818	RM(1)= .51581	RM(10)= 115.40029	Y(1)= .43516
X(2)= .02864	RM(2)= .08290	RM(11)= 2.89490	Y(2)= .26652
X(3)= .35493	RM(3)= 1.02747	RM(12)= .15781	Y(3)= .26524
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .37433	Y(4)= .01756
X(5)= .00506	RM(5)= .01463	RM(14)= .46920	Y(5)= .01550
X(6)= .15282	RM(6)= .44241	RM(15)= .30489	VRATE= .02063
X(7)= .07980	RM(7)= .23100	RM(16)= .02128	SUMY= .99998
X(8)= .20058	RM(8)= .58067	RM(17)= .01393	DY1= -.00012
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= 1.18141	DY= -.00002
HINT = 247.222	HOUT0= 259.051	HLOSS= 101.191	HMXNS= 97.500
			HOMDT= -7.398
			MOHDT= -8.123

TIME= 56.00 MINUTES NUMBER OF ITERATIONS= 8

X(1)= .18146	RM(1)= .52886	RM(10)= 115.10503	Y(1)= .44848
X(2)= .02721	RM(2)= .07931	RM(11)= 2.91449	Y(2)= .25158
X(3)= .35595	RM(3)= 1.03742	RM(12)= .15736	Y(3)= .26690
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .41108	Y(4)= .01749
X(5)= .00508	RM(5)= .01481	RM(14)= .49068	Y(5)= .01541
X(6)= .14516	RM(6)= .42306	RM(15)= .32699	VRATE= .02082
X(7)= .07926	RM(7)= .23100	RM(16)= .02283	SUMY= .99998
X(8)= .20588	RM(8)= .60002	RM(17)= .01522	DY1= -.00012
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= 1.26431	DY= -.00002
HINT = 247.222	HOUT0= 261.067	HLOSS= 93.492	HMXNS= 92.658
			HOMDT= -6.918
			MOHDT= -7.760

TIME= 60.00 MINUTES NUMBER OF ITERATIONS= 8

X(1)= .18460	RM(1)= .54149	RM(10)= 114.82168	Y(1)= .46118
X(2)= .02585	RM(2)= .07583	RM(11)= 2.93337	Y(2)= .23760
X(3)= .35694	RM(3)= 1.04705	RM(12)= .15693	Y(3)= .26846
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .44926	Y(4)= .01742
X(5)= .00509	RM(5)= .01492	RM(14)= .51115	Y(5)= .01530
X(6)= .13795	RM(6)= .40467	RM(15)= .34944	VRATE= .02101
X(7)= .07875	RM(7)= .23100	RM(16)= .02439	SUMY= .99998
X(8)= .21082	RM(8)= .61841	RM(17)= .01651	DY1= -.00011
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= 1.34795	DY= -.00002
HINT = 247.222	HOUT0= 263.050	HLOSS= 86.120	HMXNS= 88.065
			HOMDT= -6.473
			MOHDT= -7.410

TIME= 64.00 MINUTES NUMBER OF ITERATIONS= 8

X(1)= .18760	RM(1)= .55370	RM(10)= 114.54992	Y(1)= .47325
X(2)= .02455	RM(2)= .07246	RM(11)= 2.95156	Y(2)= .22427
X(3)= .35789	RM(3)= 1.05634	RM(12)= .15652	Y(3)= .26497
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .44823	Y(4)= .01733

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HINT = 247.222 HOUTO = 265.001 HLOSS = 79.663 HRXNS = 83.769 HMDT = -6.062 MDHDT = -7.072

TIME = 68.00 MINUTES NUMBER OF ITERATIONS = 8

X(1) = .19046	RM(1) = .56548	PM(10) = 114.28942	Y(1) = .48470
X(2) = .02331	RM(2) = .06921	PM(11) = 2.95908	Y(2) = .21168
X(3) = .35441	RM(3) = 1.06533	PM(12) = .15613	Y(3) = .27137
X(4) = 0.00000	RM(4) = 0.00000	PM(13) = .52974	Y(4) = .01723
X(5) = .00505	PM(5) = .01498	PM(14) = .54921	Y(5) = .01500
X(6) = .12482	PM(6) = .37059	PM(15) = .39530	VRATE = .02137
X(7) = .07740	PM(7) = .23100	PM(16) = .02753	SUMY = .99998
X(8) = .21976	PM(8) = .65240	PM(17) = .01908	DY1 = -.00011
X(9) = 0.00000	PM(9) = 0.00000	PM(18) = 1.51747	DY = -.00002

HINT = 247.222 HOUTO = 266.920 HLOSS = 72.313 HRXNS = 79.583 HMDT = -5.684 MDHDT = -6.744

TIME = 72.00 MINUTES NUMBER OF ITERATIONS = 8

X(1) = .19314	RM(1) = .57682	PM(10) = 114.03989	Y(1) = .49535
X(2) = .02214	RM(2) = .06610	PM(11) = 2.98593	Y(2) = .19940
X(3) = .35969	RM(3) = 1.07400	PM(12) = .15576	Y(3) = .27270
X(4) = 0.00000	RM(4) = 0.00000	PM(13) = .57195	Y(4) = .01712
X(5) = .00500	PM(5) = .01493	PM(14) = .56588	Y(5) = .01481
X(6) = .11843	PM(6) = .35480	PM(15) = .41870	VRATE = .02155
X(7) = .07736	PM(7) = .23100	PM(16) = .02911	SUMY = .99998
X(8) = .22381	PM(8) = .66827	PM(17) = .02036	DY1 = -.00010
X(9) = 0.00000	PM(9) = 0.00000	PM(18) = 1.60331	DY = -.00002

HINT = 247.222 HOUTO = 268.804 HLOSS = 65.859 HRXNS = 75.677 HMDT = -5.338 MDHDT = -6.426

TIME = 76.00 MINUTES NUMBER OF ITERATIONS = 8

X(1) = .19577	RM(1) = .58773	PM(10) = 113.80104	Y(1) = .50580
X(2) = .02102	RM(2) = .06311	PM(11) = 3.00213	Y(2) = .18851
X(3) = .36053	RM(3) = 1.08237	PM(12) = .15540	Y(3) = .27395
X(4) = 0.00000	RM(4) = 0.00000	PM(13) = .61542	Y(4) = .01701
X(5) = .00494	PM(5) = .01484	PM(14) = .58370	Y(5) = .01452
X(6) = .11318	PM(6) = .33979	PM(15) = .44241	VRATE = .02172
X(7) = .07695	PM(7) = .23100	PM(16) = .03069	SUMY = .99998
X(8) = .22760	PM(8) = .68328	PM(17) = .02164	DY1 = -.00010
X(9) = 0.00000	PM(9) = 0.00000	PM(18) = 1.68984	DY = -.00002

HINT = 247.222 HOUTO = 270.652 HLOSS = 59.691 HRXNS = 71.981 HMDT = -5.023 MDHDT = -6.117

TIME = 80.00 MINUTES NUMBER OF ITERATIONS = 8

X(1) = .19823	RM(1) = .59819	PM(10) = 113.57115	Y(1) = .51544
X(2) = .01997	RM(2) = .06026	PM(11) = 3.01767	Y(2) = .17808
X(3) = .36135	RM(3) = 1.09045	PM(12) = .15506	Y(3) = .27512
X(4) = 0.00000	RM(4) = 0.00000	PM(13) = .65012	Y(4) = .01686
X(5) = .00487	PM(5) = .01470	PM(14) = .59070	Y(5) = .01440
X(6) = .10747	PM(6) = .32552	PM(15) = .44441	VRATE = .02181

TIME= 84.00 MINUTES NUMBER OF ITERATIONS= 6

X(1)= .20057	RM(1)= .60824	RM(10)= 113.35327	Y(1)= .52456		
X(2)= .01827	RM(2)= .05753	RM(11)= 3.03261	Y(2)= .16819		
X(3)= .36214	RM(3)= 1.09824	RM(12)= .15473	Y(3)= .27625		
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .70597	Y(4)= .01673		
X(5)= .00479	RM(5)= .01452	RM(14)= .61493	Y(5)= .01417		
X(6)= .10286	RM(6)= .31194	RM(15)= .49070	VRATE= .02209		
X(7)= .07617	RM(7)= .23100	RM(16)= .03385	SUMY= .99991		
X(8)= .23450	RM(8)= .71114	RM(17)= .02417	DY1= -.00085		
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= 1.85499	DY= -.00009		
HINT = 247.222	HOUT0= 274.680	HL0SS= 48.170	HRXNS= 65.182	HMMDT= -4.603	MDHDT= -5.842

TIME= 88.00 MINUTES NUMBER OF ITERATIONS= 5

X(1)= .20278	RM(1)= .61786	RM(10)= 113.14449	Y(1)= .53313		
X(2)= .01803	RM(2)= .05493	RM(11)= 3.04693	Y(2)= .15890		
X(3)= .36291	RM(3)= 1.10575	RM(12)= .15442	Y(3)= .27732		
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .75295	Y(4)= .01662		
X(5)= .00470	RM(5)= .01431	RM(14)= .62942	Y(5)= .01393		
X(6)= .09813	RM(6)= .29901	RM(15)= .51527	VRATE= .02223		
X(7)= .07581	RM(7)= .23100	RM(16)= .03543	SUMY= .99991		
X(8)= .23764	RM(8)= .72407	RM(17)= .02541	DY1= -.00085		
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= 1.95355	DY= -.00009		
HINT = 247.222	HOUT0= 276.099	HL0SS= 42.785	HRXNS= 62.054	HMMDT= -4.279	MDHDT= -5.329

INITIAL CONDITIONS BASED ON ADJUSTED TIME

X(1)= .12454	RM(1)= .31602	RM(10)= 118.34000	Y(1)= .12502
X(2)= .03454	RM(2)= .08763	RM(11)= 2.53738	Y(2)= .61585
X(3)= .35676	RM(3)= .90523	RM(12)= .15563	Y(3)= .24043
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .05334	Y(4)= .01034
X(5)= .00097	RM(5)= .00246	RM(14)= .18556	Y(5)= .00836
X(6)= .29089	RM(6)= .73809	RM(15)= .08566	VRATE= .01284
X(7)= .08265	RM(7)= .20972	RM(16)= .00287	SUMY= 1.00000
X(8)= .10965	RM(8)= .27824	RM(17)= .00159	DY1= 0.00000
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= .33001	DY= 0.00000

TIME= 4.00 MINUTES

NUMBER OF ITERATIONS= 7

X(1)= .13002	RM(1)= .33488	RM(10)= 119.38584	Y(1)= .26048
X(2)= .04164	RM(2)= .10851	RM(11)= 2.60628	Y(2)= .43557
X(3)= .35620	RM(3)= .92835	RM(12)= .15849	Y(3)= .25712
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .06075	Y(4)= .03764
X(5)= .00172	RM(5)= .00449	RM(14)= .19920	Y(5)= .00815
X(6)= .26949	RM(6)= .70234	RM(15)= .09323	VRATE= .00959
X(7)= .08047	RM(7)= .20972	RM(16)= .00445	SUMY= .99997
X(8)= .12047	RM(8)= .31399	RM(17)= .00178	DY1= -.00018
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= .36023	DY= -.00003

HINT = 202.501 HOUTO= 119.611 HLOSS= 230.703 HMXNS= 180.020 HMDT= 21.947 HMDT= 10.260

TIME= 8.00 MINUTES

NUMBER OF ITERATIONS= 8

X(1)= .13325	RM(1)= .35346	RM(10)= 118.61635	Y(1)= .27198
X(2)= .04544	RM(2)= .12054	RM(11)= 2.65255	Y(2)= .43690
X(3)= .35666	RM(3)= .94606	RM(12)= .15955	Y(3)= .25478
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .07451	Y(4)= .02510
X(5)= .00243	RM(5)= .00645	RM(14)= .22179	Y(5)= .01020
X(6)= .25981	RM(6)= .66527	RM(15)= .10642	VRATE= .01337
X(7)= .07906	RM(7)= .20972	RM(16)= .00595	SUMY= .99995
X(8)= .13234	RM(8)= .35105	RM(17)= .00227	DY1= -.00025
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= .41159	DY= -.00005

HINT = 202.501 HOUTO= 170.070 HLOSS= 226.773 HMXNS= 173.428 HMDT= 5.317 HMDT= -26.232

TIME= 12.00 MINUTES

NUMBER OF ITERATIONS= 8

X(1)= .13779	RM(1)= .37157	RM(10)= 117.57141	Y(1)= .28543
X(2)= .04740	RM(2)= .12783	RM(11)= 2.69552	Y(2)= .42555
X(3)= .35719	RM(3)= .96320	RM(12)= .16041	Y(3)= .25229
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .08950	Y(4)= .02435
X(5)= .00295	RM(5)= .00799	RM(14)= .24506	Y(5)= .01135
X(6)= .23458	RM(6)= .63257	RM(15)= .12009	VRATE= .01357
X(7)= .07777	RM(7)= .20972	RM(16)= .00758	SUMY= .99996
X(8)= .14231	RM(8)= .38375	RM(17)= .00285	DY1= -.00022
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= .43551	DY= -.00004

10.00 MINUTES

NUMBER OF ITERATIONS= 8

X(1)= .14314	RM(1)= .39216	RM(10)= 116.80273	Y(1)= .30394
X(2)= .04824	RM(2)= .13217	RM(11)= 2.73965	Y(2)= .41020
X(3)= .35773	RM(3)= .98005	RM(12)= .16120	Y(3)= .25102
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .10595	Y(4)= .02273
X(5)= .00337	RM(5)= .00924	RM(14)= .26815	Y(5)= .01207
X(6)= .22020	RM(6)= .60326	RM(15)= .13399	VRATE= .01405
X(7)= .07655	RM(7)= .20972	RM(16)= .00675	SUMY= .99997
X(8)= .15077	RM(8)= .41306	RM(17)= .00551	DY1= -.00020
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= .52069	DY= -.00003

HINT = 202.501 HOUTO= 177.963 HLOSS= 179.853 HRXNS= 137.946 HMDT= 6.745 MDHDT= -24.114

TIME= 20.00 MINUTES

NUMBER OF ITERATIONS= 8

X(1)= .14986	RM(1)= .41392	RM(10)= 116.00722	Y(1)= .32291
X(2)= .04820	RM(2)= .13403	RM(11)= 2.78058	Y(2)= .39271
X(3)= .35832	RM(3)= .99634	RM(12)= .16186	Y(3)= .25055
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .12402	Y(4)= .02125
X(5)= .00359	RM(5)= .01025	RM(14)= .29121	Y(5)= .01254
X(6)= .20737	RM(6)= .57661	RM(15)= .14841	VRATE= .01469
X(7)= .07542	RM(7)= .20972	RM(16)= .01009	SUMY= .99997
X(8)= .15814	RM(8)= .43971	RM(17)= .00422	DY1= -.00018
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= .57813	DY= -.00003

HINT = 202.501 HOUTO= 185.718 HLOSS= 159.283 HRXNS= 125.873 HMDT= 5.755 MDHDT= -22.383

TIME= 24.00 MINUTES

NUMBER OF ITERATIONS= 8

X(1)= .15468	RM(1)= .43602	RM(10)= 115.29151	Y(1)= .34236
X(2)= .04748	RM(2)= .13385	RM(11)= 2.81893	Y(2)= .37415
X(3)= .35898	RM(3)= 1.01193	RM(12)= .16237	Y(3)= .25065
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .14411	Y(4)= .01998
X(5)= .00393	RM(5)= .01108	RM(14)= .31427	Y(5)= .01293
X(6)= .19587	RM(6)= .55213	RM(15)= .16350	VRATE= .01539
X(7)= .07440	RM(7)= .20972	RM(16)= .01140	SUMY= .99997
X(8)= .16467	RM(8)= .46419	RM(17)= .00498	DY1= -.00016
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= .63828	DY= -.00003

HINT = 202.501 HOUTO= 194.210 HLOSS= 140.400 HRXNS= 115.951 HMDT= 4.492 MDHDT= -20.561

TIME= 28.00 MINUTES

NUMBER OF ITERATIONS= 8

X(1)= .16042	RM(1)= .45797	RM(10)= 114.51110	Y(1)= .36184
X(2)= .04529	RM(2)= .13214	RM(11)= 2.85475	Y(2)= .35516
X(3)= .35969	RM(3)= 1.02583	RM(12)= .16274	Y(3)= .25106
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .16530	Y(4)= .01910
X(5)= .00412	RM(5)= .01176	RM(14)= .33716	Y(5)= .01300
X(6)= .18547	RM(6)= .52947	RM(15)= .17978	VRATE= .01591
X(7)= .07346	RM(7)= .20972	RM(16)= .01270	SUMY= .99997
X(8)= .17054	RM(8)= .48686	RM(17)= .00580	DY1= -.00019
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= .70106	DY= -.00003

HINT = 202.501 HOUTO= 200.352 HLOSS= 124.766 HRXNS= 107.518 HMDT= 3.735 MDHDT= -18.834

X(1)=	0.00000	RM(1)=	1.00000	PM(10)=	113.46348	Y(1)=	.39878
X(2)=	.00426	RM(2)=	.01230	PM(11)=	2.91906	Y(2)=	.31794
X(3)=	.17501	RM(3)=	.50937	PM(12)=	.16312	Y(3)=	.25279
X(4)=	.07261	RM(4)=	.20972	PM(13)=	.21717	Y(4)=	.01737
X(5)=	.17587	RM(5)=	.50795	PM(14)=	.38190	Y(5)=	.01309
X(6)=	0.00000	RM(6)=	0.00000	PM(15)=	.21286	VRATE=	.01731
HINT =	202.501	HOUT0=	209.232	PM(16)=	.01526	SUMY=	.99498
		HLOSS=	108.654	PM(17)=	.00754	DY1=	-.00013
		HRXNS=	100.316	PM(18)=	.83418	DY=	-.00002
		HOMDT=	2.134				
		MDHDT=	-17.203				

TIME= 36.00 MINUTES NUMBER OF ITERATIONS= 8

X(1)=	.17135	RM(1)=	.50018	PM(10)=	113.46348	Y(1)=	.39878
X(2)=	.04301	RM(2)=	.12554	PM(11)=	2.91906	Y(2)=	.31794
X(3)=	.36127	RM(3)=	1.05456	PM(12)=	.16312	Y(3)=	.25279
X(4)=	0.00000	RM(4)=	0.00000	PM(13)=	.21717	Y(4)=	.01737
X(5)=	.00436	RM(5)=	.01273	PM(14)=	.38190	Y(5)=	.01309
X(6)=	.16739	RM(6)=	.48861	PM(15)=	.21286	VRATE=	.01731
X(7)=	.07184	RM(7)=	.20972	PM(16)=	.01526	SUMY=	.99498
X(8)=	.18078	RM(8)=	.52771	PM(17)=	.00754	DY1=	-.00013
X(9)=	0.00000	RM(9)=	0.00000	PM(18)=	.83418	DY=	-.00002
HINT =	202.501	HOUT0=	217.176	HLOSS=	94.103	HRXNS=	94.118
				HOMDT=	.791	MDHDT=	-15.451

TIME= 40.00 MINUTES NUMBER OF ITERATIONS= 8

X(1)=	.17638	RM(1)=	.51985	PM(10)=	112.97702	Y(1)=	.41610
X(2)=	.04109	RM(2)=	.12112	PM(11)=	2.94741	Y(2)=	.30011
X(3)=	.36212	RM(3)=	1.06733	PM(12)=	.16314	Y(3)=	.25394
X(4)=	0.00000	RM(4)=	0.00000	PM(13)=	.24600	Y(4)=	.01676
X(5)=	.00443	RM(5)=	.01307	PM(14)=	.40366	Y(5)=	.01305
X(6)=	.15947	RM(6)=	.47001	PM(15)=	.23074	VRATE=	.01791
X(7)=	.07115	RM(7)=	.20972	PM(16)=	.01654	SUMY=	.99598
X(8)=	.18535	RM(8)=	.54631	PM(17)=	.00846	DY1=	-.00012
X(9)=	0.00000	RM(9)=	0.00000	PM(18)=	.90464	DY=	-.00002
HINT =	202.501	HOUT0=	224.344	HLOSS=	81.029	HRXNS=	88.726
				HOMDT=	-.343	MDHDT=	-13.804

TIME= 44.00 MINUTES NUMBER OF ITERATIONS= 8

X(1)=	.18108	RM(1)=	.53844	PM(10)=	112.54168	Y(1)=	.43245
X(2)=	.03911	RM(2)=	.11630	PM(11)=	2.97351	Y(2)=	.28201
X(3)=	.36301	RM(3)=	1.07942	PM(12)=	.16396	Y(3)=	.25527
X(4)=	0.00000	RM(4)=	0.00000	PM(13)=	.27698	Y(4)=	.01627
X(5)=	.00448	RM(5)=	.01331	PM(14)=	.42486	Y(5)=	.01298
X(6)=	.15216	RM(6)=	.45244	PM(15)=	.24930	VRATE=	.01846
X(7)=	.07053	RM(7)=	.20972	PM(16)=	.01782	SUMY=	.99998
X(8)=	.18964	RM(8)=	.56389	PM(17)=	.00941	DY1=	-.00012
X(9)=	0.00000	RM(9)=	0.00000	PM(18)=	.97729	DY=	-.00002
HINT =	202.501	HOUT0=	230.756	HLOSS=	69.305	HRXNS=	83.979
				HOMDT=	-1.276	MDHDT=	-12.305

TIME= 48.00 MINUTES NUMBER OF ITERATIONS= 8

X(1)=	.18108	RM(1)=	.53844	PM(10)=	112.54168	Y(1)=	.43245
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X(6)= .14537	RM(6)= .43576	RM(15)= .26849	VRATE= .01374
X(7)= .06996	RM(7)= .20972	RM(16)= .01910	SUMY= .99998
X(8)= .19368	RM(8)= .58056	RM(17)= .01038	DY1= -.00011
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= 1.05220	DY= -.00002
HINT = 202.501	HOUT0= 236.451	HLOSS= 58.794	HQXNS= 79.753
			MDMDT= -2.023
			MDHDT= -10.968

TIME= 52.00 MINUTES NUMBER OF ITERATIONS= 8

X(1)= .18950	RM(1)= .57229	RM(10)= 111.80161	Y(1)= .46222
X(2)= .03517	RM(2)= .10620	RM(11)= 3.01491	Y(2)= .25133
X(3)= .36484	RM(3)= 1.10177	RM(12)= .16269	Y(3)= .25813
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .34502	Y(4)= .01556
X(5)= .00451	RM(5)= .01361	RM(14)= .46525	Y(5)= .01275
X(6)= .13404	RM(6)= .41990	RM(15)= .28826	VRATE= .01937
X(7)= .06944	RM(7)= .20972	RM(16)= .02038	SUMY= .99998
X(8)= .19750	RM(8)= .59642	RM(17)= .01137	DY1= -.00011
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= 1.12844	DY= -.00002
HINT = 202.501	HOUT0= 241.486	HLOSS= 49.359	HQXNS= 75.950
			MDMDT= -2.605
			MDHDT= -9.790

