

T-3448

ENTHALPY MEASUREMENTS OF THE TERNARY SYSTEM

m-CRESOL, QUINOLINE, AND TETRALIN

In the Temperature Range of 291 to 669 K

And Pressures to 10 MPa

by

Timothy Patrick Joyce

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A thesis submitted to the Faculty and Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the Degree of Masters of Science in Chemical Engineering and Petroleum-Refining.

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## ABSTRACT

Enthalpy measurements were obtained for four ternary mixtures of quinoline, m-cresol, and tetralin with a reference fluid boil-off calorimeter. The ternary systems studied