TIME= 56.00 MINUTES NUMBER OF ITERATIONS= 6

X(1)= .19323	RM(1)= .58750	RM(10)= 111.48891	Y(1)= .47560
X(2)= .03326	RM(2)= .10112	RM(11)= 3.04040	Y(2)= .23679
X(3)= .36576	RM(3)= 1.11206	RM(12)= .16243	Y(3)= .25963
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .38195	Y(4)= .01528
X(5)= .00450	RM(5)= .01367	RM(14)= .48440	Y(5)= .01260
X(6)= .13313	RM(6)= .40477	RM(15)= .30861	VRATE= .01979
X(7)= .06898	RM(7)= .20972	RM(16)= .02167	SUMY= .99990
X(8)= .20114	RM(8)= .61155	RM(17)= .01236	DY1= -.00075
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= 1.20733	DY= -.00010
HINT = 202.501	HOUT0= 246.325	HLOSS= 40.339	HQXNS= 72.507
			MDMDT= -3.160
			MDHDT= -8.497

TIME= 60.00 MINUTES NUMBER OF ITERATIONS= 6

X(1)= .19667	RM(1)= .60172	RM(10)= 111.20688	Y(1)= .48809
X(2)= .03144	RM(2)= .09620	RM(11)= 3.05955	Y(2)= .22317
X(3)= .36668	RM(3)= 1.12188	RM(12)= .16214	Y(3)= .26113
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .42056	Y(4)= .01505
X(5)= .00447	RM(5)= .01369	RM(14)= .50276	Y(5)= .01245
X(6)= .12757	RM(6)= .39031	RM(15)= .32945	VRATE= .02616
X(7)= .06854	RM(7)= .20972	RM(16)= .02296	SUMY= .99999
X(8)= .20461	RM(8)= .62602	RM(17)= .01337	DY1= -.00075
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= 1.26718	DY= -.00010
HINT = 202.501	HOUT0= 250.566	HLOSS= 32.802	HQXNS= 69.361
			MDMDT= -3.572
			MDHDT= -8.025

TIME= 64.00 MINUTES NUMBER OF ITERATIONS= 6

X(1)= .19985	RM(1)= .61502	RM(10)= 110.94914	Y(1)= .49970
X(2)= .02972	RM(2)= .09149	RM(11)= 3.07740	Y(2)= .21043
X(3)= .36754	RM(3)= 1.13127	RM(12)= .16182	Y(3)= .26251
		RM(13)= .42056	Y(4)= .01505
		RM(14)= .50276	Y(5)= .01245

HINT = 202.501 HOUTO= 254.027 HLOSS= 26.088 HRXNS= 66.430 HQMDT= -3.789 MDHDT= -7.396

TIME= 60.00 MINUTES - - - - - NUMBER OF ITERATIONS= 6

X(1)= .20277	RM(1)= .62745	RM(10)= 110.71215	Y(1)= .51045
X(2)= .02411	RM(2)= .08699	RM(11)= 3.09434	Y(2)= .19853
X(3)= .36949	RM(3)= 1.14024	RM(12)= .16151	Y(3)= .26404
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .50241	Y(4)= .01476
X(5)= .00440	RM(5)= .01362	RM(14)= .53714	Y(5)= .01211
X(6)= .11734	RM(6)= .36320	RM(15)= .37243	VRATE= .02069
X(7)= .06777	RM(7)= .20972	RM(16)= .02556	SUMY= .99991
X(8)= .21107	RM(8)= .65312	RM(17)= .01538	OY1= -.00075
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= 1.45051	OY= -.00009

HINT = 202.501 HOUTO= 256.645 HLOSS= 19.831 HRXNS= 63.680 HQMDT= -3.797 MDHDT= -6.499

TIME= 72.00 MINUTES - - - - - NUMBER OF ITERATIONS= 6

X(1)= .20548	RM(1)= .63908	RM(10)= 110.49402	Y(1)= .52046
X(2)= .02660	RM(2)= .09274	RM(11)= 3.11023	Y(2)= .18744
X(3)= .36937	RM(3)= 1.14883	RM(12)= .16118	Y(3)= .26543
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .54543	Y(4)= .01454
X(5)= .00435	RM(5)= .01354	RM(14)= .55319	Y(5)= .01193
X(6)= .11269	RM(6)= .35048	RM(15)= .39451	VRATE= .02092
X(7)= .06743	RM(7)= .20972	RM(16)= .02686	SUMY= .99991
X(8)= .21408	RM(8)= .66595	RM(17)= .01638	OY1= -.00076
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= 1.53372	OY= -.00009

HINT = 202.501 HOUTO= 259.203 HLOSS= 14.110 HRXNS= 61.106 HQMDT= -3.823 MDHDT= -5.884

TIME= 76.00 MINUTES - - - - - NUMBER OF ITERATIONS= 6

X(1)= .20798	RM(1)= .64998	RM(10)= 110.29207	Y(1)= .52973
X(2)= .02519	RM(2)= .07473	RM(11)= 3.12525	Y(2)= .17712
X(3)= .37023	RM(3)= 1.15708	RM(12)= .16085	Y(3)= .26677
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .58973	Y(4)= .01454
X(5)= .00430	RM(5)= .01343	RM(14)= .56452	Y(5)= .01175
X(6)= .10824	RM(6)= .33827	RM(15)= .41694	VRATE= .02113
X(7)= .06710	RM(7)= .20972	RM(16)= .02817	SUMY= .99991
X(8)= .21396	RM(8)= .67906	RM(17)= .01738	OY1= -.00076
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= 1.61782	OY= -.00009

HINT = 202.501 HOUTO= 261.564 HLOSS= 9.824 HRXNS= 58.676 HQMDT= -3.825 MDHDT= -5.386

TIME= 80.00 MINUTES - - - - - NUMBER OF ITERATIONS= 6

X(1)= .21029	RM(1)= .66019	RM(10)= 110.10421	Y(1)= .53834
X(2)= .02348	RM(2)= .07497	RM(11)= 3.13949	Y(2)= .16752
X(3)= .37108	RM(3)= 1.16499	RM(12)= .16053	Y(3)= .26806
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .63522	Y(4)= .01444
X(5)= .00423	RM(5)= .01329	RM(14)= .58315	Y(5)= .01156
X(6)= .10461	RM(6)= .32854	RM(15)= .43970	VRATE= .02153
X(7)= .06710	RM(7)= .20972	RM(16)= .02848	SUMY= .99991

TIME=-- 84.00 MINUTES

NUMBER OF ITERATIONS= 6

X(1)=	.21243	RM(1)=	.66978	PM(10)=	109.92869	Y(1)=	.54632
X(2)=	.02266	RM(2)=	.07144	PM(11)=	3.15301	Y(2)=	.15859
X(3)=	.37190	RM(3)=	1.17261	PM(12)=	.16021	Y(3)=	.26930
X(4)=	0.00000	RM(4)=	0.00000	PM(13)=	.68181	Y(4)=	.01435
X(5)=	.00417	RM(5)=	.01314	PM(14)=	.59712	Y(5)=	.01137
X(6)=	.09999	RM(6)=	.31527	PM(15)=	.46277	VRATE=	.02150
X(7)=	.06651	RM(7)=	.20972	PM(16)=	.03080	SUMY=	.99991
X(8)=	.22234	RM(8)=	.70105	PM(17)=	.01935	DY1=	-.00076
X(9)=	0.00000	RM(9)=	0.00000	PM(18)=	1.78840	DY=	-.00009
HINT =	202.501	HOUT0=	265.682	WLOSS=	-.651	HRXNS=	54.187
						HQMDT=	-3.753
						WQMDT=	-4.591

INITIAL CONDITIONS BASED ON ADJUSTED TIME

X(1)= .12448	RM(1)= .33481	RM(10)= 120.77000	Y(1)= .13740
X(2)= .04719	RM(2)= .12643	RM(11)= 2.68972	Y(2)= .66852
X(3)= .35005	RM(3)= .94154	RM(12)= .16484	Y(3)= .15404
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .05261	Y(4)= .01935
X(5)= .00180	RM(5)= .00484	RM(14)= .15498	Y(5)= .02048
X(6)= .26563	RM(6)= .71446	RM(15)= .10437	VPATE= .01650
X(7)= .10397	RM(7)= .27964	RM(16)= .00421	SUMY= 1.00000
X(8)= .10449	RM(8)= .28751	RM(17)= .00077	DY1= 0.00000
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= .31693	DY= 0.00000

TIME= 4.00 MINUTES

NUMBER OF ITERATIONS= 9

X(1)= .13216	RM(1)= .36016	RM(10)= 119.34712	Y(1)= .25495
X(2)= .04363	RM(2)= .11991	RM(11)= 2.72522	Y(2)= .44905
X(3)= .35151	RM(3)= .95795	RM(12)= .16408	Y(3)= .25323
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .07529	Y(4)= .02211
X(5)= .00242	RM(5)= .00659	RM(14)= .14706	Y(5)= .01059
X(6)= .24870	RM(6)= .67775	RM(15)= .12706	VPATE= .01637
X(7)= .10261	RM(7)= .27964	RM(16)= .00581	SUMY= .49993
X(8)= .11997	RM(8)= .32422	RM(17)= .00165	DY1= -.00040
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= .40535	DY= -.00007
HINT = 320.473	HOUT0= 209.828	HLOSS= 253.369	HRXNS= 170.368
			RDMDT= 14.766
			MDMDT= 12.879

TIME= 8.00 MINUTES

NUMBER OF ITERATIONS= 8

X(1)= .14012	RM(1)= .38778	RM(10)= 118.70994	Y(1)= .29509
X(2)= .04124	RM(2)= .11413	RM(11)= 2.76734	Y(2)= .41699
X(3)= .35259	RM(3)= .97575	RM(12)= .16403	Y(3)= .25714
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .09880	Y(4)= .01876
X(5)= .00293	RM(5)= .00812	RM(14)= .23312	Y(5)= .01197
X(6)= .23271	RM(6)= .64400	RM(15)= .14837	VPATE= .02023
X(7)= .10105	RM(7)= .27964	RM(16)= .00739	SUMY= .49995
X(8)= .12935	RM(8)= .35797	RM(17)= .00260	DY1= -.00058
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= .48948	DY= -.00005
HINT = 320.473	HOUT0= 257.953	HLOSS= 234.036	HRXNS= 161.055
			RDMDT= .267
			MDMDT= -10.728

TIME= 12.00 MINUTES

NUMBER OF ITERATIONS= 8

X(1)= .14749	RM(1)= .41385	RM(10)= 118.05045	Y(1)= .32305
X(2)= .03973	RM(2)= .10869	RM(11)= 2.80597	Y(2)= .34543
X(3)= .35367	RM(3)= .99239	RM(12)= .16385	Y(3)= .25016
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .12581	Y(4)= .01800
X(5)= .00336	RM(5)= .00943	RM(14)= .25794	Y(5)= .01292
X(6)= .21418	RM(6)= .61222	RM(15)= .17083	VPATE= .02170
X(7)= .09965	RM(7)= .27964	RM(16)= .00903	SUMY= .99997
X(8)= .13890	RM(8)= .38975	RM(17)= .00359	DY1= -.00015
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= .57525	DY= -.00003

TIME= 20.00 MINUTES NUMBER OF ITERATIONS= 7

X(1)= .15434	RM(1)= .43863	RM(10)= 117.44119	Y(1)= .34933
X(2)= .03628	RM(2)= .10312	RM(11)= 2.84208	Y(2)= .35650
X(3)= .35473	RM(3)= 1.00817	RM(12)= .16362	Y(3)= .26276
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .15603	Y(4)= .01771
X(5)= .00371	RM(5)= .01055	RM(14)= .30109	Y(5)= .01357
X(6)= .20489	RM(6)= .58232	RM(15)= .19430	VRATE= .02250
X(7)= .02839	RM(7)= .27964	RM(16)= .01072	SUMY= .99996
X(8)= .14765	RM(8)= .41965	RM(17)= .00485	DY1= -.00010
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= .66558	DY= -.00002

HINT = 320.473 HOUTO= 284.998 HLOSS= 199.108 HPRXNS= 142.643 HMDT= -4.551 MDHDT= -16.439

TIME= 20.00 MINUTES NUMBER OF ITERATIONS= 7

X(1)= .16070	RM(1)= .46219	RM(10)= 116.86184	Y(1)= .37393
X(2)= .03254	RM(2)= .09762	RM(11)= 2.87610	Y(2)= .32944
X(3)= .35875	RM(3)= 1.02318	RM(12)= .16337	Y(3)= .26505
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .18930	Y(4)= .01752
X(5)= .00400	RM(5)= .01150	RM(14)= .33246	Y(5)= .01402
X(6)= .19270	RM(6)= .55423	RM(15)= .21851	VRATE= .02309
X(7)= .09723	RM(7)= .27964	RM(16)= .01243	SUMY= .99995
X(8)= .15568	RM(8)= .44774	RM(17)= .00616	DY1= -.00044
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= .75710	DY= -.00005

HINT = 320.473 HOUTO= 291.610 HLOSS= 183.475 HPRXNS= 134.075 HMDT= -4.690 MDHDT= -15.849

TIME= 24.00 MINUTES NUMBER OF ITERATIONS= 7

X(1)= .16663	RM(1)= .48460	RM(10)= 116.31957	Y(1)= .39690
X(2)= .03173	RM(2)= .09229	RM(11)= 2.90828	Y(2)= .30434
X(3)= .35674	RM(3)= 1.03749	RM(12)= .16312	Y(3)= .26708
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .22550	Y(4)= .01732
X(5)= .00423	RM(5)= .01229	RM(14)= .36206	Y(5)= .01430
X(6)= .18150	RM(6)= .52784	RM(15)= .24343	VRATE= .02357
X(7)= .09615	RM(7)= .27964	RM(16)= .01417	SUMY= .99995
X(8)= .16303	RM(8)= .47413	RM(17)= .00749	DY1= -.00044
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= .85053	DY= -.00005

HINT = 320.473 HOUTO= 297.066 HLOSS= 168.887 HPRXNS= 125.978 HMDT= -4.527 MDHDT= -14.976

TIME= 28.00 MINUTES NUMBER OF ITERATIONS= 7

X(1)= .17214	RM(1)= .50587	RM(10)= 115.81073	Y(1)= .41825
X(2)= .02967	RM(2)= .08719	RM(11)= 2.93877	Y(2)= .28122
X(3)= .35769	RM(3)= 1.05116	RM(12)= .16288	Y(3)= .26849
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .25450	Y(4)= .01712
X(5)= .00440	RM(5)= .01294	RM(14)= .38992	Y(5)= .01447
X(6)= .17118	RM(6)= .50306	RM(15)= .26091	VRATE= .02401
X(7)= .09515	RM(7)= .27964	RM(16)= .01592	SUMY= .99995
X(8)= .16977	RM(8)= .49491	RM(17)= .00886	DY1= -.00045
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= .94575	DY= -.00005

HINT = 320.473 HOUTO= 301.896 HLOSS= 155.232 HPRXNS= 118.356 HMDT= -4.247 MDHDT= -14.052

X(3)= .35461	RM(3)= 1.06423	RM(12)= .16265	Y(3)= .27050
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .30617	Y(4)= .01689
X(5)= .00453	RM(5)= .01346	RM(14)= .41513	Y(5)= .01453
X(6)= .16167	RM(6)= .47978	RM(15)= .29520	VRATE= .02442
X(7)= .09423	RM(7)= .27964	RM(16)= .01768	SUMY= .94495
X(8)= .17596	RM(8)= .52219	RM(17)= .01027	RY1= -.00045
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= 1.04253	DY= -.00005
HINT= 320.473	HOUT0= 306.356	HLOSS= 142.429	HRXNS= 111.209
			HOMDT= -3.941
			WOMDT= -13.162

TIME= 36.00 MINUTES NUMBER OF ITERATIONS= 7

X(1)= .18197	RM(1)= .54493	RM(10)= 114.90041	Y(1)= .45630
X(2)= .02593	RM(2)= .07764	RM(11)= 2.99460	Y(2)= .24045
X(3)= .35051	RM(3)= 1.07658	RM(12)= .16239	Y(3)= .27206
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .35053	Y(4)= .01661
X(5)= .00462	RM(5)= .01385	RM(14)= .44088	Y(5)= .01453
X(6)= .15290	RM(6)= .45789	RM(15)= .32212	VRATE= .02490
X(7)= .09338	RM(7)= .27964	RM(16)= .01945	SUMY= .99996
X(8)= .18169	RM(8)= .54408	RM(17)= .01171	RY1= -.00044
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= 1.14162	DY= -.00004
HINT= 320.473	HOUT0= 311.862	HLOSS= 128.890	HRXNS= 104.683
			HOMDT= -4.052
			WOMDT= -11.543

TIME= 40.00 MINUTES NUMBER OF ITERATIONS= 7

X(1)= .18634	RM(1)= .56277	RM(10)= 114.48983	Y(1)= .47306
X(2)= .02425	RM(2)= .07325	RM(11)= 3.02014	Y(2)= .22263
X(3)= .36038	RM(3)= 1.08838	RM(12)= .16214	Y(3)= .27342
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .39749	Y(4)= .01638
X(5)= .00468	RM(5)= .01413	RM(14)= .46413	Y(5)= .01446
X(6)= .14479	RM(6)= .43728	RM(15)= .34958	VRATE= .02526
X(7)= .09259	RM(7)= .27964	RM(16)= .02122	SUMY= .99994
X(8)= .18607	RM(8)= .56469	RM(17)= .01317	RY1= -.00046
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= 1.24204	DY= -.00006
HINT= 320.473	HOUT0= 315.728	HLOSS= 118.104	HRXNS= 98.561
			HOMDT= -3.750
			WOMDT= -11.049

TIME= 44.00 MINUTES NUMBER OF ITERATIONS= 7

X(1)= .19040	RM(1)= .57956	RM(10)= 114.10126	Y(1)= .48946
X(2)= .02272	RM(2)= .06918	RM(11)= 3.04446	Y(2)= .20538
X(3)= .36121	RM(3)= 1.09970	RM(12)= .16191	Y(3)= .27453
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .44550	Y(4)= .01613
X(5)= .00470	RM(5)= .01431	RM(14)= .48595	Y(5)= .01435
X(6)= .13725	RM(6)= .41788	RM(15)= .37752	VRATE= .02559
X(7)= .09145	RM(7)= .27964	RM(16)= .02298	SUMY= .99996
X(8)= .19185	RM(8)= .58400	RM(17)= .01455	RY1= -.00046
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= 1.34376	DY= -.00006
HINT= 320.473	HOUT0= 319.321	HLOSS= 107.911	HRXNS= 92.824
			HOMDT= -3.453
			WOMDT= -10.482

TIME= 48.00 MINUTES NUMBER OF ITERATIONS= 7

X(6)= .13027	RM(6)= .39961	RM(15)= .40583	VPATE= .02590
Y(7)= .09116	RM(7)= .27464	RM(16)= .02475	SUMY= .99994
X(8)= .19436	RM(8)= .60236	RM(17)= .01512	DY1= -.00045
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= 1.44574	DY= -.00006
HINT = 320.473	HOUTO= 322.733	HLOSS= 98.242	42XNS= 87.465
			-DMDT= -3.187
			MDHDT= -9.889

TIME= 52.00 MINUTES NUMBER OF ITERATIONS= 7

X(1)= .19768	RM(1)= .61075	RM(10)= 113.38692	Y(1)= .51558
X(2)= .02002	RM(2)= .06187	RM(11)= 3.08960	Y(2)= .17805
X(3)= .36291	RM(3)= 1.12095	RM(12)= .16148	Y(3)= .27669
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .55110	Y(4)= .01563
X(5)= .00467	RM(5)= .01443	RM(14)= .52570	Y(5)= .01400
Y(6)= .12376	RM(6)= .38238	RM(15)= .43479	VPATE= .02620
X(7)= .04061	RM(7)= .27964	RM(16)= .02651	SUMY= .99994
X(8)= .20054	RM(8)= .61959	RM(17)= .01759	DY1= -.00045
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= 1.55094	DY= -.00006
HINT = 320.473	HOUTO= 326.012	HLOSS= 89.196	42XNS= 82.474
			-DMDT= -2.263
			MDHDT= -9.298

TIME= 56.00 MINUTES NUMBER OF ITERATIONS= 7

X(1)= .20004	RM(1)= .62502	RM(10)= 113.05989	Y(1)= .52748
X(2)= .01883	RM(2)= .05858	RM(11)= 3.11050	Y(2)= .16573
X(3)= .36354	RM(3)= 1.13092	RM(12)= .16128	Y(3)= .27758
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .60626	Y(4)= .01538
X(5)= .00462	RM(5)= .01437	RM(14)= .54382	Y(5)= .01378
X(6)= .11771	RM(6)= .36614	RM(15)= .46406	VPATE= .02649
X(7)= .04990	RM(7)= .27964	RM(16)= .02826	SUMY= .99995
X(8)= .20441	RM(8)= .63583	RM(17)= .01906	DY1= -.00046
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= 1.65632	DY= -.00005
HINT = 320.473	HOUTO= 329.173	HLOSS= 80.636	42XNS= 77.833
			-DMDT= -2.781
			MDHDT= -8.721

TIME= 60.00 MINUTES NUMBER OF ITERATIONS= 7

X(1)= .20397	RM(1)= .63848	RM(10)= 112.75200	Y(1)= .53830
X(2)= .01774	RM(2)= .05552	RM(11)= 3.13034	Y(2)= .15409
X(3)= .36433	RM(3)= 1.14047	RM(12)= .16109	Y(3)= .27840
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .66324	Y(4)= .01513
X(5)= .00455	RM(5)= .01425	RM(14)= .55088	Y(5)= .01354
X(6)= .11206	RM(6)= .35080	RM(15)= .49375	VPATE= .02676
X(7)= .08933	RM(7)= .27964	RM(16)= .03000	SUMY= .99995
X(8)= .20202	RM(8)= .65117	RM(17)= .02052	DY1= -.00045
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= 1.76282	DY= -.00005
HINT = 320.473	HOUTO= 332.217	HLOSS= 72.580	42XNS= 73.524
			-DMDT= -2.637
			MDHDT= -8.162

TIME= 64.00 MINUTES NUMBER OF ITERATIONS= 7

X(1)= .20678	RM(1)= .65117	RM(10)= 112.46249	Y(1)= .54839
X(2)= .01673	RM(2)= .05257	RM(11)= 3.14915	Y(2)= .14023
X(3)= .36505	RM(3)= 1.14962	RM(12)= .16090	Y(3)= .27917

Y(4) = 0.00000 RM(9) = 0.00000 PM(18) = 1.87040 DY = -0.00005
 HINT = 320.473 HOUTO = 335.141 HLOSS = 65.008 HRXNS = 69.525 HOMDT = -2.525 MOHDT = -7.626

TIME = 68.00 MINUTES NUMBER OF ITERATIONS = 7

X(1) = .20939	RM(1) = .66312	PM(10) = 112.19052	Y(1) = .55755
X(2) = .01579	RM(2) = .05001	PM(11) = 3.16098	Y(2) = .13485
X(3) = .36577	RM(3) = 1.15840	PM(12) = .16071	Y(3) = .27989
X(4) = 0.00000	RM(4) = 0.00000	PM(13) = .78220	Y(4) = .01454
X(5) = .00437	RM(5) = .01345	PM(14) = .59712	Y(5) = .01301
X(6) = .10186	RM(6) = .32259	PM(15) = .55426	VRATE = .02728
X(7) = .08837	RM(7) = .27964	PM(16) = .03344	SHMY = .99995
X(8) = .21452	RM(8) = .67938	PM(17) = .02340	DY1 = -.00046
X(9) = 0.00000	RM(9) = 0.00000	PM(18) = 1.97903	DY = -.00005

HINT = 320.473 HOUTO = 337.940 HLOSS = 57.898 HRXNS = 65.815 HOMDT = -2.438 MOHDT = -7.112

TIME = 72.00 MINUTES NUMBER OF ITERATIONS = 7

X(1) = .21180	RM(1) = .67436	PM(10) = 111.93526	Y(1) = .56594
X(2) = .01493	RM(2) = .04753	PM(11) = 3.18388	Y(2) = .12629
X(3) = .36647	RM(3) = 1.16680	PM(12) = .16052	Y(3) = .28058
X(4) = 0.00000	RM(4) = 0.00000	PM(13) = .84400	Y(4) = .01442
X(5) = .00427	RM(5) = .01358	PM(14) = .60644	Y(5) = .01272
X(6) = .09724	RM(6) = .30960	PM(15) = .58507	VRATE = .02752
X(7) = .08783	RM(7) = .27964	PM(16) = .03515	SHMY = .99995
X(8) = .21746	RM(8) = .69237	PM(17) = .02481	DY1 = -.00045
X(9) = 0.00000	RM(9) = 0.00000	PM(18) = 2.05854	DY = -.00005

HINT = 320.473 HOUTO = 340.610 HLOSS = 51.228 HRXNS = 62.371 HOMDT = -2.372 MOHDT = -6.622

TIME = 76.00 MINUTES NUMBER OF ITERATIONS = 7

X(1) = .21465	RM(1) = .68493	PM(10) = 111.69583	Y(1) = .57353
X(2) = .01413	RM(2) = .04522	PM(11) = 3.19988	Y(2) = .11846
X(3) = .36715	RM(3) = 1.17485	PM(12) = .16033	Y(3) = .28124
X(4) = 0.00000	RM(4) = 0.00000	PM(13) = .90722	Y(4) = .01420
X(5) = .00415	RM(5) = .01328	PM(14) = .61598	Y(5) = .01242
X(6) = .09261	RM(6) = .29729	PM(15) = .61621	VRATE = .02775
X(7) = .08739	RM(7) = .27964	PM(16) = .03645	SHMY = .99995
X(8) = .22622	RM(8) = .70468	PM(17) = .02520	DY1 = -.00045
X(9) = 0.00000	RM(9) = 0.00000	PM(18) = 2.19920	DY = -.00005

HINT = 320.473 HOUTO = 343.149 HLOSS = 44.974 HRXNS = 59.172 HOMDT = -2.322 MOHDT = -6.157

TIME = 80.00 MINUTES NUMBER OF ITERATIONS = 7

X(1) = .21613	RM(1) = .69486	PM(10) = 111.47134	Y(1) = .58069
X(2) = .01339	RM(2) = .04306	PM(11) = 3.21504	Y(2) = .11128
X(3) = .36722	RM(3) = 1.18257	PM(12) = .16014	Y(3) = .28187
X(4) = 0.00000	RM(4) = 0.00000	PM(13) = .97178	Y(4) = .01400
X(5) = .00403	RM(5) = .01294	PM(14) = .63246	Y(5) = .01211
X(6) = .09143	RM(6) = .28560	PM(15) = .64457	VRATE = .02777

TIME= 84.00 MINUTES NUMBER OF ITERATIONS= 7

X(1)= .21806	RM(1)= .70420	PM(10)= 111.26093	Y(1)= .58717
X(2)= .01271	RM(2)= .04104	PM(11)= 3.22939	Y(2)= .10470
X(3)= .36448	RM(3)= 1.18996	PM(12)= .15996	Y(3)= .28248
X(4)= 0.00000	RM(4)= 0.00000	PM(13)= 1.03759	Y(4)= .01381
X(5)= .00390	RM(5)= .01259	PM(14)= .64494	Y(5)= .01179
X(6)= .08500	RM(6)= .27449	PM(15)= .67945	VRATE= .02818
X(7)= .04659	RM(7)= .27964	PM(16)= .04021	SUMY= .99495
X(8)= .22527	RM(8)= .72748	PM(17)= .02892	DY1= -.00045
X(9)= 0.00000	RM(9)= 0.00000	PM(18)= 2.42297	DY= -.00005

HINT = 320.473 HOUTO= 347.832 HLOSS= 33.626 HRXNS= 53.431 HOMDT= -2.251 MDHDT= -5.302

TIME= 88.00 MINUTES NUMBER OF ITERATIONS= 7

X(1)= .21985	RM(1)= .71297	PM(10)= 111.06374	Y(1)= .59312
X(2)= .01207	RM(2)= .03915	PM(11)= 3.24298	Y(2)= .09866
X(3)= .36912	RM(3)= 1.19705	PM(12)= .15977	Y(3)= .28307
X(4)= 0.00000	RM(4)= 0.00000	PM(13)= 1.10457	Y(4)= .01363
X(5)= .00376	RM(5)= .01221	PM(14)= .65645	Y(5)= .01147
X(6)= .08138	RM(6)= .26392	PM(15)= .71153	VRATE= .02837
X(7)= .08423	RM(7)= .27964	PM(16)= .04187	SUMY= .99495
X(8)= .22758	RM(8)= .73805	PM(17)= .03024	DY1= -.00045
X(9)= 0.00000	RM(9)= 0.00000	PM(18)= 2.53608	DY= -.00005

HINT = 320.473 HOUTO= 349.977 HLOSS= 28.485 HRXNS= 50.852 HOMDT= -2.225 MDHDT= -4.912

TIME= 92.00 MINUTES NUMBER OF ITERATIONS= 7

X(1)= .22151	RM(1)= .72120	PM(10)= 110.87892	Y(1)= .59859
X(2)= .01148	PM(2)= .03738	PM(11)= 3.25585	Y(2)= .09311
X(3)= .36975	PM(3)= 1.20385	PM(12)= .15958	Y(3)= .28365
X(4)= 0.00000	RM(4)= 0.00000	PM(13)= 1.17266	Y(4)= .01346
X(5)= .00363	RM(5)= .01181	PM(14)= .66738	Y(5)= .01115
X(6)= .07797	RM(6)= .25386	PM(15)= .74388	VRATE= .02856
X(7)= .08589	RM(7)= .27964	PM(16)= .04353	SUMY= .99495
X(8)= .22977	RM(8)= .74811	PM(17)= .03153	DY1= -.00043
X(9)= 0.00000	RM(9)= 0.00000	PM(18)= 2.64995	DY= -.00005

HINT = 320.473 HOUTO= 351.995 HLOSS= 23.670 HRXNS= 48.445 HOMDT= -2.201 MDHDT= -4.546

INITIAL CONDITIONS BASED ON ADJUSTED TIME

X(1)= .11773	RM(1)= .30682	RM(10)= 115.71000	Y(1)= .10836
X(2)= .05622	RM(2)= .14651	RM(11)= 2.60603	Y(2)= .56238
X(3)= .33318	RM(3)= .86828	RM(12)= .16586	Y(3)= .29193
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .03278	Y(4)= .02487
X(5)= .00069	RM(5)= .00180	RM(14)= .08622	Y(5)= .01246
X(6)= .29384	RM(6)= .76575	RM(15)= .01058	VRATE= .02082
X(7)= .10434	RM(7)= .28234	RM(16)= .00346	SUMY= 1.00000
X(8)= .04099	RM(8)= .23453	RM(17)= 0.00000	DY1= 0.00000
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= .13304	DY= 0.00000

TIME= 4.00 MINUTES

NUMBER OF ITERATIONS= 4

X(1)= .12039	RM(1)= .32035	RM(10)= 118.03739	Y(1)= .19917
X(2)= .06066	RM(2)= .16141	RM(11)= 2.66098	Y(2)= .54059
X(3)= .33512	RM(3)= .89176	RM(12)= .16692	Y(3)= .21541
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .04287	Y(4)= .03630
X(5)= .00182	RM(5)= .00484	RM(14)= .11426	Y(5)= .00857
X(6)= .27037	RM(6)= .71944	RM(15)= .02166	VRATE= .01908
X(7)= .10611	RM(7)= .28234	RM(16)= .00615	SUMY= 1.00004
X(8)= .10554	RM(8)= .28084	RM(17)= .00033	DY1= .00188
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= .18675	DY= .00004

HINT = 296.337 HOUTO= 236.782 HLOSS= 301.731 HPRXNS= 241.395 HMDT= -21.723 WMDT= 20.943

TIME= 8.00 MINUTES

NUMBER OF ITERATIONS= 8

X(1)= .11938	RM(1)= .32043	RM(10)= 117.88885	Y(1)= .20154
X(2)= .06114	RM(2)= .16410	RM(11)= 2.68411	Y(2)= .53512
X(3)= .33463	RM(3)= .90892	RM(12)= .16522	Y(3)= .21744
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .05948	Y(4)= .03424
X(5)= .00299	RM(5)= .00803	RM(14)= .15893	Y(5)= .01157
X(6)= .24888	RM(6)= .66802	RM(15)= .03962	VRATE= .01987
X(7)= .10519	RM(7)= .28234	RM(16)= .00910	SUMY= .99972
X(8)= .12379	RM(8)= .33226	RM(17)= .00119	DY1= -.00026
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= .26944	DY= -.00002

HINT = 296.337 HOUTO= 255.523 HLOSS= 315.838 HPRXNS= 243.566 HMDT= -25.782 WMDT= -2.676

TIME= 12.00 MINUTES

NUMBER OF ITERATIONS= 8

X(1)= .12021	RM(1)= .32603	RM(10)= 117.53882	Y(1)= .20821
X(2)= .06115	RM(2)= .16583	RM(11)= 2.71210	Y(2)= .52363
X(3)= .34175	RM(3)= .92686	RM(12)= .16395	Y(3)= .21937
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .07553	Y(4)= .03546
X(5)= .00396	RM(5)= .01075	RM(14)= .20943	Y(5)= .01326
X(6)= .22901	RM(6)= .62109	RM(15)= .05674	VRATE= .01903
X(7)= .10411	RM(7)= .28234	RM(16)= .01261	SUMY= .99993
X(8)= .12062	RM(8)= .37920	RM(17)= .00214	DY1= -.00031
		RM(18)= .36370	DY= -.00007

TIME= 16.00 MINUTES NUMBER OF ITERATIONS= 8

X(1)= .12246	RM(1)= .33602	RM(10)= 117.09798	Y(1)= .21867
X(2)= .06090	RM(2)= .16684	RM(11)= 2.74404	Y(2)= .50867
X(3)= .34454	RM(3)= .94543	RM(12)= .16307	Y(3)= .22154
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .09149	Y(4)= .03672
X(5)= .00478	RM(5)= .01312	RM(14)= .23898	Y(5)= .01433
X(6)= .21048	RM(6)= .57812	RM(15)= .07321	VRATE= .01830
X(7)= .10240	RM(7)= .28234	RM(16)= .01489	SUMY= .99993
X(8)= .15385	RM(8)= .42216	RM(17)= .00322	DY1= -.00031
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= .42230	DY= -.00007

HINT = -246.337 HOUTO= 233.393 HLOSS= 293.333 HRXNS= 203.644 HDMOT= -15.786 MDHDT= -10.959

TIME= 20.00 MINUTES NUMBER OF ITERATIONS= 8

X(1)= .12573	RM(1)= .34931	RM(10)= 116.63312	Y(1)= .23220
X(2)= .06002	RM(2)= .16675	RM(11)= 2.77815	Y(2)= .49148
X(3)= .34708	RM(3)= .95425	RM(12)= .16242	Y(3)= .22412
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .10792	Y(4)= .03711
X(5)= .00548	RM(5)= .01522	RM(14)= .27535	Y(5)= .01507
X(6)= .19340	RM(6)= .53867	RM(15)= .08943	VRATE= .01825
X(7)= .10163	RM(7)= .28234	RM(16)= .01777	SUMY= .99494
X(8)= .16616	RM(8)= .46161	RM(17)= .00429	DY1= -.00014
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= .49498	DY= -.00002

HINT = -296.337 HOUTO= 232.245 HLOSS= 276.541 HRXNS= 187.466 HDMOT= -13.104 MDHDT= -11.889

TIME= 24.00 MINUTES NUMBER OF ITERATIONS= 8

X(1)= .12269	RM(1)= .36477	RM(10)= 116.12467	Y(1)= .24758
X(2)= .05875	RM(2)= .16524	RM(11)= 2.81266	Y(2)= .47210
X(3)= .34947	RM(3)= .98295	RM(12)= .16187	Y(3)= .22472
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .12538	Y(4)= .03796
X(5)= .00607	RM(5)= .01708	RM(14)= .31028	Y(5)= .01554
X(6)= .17858	RM(6)= .50228	RM(15)= .10580	VRATE= .01801
X(7)= .10038	RM(7)= .28234	RM(16)= .02067	SUMY= .99493
X(8)= .17706	RM(8)= .49801	RM(17)= .00541	DY1= -.00030
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= .56746	DY= -.00007

HINT = -296.337 HOUTO= 228.611 HLOSS= 263.452 HRXNS= 172.892 HDMOT= -9.548 MDHDT= -13.146

TIME= 28.00 MINUTES NUMBER OF ITERATIONS= 8

X(1)= .13420	RM(1)= .38219	RM(10)= 115.59411	Y(1)= .26453
X(2)= .05717	RM(2)= .16281	RM(11)= 2.84798	Y(2)= .45149
X(3)= .35170	RM(3)= 1.00163	RM(12)= .16146	Y(3)= .22939
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .14385	Y(4)= .03455
X(5)= .00658	RM(5)= .01873	RM(14)= .34347	Y(5)= .01592
X(6)= .16458	RM(6)= .46873	RM(15)= .12221	VRATE= .01743
X(7)= .09914	RM(7)= .28234	RM(16)= .02361	SUMY= .99493
X(8)= .14664	RM(8)= .53155	RM(17)= .00654	DY1= -.00030
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= .62930	DY= -.00007

HINT = -296.337 HOUTO= 227.131 HLOSS= 247.691 HRXNS= 159.450 HDMOT= -7.122 MDHDT= -13.913

X(3)= .35979	RM(3)= 1.02016	RM(12)= .16115	Y(3)= .23197
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .16359	Y(4)= .03889
X(5)= .00700	RM(5)= .02018	RM(14)= .37512	Y(5)= .01615
X(6)= .15143	RM(6)= .43780	RM(15)= .13881	VRATE= .01799
X(7)= .09792	RM(7)= .28234	RM(16)= .02657	SUMY= .99994
X(8)= .14507	RM(8)= .56248	RM(17)= .00779	DY1= -.00030
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= .71112	DY= -.00006

HINT = 296.337 HOUT0 = 227.239 HLOSS = 235.689 HRXNS = 147.137 HQMDT = -5.203 MQHDT = -14.251

TIME= 36.00 MINUTES

NUMBER OF ITERATIONS= 8

X(1)= .14422	RM(1)= .42095	RM(10)= 114.51532	Y(1)= .30199
X(2)= .05321	RM(2)= .15531	RM(11)= 2.91879	Y(2)= .40814
X(3)= .35578	RM(3)= 1.03844	RM(12)= .16090	Y(3)= .23457
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .18479	Y(4)= .03905
X(5)= .00735	RM(5)= .02146	RM(14)= .40538	Y(5)= .01629
X(6)= .14021	RM(6)= .40925	RM(15)= .15569	VRATE= .01813
X(7)= .09673	RM(7)= .28234	RM(16)= .02957	SUMY= .99994
X(8)= .20249	RM(8)= .59103	RM(17)= .00887	DY1= -.00029
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= .78334	DY= -.00006

HINT = 296.337 HOUT0 = 228.519 HLOSS = 221.715 HRXNS = 135.865 HQMDT = -3.772 MQHDT = -14.261

TIME= 40.00 MINUTES

NUMBER OF ITERATIONS= 8

X(1)= .14948	RM(1)= .44148	RM(10)= 113.98669	Y(1)= .32134
X(2)= .05093	RM(2)= .15041	RM(11)= 2.95349	Y(2)= .38606
X(3)= .35768	RM(3)= 1.05639	RM(12)= .16069	Y(3)= .23715
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .20762	Y(4)= .03904
X(5)= .00764	RM(5)= .02258	RM(14)= .43433	Y(5)= .01635
X(6)= .12964	RM(6)= .38289	RM(15)= .17293	VRATE= .01834
X(7)= .09560	RM(7)= .28234	RM(16)= .03261	SUMY= .99994
X(8)= .20904	RM(8)= .61739	RM(17)= .01007	DY1= -.00028
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= .85628	DY= -.00006

HINT = 296.337 HOUT0 = 230.631 HLOSS = 207.986 HRXNS = 125.560 HQMDT = -2.700 MQHDT = -14.020

TIME= 44.00 MINUTES

NUMBER OF ITERATIONS= 8

X(1)= .15477	RM(1)= .46235	RM(10)= 113.47431	Y(1)= .34091
X(2)= .04451	RM(2)= .14491	RM(11)= 2.98739	Y(2)= .36407
X(3)= .35990	RM(3)= 1.07397	RM(12)= .16050	Y(3)= .23959
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .23219	Y(4)= .03893
X(5)= .00798	RM(5)= .02353	RM(14)= .46203	Y(5)= .01635
X(6)= .12002	RM(6)= .35853	RM(15)= .19058	VRATE= .01850
X(7)= .09451	RM(7)= .28234	RM(16)= .03568	SUMY= .99994
X(8)= .21482	RM(8)= .64175	RM(17)= .01128	DY1= -.00027
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= .93016	DY= -.00006

HINT = 296.337 HOUT0 = 233.308 HLOSS = 194.661 HRXNS = 116.147 HQMDT = -1.840 MQHDT = -13.596

TIME= 48.00 MINUTES

NUMBER OF ITERATIONS= 8

X(5)= .01124 RM(6)= .20854 RM(15)= .03878 VDATE= .01449
 X(7)= .04348 RM(7)= .24534 RM(16)= .03878 SUMY= .99994
 X(1)= .21994 RM(8)= .64429 RM(17)= .01250 DY1= -.00026
 X(9)= 0.00000 RM(9)= 0.00000 RM(18)= 1.00512 DY= -.00005
 HINT = 246.337 HOUTO= 236.346 HLOSS= 161.856 HRYNS= 107.555 HMDT= -1.266 MDHDT= -13.045

--TIME= 52.00 MINUTES-- NUMBER OF ITERATIONS= 8
 X(1)= .16514 RM(1)= .50405 RM(10)= 112.51390 Y(1)= .37943
 X(2)= .04347 RM(2)= .13267 RM(11)= 3.05220 Y(2)= .32118
 X(3)= .36295 RM(3)= 1.10784 RM(12)= .16016 Y(3)= .24465
 X(4)= 0.00000 RM(4)= 0.00000 RM(13)= .28686 Y(4)= .03848
 X(5)= .00820 RM(5)= .02501 RM(14)= .51373 Y(5)= .01621
 X(6)= .10324 RM(6)= .31512 RM(15)= .22725 VDATE= .01919
 X(7)= .00251 RM(7)= .28234 RM(16)= .04192 SUMY= .99994
 X(8)= .22448 RM(8)= .64416 RM(17)= .01375 DY1= -.00025
 X(9)= 0.00000 RM(9)= 0.00000 RM(18)= 1.08126 DY= -.00005
 HINT = 296.337 HOUTO= 239.591 HLOSS= 169.646 HRYNS= 99.711 HMDT= -.773 MDHDT= -12.416

--TIME= 56.00 MINUTES-- NUMBER OF ITERATIONS= 8
 X(1)= .17013 RM(1)= .52450 RM(10)= 112.06992 Y(1)= .39801
 X(2)= .04093 RM(2)= .12619 RM(11)= 3.08297 Y(2)= .30062
 X(3)= .35461 RM(3)= 1.12409 RM(12)= .16001 Y(3)= .24706
 X(4)= 0.00000 RM(4)= 0.00000 RM(13)= .31796 Y(4)= .03819
 X(5)= .00429 RM(5)= .02556 RM(14)= .53777 Y(5)= .01608
 X(6)= .09503 RM(6)= .29576 RM(15)= .24631 VDATE= .01949
 X(7)= .09158 RM(7)= .28234 RM(16)= .04508 SUMY= .99995
 X(8)= .22852 RM(8)= .70452 RM(17)= .01500 DY1= -.00024
 X(9)= 0.00000 RM(9)= 0.00000 RM(18)= 1.15862 DY= -.00005
 HINT = 296.337 HOUTO= 242.933 HLOSS= 154.069 HRYNS= 92.546 HMDT= -.374 MDHDT= -11.745

--TIME= 60.00 MINUTES-- NUMBER OF ITERATIONS= 8
 X(1)= .17492 RM(1)= .54447 RM(10)= 111.65089 Y(1)= .41595
 X(2)= .03944 RM(2)= .11954 RM(11)= 3.11261 Y(2)= .28080
 X(3)= .35621 RM(3)= 1.13988 RM(12)= .15946 Y(3)= .24940
 X(4)= 0.00000 RM(4)= 0.00000 RM(13)= .34817 Y(4)= .03787
 X(5)= .00435 RM(5)= .02599 RM(14)= .56059 Y(5)= .01593
 X(6)= .08925 RM(6)= .27779 RM(15)= .26586 VDATE= .01980
 X(7)= .09071 RM(7)= .24234 RM(16)= .04227 SUMY= .99995
 X(8)= .23212 RM(8)= .72249 RM(17)= .01626 DY1= -.00023
 X(9)= 0.00000 RM(9)= 0.00000 RM(18)= 1.23720 DY= -.00005
 HINT = 296.337 HOUTO= 246.294 HLOSS= 147.141 HRYNS= 85.994 HMDT= -.040 MDHDT= -11.063

--TIME= 64.00 MINUTES-- NUMBER OF ITERATIONS= 8
 X(1)= .17951 RM(1)= .56347 RM(10)= 111.25643 Y(1)= .43315
 X(2)= .03601 RM(2)= .11312 RM(11)= 3.14112 Y(2)= .26182
 X(3)= .35775 RM(3)= 1.15519 RM(12)= .15972 Y(3)= .25150
 X(4)= 0.00000 RM(4)= 0.00000 RM(13)= .36113 Y(4)= .03751

X(9)= 0.00000 RM(9)= 0.00000 PM(9)= 1.31707 DY= -0.00005
 HINT = 296.337 HOUTO= 249.624 HLOSS= 136.853 HRXNS= 79.994 HMDT= .245 MDHDT= -10.391

TIME= 68.00 MINUTES NUMBER OF ITERATIONS= 8

X(1)= .18308	RM(1)= .58261	PM(10)= 110.89564	Y(1)= .44955
X(2)= .03367	RM(2)= .10669	PM(11)= 3.15852	Y(2)= .24374
X(3)= .36927	RM(3)= 1.17004	PM(12)= .15959	Y(3)= .25390
X(4)= 0.00000	RM(4)= 0.00000	PM(13)= .41907	Y(4)= .03720
X(5)= .00238	RM(5)= .02655	PM(14)= .60269	Y(5)= .01555
X(6)= .07750	RM(6)= .24556	PM(15)= .30642	VRATE= .02040
X(7)= .00411	RM(7)= .28234	PM(16)= .05471	SUMY= .99995
X(8)= .23819	RM(8)= .75472	PM(17)= .01679	DY1= -.00021
X(9)= 0.00000	RM(9)= 0.00000	PM(18)= 1.39803	DY= -.00005

HINT = 296.337 HOUTO= 252.891 HLOSS= 127.185 HRXNS= 74.490 HMDT= .492 MDHDT= -9.742

TIME= 72.00 MINUTES NUMBER OF ITERATIONS= 8

X(1)= .16901	RM(1)= .60065	PM(10)= 110.53733	Y(1)= .46510
X(2)= .03144	RM(2)= .10044	PM(11)= 3.19482	Y(2)= .22661
X(3)= .37073	RM(3)= 1.18443	PM(12)= .15947	Y(3)= .25604
X(4)= 0.00000	RM(4)= 0.00000	PM(13)= .45630	Y(4)= .03685
X(5)= .00875	RM(5)= .02668	PM(14)= .62200	Y(5)= .01535
X(6)= .07214	RM(6)= .23110	PM(15)= .32742	VRATE= .02059
X(7)= .08234	RM(7)= .28234	PM(16)= .05796	SUMY= .99995
X(8)= .24075	RM(8)= .76918	PM(17)= .02007	DY1= -.00020
X(9)= 0.00000	RM(9)= 0.00000	PM(18)= 1.49023	DY= -.00005

HINT = 296.337 HOUTO= 256.078 HLOSS= 118.108 HRXNS= 69.433 HMDT= .709 MDHDT= -9.125

TIME= 76.00 MINUTES NUMBER OF ITERATIONS= 8

X(1)= .19190	RM(1)= .61794	PM(10)= 110.21013	Y(1)= .47978
X(2)= .02932	RM(2)= .09440	PM(11)= 3.22005	Y(2)= .21045
X(3)= .37215	RM(3)= 1.19835	PM(12)= .15935	Y(3)= .25811
X(4)= 0.00000	RM(4)= 0.00000	PM(13)= .49631	Y(4)= .02630
X(5)= .00839	RM(5)= .02673	PM(14)= .64019	Y(5)= .01513
X(6)= .06754	RM(6)= .21762	PM(15)= .34850	VRATE= .02055
X(7)= .08714	RM(7)= .28234	PM(16)= .06122	SUMY= .99995
X(8)= .24306	RM(8)= .78266	PM(17)= .02134	DY1= -.00019
X(9)= 0.00000	RM(9)= 0.00000	PM(18)= 1.56387	DY= -.00004

HINT = 296.337 HOUTO= 259.175 HLOSS= 102.586 HRXNS= 64.778 HMDT= .898 MDHDT= -8.544

TIME= 80.00 MINUTES NUMBER OF ITERATIONS= 8

X(1)= .19557	RM(1)= .63447	PM(10)= 109.90266	Y(1)= .49357
X(2)= .02731	RM(2)= .08861	PM(11)= 3.24425	Y(2)= .19526
X(3)= .37353	RM(3)= 1.21184	PM(12)= .15924	Y(3)= .26009
X(4)= 0.00000	RM(4)= 0.00000	PM(13)= .53756	Y(4)= .03613
X(5)= .00853	RM(5)= .02671	PM(14)= .68750	Y(5)= .01450
X(6)= .06320	RM(6)= .21505	PM(15)= .35073	VRATE= .02125
X(7)= .08714	RM(7)= .28234	PM(16)= .05550	SUMY= .99995
X(8)= .24306	RM(8)= .78266	PM(17)= .02134	DY1= -.00019
X(9)= 0.00000	RM(9)= 0.00000	PM(18)= 1.64023	DY= -.00004

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TIME= 84.00 MINUTES

NUMBER OF ITERATIONS= 8

X(1)= .19900	RM(1)= .65022	RM(10)= 109.61354	Y(1)= .50649
X(2)= .02543	RM(2)= .08310	RM(11)= 3.26745	Y(2)= .18106
X(3)= .37487	RM(3)= 1.22488	RM(12)= .15914	Y(3)= .26198
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .58047	Y(4)= .03576
X(5)= .00915	RM(5)= .02662	RM(14)= .67338	Y(5)= .01467
X(6)= .05916	RM(6)= .19331	RM(15)= .39320	VRATE= .02151
X(7)= .08641	RM(7)= .28234	RM(16)= .06778	SUMY= .99996
X(8)= .24647	RM(8)= .80697	RM(17)= .02384	OY1= -.00014
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= 1.73354	OY= -.00004
HINT = 256.337	HOUTO= 265.091	HLOSS= 94.064	HDXNS= 56.523
		HDMOT= 1.199	MDHDT= -7.495

TIME= 88.00 MINUTES

NUMBER OF ITERATIONS= 8

X(1)= .20221	RM(1)= .66520	RM(10)= 109.34149	Y(1)= .51855
X(2)= .02347	RM(2)= .07788	RM(11)= 3.28966	Y(2)= .16740
X(3)= .37618	RM(3)= 1.23750	RM(12)= .15905	Y(3)= .26380
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .62498	Y(4)= .03539
X(5)= .00404	RM(5)= .02646	RM(14)= .68846	Y(5)= .01442
X(6)= .05543	RM(6)= .18234	RM(15)= .41601	VRATE= .02177
X(7)= .08583	RM(7)= .28234	RM(16)= .07108	SUMY= .99996
X(8)= .24864	RM(8)= .81794	RM(17)= .02514	OY1= -.00017
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= 1.82010	OY= -.00004
HINT = 296.337	HOUTO= 267.913	HLOSS= 86.994	HDXNS= 52.860
		HDMOT= 1.313	MDHDT= -7.023

TIME= 92.00 MINUTES

NUMBER OF ITERATIONS= 8

X(1)= .20520	RM(1)= .67942	RM(10)= 109.08530	Y(1)= .52977
X(2)= .02203	RM(2)= .07295	RM(11)= 3.31094	Y(2)= .15547
X(3)= .37745	RM(3)= 1.24970	RM(12)= .15897	Y(3)= .26553
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .67103	Y(4)= .03501
X(5)= .00793	RM(5)= .02624	RM(14)= .70260	Y(5)= .01418
X(6)= .05198	RM(6)= .17209	RM(15)= .43924	VRATE= .02202
X(7)= .08528	RM(7)= .28234	RM(16)= .07437	SUMY= .99996
X(8)= .25014	RM(8)= .82819	RM(17)= .02639	OY1= -.00016
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= 1.90787	OY= -.00004
HINT = 256.337	HOUTO= 270.647	HLOSS= 80.340	HDXNS= 49.471
		HDMOT= 1.406	MDHDT= -6.582

TIME= 96.00 MINUTES

NUMBER OF ITERATIONS= 8

X(1)= .20799	RM(1)= .69289	RM(10)= 108.84390	Y(1)= .54019
X(2)= .02051	RM(2)= .06832	RM(11)= 3.33130	Y(2)= .14604
X(3)= .37848	RM(3)= 1.26142	RM(12)= .15889	Y(3)= .26718
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .71855	Y(4)= .03463
X(5)= .00780	RM(5)= .02597	RM(14)= .71886	Y(5)= .01393
X(6)= .04878	RM(6)= .16250	RM(15)= .46248	VRATE= .02225
X(7)= .08475	RM(7)= .28234	RM(16)= .07767	SUMY= .99997
X(8)= .25169	RM(8)= .83778	RM(17)= .02764	OY1= -.00015
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= 1.99121	OY= -.00003
HINT = 256.337	HOUTO= 273.294	HLOSS= 71.076	HDXNS= 46.332
		HDMOT= 1.472	MDHDT= -6.171

INITIAL CONDITIONS BASED ON ADJUSTED TIME

X(1)= .15837	RM(1)= .44740	PM(10)= 110.80000	Y(1)= .25624
X(2)= .05435	RM(2)= .15356	PM(11)= 2.42511	Y(2)= .56995
X(3)= .32973	RM(3)= .92869	PM(12)= .17550	Y(3)= .15032
X(4)= 0.00000	RM(4)= 0.00000	PM(13)= .04207	Y(4)= .01111
X(5)= .00094	RM(5)= .00264	PM(14)= .12265	Y(5)= .01237
X(6)= .25724	RM(6)= .72672	PM(15)= .06848	VRATE= .01750
X(7)= .10146	RM(7)= .28663	PM(16)= .00251	SUMY= 1.00000
X(8)= .09402	RM(8)= .27947	PM(17)= .00062	DY1= 0.00000
X(9)= 0.00000	RM(9)= 0.00000	PM(18)= .23642	DY= 0.00000

TIME= 4.00 MINUTES

NUMBER OF ITERATIONS= 10

X(1)= .16600	RM(1)= .48561	PM(10)= 111.84853	Y(1)= .31092
X(2)= .06259	RM(2)= .18349	PM(11)= 2.93146	Y(2)= .40906
X(3)= .32867	RM(3)= .96349	PM(12)= .18039	Y(3)= .20009
X(4)= 0.00000	RM(4)= 0.00000	PM(13)= .04913	Y(4)= .07189
X(5)= .00172	RM(5)= .00505	PM(14)= .13240	Y(5)= .00798
X(6)= .23350	RM(6)= .68449	PM(15)= .07376	VRATE= .00390
X(7)= .09778	RM(7)= .28663	PM(16)= .00431	SUMY= .99994
X(8)= .10074	RM(8)= .32170	PM(17)= .00077	DY1= -.00023
X(9)= 0.00000	RM(9)= 0.00000	PM(18)= .26181	DY= -.00006
HINT = 45.057	HOUT0= 46.754	HLOSS= 151.781	HMXNS= 214.124
			HOMDT= 63.655
			MOHDT= 46.992

TIME= 8.00 MINUTES

NUMBER OF ITERATIONS= 6

X(1)= .17018	RM(1)= .51503	PM(10)= 111.98112	Y(1)= .33698
X(2)= .07072	RM(2)= .21403	PM(11)= 3.02635	Y(2)= .42230
X(3)= .32929	RM(3)= .99656	PM(12)= .18450	Y(3)= .20442
X(4)= 0.00000	RM(4)= 0.00000	PM(13)= .06014	Y(4)= .02545
X(5)= .00262	RM(5)= .00792	PM(14)= .14646	Y(5)= .01080
X(6)= .21038	RM(6)= .63669	PM(15)= .08059	VRATE= .01233
X(7)= .09471	RM(7)= .28663	PM(16)= .00550	SUMY= .99995
X(8)= .12209	RM(8)= .36950	PM(17)= .00110	DY1= -.00029
X(9)= 0.00000	RM(9)= 0.00000	PM(18)= .29525	DY= -.00005
HINT = 95.057	HOUT0= 154.147	HLOSS= 174.221	HMXNS= 228.546
			HOMDT= 27.557
			MOHDT= -32.321

TIME= 12.00 MINUTES

NUMBER OF ITERATIONS= 8

X(1)= .17506	RM(1)= .54401	PM(10)= 110.80169	Y(1)= .35137
X(2)= .07523	RM(2)= .23379	PM(11)= 3.10761	Y(2)= .41095
X(3)= .33042	RM(3)= 1.02681	PM(12)= .18745	Y(3)= .20099
X(4)= 0.00000	RM(4)= 0.00000	PM(13)= .07548	Y(4)= .02459
X(5)= .00328	RM(5)= .01019	PM(14)= .16624	Y(5)= .01197
X(6)= .19125	RM(6)= .59433	PM(15)= .09020	VRATE= .01151
X(7)= .09223	RM(7)= .28663	PM(16)= .00677	SUMY= .99997
X(8)= .13252	RM(8)= .41186	PM(17)= .00164	DY1= -.00018
X(9)= 0.00000	RM(9)= 0.00000	PM(18)= .30264	DY= -.00003

TIME= 16.00 MINUTES NUMBER OF ITERATIONS= 8

X(1)= .18170	RM(1)= .57976	RM(10)= 109.67272	Y(1)= .37072
X(2)= .07797	RM(2)= .24879	RM(11)= 3.19068	Y(2)= .39524
X(3)= .33139	RM(3)= 1.05736	RM(12)= .19053	Y(3)= .19479
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .09317	Y(4)= .02259
X(5)= .00375	RM(5)= .01196	RM(14)= .18462	Y(5)= .01254
X(6)= .17502	RM(6)= .55842	RM(15)= .09941	VRATE= .01153
X(7)= .08043	RM(7)= .28663	RM(16)= .00793	SUMY= .99997
X(8)= .14134	RM(8)= .44777	RM(17)= .00221	OY1= -.00015
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= .38876	OY= -.00003

TIME= 16.057 HOUTO= 145.686 HLOSS= 114.252 HPRXNS= 166.222 HMDT= 35.073 MDHDT= -34.731

TIME= 20.00 MINUTES NUMBER OF ITERATIONS= 8

X(1)= .18925	RM(1)= .61930	RM(10)= 108.61203	Y(1)= .39212
X(2)= .07926	RM(2)= .25938	RM(11)= 3.27243	Y(2)= .37744
X(3)= .33235	RM(3)= 1.06759	RM(12)= .19353	Y(3)= .19742
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .11145	Y(4)= .02021
X(5)= .00408	RM(5)= .01334	RM(14)= .20325	Y(5)= .01278
X(6)= .16116	RM(6)= .52740	RM(15)= .10888	VRATE= .01231
X(7)= .08759	RM(7)= .28663	RM(16)= .00901	SUMY= .99997
X(8)= .14631	RM(8)= .47880	RM(17)= .00282	OY1= -.00015
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= .43552	OY= -.00003

TIME= 20.057 HOUTO= 153.872 HLOSS= 83.743 HPRXNS= 144.290 HMDT= 35.505 MDHDT= -33.773

TIME= 24.00 MINUTES NUMBER OF ITERATIONS= 8

X(1)= .19714	RM(1)= .66062	RM(10)= 107.62619	Y(1)= .41397
X(2)= .07939	RM(2)= .26604	RM(11)= 3.35103	Y(2)= .35883
X(3)= .33337	RM(3)= 1.11714	RM(12)= .19630	Y(3)= .19654
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .13215	Y(4)= .01782
X(5)= .00430	RM(5)= .01441	RM(14)= .22206	Y(5)= .01282
X(6)= .14927	RM(6)= .50020	RM(15)= .11896	VRATE= .01330
X(7)= .08553	RM(7)= .28663	RM(16)= .01003	SUMY= .99998
X(8)= .15100	RM(8)= .50599	RM(17)= .00348	OY1= -.00013
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= .48768	OY= -.00002

TIME= 24.057 HOUTO= 165.891 HLOSS= 54.909 HPRXNS= 126.979 HMDT= 33.410 MDHDT= -32.174

TIME= 28.00 MINUTES NUMBER OF ITERATIONS= 8

X(1)= .20504	RM(1)= .70237	RM(10)= 106.71967	Y(1)= .43501
X(2)= .07962	RM(2)= .26930	RM(11)= 3.42554	Y(2)= .34016
X(3)= .33459	RM(3)= 1.14583	RM(12)= .19879	Y(3)= .19534
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .15577	Y(4)= .01575
X(5)= .00444	RM(5)= .01522	RM(14)= .24142	Y(5)= .01273
X(6)= .13898	RM(6)= .47507	RM(15)= .12947	VRATE= .01443
X(7)= .08367	RM(7)= .28663	RM(16)= .01109	SUMY= .99998
X(8)= .15476	RM(8)= .53012	RM(17)= .00418	OY1= -.00011
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= .54312	OY= -.00002

TIME= 28.057 HOUTO= 179.702 HLOSS= 27.945 HPRXNS= 113.046 HMDT= 30.584 MDHDT= -30.126

X(3)= .33573	RM(3)= 1.17357	RM(12)= .20597	Y(3)= .19643
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .18264	Y(4)= .01402
X(5)= .00452	RM(5)= .01542	RM(14)= .26129	Y(5)= .01254
X(6)= .13000	RM(6)= .45443	RM(15)= .14169	VRATE= .01565
X(7)= .06200	RM(7)= .28563	RM(16)= .01194	SHMY= .99990
X(8)= .15785	RM(8)= .55176	RM(17)= .00495	DY1= -.00056
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= .60325	DY= -.00010
HINT = 95.057	HOUTO= 194.490	HLOSS= 2.911	H2XNS= 101.684
			HMDT= 27.366
			MDHDT= -28.026

TIME= 36.00 MINUTES

NUMBER OF ITERATIONS= 6

X(1)= .22010	RM(1)= .78377	RM(10)= 105.14541	Y(1)= .47378
X(2)= .07521	RM(2)= .26793	RM(11)= 3.56100	Y(2)= .30428
X(3)= .33708	RM(3)= 1.20035	RM(12)= .20287	Y(3)= .19687
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .21281	Y(4)= .01271
X(5)= .00456	RM(5)= .01624	RM(14)= .28154	Y(5)= .01225
X(6)= .12211	RM(6)= .43484	RM(15)= .15444	VRATE= .01675
X(7)= .08049	RM(7)= .28663	RM(16)= .01286	SHMY= .99992
X(8)= .16045	RM(8)= .57135	RM(17)= .00575	DY1= -.00052
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= .66800	DY= -.00008
HINT = 95.057	HOUTO= 207.760	HLOSS= -19.490	H2XNS= 92.299
			HMDT= 24.547
			MDHDT= -25.461

TIME= 40.00 MINUTES

NUMBER OF ITERATIONS= 6

X(1)= .22706	RM(1)= .82246	RM(10)= 104.47341	Y(1)= .49118
X(2)= .07293	RM(2)= .26415	RM(11)= 3.62212	Y(2)= .28752
X(3)= .33853	RM(3)= 1.22619	RM(12)= .20451	Y(3)= .19761
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .24532	Y(4)= .01163
X(5)= .00456	RM(5)= .01652	RM(14)= .30199	Y(5)= .01199
X(6)= .11511	RM(6)= .41695	RM(15)= .16811	VRATE= .01785
X(7)= .07913	RM(7)= .28663	RM(16)= .01374	SHMY= .99993
X(8)= .16268	RM(8)= .58924	RM(17)= .00659	DY1= -.00049
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= .73720	DY= -.00007
HINT = 95.057	HOUTO= 220.949	HLOSS= -40.008	H2XNS= 84.507
			HMDT= 21.720
			MDHDT= -23.097

TIME= 44.00 MINUTES

NUMBER OF ITERATIONS= 6

X(1)= .23359	RM(1)= .85939	RM(10)= 103.87153	Y(1)= .50726
X(2)= .07042	RM(2)= .25906	RM(11)= 3.67903	Y(2)= .27154
X(3)= .34006	RM(3)= 1.25109	RM(12)= .20589	Y(3)= .19550
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .28314	Y(4)= .01076
X(5)= .00453	RM(5)= .01667	RM(14)= .32251	Y(5)= .01168
X(6)= .10886	RM(6)= .40049	RM(15)= .18270	VRATE= .01849
X(7)= .07791	RM(7)= .28663	RM(16)= .01451	SHMY= .99994
X(8)= .16464	RM(8)= .60570	RM(17)= .00746	DY1= -.00047
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= .81070	DY= -.00006
HINT = 95.057	HOUTO= 233.495	HLOSS= -58.691	H2XNS= 77.960
			HMDT= 19.063
			MDHDT= -20.850

TIME= 48.00 MINUTES

NUMBER OF ITERATIONS= 6

477

X(1)= .10322	RM(6)= .38523	RM(15)= .19817	VRATE= .01947
X(7)= .07680	RM(7)= .28663	RM(16)= .01546	SUMY= .99995
X(8)= .16639	RM(8)= .62096	RM(17)= .00836	DY1= -.00045
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= .88825	DY= -.00005
HINT = 95.057	HOUT0= 245.179	HLOSS= -75.605	HRYNS= 72.404
			HDMDT= 16.643
			MDHDT= -18.755

TIME=52.00 MINUTES NUMBER OF ITERATIONS= 6

X(1)= .24528	RM(1)= .92744	RM(10)= 102.45313	Y(1)= .53570
X(2)= .06505	RM(2)= .24547	RM(11)= 3.78115	Y(2)= .24254
X(3)= .34334	RM(3)= 1.29821	RM(12)= .20802	Y(3)= .20122
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .36632	Y(4)= .00948
X(5)= .00442	RM(5)= .01671	RM(14)= .36324	Y(5)= .01102
X(6)= .09812	RM(6)= .37100	RM(15)= .21451	VRATE= .02077
X(7)= .07580	RM(7)= .28663	RM(16)= .01631	SUMY= .99995
X(8)= .16749	RM(8)= .63519	RM(17)= .00927	DY1= -.00044
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= .96956	DY= -.00004
HINT = 95.057	HOUT0= 255.914	HLOSS= -90.864	HRYNS= 67.639
			HDMDT= 14.484
			MDHDT= -16.837

TIME=56.00 MINUTES NUMBER OF ITERATIONS= 6

X(1)= .25046	RM(1)= .95850	RM(10)= 102.42329	Y(1)= .54824
X(2)= .06232	RM(2)= .23850	RM(11)= 3.82695	Y(2)= .22925
X(3)= .34505	RM(3)= 1.32051	RM(12)= .20881	Y(3)= .20276
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .41240	Y(4)= .00902
X(5)= .00435	RM(5)= .01663	RM(14)= .38321	Y(5)= .01068
X(6)= .09346	RM(6)= .35766	RM(15)= .23166	VRATE= .02150
X(7)= .07490	RM(7)= .28663	RM(16)= .01714	SUMY= .99995
X(8)= .16946	RM(8)= .64853	RM(17)= .01019	DY1= -.00043
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= 1.05432	DY= -.00004
HINT = 95.057	HOUT0= 265.692	HLOSS= -104.602	HRYNS= 63.510
			HDMDT= 12.584
			MDHDT= -15.107

TIME=60.00 MINUTES NUMBER OF ITERATIONS= 2

X(1)= .25523	RM(1)= .98765	RM(10)= 102.04090	Y(1)= .55944
X(2)= .05962	RM(2)= .23070	RM(11)= 3.86970	Y(2)= .21681
X(3)= .34690	RM(3)= 1.34202	RM(12)= .20947	Y(3)= .20444
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .46121	Y(4)= .00859
X(5)= .00426	RM(5)= .01650	RM(14)= .40279	Y(5)= .01035
X(6)= .08918	RM(6)= .34508	RM(15)= .24050	VRATE= .02248
X(7)= .07407	RM(7)= .28663	RM(16)= .01707	SUMY= 1.00002
X(8)= .17044	RM(8)= .66111	RM(17)= .01111	DY1= -.01885
X(9)= 0.00000	RM(9)= 0.00000	RM(18)= 1.14035	DY= .00002
HINT = 95.057	HOUT0= 276.240	HLOSS= -117.004	HRYNS= 59.883
			HDMDT= 10.473
			MDHDT= -14.769

TIME=64.00 MINUTES NUMBER OF ITERATIONS= 7

X(1)= .25960	RM(1)= 1.01492	RM(10)= 101.69270	Y(1)= .57042
X(2)= .05696	RM(2)= .22270	RM(11)= 3.89854	Y(2)= .20507
X(3)= .34350	RM(3)= 1.36278	RM(12)= .20990	Y(3)= .20616
X(4)= 0.00000	RM(4)= 0.00000	RM(13)= .51336	Y(4)= .00831

X(9)= 0.00000 RM(9)= 0.00000 PM(9)= 1.23313 DY= -0.00002
 HINT = 95.057 HOUT0= 293.085 HLOSS= -129.091 HRYNS= 56.692 HMDT= 9.355 MDHDT= -12.600

TIME= 68.00 MINUTES NUMBER OF ITERATIONS= 7

X(1)= .26361	RM(1)= 1.04045	PM(10)= 101.38041	Y(1)= .58021
X(2)= .05438	RM(2)= .21464	PM(11)= 3.94687	Y(2)= .19406
X(3)= .35036	RM(3)= 1.38284	PM(12)= .21039	Y(3)= .20796
X(4)= 0.00000	RM(4)= 0.00000	PM(13)= .56652	Y(4)= .00805
X(5)= .00408	RM(5)= .01612	PM(14)= .44054	Y(5)= .00970
X(6)= .04157	RM(6)= .32194	PM(15)= .28763	VRATE= .02355
X(7)= .07252	RM(7)= .28663	PM(16)= .01955	SUMY= .94998
X(8)= .17337	RM(8)= .68425	PM(17)= .01296	DY1= -.00021
X(9)= 0.00000	RM(9)= 0.00000	PM(18)= 1.32646	DY= -.00002

HINT = 95.057 HOUT0= 299.973 HLOSS= -138.127 HRYNS= 53.833 HMDT= 8.212 MDHDT= -11.166

TIME= 72.00 MINUTES NUMBER OF ITERATIONS= 7

X(1)= .26729	RM(1)= 1.06432	PM(10)= 101.09809	Y(1)= .58925
X(2)= .04182	RM(2)= .20662	PM(11)= 3.98189	Y(2)= .18372
X(3)= .35216	RM(3)= 1.40224	PM(12)= .21071	Y(3)= .20980
X(4)= 0.00000	RM(4)= 0.00000	PM(13)= .62261	Y(4)= .00783
X(5)= .00399	RM(5)= .01588	PM(14)= .45859	Y(5)= .00938
X(6)= .07816	RM(6)= .31122	PM(15)= .30766	VRATE= .02420
X(7)= .07198	RM(7)= .28663	PM(16)= .02036	SUMY= .99948
X(8)= .17453	RM(8)= .69497	PM(17)= .01387	DY1= -.00021
X(9)= 0.00000	RM(9)= 0.00000	PM(18)= 1.42212	DY= -.00002

HINT = 95.057 HOUT0= 296.309 HLOSS= -147.200 HRYNS= 51.255 HMDT= 7.201 MDHDT= -9.997

TIME= 76.00 MINUTES NUMBER OF ITERATIONS= 7

X(1)= .27066	RM(1)= 1.08665	PM(10)= 100.84182	Y(1)= .59759
X(2)= .04949	RM(2)= .19871	PM(11)= 4.01482	Y(2)= .17401
X(3)= .35394	RM(3)= 1.42102	PM(12)= .21095	Y(3)= .21166
X(4)= 0.00000	RM(4)= 0.00000	PM(13)= .68079	Y(4)= .00765
X(5)= .00389	RM(5)= .01563	PM(14)= .47507	Y(5)= .00906
X(6)= .07497	RM(6)= .30101	PM(15)= .32831	VRATE= .02459
X(7)= .07139	RM(7)= .28663	PM(16)= .02117	SUMY= .99998
X(8)= .17565	RM(8)= .70519	PM(17)= .01478	DY1= -.00022
X(9)= 0.00000	RM(9)= 0.00000	PM(18)= 1.51988	DY= -.00002

HINT = 95.057 HOUT0= 302.072 HLOSS= -155.417 HRYNS= 48.912 HMDT= 6.326 MDHDT= -9.011

TIME= 80.00 MINUTES NUMBER OF ITERATIONS= 7

X(1)= .27374	RM(1)= 1.10753	PM(10)= 100.60828	Y(1)= .60530
X(2)= .04720	RM(2)= .19097	PM(11)= 4.04584	Y(2)= .16488
X(3)= .35572	RM(3)= 1.43920	PM(12)= .21113	Y(3)= .21353
X(4)= 0.00000	RM(4)= 0.00000	PM(13)= .74090	Y(4)= .00749
X(5)= .00381	RM(5)= .01537	PM(14)= .46294	Y(5)= .00878
X(6)= .07315	RM(6)= .30120	PM(15)= .34455	VRATE= .02514

```

PROGRAM CHEMACT(INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
COMMON K,N,MG,X(60,7),XLAMDA(5,5),NN,NCOMP,SUM(60,5),KK
COMMON /G1/ Y(240),YCAL(240),IBCODE(24),BMAX(24),BMIN(24),B(25),
1PHI,FNU,FLAMDA,TAU,EPSILN,PHIMIN,INDEX,KODE,ITER,STDEVS
DIMENSION DEV(240),TITLE(20)
READ(5,103) (TITLE(I),I=1,20)
103 FORMAT(20A4)
50 READ(5,9) K,N,IDUMMY,MG,NCOMP,NSET,KK
9 FORMAT(8I5)
NN=N*MG
DO 10 I=1,KK
BMAX(I)=10000.
10 BMIN(I)=0.
IF(KK.EQ.K) GO TO 60
KK)=KK+1
DO 31 I=KK1,K
BMIN(I)=-100.
31 BMAX(I)=1000.
60 READ(5,14) (B(I),I=1,K)
B(K+1)=0.
NCOMP1=NCOMP-1
70 DO 1000 I=1,N
000 READ(5,14) (X(I,J),J=1,NCOMP1),Y(I),Y(I+N),Y(I+2*N),Y(I+3*N)
DO 62 J=1,N
XS=0.
DO 83 J=1,NCOMP1
83 XS=XS+X(I,J)
62 X(I,NCOMP)=1.-XS
IF(IDUMMY.EQ.NCOMP) GO TO 80
NCOMP2=NCOMP+1
DO 63 J=NCOMP2,IDUMMY
63 READ(5,14) (X(I,J),I=1,N)
DO 64 I=1,N
DO 64 J=NCOMP2,IDUMMY
64 X(I,J)=X(I,J)+273.16
14 FORMAT(8F10.0)
80 DO 81 I=1,NN
81 Y(I)=ALOG(Y(I))
READ(5,14) STDEVS
FNU=0.
FLAMDA=0.
TAU=0.
EPSILN=0.
PHIMIN=0.
INDEX=0
DO 12 I=1,K
12 IBCODE(I)=-1
WRITE(6,100)
100 FORMAT(1H1///2X,5HINDEX,1X,4HKODE,8X,5HSTDEV,11X,2HB1,11X,2HB2,11X
1,2HB3,11X,2HB4,11X,2HB5,11X,2HB6,11X,2HB7/)
30 CALL RSOLVE
STDEV=SQRT(PHI/FL0AT(NN-1))
IF(INDEX.GE.NSET) KODE=-1
WRITE(6,102) INDEX,KODE,STDEV,(B(I),I=1,K)
102 FORMAT(2X,2I5,5F13.5,/, (25X,7F13.5))

```



```
IF(KODF) 40,40,27
27 IF(INDEX.LT.NSET) GO TO 30
40 DO 25 I=1,NN
   DEV(I)=YCAL(I)-Y(I)
25 CONTINUE
   WRITE(6,203) (TITLE(I),I=1,20)
203 FORMAT(1H1//1X,20A4)
   WRITE(6,104)
104 FORMAT(//1X,5HPOINT,9X,2HX1,9X,2HX2,9X,2HX3,9X,2HX4,9X,2HX5,
17X,4HTSYS,7X,4HTSUR/)
   WRITE(6,106) (I,(X(I,J),J=1,7),I=1,N)
106 FORMAT(1X,15,7F11.5)
   WRITE(6,120)
120 FORMAT(1H1///1X,5HPOINT,7X,4HLNG1,6X,5HLNGC1,8X,3HDEV,7X,4HLNG2,
16X,5HLNGC2,8X,3HDEV/)
   DO 92 I=1,N
     L1=I+N
92  WRITE(6,94) I, Y(I),YCAL(I),DEV(I),Y(L1),YCAL(L1),DEV(L1)
94  FORMAT(1X,15,6F11.5)
     WRITE(6,122)
122 FORMAT(1H1///1X,5HPOINT,7X,4HLNG3,6X,5HLNGC3,8X,3HDEV,7X,4HLNG4,
16X,5HLNGC4,8X,3HDEV/)
     DO 96 J=1,N
       L2=I+2*N
       L3=I+3*N
96  WRITE(6,94) I,Y(L2),YCAL(L2),DEV(L2),Y(L3),YCAL(L3),DEV(L3)
     DO 82 I=1,NN
       Y(I)=EXP(Y(I))
82  YCAL(I)=EXP(YCAL(I))
     WRITE(6,129)
129 FORMAT(1H1///1X,5HPOINT,9X,2HG1,8X,3HG1C,9X,2HG2,8X,3HG2C,9X,
12HG3,8X,3HG3C,9X,2HG4,8X,3HG4C/)
     DO 84 I=1,N
       L1=I+N
       L2=I+2*N
       L3=I+3*N
84  WRITE(6,90) I,Y(I),YCAL(I),Y(L1),YCAL(L1),Y(L2),YCAL(L2),Y(L3),
1YCAL(L3)
90  FORMAT(1X,15,8F11.5)
     WRITE(6,108) STDEV
108 FORMAT(1H1//20X,19HSTANDARD DEVIATION=,F10.5//20X,
116HFITTED CONSTANTS)
     WRITE(6,114) (I,B(I),I=1,K)
114 FORMAT(22X,2H8(,12,2H)=,E13.5)
77 READ(5,9) IDT
   GO TO (50,60,70,80,90),IDT
90 STOP
END
```

```

SUBROUTINE RSOLVE
COMMON K,NPOINT,MG,X(60,7),XLAMDA(5,5),N,NCOMP,SUM(60,5),KK
COMMON /G1/ Y(240),Z(240),IRCODE(24),RMAX(24),RMIN(24),B(25),
1PHI,FNU,FLAMDA,TAU,EPSILN,PHIMIN,INDEX,KODE,ITER,STDEVS
DIMENSION ZETA(240),ALPHA(24),AJACOB(240,24),G(24),A(24,24),
1OMEGA(24),ASCALE(24,25),DELTA(24)
KPI=K+1
IF(FLAMDA.LE.0.0) FLAMDA=0.01
IF(INDEX.GT.0) GO TO 300
IF(FNU.LE.0.0) FNU=10.0
IF(TAU.LE.0.0) TAU=0.001
IF(EPSILN.LE.0.0) EPSILN=0.00002
IF(PHIMIN.LT.0.0) PHIMIN=0.0
KEY=0
DO 100 J=1,K
100 IF(IRCODE(J).NE.0) KEY=KEY+1
IF(KEY.GT.0) GO TO 101
KODE=-3
GO TO 1500
101 IF(N.GE.KEY) GO TO 102
KODE=-2
GO TO 1500
102 IF(INDEX.GT.0) GO TO 300
DO 200 J=1,K
200 ALPHA(J)=B(J)
GO TO 400
300 IF(PHIMIN.GT.PHI.AND.INDEX.GT.1) GO TO 400
DO 307 J=1,K
IF(IRCODE(J)) 301,307,303
301 CALL DERIV(J,JTEST,B,ZETA)
DO 302 I=1,N
302 AJACOB(I,J)=ZETA(I)
IF(JTEST.NE.-1) GO TO 307
IRCODE(J)=1
303 DEL=0.001*ABS(B(J))
IF(ABS(B(J)).LT.1.0E-04) DEL=0.00001
IF(B(J)+DEL.LE.RMAX(J)) GO TO 304
ALPHA(J)=B(J)-DEL
DEL=-DEL
GO TO 305
304 ALPHA(J)=B(J)+DEL
305 CALL FUNC(ALPHA,ZETA)
ALPHA(J)=B(J)
DO 306 I=1,N
306 AJACOB(I,J)=(ZETA(I)-Z(I))/DEL
307 CONTINUE
400 DO 406 LL=1,K
IF(IRCODE(LL)) 401,404,401
401 G(LL)=0.0
DO 402 JJ=1,N
402 G(LL)=G(LL)+AJACOB(JJ,LL)*(Y(JJ)-Z(JJ))
DO 403 JJ=1,K
A(LL,JJ)=0.0
DO 403 MM=1,N
403 A(LL,JJ)=A(LL,JJ)+AJACOB(MM,LL)*AJACOB(MM,JJ)

```

```

      IF(A(LL,LL).GT.1.0E-20) GO TO 406
04  DO 405 JJ=1,K
05  A(LL,JJ)=0.0
      A(LL,LL)=1.0
      G(LL)=0.0
06  CONTINUE
      GNORM=0.0
      DO 407 I=1,K
07  GNORM=GNORM+G(I)**2
      DO 500 I=1,K
500  OMEGA(I)=SQRT(A(I,I))
      DO 501 I=1,K
      G(I)=G(I)/OMEGA(I)
      DO 501 J=1,K
501  A(I,J)=A(I,J)/(OMEGA(I)*OMEGA(J))
      FLAM=FLAMDA/FNU
      ITER=1
      GO TO 503
502  FLAM=FLAM*FNU
503  DO 504 I=1,K
504  A(I,I)=A(I,I)+FLAM
      DO 506 I=1,K
      DO 505 J=1,K
505  ASCALE(I,J)=A(I,J)
506  ASCALE(I,KP1)=G(I)
      DO 603 L=1,K
      LL=L+1
      DO 600 M=LL,KP1
600  ASCALE(L,M)=ASCALE(L,M)/ASCALE(L,L)
      DO 603 M=1,K
      IF(L-M) 601,603,601
601  DO 602 J=LL,KP1
602  ASCALE(M,J)=ASCALE(M,J)-ASCALE(L,J)*ASCALE(M,L)
603  CONTINUE
      DLNORM=0.0
      DGPROD=0.0
      DO 701 I=1,K
      DELTA(I)=ASCALE(I,KP1)/OMEGA(I)
      IF(IBCDE(I).EQ.0) GO TO 700
      ALPHA(I)=AMAX1(RMIN(I),AMIN1(BMAX(I),R(I)+DELTA(I)))
700  DLNORM=DLNORM+DELTA(I)**2
      DGPROD=DGPROD+DELTA(I)*G(I)*OMEGA(I)
701  DELTA(I)=ALPHA(I)-B(I)
      COSGAM=DGPROD/(SQRT(DLNORM*GNORM))
      JQUAD=1
      IF(COSGAM) 800,801,801
800  JQUAD=2
      COSGAM=-COSGAM
801  COSGAM=AMIN1(COSGAM,1.0)
      GAMMA=ARCO(COSGAM)*180.0/3.14159265
      IF(JQUAD.GT.1) GAMMA=180.0-GAMMA
900  CALL FUNC(ALPHA,ZETA)
      XPHI=0.0
      DO 901 I=1,N
      XPHI=XPHI+(Y(I)-ZETA(I))**2

```

```
1  CONTINUE
   STDEV=SQRT(XPHI/FLOAT(N-1))
   IF(STDEV.LT.STDEVS) GO TO 1400
   IF(INDEX.GT.0) GO TO 1000
   KODE=K
   GO TO 1404
000  IF(XPHI.GE.PHI) GO TO 1300
   KODE=0
   DO 1100 I=1,K
100  IF(ABS(DELTA(I))/(TAU+ABS(ALPHA(I))).GT.EPSILN) KODE=KODE+1
   IF(KODE.EQ.0) GO TO 1200
   IF(FLAM.GT.1.0.AND.GAMMA.GT.90.0) KODE=-1
   GO TO 1401
200  IF(FLAM.GT.1.0.AND.GAMMA.LE.45.0) KODE=-4
   GO TO 1401
300  IF(FLAM.GE.1.0E+08) GO TO 1301
   ITER=ITER+1
   GO TO 502
301  KODE=-1
   GO TO 1500
400  KODE=0
   IF(INDEX.EQ.0) GO TO 1402
401  FLAMDA=FLAM
402  DO 1403 I=1,K
403  B(I)=ALPHA(I)
404  DO 1405 J=1,N
405  Z(J)=ZETA(J)
   PHI=XPHI
500  INDEX=INDEX+1
   RETURN
   END
```

CHEMACT

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FUNCTION ARCO(Z)

X=7

KEY=0

IF(X.LT.(-1.0)) X=-1.0

IF(X.GT.1.0) X=1.0

IF(X.GE.(-1.0).AND.X.LT.0.0) KEY=1

EPS=1.E-12

IF(ABS(X)-EPS) 20,20,30

20 ARCO=1.57079633

GO TO 40

30 X=ABS(X)

ARCO= ATAN(SQRT(1.0-X*X)/X)

IF(KEY.EQ.1) ARCO=3.14159265-ARCO

40 RETURN

END

```
SUBROUTINE LAMDA(R)
COMMON K,N,MG,X(60,7),XLAMDA(5,5),NN,NCOMP,SUM(60,5),KK
DIMENSION B(1)
DO 70 J1=1,NCOMP
DO 70 J2=1,NCOMP
IF(J1-J2) 40,42,44
40 J=(J1-1)*(NCOMP-1)+J2-1
GO TO 46
44 J=(J1-1)*(NCOMP-1)+J2
46 XLAMDA(J1,J2)=B(J)
GO TO 70
42 XLAMDA(J1,J2)=1.0
70 CONTINUE
DO 10 I=1,N
DO 10 IS=1,NCOMP
SUM(I,IS)=0.
IF(IS.EQ.5.AND.KK.LT.K) GO TO 20
DO 25 J=1,NCOMP
25 SUM(I,IS)=SUM(I,IS)+X(I,J)*XLAMDA(IS,J)
GO TO 10
20 DO 30 J=1,NCOMP
30 SUM(I,IS)=SUM(I,IS)+X(I,J)*XLAMDA(IS,J)*EXP(B(J+KK)*(1000./
1X(I,7)-1000./X(I,6)))
10 CONTINUE
RETURN
END
```

```
SUBROUTINE FUNC(R,YCAL)
COMMON K,N,MG,X(60,7),XLAMDA(5,5),NN,NCOMP,SUM(60,5),KK
DIMENSION R(1),YCAL(1),SUM(60,5)
CALL LAMDA(R)
DO 20 J=1,N
DO 20 M=1,MG
J=(M-1)*N+I
SUMT=0.
DO 30 KS=1,NCOMP
F=1.
IF(KS.EQ.5.AND.KK.LT.K) F=EXP(B(KS+KK)*(1000./X(I,7)-1000./X(I,6))
1)
SUMT=SUMT+X(I,KS)*XLAMDA(KS,M)/SUM(I,KS)*F
YCAL(J)=1.-ALOG(SUM(I,M))-SUMT
RETURN
END
```

```

SUBROUTINE DERIV(J,JTEST,B,ZETA)
COMMON K,N,MG,X(60,7),XLAMDA(5,5),NN,NCOMP,SUM(60,5),KK
DIMENSION B(1),ZETA(1),SUM(60,5)
IF(J.GT.KK) GO TO 30
J1=FLOAT(J-1)/FLOAT(NCOMP-1)+1
J2=J-(J1-1)*(NCOMP-1)
IF(J2.GE.J1) J2=J2+1
GO TO 35
30 J1=5
J2=J-KK
35 DO 20 M=1,MG
DO 20 I=1,N
L=(M-1)*N+I
F=1.
IF(J1.EQ.5.AND.KK.LT.K) F=EXP(B(J)*(1000./X(I,7)-1000./X(I,6)))
IF(J.GT.KK) GO TO 50
IF(J1.NE.M.AND.J2.NE.M) GO TO 40
JJ=J1
IF(J1.EQ.M) JJ=J2
ZETA(L)=(-X(I,JJ)/SUM(I,J1)+X(I,J1)*X(I,J2)*XLAMDA(J1,M)/SUM(I,J1)
1**2*F)*F
GO TO 20
40 ZETA(L)=X(I,J1)*X(I,J2)*XLAMDA(J1,M)/SUM(I,J1)**2*F**2
GO TO 20
50 G=1000./X(I,7)-1000./X(I,6)
IF(J2.NE.M) GO TO 60
ZETA(L)=X(I,J1)*XLAMDA(J1,M)*F*G/SUM(I,J1)*(-1.+X(I,M)*F/SUM(I,J1)
1)
GO TO 20
60 FM=EXP(B(KK+M)*(1000./X(I,7)-1000./X(I,6)))
ZETA(L)=X(I,J1)*XLAMDA(J1,M)*X(I,J2)*F*FM*G/SUM(I,J1)**2
20 CONTINUE
JTEST=0
RETURN
END

```


0.	0.	.68	.486	.0	.41	0.
9.2	11.	6.05	0.	0.	.028	0.
0.	4.1	6.73	10.	-10.	10.	-10.
.03357	.3324	.003773	.6595	7.0727	.2878	22.53
.02583	.3428	.00383	.7080	7.370	.3520	22.96
.0177	.3516	.005088	.7810	8.06	.4118	19.18
.01187	.3561	.005278	.8347	9.2835	.4470	17.28
.01007	.3602	.00478	.9173	7.496	.4757	15.66
.007505	.3637	.004006	.9944	5.944	.4867	12.29
.02239	.3437	.001594	.6503	8.837	.3726	57.87
.01648	.3584	.0020	.9740	5.405	.4824	39.03
.01524	.3630	.002220	1.0208	3.944	.5404	32.69
.009457	.3647	.001683	.9969	4.369	.6128	40.96
.00815	.3621	.001631	.9611	4.024	.7228	42.30
.0358	.3503	.0026	.4772	7.91	.502	29.53
.0314	.3507	.00372	.5625	7.64	.511	22.19
.0345	.352	.00527	.719	4.565	.531	18.51
.0195	.3536	.00758	.7546	6.63	.5614	14.53
.0203	.3533	.00474	.8785	5.01	.5507	29.42
.0172	.354	.005844	.9404	4.34	.687	26.7
.01237	.3533	.003961	.9804	3.497	.7301	44.44
.03559	.3461	.00317	.4655	9.165	.3931	32.73
.0157	.3544	.004517	.6696	11.73	.479	25.78
.0119	.359	.00466	.7856	10.99	.498	23.69
.00855	.3639	.00365	.875	11.36	.4969	26.67
.006256	.3708	.00334	.9962	10.72	.4742	21.94
.03172	.3436	.00356	.5467	11.0	.3778	17.57
.0262	.3524	.00599	.7214	10.49	.385	18.17
.01982	.3593	.00752	.8135	10.99	.4356	17.73
.01807	.3636	.006432	.865	8.744	.531	22.13
.01615	.3633	.005306	.8569	7.502	.615	25.7
.01249	.3574	.003333	.8261	6.968	.7536	37.15
.03999	.3587	.002033	.5444	9.018	.3784	24.68
.0242	.3633	.00323	.6813	12.06	.391	16.64
.01538	.3697	.003848	.8363	14.63	.4256	15.35
.01313	.3764	.003504	1.023	11.26	.478	18.51
.008465	.3801	.002824	1.145	10.61	.5315	24.73
.00582	.3817	.002485	1.24	7.81	.579	29.75
.04246	.3594	.003487	.6433	7.085	.3015	24.24
.03678	.3673	.003213	.8495	5.584	.3688	21.81
.02994	.3732	.0028	.9726	4.846	.423	21.56
.01943	.3802	.00238	1.087	4.38	.484	20.19
.01723	.3844	.00197	1.167	3.19	.5166	19.9
.00847	.3874	.001696	1.181	4.478	.541	18.89
.0525	.3357	.002982	.517	6.63	.531	26.87
.0513	.3378	.004247	.7067	5.892	.544	20.05
.046	.3402	.004818	.870	5.434	.5529	18.71
.03818	.343	.004976	.9932	5.148	.5535	19.63
.02659	.3552	.00435	1.2657	3.03	.5075	22.42
.0429	.3375	.002863	.6606	10.02	.4192	31.94
.0411	.3443	.00325	.8479	8.327	.524	31.0
.03535	.3487	.004493	.9898	7.79	.5757	26.45
.02601	.3537	.004164	1.117	8.05	.596	35.79

C.3.3 Results from Program CHEMACT

This program correlates liquid activity coefficient under the frame work of Wilson's Equation. The BSOLVE technique is used for data regression. The terms in the computer outputs are explained as follows.

Pages 1 to 3 -

INDEX = number of iterations

KODE = an indication for program convergence

0 = Program converges to a preset accuracy.

-1 = Program converges but does not converge to a preset accuracy after certain number of iterations. The final standard deviation represents the accuracy that the selected function can get at this point.

positive numbers = Program requires more iterations

STDEV = standard deviation

B1 = constants B_1 , B_8 , and B_{15}

B2 = constants B_2 , B_9 , and B_{16}

B3 = constants B_3 , B_{10} and B_{17}

B4 = constants B_4 , B_{11} and B_{18}

B5 = constants B_5 , B_{12} and B_{19}

B6 = constants B_6 , B_{13} and B_{20}

$B_7 = \text{constants } B_7 \text{ and } B_{14}$

Page 4 -

$X_1 \text{ to } X_5 = \text{liquid mole fraction for components}$
 $1 \text{ to } 5$

Page 5 and 6 -

$\text{LNGi} = \ln \gamma_i, i = 1, \dots, 4$

$\text{LNGCi} = \text{calculated } \ln \gamma_i$

$\text{DEV} = \text{LNGCi} - \text{LNGi}$

Page 7 -

$G_i = \gamma_i, i = 1, \dots, 4$

$G_iC = \text{Calculated } \gamma_i$

Page 8 -

	Wilson's Constant		Wilson's Constant
$B(1) =$	\wedge_{12}	$B(11) =$	\wedge_{34}
$B(2) =$	\wedge_{13}	$B(12) =$	\wedge_{35}
$B(3) =$	\wedge_{14}	$B(13) =$	\wedge_{41}
$B(4) =$	\wedge_{15}	$B(14) =$	\wedge_{42}
$B(5) =$	\wedge_{21}	$B(15) =$	\wedge_{43}
$B(6) =$	\wedge_{23}	$B(16) =$	\wedge_{45}
$B(7) =$	\wedge_{24}	$B(17) =$	\wedge_{51}
$B(8) =$	\wedge_{25}	$B(18) =$	\wedge_{52}
$B(9) =$	\wedge_{31}	$B(19) =$	\wedge_{53}
$B(10) =$	\wedge_{32}	$B(20) =$	\wedge_{54}

1	20	.24763	.10000	0.00000	0.00000	.68000	.48600	0.00000	.41000
			0.00000	1.46000	9.20000	11.00000	6.05000	0.00000	0.00000
			.02800	0.00000	13.10000	0.00000	4.10000	6.73000	
2	12	.24746	.10345	0.00000	0.00000	.68738	.48442	0.00000	.28744
			0.00000	1.45132	9.21373	10.99300	6.02411	0.00000	0.00000
			.02790	0.00000	13.18269	0.00000	4.03170	6.75986	
3	12	.24716	.10076	0.00000	0.00000	.68761	.48442	0.00000	.37829
			0.00000	1.45628	9.20397	10.97905	6.02855	0.00000	0.00000
			.02781	0.00000	13.20183	0.00000	4.03019	6.75458	
4	12	.24698	.09853	0.00000	0.00000	.68756	.48414	0.00000	.37081
			0.00000	1.45409	9.19541	10.96544	6.03162	0.00000	0.00000
			.02774	0.00000	13.21520	0.00000	4.02803	6.75120	
5	12	.24697	.09667	0.00000	0.00000	.68753	.48445	0.00000	.36452
			0.00000	1.46033	9.18496	10.95749	6.03342	0.00000	0.00000
			.02769	0.00000	13.22590	0.00000	4.02545	6.74573	
6	12	.24679	.09509	0.00000	0.00000	.68740	.48442	0.00000	.35939
			0.00000	1.46044	9.18313	10.95045	6.03434	0.00000	0.00000
			.02764	0.00000	13.23483	0.00000	4.02260	6.74441	
7	12	.24674	.09372	0.00000	0.00000	.68715	.48475	0.00000	.35458
			0.00000	1.45975	9.17810	10.94484	6.03474	0.00000	0.00000
			.02760	0.00000	13.24068	0.00000	4.01957	6.74370	
8	11	.24670	.09252	0.00000	0.00000	.68657	.48473	0.00000	.35091
			0.00000	1.45842	9.17370	10.94024	6.03457	0.00000	0.00000
			.02757	0.00000	13.24493	0.00000	4.01643	6.74418	
9	11	.24667	.09145	0.00000	0.00000	.68655	.48573	0.00000	.34736
			0.00000	1.45692	9.16979	10.93450	6.03431	0.00000	0.00000
			.02754	0.00000	13.24797	0.00000	4.01324	6.74555	
10	12	.24665	.09049	0.00000	0.00000	.68621	.48576	0.00000	.34413
			0.00000	1.45507	9.16627	10.92330	6.03374	0.00000	0.00000
			.02752	0.00000	13.25007	0.00000	4.01094	6.74758	
11	12	.24663	.08961	0.00000	0.00000	.68526	.48482	0.00000	.34115
			0.00000	1.45308	9.16308	10.93053	6.03304	0.00000	0.00000
			.02749	0.00000	13.25144	0.00000	4.00684	6.75011	
12	12	.24661	.08879	0.00000	0.00000	.68551	.48588	0.00000	.33837
			0.00000	1.45102	9.16015	10.92407	6.03227	0.00000	0.00000
			.02747	0.00000	13.25224	0.00000	4.00368	6.75302	
13	12	.24659	.08803	0.00000	0.00000	.68515	.48497	0.00000	.33574
			0.00000	1.44893	9.15744	10.92546	6.03145	0.00000	0.00000
			.02745	0.00000	13.25257	0.00000	4.00055	6.75623	
14	11	.24658	.08731	0.00000	0.00000	.68481	.48406	0.00000	.33323
			0.00000	1.44684	9.15492	10.92383	6.03061	0.00000	0.00000
			.02744	0.00000	13.25252	0.00000	3.99747	6.75955	
15	12	.24656	.08662	0.00000	0.00000	.68446	.48315	0.00000	.33083
			0.00000	1.44480	9.15254	10.92194	6.02977	0.00000	0.00000
			.02742	0.00000	13.25217	0.00000	3.99443	6.76325	
16	12	.24655	.08597	0.00000	0.00000	.68413	.48327	0.00000	.32852
			0.00000	1.44280	9.15030	10.92015	6.02895	0.00000	0.00000
			.02740	0.00000	13.25156	0.00000	3.99145	6.76658	
17	12	.24654	.08535	0.00000	0.00000	.68380	.48334	0.00000	.32628
			0.00000	1.44087	9.14819	10.91844	6.02815	0.00000	0.00000
			.02739	0.00000	13.25074	0.00000	3.98853	6.77042	
18	12	.24653	.08474	0.00000	0.00000	.68348	.48351	0.00000	.32411
			0.00000	1.43901	9.14616	10.91680	6.02734	0.00000	0.00000
			.02737	0.00000	13.24972	0.00000	3.98555	6.77475	
19	12	.24652	.08416	0.00000	0.00000	.68317	.48363	0.00000	.32199
			0.00000	1.43723	9.14423	10.91521	6.02655	0.00000	0.00000
			.02735	0.00000	13.24854	0.00000	3.98264	6.77908	

22	12	.24649	.02732	0.00000	13.24575	0.00000	3.47736	5.78594	
			.08252	0.00000	0.00000	.68229	.49003	0.00000	.31593
			0.00000	1.43234	9.13889	10.91054	6.02467	0.00000	0.00000
23	12	.24649	.02731	0.00000	13.24417	0.00000	3.47459	6.79110	
			.08199	0.00000	0.00000	.68201	.49017	0.00000	.31399
			0.00000	1.43037	9.13725	10.90915	6.02409	0.00000	0.00000
24	12	.24647	.02729	0.00000	13.24248	0.00000	3.47207	5.79529	
			.08149	0.00000	0.00000	.68175	.49031	0.00000	.31208
			0.00000	1.42947	9.13566	10.90771	6.02355	0.00000	0.00000
25	12	.24646	.02728	0.00000	13.24069	0.00000	3.46950	6.79953	
			.08099	0.00000	0.00000	.68149	.49046	0.00000	.31022
			0.00000	1.42814	9.13413	10.90529	6.02304	0.00000	0.00000
26	12	.24645	.02726	0.00000	13.23981	0.00000	3.46597	6.40379	
			.08050	0.00000	0.00000	.68124	.49061	0.00000	.30838
			0.00000	1.42689	9.13264	10.90436	6.02257	0.00000	0.00000
27	12	.24644	.02725	0.00000	13.23584	0.00000	3.46448	6.40308	
			.08003	0.00000	0.00000	.68100	.49075	0.00000	.30558
			0.00000	1.42570	9.13120	10.90346	6.02214	0.00000	0.00000
28	12	.24643	.02724	0.00000	13.23478	0.00000	3.46203	6.41240	
			.07956	0.00000	0.00000	.68076	.49091	0.00000	.30480
			0.00000	1.42458	9.12931	10.90206	6.02174	0.00000	0.00000
29	12	.24642	.02722	0.00000	13.23266	0.00000	3.45962	6.41574	
			.07910	0.00000	0.00000	.68054	.49106	0.00000	.30305
			0.00000	1.42352	9.12846	10.90068	6.02137	0.00000	0.00000
30	12	.24642	.02721	0.00000	13.23046	0.00000	3.45724	6.42110	
			.07865	0.00000	0.00000	.68032	.49121	0.00000	.30133
			0.00000	1.42252	9.12715	10.89931	6.02104	0.00000	0.00000
31	12	.24641	.02719	0.00000	13.22819	0.00000	3.45490	6.42548	
			.07820	0.00000	0.00000	.68010	.49137	0.00000	.29963
			0.00000	1.42157	9.12587	10.89795	6.02073	0.00000	0.00000
32	12	.24640	.02718	0.00000	13.22586	0.00000	3.45260	6.42948	
			.07777	0.00000	0.00000	.67989	.49152	0.00000	.29795
			0.00000	1.42069	9.12463	10.89660	6.02046	0.00000	0.00000
33	12	.24639	.02717	0.00000	13.22347	0.00000	3.45032	6.43429	
			.07734	0.00000	0.00000	.67969	.49168	0.00000	.29530
			0.00000	1.41985	9.12343	10.89526	6.02021	0.00000	0.00000
34	12	.24639	.02715	0.00000	13.22102	0.00000	3.44804	6.43872	
			.07692	0.00000	0.00000	.67950	.49184	0.00000	.29467
			0.00000	1.41907	9.12225	10.89392	6.01999	0.00000	0.00000
35	12	.24638	.02714	0.00000	13.21852	0.00000	3.44586	6.44317	
			.07650	0.00000	0.00000	.67931	.49200	0.00000	.29306
			0.00000	1.41833	9.12111	10.89253	6.01980	0.00000	0.00000
36	12	.24637	.02713	0.00000	13.21597	0.00000	3.44367	6.44762	
			.07609	0.00000	0.00000	.67912	.49216	0.00000	.29148
			0.00000	1.41764	9.11999	10.89127	6.01963	0.00000	0.00000
37	12	.24636	.02711	0.00000	13.21336	0.00000	3.44151	6.45209	
			.07569	0.00000	0.00000	.67894	.49232	0.00000	.28991
			0.00000	1.41699	9.11891	10.88996	6.01948	0.00000	0.00000
38	12	.24636	.02710	0.00000	13.21072	0.00000	3.43934	6.45657	
			.07529	0.00000	0.00000	.67877	.49249	0.00000	.28835
			0.00000	1.41633	9.11785	10.88865	6.01935	0.00000	0.00000
39	11	.24635	.02709	0.00000	13.20803	0.00000	3.43726	6.46106	
			.07490	0.00000	0.00000	.67859	.49265	0.00000	.28582
			0.00000	1.41581	9.11681	10.88735	6.01925	0.00000	0.00000
40	11	.24634	.02707	0.00000	13.20530	0.00000	3.43518	6.46556	
			.07451	0.00000	0.00000	.67843	.49282	0.00000	.28530
			0.00000	1.41528	9.11580	10.88605	6.01917	0.00000	0.00000
			.02705	0.00000	12.20234	0.00000	3.43311	6.47037	
			.02712	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000

43	11	.24632	.02704	0.00000	13.10590	0.00000	3.92904	6.97910	.28085
			.07339	0.00000	0.00000	.67795	.49332	0.00000	0.00000
			0.00000	1.41290	9.11291	10.88218	6.01984	0.00000	0.00000
			.02702	0.00000	13.10403	0.00000	3.92703	6.88363	0.00000
44	11	.24632	.07301	0.00000	0.00000	.67780	.49348	0.00000	.27939
			0.00000	1.41351	9.11198	10.88090	6.01963	0.00000	0.00000
			.02701	0.00000	13.10113	0.00000	3.92505	6.88816	0.00000
45	11	.24631	.07284	0.00000	0.00000	.67745	.49355	0.00000	.27795
			0.00000	1.41314	9.11108	10.87962	6.01904	0.00000	0.00000
			.02700	0.00000	13.18820	0.00000	3.92308	6.89269	0.00000
46	11	.24630	.07228	0.00000	0.00000	.67751	.49382	0.00000	.27652
			0.00000	1.41280	9.11019	10.87835	6.01906	0.00000	0.00000
			.02699	0.00000	13.18525	0.00000	3.92112	6.89723	0.00000
47	11	.24630	.07192	0.00000	0.00000	.67737	.49399	0.00000	.27511
			0.00000	1.41249	9.10933	10.87708	6.01910	0.00000	0.00000
			.02697	0.00000	13.18227	0.00000	3.91919	6.90178	0.00000
48	11	.24629	.07157	0.00000	0.00000	.67723	.49416	0.00000	.27370
			0.00000	1.41221	9.10848	10.87591	6.01915	0.00000	0.00000
			.02696	0.00000	13.17926	0.00000	3.91727	6.90632	0.00000
49	11	.24628	.07122	0.00000	0.00000	.67709	.49433	0.00000	.27231
			0.00000	1.41194	9.10764	10.87455	6.01922	0.00000	0.00000
			.02695	0.00000	13.17624	0.00000	3.91536	6.91087	0.00000
50	-1	.24628	.07087	0.00000	0.00000	.67696	.49450	0.00000	.27093
			0.00000	1.41171	9.10582	10.87329	6.01930	0.00000	0.00000
			.02694	0.00000	13.17319	0.00000	3.91347	6.91542	0.00000

POINT	X1	X2	X3	X4	X5	TSYS	TSUR
1	.14860	.03357	.33240	.00377	.48166	0.00000	0.00000
2	.16980	.02583	.34280	.00383	.45774	0.00000	0.00000
3	.18660	.01770	.35160	.00509	.43501	0.00000	0.00000
4	.19710	.01187	.35610	.00528	.42965	0.00000	0.00000
5	.20210	.01007	.36020	.00478	.42285	0.00000	0.00000
6	.20450	.00751	.36370	.00401	.42029	0.00000	0.00000
7	.20690	.00239	.36370	.00159	.42542	0.00000	0.00000
8	.22870	.01648	.35840	.00200	.39442	0.00000	0.00000
9	.23090	.01524	.36300	.00222	.38864	0.00000	0.00000
10	.23810	.00946	.36470	.00168	.38606	0.00000	0.00000
11	.24110	.00815	.36210	.00163	.38702	0.00000	0.00000
12	.17970	.03580	.35030	.00260	.43160	0.00000	0.00000
13	.19810	.03140	.35070	.00372	.41608	0.00000	0.00000
14	.21510	.03450	.35200	.00527	.39313	0.00000	0.00000
15	.23220	.01950	.35360	.00758	.38712	0.00000	0.00000
16	.24100	.02030	.35330	.00474	.38066	0.00000	0.00000
17	.24350	.01720	.35400	.00584	.37845	0.00000	0.00000
18	.25030	.01237	.35330	.00396	.38007	0.00000	0.00000
19	.15830	.03559	.34610	.00317	.45684	0.00000	0.00000
20	.20520	.01570	.35440	.00452	.42918	0.00000	0.00000
21	.21610	.01170	.35900	.00465	.40834	0.00000	0.00000
22	.22240	.00855	.36390	.00365	.40150	0.00000	0.00000
23	.22210	.00626	.37080	.00334	.39750	0.00000	0.00000
24	.15090	.03172	.34360	.00356	.47032	0.00000	0.00000
25	.16500	.02620	.35240	.00599	.45041	0.00000	0.00000
26	.17550	.01982	.35930	.00752	.43786	0.00000	0.00000
27	.18450	.01807	.36260	.00643	.42740	0.00000	0.00000
28	.19150	.01615	.36330	.00531	.42374	0.00000	0.00000
29	.20220	.01249	.35740	.00333	.42398	0.00000	0.00000
30	.13940	.03999	.35870	.00203	.45988	0.00000	0.00000
31	.16960	.02420	.36330	.00323	.43967	0.00000	0.00000
32	.18710	.01538	.36470	.00345	.42297	0.00000	0.00000
33	.19420	.01313	.37640	.00350	.41277	0.00000	0.00000
34	.20100	.00847	.38010	.00282	.40761	0.00000	0.00000
35	.20480	.00582	.38170	.00249	.40520	0.00000	0.00000
36	.14750	.04246	.35940	.00349	.44715	0.00000	0.00000
37	.16770	.03678	.36730	.00321	.42501	0.00000	0.00000
38	.18180	.02994	.37320	.00280	.41226	0.00000	0.00000
39	.19540	.01943	.38020	.00238	.40259	0.00000	0.00000
40	.19640	.01723	.38440	.00197	.40060	0.00000	0.00000
41	.20230	.00347	.38740	.00170	.40013	0.00000	0.00000
42	.12880	.05250	.33570	.00298	.48002	0.00000	0.00000
43	.13630	.05130	.33780	.00425	.47035	0.00000	0.00000
44	.14900	.04600	.34020	.00482	.45998	0.00000	0.00000
45	.16440	.03818	.34300	.00498	.44944	0.00000	0.00000
46	.18570	.02659	.35520	.00435	.42816	0.00000	0.00000
47	.18790	.04220	.33750	.00286	.42864	0.00000	0.00000
48	.21580	.04110	.34430	.00325	.39555	0.00000	0.00000
49	.23590	.03535	.34470	.00449	.37554	0.00000	0.00000
50	.25910	.02601	.35370	.00416	.35703	0.00000	0.00000

1	-.41627	-.53357	-.11730	1.95624	2.09314	.13690
2	-.34531	-.35518	-.09987	1.99742	2.07402	.08061
3	-.24718	-.22501	.02217	2.08691	2.09717	.00025
4	-.18068	-.15901	.02168	2.22824	2.10686	-.12138
5	-.08632	-.12545	-.03912	2.01437	2.09198	.07761
6	-.00562	-.10591	-.10030	1.78238	2.10639	.32401
7	-.43032	-.19037	.23995	2.17895	1.95409	-.22486
8	-.02634	-.05744	-.03109	1.68732	1.86870	.19138
9	.02059	-.03345	-.05454	1.37220	1.85390	.48170
10	-.00310	-.00937	-.00627	1.47453	1.89919	.41466
11	-.03968	-.00942	.03025	1.39228	1.90391	.51164
12	-.73942	-.27106	.46876	2.06813	1.86795	-.20107
13	-.57536	-.18230	.39306	2.02340	1.84469	-.18870
14	-.22989	-.10066	.22923	1.51842	1.73126	.21284
15	-.28157	-.03441	.24715	1.89160	1.83187	-.05474
16	-.12954	-.02393	.10561	1.61144	1.78352	.17208
17	-.06145	-.00982	.05153	1.46787	1.80710	.33922
18	-.01979	-.00297	.01682	1.25101	1.83979	.58788
19	-.75464	-.40394	.38071	2.21539	1.97416	-.24123
20	-.40107	-.13936	.26172	2.46215	2.01247	-.44988
21	-.24131	-.08140	.15991	2.39699	1.99344	-.40355
22	-.13353	-.04754	.08599	2.43019	1.95922	-.44088
23	-.00381	-.02479	-.02099	2.37211	1.99505	-.37766
24	-.60384	-.46490	.13985	2.39790	2.07186	-.32504
25	-.32656	-.32208	.00448	2.35042	2.05696	-.29346
26	-.20541	-.22450	-.02209	2.39699	2.07742	-.31957
27	-.14603	-.17584	-.03086	2.16837	2.04251	-.12586
28	-.15443	-.15407	.00036	2.01517	2.03835	.02318
29	-.19104	-.14291	.04813	1.94133	2.05241	.12108
30	-.60407	-.46496	.14311	2.19922	1.94448	-.25474
31	-.38375	-.26708	.11667	2.48989	2.02516	-.46473
32	-.17877	-.15486	-.02391	2.68307	2.04813	-.63494
33	.02274	-.10108	-.12383	2.42126	2.01702	-.40424
34	.13540	-.05360	-.19900	2.36180	2.03883	-.32297
35	.21511	-.04459	-.25971	2.05540	2.05378	-.00153
36	-.44114	-.39393	.04721	1.95798	1.87470	-.08322
37	-.16311	-.25754	-.08743	1.71991	1.83749	.11758
38	-.02175	-.16650	-.13871	1.57815	1.84383	.26567
39	.08342	-.08926	-.17268	1.47705	1.89723	.42019
40	.15444	-.07173	-.22617	1.16002	1.90626	.74624
41	.16636	-.03820	-.20486	1.49918	1.99829	.49910
42	-.65971	-.64334	.01637	1.89160	1.89651	.00491
43	-.24715	-.56492	-.21777	1.77360	1.87847	.10489
44	-.13926	-.46731	-.32805	1.69268	1.89178	.19910
45	-.00682	-.36758	-.36076	1.63661	1.92440	.29580
46	.23583	-.21683	-.45245	1.10856	1.94528	.83672
47	.61461	-.27739	.13722	2.30458	1.74564	-.50705
48	-.18499	-.13177	.03322	2.11450	1.88542	-.43309
49	-.81925	-.04758	-.03733	2.05244	1.85275	-.40009
50	.11045	.02370	-.08695	2.08567	1.63523	-.44944

1	-1.24549	-.92911	.31737	3.11485	3.14490	.03006
2	-1.04412	-.82867	.21545	3.13375	3.17123	.03748
3	-.88722	-.75473	.13249	2.95387	3.03188	.07802
4	-.80520	-.71172	.09348	2.84955	3.01415	.16460
5	-.74297	-.68670	.05627	2.75111	3.05985	.30874
6	-.72011	-.67066	.04945	2.50879	3.13697	.62818
7	-.68725	-.70289	.28436	4.05820	3.58183	-.47637
8	-.72698	-.60730	.12158	3.66433	3.47016	-.19117
9	-.61548	-.59169	.02376	3.48707	3.41711	-.06996
10	-.48972	-.56574	-.07662	3.71260	3.49308	-.21952
11	-.42462	-.56232	-.23770	3.74479	3.51843	-.22636
12	-.68915	-.77636	-.08720	3.38541	3.34268	-.04273
13	-.67139	-.71854	-.04726	3.09964	3.23017	.13052
14	-.63299	-.66574	-.03175	2.91831	3.07977	.16146
15	-.57732	-.61551	-.03828	2.67622	2.85296	.14674
16	-.42071	-.58919	-.15838	3.38167	3.15684	-.22484
17	-.27542	-.59030	-.20538	3.28466	3.03567	-.24899
18	-.31457	-.55988	-.24531	3.79414	3.25227	-.54187
19	-.03387	-.83955	.07413	3.48429	2.21541	-.27289
20	-.73605	-.68958	.04648	3.24960	3.12221	-.12739
21	-.69716	-.64690	.05025	3.16505	3.10180	-.06325
22	-.69937	-.61622	.04315	3.28354	3.20529	-.07825
23	-.74613	-.60180	.14432	3.08831	3.20807	.11976
24	-.07339	-.49342	.07497	2.86619	3.14347	.27728
25	-.05451	-.82511	.12940	2.89977	2.88185	-.01742
26	-.63103	-.77569	.05534	2.87525	2.74201	-.13325
27	-.63299	-.73626	-.10327	3.09693	2.84507	-.25186
28	-.48613	-.71369	-.22756	3.24649	2.97219	-.27430
29	-.28289	-.68874	-.40585	3.61495	3.24825	-.36661
30	-.07180	-.89695	.07485	3.20599	3.26420	.05220
31	-.03905	-.74230	.15675	2.81181	3.16775	.35595
32	-.65426	-.71190	.14236	2.73112	3.05989	.36877
33	-.73814	-.67448	.06366	2.91831	3.12363	.20532
34	-.63205	-.64430	-.01224	3.20802	3.20141	-.00660
35	-.54645	-.62855	-.08209	3.39283	3.24322	-.14961
36	-1.19099	-.96663	.33236	3.18800	3.09613	-.09188
37	-.09750	-.77879	.21871	3.08237	3.15422	.07585
38	-.86038	-.71953	.14086	3.07084	3.21552	.14478
39	-.72567	-.66103	.06464	3.00519	3.25785	.25266
40	-.66049	-.64808	.01241	2.99072	3.29473	.30401
41	-.61434	-.62251	-.00628	2.93863	3.32279	.38416
42	-.63299	-.90284	-.35985	3.29101	3.17402	-.11599
43	-.60881	-.95912	-.35031	2.99823	3.03518	.03695
44	-.59258	-.90684	-.31427	2.92906	3.00667	.07761
45	-.59149	-.84672	-.25522	2.97706	3.02632	.04926
46	-.67826	-.74872	-.07947	3.10995	3.10380	-.00615
47	-.66941	-.77799	.09142	3.46386	3.38572	-.07814
48	-.64626	-.67434	-.03207	3.43399	3.36358	-.07031
49	-.55217	-.61310	-.06493	3.27525	3.21408	-.05118
50	-.51751	-.53763	-.02012	3.57767	3.24446	-.33321

1	.65950	.59651	7.07270	8.11034	.29720	.39530	22.53000	23.21745
2	.70820	.70105	7.37000	7.98467	.35200	.43663	22.96000	23.83679
3	.75160	.79251	8.06000	8.06206	.41180	.47014	19.18000	20.73626
4	.83479	.85299	9.24350	8.22237	.44700	.49060	17.28000	20.37174
5	.91739	.92210	7.49600	8.10995	.47570	.50324	15.66000	21.32429
6	.99440	.89950	5.94400	8.21852	.49670	.51137	12.29000	23.03385
7	.65030	.82665	8.83700	7.05749	.37260	.49515	57.97000	35.93021
8	.97400	.94414	5.40500	5.47990	.48240	.54492	34.03000	32.23442
9	1.02080	.96652	3.94400	6.38465	.54040	.55339	32.69000	30.48110
10	.60690	.99067	4.36900	6.61401	.61280	.55794	40.96000	32.84695
11	.64110	.99062	4.02400	6.71212	.72280	.56484	42.30000	33.73143
12	.67720	.75257	7.91000	6.44920	.50200	.46008	24.53000	28.23490
13	.66250	.83335	7.64000	6.32617	.51100	.48741	22.19000	25.28385
14	.71900	.94424	4.56500	5.64775	.53100	.51234	18.51000	21.75342
15	.75460	.96617	6.63000	6.24553	.56140	.54031	14.53000	17.51324
16	.87450	.97636	5.01000	5.95075	.65070	.55534	29.42000	23.49617
17	.64040	.99023	4.34000	6.09274	.69700	.55945	26.75000	20.81501
18	.98040	.94703	3.40700	6.29521	.73010	.57128	44.44000	25.84895
19	.66550	.66769	9.16500	7.20059	.39310	.42335	32.73000	24.91242
20	.66960	.86992	11.73000	7.48178	.47900	.50179	25.78000	22.69640
21	.78560	.92182	10.99000	7.34072	.49200	.52366	23.69000	22.23795
22	.67500	.95357	11.36000	7.30904	.49690	.53998	26.67000	24.56254
23	.89620	.97552	10.72000	7.35258	.47420	.54782	21.94000	24.73128
24	.54670	.62876	11.00000	7.43955	.37780	.40925	17.57000	23.18415
25	.72140	.72464	10.49000	7.82215	.38500	.43814	18.17000	17.84723
26	.81350	.79573	10.99000	7.98344	.43560	.46039	17.73000	15.51818
27	.86500	.83471	8.74400	7.70994	.53100	.47890	22.13000	17.20293
28	.85690	.85721	7.50200	7.67795	.61500	.48983	25.70000	19.53463
29	.92610	.86683	6.96800	7.86490	.75360	.50221	37.15000	25.74745
30	.54440	.62816	9.01800	6.99002	.37840	.40781	24.68000	26.26397
31	.68130	.76561	12.06000	7.57733	.39100	.45735	16.64000	23.75409
32	.63630	.85654	14.63000	7.75341	.42560	.49071	15.35000	22.19540
33	1.02300	.90385	11.26000	7.51586	.47800	.50942	18.51000	22.72477
34	1.14500	.93834	10.61000	7.68153	.53150	.52503	24.73000	24.56725
35	1.24000	.95639	7.81000	7.79728	.57900	.52337	29.75000	25.61609
36	.64330	.67440	7.08500	6.51846	.30150	.42037	24.24000	22.11215
37	.64090	.77838	5.58400	6.28074	.36820	.45895	21.81000	23.52862
38	.67260	.84663	4.84600	6.32068	.42300	.48698	21.56000	24.41865
39	1.04700	.91461	4.38000	6.66743	.48400	.51632	20.19000	25.99347
40	1.16700	.93078	3.19000	6.72786	.51650	.52305	19.90000	25.97008
41	1.18100	.96252	4.47800	7.37633	.54100	.53654	18.89000	27.72752
42	.51700	.52553	6.63000	6.66263	.53100	.37052	26.87000	23.51343
43	.70670	.55841	5.89200	6.54350	.54400	.38323	20.05000	20.80479
44	.87000	.62669	5.43400	6.63115	.55220	.40380	18.71000	20.22000
45	.09320	.69241	5.14800	6.85107	.55350	.42882	19.63000	20.52120
46	1.26570	.80507	3.03000	6.99560	.50750	.47297	22.42000	22.28245
47	.66060	.75776	10.02000	6.02033	.41920	.49023	31.94000	24.43913
48	.84700	.87654	8.32700	5.40009	.52400	.50745	31.00000	24.89525
49	.68020	.95354	7.79000	5.22130	.57570	.56117	26.45000	24.49835
50	1.11700	1.02398	8.05000	5.13577	.59500	.59413	35.79000	25.64758

FITTED CONSTANTS

R(1)= .70872E-01
 R(2)= 0.
 R(3)= 0.
 R(4)= .67696E+00
 R(5)= .49460E+00
 R(6)= 0.
 R(7)= .27093E+00
 R(8)= 0.
 R(9)= .14117E+01
 R(10)= .91062E+01
 R(11)= .10873E+02
 R(12)= .60193E+01
 R(13)= 0.
 R(14)= 0.
 R(15)= .26937E-01
 R(16)= 0.
 R(17)= .15173E+02
 R(18)= 0.
 R(19)= .39135E+01
 R(20)= .69154E+01

RXNRATE

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PROGRAM RXNPATE(INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
DIMENSION NSET(10),SETID(7,10),X(7,10),Y(7,10),XSUM(10),YSUM(10)
1,YCAL(7,10),DELT(7,10),FKM(10),TITLE(20)
1 READ(5,10) L,ICONTD
10 FORMAT(16I5)
   READ(5,10) (NSET(I),I=1,L)
   READ(5,10) (TITLE(I),I=1,20)
16 FORMAT(20A4)
   XYS=0.
   XXS=0.
   DO 20 J=1,L
     NS=NSET(J)
     XSUM(J)=0.
     YSUM(J)=0.
     DO 20 I=1,NS
       READ(5,30) SETID(I,J),X(I,J),Y(I,J)
       Y(I,J)=ALOG10(Y(I,J))
       XSUM(J)=XSUM(J)+X(I,J)
       YSUM(J)=YSUM(J)+Y(I,J)
       XYS=XYS+X(I,J)*Y(I,J)
       XXS=XXS+X(I,J)**2
20 CONTINUE
30 FORMAT(A8,2X,2F10.0)
   XSYS=0.
   XSYS=0.
   DO 50 J=1,L
     XSYS=XSYS+XSUM(J)**2/FLOAT(NS)
     XSYS=XSYS+XSUM(J)*YSUM(J)/FLOAT(NS)
50 CONTINUE
   STDEV=0.
   NSUM=0
   E=(XYS-XSYS)/(XXS-XXS)
   DO 70 J=1,L
     FKM(J)=(XSUM(J)*E+YSUM(J))/FLOAT(NS)
     NS=NSET(J)
     DO 80 I=1,NS
       YCAL(I,J)=FKM(J)-X(I,J)*E
       DELT(I,J)=YCAL(I,J)-Y(I,J)
80 STDEV=STDEV+DELT(I,J)*DELT(I,J)
       NSUM=NSUM+NS
       FKM(J)=10.**(FKM(J))
70 CONTINUE
   STDEV=SQRT(STDEV/FLOAT(NSUM-1))
   WRITE(6,110) (TITLE(I),I=1,20)
115 FORMAT(1H1///1X,20A4)
   WRITE(6,100) E
100 FORMAT(/1X,20HUNIVERSAL ACTIVATION ENERGY=.F7.2,12H KCAL/G MOLE//)
   WRITE(6,102)
102 FORMAT(1X,6HSET ID,4X,16HFREQUENCY FACTOR,5X,10H1000/2.3PT,10X,
15HLOG K,5X,10HCALC LOG K,6X,9HDEVIATION/)
   DO 104 J=1,L
     NS=NSET(J)
     DO 104 I=1,NS
104 WRITE(6,105) SETID(I,J),FKM(J),X(I,J),Y(I,J),YCAL(I,J),DELT(I,J)
106 FORMAT(1X,AP,2X,E16.4,4F15.6)

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PDATE

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WRITE(6,110) STDEV  
10 FORMAT(//2X,20HSTANDARD DEVIATION =,F11.5)  
IF(ICONTD.EQ.1) GO TO 1  
STOP  
END
```

	1	5	5	5	5	4	5	4
RIFICATION								
01-1	.548285		6.1154					
01-2	.551398		5.4563					
01-3	.554659		4.4523					
01-4	.558001		3.6883					
01-5	.560118		3.1076					
02-1	.550828		6.209					
02-2	.554912		4.556					
02-3	.558301		3.5236					
02-4	.564342		2.552					
02-5	.568437		1.683					
03-1	.558629		3.8535					
03-2	.560305		3.3351					
03-3	.561832		2.9275					
03-4	.563788		2.4808					
03-5	.566052		1.8720					
04-1	.556594		5.1834					
04-2	.558800		4.0379					
04-3	.562815		2.5650					
04-4	.565027		2.1242					
04-5	.566624		1.7412					
05-1	.557446		4.7906					
05-2	.560391		3.8965					
05-3	.562309		3.5290					
05-4	.56421		3.1574					
05-5	.565803		2.6952					
06-1	.558186		5.2394					
06-2	.560376		4.5406					
06-3	.562989		3.2333					
06-4	.566345		2.4727					
06-5	.569444		1.8621					
07-1	.554743		7.4735					
07-2	.557361		5.5545					
07-3	.561081		3.9622					
07-4	.564342		2.7179					
08-1	.561962		8.0225					
08-2	.563077		6.5505					
08-3	.56529		5.5596					
08-4	.567419		4.2723					
08-5	.569148		2.9923					
09-1	.569148		5.0426					
09-2	.572623		3.7125					
09-3	.577877		2.6981					
09-4	.581568		1.9791					

	1	5	5	5	5	4	5	4
PAYION								
1-1	.548285	.5370						
1-2	.551398	.3769						
1-3	.554659	.2400						
1-4	.558001	.1655						
1-5	.560118	.1310						
2-1	.550828	.3689						
2-2	.554912	.1941						
2-3	.558301	.1262						
2-4	.564342	.0827						
2-5	.568437	.05679						
3-1	.558629	.450						
3-2	.560305	.2963						
3-3	.561832	.20095						
3-4	.563788	.1184						
3-5	.566052	.0887						
4-1	.556594	.6049						
4-2	.558800	.4821						
4-3	.562815	.3107						
4-4	.565027	.2646						
4-5	.566624	.2239						
5-1	.557446	.5164						
5-2	.560391	.3294						
5-3	.562309	.2591						
5-4	.56421	.2191						
5-5	.565803	.1893						
6-2	.560376	.2266						
6-3	.562969	.1770						
6-4	.566345	.1469						
6-5	.569444	.1196						
6-6	.571829	.09084						
7-1	.554743	.4778						
7-2	.557361	.2868						
7-3	.561081	.1892						
7-4	.564342	.1421						
8-1	.561962	.9124						
8-2	.563077	.6906						
8-3	.56529	.5621						
8-4	.567419	.4184						
8-5	.569128	.2968						
9-1	.569148	.1705						
9-2	.572623	.1086						
9-3	.577577	.0702						
9-4	.581568	.05157						

	0								
	5	5	5	5	5	4	5	4	
SSIVE REACTION									
1-1	.548285								284.4
1-2	.551398								232.0
1-3	.554659								165.4
1-4	.558001								123.6
1-5	.560118								95.1
2-1	.550828								109.3
2-2	.554912								79.21
2-3	.558301								65.96
2-4	.564342								58.40
2-5	.568437								53.26
3-1	.558629								183.7
3-2	.550305								131.6
3-3	.561832								99.30
3-4	.563788								75.51
3-5	.566052								55.85
4-1	.556594								329.1
4-2	.558800								190.6
4-3	.562815								75.08
4-4	.565027								50.32
4-5	.566624								33.94
5-1	.557446								194.3
5-2	.560391								148.8
5-3	.562309								128.7
5-4	.56421								102.1
5-5	.565803								61.27
6-1	.558186								149.1
6-2	.560376								110.6
6-3	.562989								60.52
6-4	.566345								37.02
6-5	.569444								19.31
7-1	.554743								237.6
7-2	.557361								124.2
7-3	.561081								62.60
7-4	.564342								32.54
8-1	.561962								318.0
8-2	.563077								233.7
8-3	.56529								186.8
8-4	.567419								132.4
8-5	.569148								86.22
9-1	.569148								151.0
9-2	.572623								85.21
9-3	.577877								49.34
9-4	.581568								32.75

C.4.3 Results from Program RXNRATE

The program is used to fit reaction rate constants into the Arrhenious equation. The terms shown on the printouts are explained as follows:

Pages 1 to 3 -

$1000/2.3RT$ = see definition shown in Section C.1.3

K = rate constants, units being the same as those for ACR RCONST, ROR RCONST, and PRO RCONST given in Section C.1.3

ESTERIFICATION

UNIVERSAL ACTIVATION ENERGY= 35.65 KCAL/G MOLE

SET ID	FREQUENCY FACTOR	1000/2.3RT	LOG K	CALC LOG K	DEVIATION
SET 01-1	.2591F+21	.548285	.786425	.867515	.081090
SET 01-2	.2591F+21	.551398	.736898	.755538	.019640
SET 01-3	.2591F+21	.554659	.648584	.640285	-.008299
SET 01-4	.2591F+21	.558001	.566826	.521145	-.045681
SET 01-5	.2591F+21	.560118	.492425	.445675	-.046750
SET 02-1	.2933F+21	.550828	.793022	.830615	.037593
SET 02-2	.2933F+21	.554912	.658584	.685023	.026439
SET 02-3	.2933F+21	.558301	.546987	.564207	.017220
SET 02-4	.2933F+21	.564342	.406881	.348849	-.058032
SET 02-5	.2933F+21	.568437	.226084	.202864	-.023220
SET 03-1	.3079F+21	.558629	.589223	.573640	-.015583
SET 03-2	.3079F+21	.560305	.523109	.513892	-.009217
SET 03-3	.3079F+21	.561832	.466497	.459455	-.007042
SET 03-4	.3079F+21	.563788	.394592	.389725	-.004857
SET 03-5	.3079F+21	.566052	.272306	.309015	.036709
SET 04-1	.3116F+21	.566594	.714615	.651303	-.053312
SET 04-2	.3116F+21	.568800	.606156	.572660	-.033495
SET 04-3	.3116F+21	.562815	.409087	.429528	.020441
SET 04-4	.3116F+21	.565027	.327195	.350671	.023476
SET 04-5	.3116F+21	.566624	.240849	.293739	.052891
SET 05-1	.3853F+21	.557446	.680390	.713208	.032819
SET 05-2	.3853F+21	.560391	.590675	.604221	.017546
SET 05-3	.3853F+21	.562309	.547652	.539845	-.007806
SET 05-4	.3853F+21	.564210	.449330	.472076	.027254
SET 05-5	.3853F+21	.565803	.430591	.415286	-.015305
SET 06-1	.3955F+21	.558186	.719282	.698143	-.021138
SET 06-2	.3955F+21	.560376	.657113	.620071	-.037042
SET 06-3	.3955F+21	.562989	.509646	.526419	.017273
SET 06-4	.3955F+21	.565345	.393171	.407280	.014108
SET 06-5	.3955F+21	.569444	.270003	.295802	.026799
SET 07-1	.4020F+21	.554743	.873524	.827953	-.045571
SET 07-2	.4020F+21	.557361	.744545	.734623	-.010022
SET 07-3	.4020F+21	.561081	.597936	.602907	.004071
SET 07-4	.4020F+21	.564342	.434233	.485755	.051521
SET 08-1	.7411F+21	.561962	.904310	.835280	-.068030
SET 08-2	.7411F+21	.563077	.816274	.796531	-.019743
SET 08-3	.7411F+21	.565290	.745040	.717639	-.027405
SET 08-4	.7411F+21	.567419	.630552	.641741	.011080
SET 08-5	.7411F+21	.569148	.476005	.580103	.104096
SET 09-1	.1021F+22	.569148	.702655	.719419	.016765
SET 09-2	.1021F+22	.572623	.569566	.585538	.025871
SET 09-3	.1021F+22	.577877	.421058	.408236	-.022822
SET 09-4	.1021F+22	.581568	.296468	.276554	-.020914

STANDARD DEVIATION = .03689

DEHYDRATION

UNIVERSAL ACTIVATION ENERGY= 47.97 KCAL/G MOLE

SET ID	FREQUENCY FACTOR	1000/2.3PT	LOG K	CALC LOG K	DEVIATION
SET 01-1	.1013E+27	.548285	-.270026	-.297721	-.027696
SET 01-2	.1013E+27	.551398	-.423774	-.447064	-.023290
SET 01-3	.1013E+27	.554459	-.619789	-.603506	.016283
SET 01-4	.1013E+27	.558001	-.781202	-.743434	.037368
SET 01-5	.1013E+27	.560118	-.882729	-.865394	.017334
SET 02-1	.9127E+26	.550828	-.433091	-.464942	-.031851
SET 02-2	.9127E+26	.554912	-.711974	-.660867	.051108
SET 02-3	.9127E+26	.558301	-.808941	-.823450	.015491
SET 02-4	.9127E+26	.564342	-1.082494	-1.113259	-.030764
SET 02-5	.9127E+26	.568427	-1.245728	-1.309711	-.063983
SET 03-1	.1807E+27	.548629	-.346787	-.542605	-.195817
SET 03-2	.1807E+27	.560305	-.528268	-.623009	-.094740
SET 03-3	.1807E+27	.561832	-.696412	-.696265	.000147
SET 03-4	.1807E+27	.563788	-.926648	-.790101	.136547
SET 03-5	.1807E+27	.566052	-1.052076	-.893714	.153363
SET 04-1	.3205E+27	.556594	-.218314	-.196036	.022280
SET 04-2	.3205E+27	.558800	-.315863	-.301866	.014997
SET 04-3	.3205E+27	.562815	-.507659	-.494481	.013178
SET 04-4	.3205E+27	.565027	-.577410	-.600598	-.023188
SET 04-5	.3205E+27	.566624	-.649946	-.677212	-.027267
SET 05-1	.2601E+27	.557446	-.287014	-.327608	-.040594
SET 05-2	.2601E+27	.560391	-.482276	-.468891	.013386
SET 05-3	.2601E+27	.562309	-.586533	-.560904	.025628
SET 05-4	.2601E+27	.564210	-.659358	-.652102	.007255
SET 05-5	.2601E+27	.565803	-.722849	-.724524	-.001675
SET 06-1	.2108E+27	.560376	-.644740	-.550512	.094228
SET 06-2	.2108E+27	.562989	-.752027	-.684867	.067160
SET 06-3	.2108E+27	.566345	-.832974	-.845467	-.012488
SET 06-4	.2108E+27	.569444	-.922269	-.994537	-.072256
SET 06-5	.2108E+27	.571829	-1.041723	-1.104954	-.063232
SET 07-1	.1687E+27	.554743	-.320754	-.395877	-.075123
SET 07-2	.1687E+27	.557361	-.542421	-.511472	.030949
SET 07-3	.1687E+27	.561081	-.723079	-.689934	.033145
SET 07-4	.1687E+27	.564342	-.847406	-.846376	.001029
SET 08-1	.7112E+27	.561962	-.039815	-.107408	-.067593
SET 08-2	.7112E+27	.563077	-.160773	-.160899	-.000125
SET 08-3	.7112E+27	.565290	-.250186	-.267065	-.016878
SET 08-4	.7112E+27	.567419	-.378408	-.369201	.009208
SET 08-5	.7112E+27	.569148	-.527536	-.452147	.075389
SET 09-1	.3598E+27	.569148	-.768276	-.748102	.020174
SET 09-2	.3598E+27	.572623	-.964170	-.914810	.049350
SET 09-3	.3598E+27	.577877	-1.153663	-1.166864	-.013201
SET 09-4	.3598E+27	.581560	-1.287603	-1.343935	-.056332

STANDARD DEVIATION = .06085

SUCCESSIVE REACTION

UNIVERSAL ACTIVATION ENERGY= 52.88 KCAL/G MOLE

SET ID	FREQUENCY FACTOR	1000/2.3RT	LOG K	CALC LOG K	DEVIATION
SET 01-1	.3512E+32	.548285	2.453930	2.540894	.095964
SET 01-2	.3512E+32	.551398	2.365408	2.385265	.019777
SET 01-3	.3512E+32	.554659	2.212536	2.212800	-.000264
SET 01-4	.3512E+32	.558001	2.092018	2.036070	-.055948
SET 01-5	.3512E+32	.560118	1.978181	1.924114	-.054066
SET 02-1	.2701E+32	.550828	2.038520	2.301319	.262699
SET 02-2	.2701E+32	.554912	1.898780	2.085340	.186560
SET 02-3	.2701E+32	.558301	1.819281	1.906115	.086934
SET 02-4	.2701E+32	.564342	1.766413	1.585641	-.179772
SET 02-5	.2701E+32	.568437	1.726401	1.370080	-.356321
SET 03-1	.5351E+32	.558629	2.264109	2.185751	-.078358
SET 03-2	.5351E+32	.560305	2.119256	2.097117	-.022139
SET 03-3	.5351E+32	.561832	1.996949	2.015363	.019413
SET 03-4	.5351E+32	.563788	1.878004	1.912921	.034916
SET 03-5	.5351E+32	.566052	1.747023	1.793191	.046168
SET 04-1	.5018E+32	.556594	2.517328	2.265497	-.251831
SET 04-2	.5018E+32	.558800	2.280123	2.148834	-.131288
SET 04-3	.5018E+32	.562815	1.875524	1.936504	.060980
SET 04-4	.5018E+32	.565027	1.701741	1.819524	.117783
SET 04-5	.5018E+32	.566624	1.530712	1.735068	.204356
SET 05-1	.6252E+32	.557446	2.288473	2.315902	.027430
SET 05-2	.6252E+32	.560391	2.172603	2.160158	-.012445
SET 05-3	.6252E+32	.562309	2.109579	2.058726	-.050852
SET 05-4	.6252E+32	.564210	2.009026	1.958193	-.050833
SET 05-5	.6252E+32	.565803	1.787248	1.873448	.086701
SET 06-1	.3709E+32	.558186	2.173478	2.050005	-.123473
SET 06-2	.3709E+32	.560376	2.043755	1.934188	-.109567
SET 06-3	.3709E+32	.562989	1.781899	1.796002	.014103
SET 06-4	.3709E+32	.566375	1.569435	1.618522	.050096
SET 06-5	.3709E+32	.569444	1.285782	1.454634	.168851
SET 07-1	.3367E+32	.554743	2.375846	2.190057	-.185790
SET 07-2	.3367E+32	.557361	2.094122	2.051606	-.042516
SET 07-3	.3367E+32	.561081	1.796574	1.854876	.058302
SET 07-4	.3367E+32	.564342	1.512418	1.582421	.070003
SET 08-1	.1379E+33	.551962	2.502427	2.420708	-.081719
SET 08-2	.1379E+33	.563077	2.348659	2.361742	-.006917
SET 08-3	.1379E+33	.565290	2.271377	2.244709	-.026668
SET 08-4	.1379E+33	.567419	2.121888	2.132118	.010230
SET 08-5	.1379E+33	.569148	1.935608	2.040681	.105073
SET 09-1	.1795E+33	.569148	2.178977	2.155025	-.023952
SET 09-2	.1795E+33	.572623	1.930491	1.971252	.040762
SET 09-3	.1795E+33	.577877	1.693100	1.693398	.000298
SET 09-4	.1795E+33	.581568	1.515211	1.498202	-.017009

STANDARD DEVIATION = .11937

BSOLFIT

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PROGRAM BSOLFIT(INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
COMMON K,N,X(40,4),STDEVS
COMMON /G1/ Y(60),YCAL(60),IBCODE(7),RMAX(7),RMIN(7),R(7),PHI,FNU,
+FLAMDA,TAU,EPSILN,PHIMIN,INDEX,KODE,ITER
DIMENSION DEV(60),PCTDEV(60),XX(60,4),YY(60),YYCAL(60),XNAME(4)
DATA XNAME/2HX1,2HX2,2HX3,2HX4/
50 READ(5,9) K,N,IDUMMY,IXF,IYF
9  FORMAT(6I5)
  READ(5,14) STDEVS
  READ(5,14) (RMAX(I),I=1,K)
  READ(5,14) (RMIN(I),I=1,K)
60 READ(5,14) (R(I),I=1,K)
70 DO 1000 J=1,IDUMMY
000 READ(5,14) (XX(I,J),I=1,N)
  ITER1=100
  DO 1020 J=1,IDUMMY
  DO 1020 I=1,N
020 X(I,J)=XX(I,J)
80 READ(5,14) (YY(I),I=1,N)
  IF (IYF.EQ.2.OR.IYF.EQ.3.OR.IYF.EQ.4) READ(5,14) BB
  CALL NEWFUNC(Y,YY,N,IYF,BB)
14  FORMAT(8F10.0)
  FNU=0.
  FLAMDA=0.
  TAU=0.
  EPSILN=0.
  PHIMIN=0.
  INDEX=0
  DO 12 I=1,K
12  IBCODE(I)=-1
  WRITE(6,100)
100 FORMAT(1H1///,2X,5HINDEX,1X,4HKODE, 8X,4HPHIN,10X,2HB1,10X,2HB2,
  110X,2HB3,10X,2HB4,10X,2HB5,10X,2HB6)
30  CALL PSOLVE
  STDEV=SQRT(PHI/FLGAT(N-1))
  IF (INDEX.GE.ITER1) KODE=-1
  WRITE(6,102) INDEX,KODE,STDEV,(R(I),I=1,K)
102 FORMAT(2X,2I5,8F12.5)
  IF (KODE) 40,40,27
27  IF (INDEX-ITER1) 30,40,40
40  PCTV=0.
  DO 25 J=1,N
  DEV(I)=YCAL(I)-Y(I)
25  CONTINUE
  WRITE(6,104)
104 FORMAT(1H1///3X,*MODIFIED VARIABLES*/5X,5HPOINT,15X,2HYM,12X,
  15HYCAL,13X,4HDEV)
  WRITE(6,105) (I,Y(I),YCAL(I),DEV(I),I=1,N)
105 FORMAT(110,3E17.5)
  CALL REVFUNC(YCAL,YYCAL,N,IYF,BB)
  DO 55 I=1,N
  DEV(I)=YYCAL(I)-YY(I)
  IF (ABS(YY(I)).GT.1.0E-06) GO TO 56
  PCTDEV(I)=0.
  GO TO 57

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56 PCTDEV(I)=DEV(I)/YY(I)/.01
57 PCTM=PCTM+ABS(PCTDEV(I))
55 CONTINUE
   PCTM=PCTM/FLOAT(N)
   WRITE(6,207) (XNAME(J),J=1,IDUMMY)
207 FORMAT(1H1///,3X,*ORIGINAL VARIABLES*,//15X,1HY,12X,4HYCAL,13X,
13HDEV,4(14X,A2))
   DO 700 I=1,N
700 WRITE(6,208)YY(I),YYCAL(I),DEV(I),(XX(I,J),J=1,IDUMMY)
208 FORMAT(7E16.5)
   WRITE(6,108) PCTM,STDEV
108 FORMAT(///20X22HMEAN PERCENTAGE ERROR=,F8.3/20X,22HSTANDARD DEVIAT
110N   =,F10.5//20X,16HFITTED CONSTANTS)
   WRITE(6,114) (I,B(I),I=1,K)
114 FORMAT(22X,2HR(,I2,2H)=,E13.5)
77 READ(5,9) IDT
   GO TO (50,60,70,80,90),IDT
90 STOP
END
```

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SUBROUTINE BSOLVE
COMMON K,N,X(40,4),STDEVS
COMMON /G1/ Y(60), Z(60),IRCODE(7),RMAX(7),RMIN(7),B(7),PHI,FNU,
+FLAMDA,TAU,EPSILN,PHIMIN,INDEX,KODE,ITER
DIMENSION ZETA(60),ALPHA(7),AJACOB(60,7),G(7),A(7,7),OMEGA(7),
+ASCALE(7,8),DELTA(7)
K01=K+1
IF(FLAMDA.LE.0.0) FLAMDA=0.01
IF(INDEX.GT.0) GO TO 300
IF(FNU.LE.0.0) FNU=10.0
IF(TAU.LE.0.0) TAU=0.001
IF(EPSILN.LE.0.0) EPSILN=0.00002
IF(PHIMIN.LT.0.0) PHIMIN=0.0
KEY=0
DO 100 J=1,K
00 IF(IRCODE(J).NE.0) KEY=KEY+1
IF(KEY.GT.0) GO TO 101
KODE=-3
GO TO 1500
01 IF(N.GE.KEY) GO TO 102
KODE=-2
GO TO 1500
02 IF(INDEX.GT.0) GO TO 300
DO 200 J=1,K
00 ALPHA(J)=B(J)
GO TO 900
00 IF(PHIMIN.GT.PHI.AND.INDEX.GT.1) GO TO 400
DO 307 J=1,K
IF(IRCODE(J)) 301,307,303
301 CALL DERIV(J,JTEST,B,ZETA)
DO 302 I=1,N
302 AJACOB(I,J)=ZETA(I)
IF(JTEST.NE.-1) GO TO 307
IRCODE(J)=1
303 DEL=0.001*ABS(B(J))
IF(ABS(B(J)).LT.1.0E-04) DEL=0.00001
IF(B(J)+DEL.LE.BMAX(J)) GO TO 304
ALPHA(J)=B(J)-DEL
DEL=-DEL
GO TO 305
304 ALPHA(J)=B(J)+DEL
305 CALL FINE(ALPHA,ZETA)
ALPHA(J)=B(J)
DO 306 I=1,N
306 AJACOB(I,J)=(ZETA(I)-Z(I))/DEL
307 CONTINUE
400 DO 405 LL=1,K
IF(IRCODE(LL)) 401,404,401
401 G(LL)=0.0
DO 402 JJ=1,N
402 G(LL)=G(LL)+AJACOB(JJ,LL)*(Y(JJ)-Z(JJ))
DO 403 JJ=1,K
A(LL,JJ)=0.0
DO 403 MM=1,N
403 A(LL,JJ)=A(LL,JJ)+AJACOB(MM,LL)*AJACOB(MM,JJ)

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      IF(A(LL,LL).GT.1.0E-20) GO TO 406
404 DO 405 JJ=1,K
405 A(LL,JJ)=0.0
      A(LL,LL)=1.0
      G(LL)=0.0
406 CONTINUE
      GNORM=0.0
      DO 407 I=1,K
407 GNORM=GNORM+G(I)**2
      DO 500 I=1,K
500 OMEGA(I)=SQRT(A(I,I))
      DO 501 I=1,K
      G(I)=G(I)/OMEGA(I)
      DO 501 J=1,K
501 A(I,J)=A(I,J)/(OMEGA(I)*OMEGA(J))
      FLAM=FLAMDA/FNU
      ITPR=1
      GO TO 503
502 FLAM=FLAM*FNU
503 DO 504 I=1,K
504 A(I,I)=A(I,I)+FLAM
      DO 506 I=1,K
      DO 505 J=1,K
505 ASCALE(I,J)=A(I,J)
506 ASCALE(I,KP1)=G(I)
      DO 603 L=1,K
      LL=L+1
      DO 600 M=LL,KP1
600 ASCALE(L,M)=ASCALE(L,M)/ASCALE(L,L)
      DO 603 M=1,K
      IF(L-M) 601,603,601
601 DO 602 J=LL,KP1
602 ASCALE(M,J)=ASCALE(M,J)-ASCALE(L,J)*ASCALE(M,L)
603 CONTINUE
      ULNORM=0.0
      DGPROD=0.0
      DO 701 I=1,K
      DELTA(I)=ASCALE(I,KP1)/OMEGA(I)
      IF(I-CODE(I).EQ.0) GO TO 700
      ALPHA(J)=AMAX1(BMIN(I),AMIN1(BMAX(I),B(I)+DELTA(I)))
700 ULNORM=ULNORM+DELTA(I)**2
      DGPROD=DGPROD+DELTA(I)*G(I)*OMEGA(I)
701 DELTA(I)=ALPHA(I)-B(I)
      COSGAM=DGPROD/(SQRT(ULNORM*GNORM))
      JQUAD=1
      IF(COSGAM) 800,801,801
800 JQUAD=2
      COSGAM=-COSGAM
801 COSGAM=AMIN1(COSGAM,1.0)
      GAMMA=APCO(COSGAM)*180.0/3.14159265
      IF(JQUAD.GT.1) GAMMA=180.0-GAMMA
900 CALL FUNC(ALPHA,ZETA)
      XPHI=0.0
      DO 901 I=1,N
      XPHI=XPHI+(Y(I)-ZETA(I))**2

```


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```
1  CONTINUE
   STDEV=SQRT(XPHI/FLOAT(N-1))
   IF(STDEV.LT.STDEVS) GO TO 1400
   IF(INDEX.GT.0) GO TO 1000
   KODE=K
   GO TO 1404
000 IF(XPHI.GE.PHI) GO TO 1300
   KODE=0
   DO 1100 I=1,K
100 IF(ABS(DELTA(I))/(TAU+ABS(ALPHA(I))).GT.EPSILN) KODE=KODE+1
   IF(KODE.EQ.0) GO TO 1200
   IF(FLAM.GT.1.0.AND.GAMMA.GT.90.0) KODE=-1
   GO TO 1401
200 IF(FLAM.GT.1.0.AND.GAMMA.LE.45.0) KODE=-4
   GO TO 1401
300 IF(FLAM.GE.1.0E+08) GO TO 1301
   ITER=ITER+1
   GO TO 502
301 KODE=-1
   GO TO 1500
400 KODE=0
   IF(INDEX.EQ.0) GO TO 1402
401 FLAMDA=FLAM
402 DO 1403 I=1,K
403 B(I)=ALPHA(I)
404 DO 1405 J=1,N
405 Z(J)=ZETA(J)
   PHI=XPHI
1500 INDEX=INDEX+1
   RETURN
END
```

```
SUBROUTINE NEWFUNC(Z,ZZ,N,IFUNC,A)
  DIMENSION Z(1),ZZ(1)
  GO TO (10,20,30,40,50,60,70,80),IFUNC
10 DO 15 I=1,N
15 Z(I)=ZZ(I)
   RETURN
20 DO 25 I=1,N
25 Z(I)=ZZ(I)+A
   RETURN
30 DO 35 I=1,N
35 Z(I)=(ZZ(I)+A)/100.
   RETURN
40 DO 45 I=1,N
45 Z(I)=1./(ZZ(I)+A)
   RETURN
50 DO 55 I=1,N
55 Z(I)=ALOG10(ZZ(I))
   RETURN
60 DO 65 I=1,N
65 Z(I)=ALOG(ZZ(I))
   RETURN
70 DO 75 I=1,N
75 Z(I)=10.**(ZZ(I))
   RETURN
80 DO 85 I=1,N
85 Z(I)=EXP(ZZ(I))
   RETURN
END
```

```
SUBROUTINE PEVFUNC(Z,ZZ,N,IFUNC,A)
  DIMENSION Z(1),ZZ(1)
  GO TO (10,20,30,40,50,60,70,80),IFUNC
10 DO 15 I=1,N
15 Z7(I)=Z(I)
   RETURN
20 DO 25 I=1,N
25 Z7(I)=Z(I)-A
   RETURN
30 DO 35 I=1,N
35 Z7(I)=100.*Z(I)-A
   RETURN
40 DO 45 I=1,N
45 Z7(I)=1./Z(I)-A
   RETURN
50 DO 55 I=1,N
55 Z7(I)=10.**Z(I)
   RETURN
60 DO 65 I=1,N
65 Z7(I)=EXP(Z(I))
   RETURN
70 DO 75 I=1,N
75 Z7(I)=ALOG10(Z(I))
   RETURN
80 DO 85 I=1,N
85 Z7(I)=ALOG(Z(I))
   RETURN
END
```

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```
FUNCTION ARCO(7)
DOUBLE PRECISION X,Z,EPS
X=Z
KEY=0
IF(X.LT.(-1.0)) X=-1.0
IF(X.GT.1.0 ) X=1.0
IF(X.GE.(-1.0).AND.X.LT.0.0) KEY=1
EPS=1.0D-12
IF(DABS(X)-EPS) 20,20,30
20 ARCO=1.570796325
GO TO 40
30 X=DABS(X)
ARCO=DATAN(DSQRT(1.0-X*X)/X)
IF(KEY.EQ.1) ARCO=3.14159265-ARCO
40 RETURN
END
```

```
SUBROUTINE FUNC(B,YCAL)
COMMON K,N,X(40,4),STDEVS
DIMENSION B(1),YCAL(1)
DO 10 I=1,N
  YCAL(I)=B(1)*ALOG10(X(I,1)+B(2))+B(3)*ALOG10(X(I,2)+B(4))+B(5)*
1ALOG10(X(I,3)+B(6))+B(7)
10 CONTINUE
RETURN
END
```

```
SUBROUTINE DERIV(J,JTEST,B,ZETA)
COMMON K,N,X(40,4),STDEVS
DIMENSION B(1),ZETA(1)
GO TO (10,20,30,40,50,60,72),J
10 DO 15 I=1,N
15 ZETA(I)=ALOG10(X(I,1)+B(2))
GO TO 70
20 DO 25 I=1,N
25 ZETA(I)= B(1)/(X(I,1)+B(2))
GO TO 70
30 DO 35 I=1,N
35 ZETA(I)=ALOG10(X(I,2)+B(4))
GO TO 70
40 DO 45 I=1,N
45 ZETA(I)=B(3)/(X(I,2)+B(4))
GO TO 70
50 DO 55 I=1,N
55 ZETA(I)=ALOG10(X(I,3)+B(6))
GO TO 70
60 DO 65 I=1,N
65 ZETA(I)= B(5)/(X(I,3)+B(6))
GO TO 70
72 DO 74 I=1,N
74 ZETA(I)=1.
70 JTEST=0
RETURN
END
```

POLYFIT

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```
PROGRAM POLYFIT(INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
DIMENSION X(70),Y(70),YY(70),XX(70),YYCAL(70)
COMMON C(6),JJJ,YPN(70),YCAL(70),PCT(70),PERR,STDEV
20 READ(5,10) N,IX,IY,JJJ
10 FORMAT(6I5)
   READ(5,12) XF,YF
12 FORMAT(8F10.0)
22 READ(5,12) (XX(I),I=1,N)
   IF(IX.EQ.2.OR.IX.EQ.3.OR.IX.EQ.4) READ(5,12) A
   CALL FUNC(X,XX,N,IX,A)
24 READ(5,12) (YY(I),I=1,N)
   IF(IY.EQ.2.OR.IY.EQ.3.OR.IY.EQ.4) READ(5,12) B
   CALL FUNC(Y,YY,N,IY,B)
26 READ(5,10) K
   KJ=K+1
   CALL LSTSQF(N,K,X,Y,YF,YF)
   CALL REVFUNC(YCAL,YYCAL,N,IY,B)
   WRITE(6,100)
100 FORMAT(1H)///,8X,6HORIG X,8X,6HORIG Y,5X,9HORIG YCAL,7X,7HMODIF X,
   17X,7HMODIF Y,4X,10HMODIF YCAL,7X,7HPCT ERR,4X,10HDERIVATIVE/)
   WRITE(6,102) (XX(I),YY(I),YYCAL(I),X(I),Y(I),YCAL(I),PCT(I),YPN(I)
   1,I=1,N)
102 FORMAT(8E14.5)
   WRITE(6,104) PERR,STDEV
104 FORMAT(///3X,19HABS. PERCENT ERROR=,F6.3/3X,19HSTANDARD DEVIATION=
   1,F 8.5//3X,16HFITTED CONSTANTS)
   WRITE(6,120) (J,C(I),I=1,K1)
120 FORMAT(5X,2HC(,12,2H)=,E13.5)
   READ(5,10) IDT
   GO TO (20,22,24,26,28),IDT
28 STOP
END
```

```

SUBROUTINE LSTSOR(N,K,XA,YA,XF,YF)
DIMENSION XA(1),YA(1),YCAL(70),XSUM(70),A(6,6)
COMMON CA(6),JJJ,YPN(70),YCAL(70),PCT(70),PERR,STDEV
DO 10 I=1,N
  XA(I)=XA(I)*XF
10 YA(I)=YA(I)*YF
  CA(1)=0.
  DO 12 J=1,M
12 CA(1)=CA(1)+YA(J)
  XSUM(1)=N
  K1=K+1
  DO 14 I=2,K1
  CA(I)=0.
  DO 14 J=1,N
14 CA(J)=CA(I)+YA(J)*(XA(J))**(I-1)
  KK=2*K+1
  DO 16 I=2,KK
  XSUM(I)=0.
  DO 16 J=1,N
16 XSUM(I)=XSUM(I)+XA(J)**(I-1)
  DO 18 I=1,K1
  DO 18 J=1,K1
  L=I+J-1
18 A(I,J)=XSUM(L)
  DO 20 J=1,K1
  DO 24 J=1,K1
  DET=A(J,I)
  CA(J)=CA(J)/A(J,I)
  DO 24 L=1,K1
24 A(J,L)=A(J,L)/DET
  DO 20 J=1,K1
  IF(J.EQ.1) GO TO 20
  CA(J)=CA(J)-CA(I)
  DO 26 L=1,K1
26 A(J,L)=A(J,L)-A(I,L)
20 CONTINUE
  DO 28 I=1,K1
28 CA(I)=CA(I)/A(I,I)
  CA(1)=CA(1)/YF
  DO 30 J=2,K1
30 CA(I)=CA(I)/YF*XF**(I-1)
  DO 32 I=1,M
  XA(I)=XA(I)/XF
  YA(I)=YA(I)/YF
  YCAL(I)=CA(1)
  DO 32 J=2,K1
32 YCAL(I)=YCAL(I)+CA(J)*XA(I)**(J-1)
  DO 34 I=1,N
  YPN(I)=CA(2)
  IF(K1.LT.3) GO TO 34
  DO 36 J=3,K1
36 YPN(I)=YPN(I)+FLOAT(J-1)*CA(J)*XA(I)**(J-2)
  GO TO (38,34),JJJ
38 IF(YPN(I).LT.0.) YPN(I)=0.
34 CONTINUE

```



```
PEPR=0.
STDEV=0.
NM=N
DO 42 I=1,N
DELY=YCAL(I)-YA(I)
IF (ABS(YA(I))*YF-.001) 44,46,46
44 NM=NM-1
GO TO 42
46 PEPR=PEPR+ABS(DELY/YA(I))
PCT(I)=DELY/YA(I)*100.
STDEV=STDEV+DELY*DELY
42 CONTINUE
STDEV=SQRT(STDEV/FLOAT(NM-1))
PEPR=PEPR/FLOAT(NM)*100.
RETURN
END
```

```
SUBROUTINE FUNC(Z,ZZ,N,IFUNC,A)
  DIMENSION Z(1),ZZ(1)
  GO TO (10,20,30,40,50,60,70,80),IFUNC
10 DO 15 I=1,N
15 Z(I)=ZZ(I)
   RETURN
20 DO 25 I=1,N
25 Z(I)=ZZ(I)+A
   RETURN
30 DO 35 I=1,N
35 Z(I)=(ZZ(I)+A)/100.
   RETURN
40 DO 45 I=1,N
45 Z(I)=1./(ZZ(I)+A)
   RETURN
50 DO 55 I=1,N
55 Z(I)=ALOG10(ZZ(I))
   RETURN
60 DO 65 I=1,N
65 Z(I)=ALOG(ZZ(I))
   RETURN
70 DO 75 I=1,N
75 Z(I)=10.**(ZZ(I))
   RETURN
80 DO 85 I=1,N
85 Z(I)=EXP(ZZ(I))
   RETURN
END
```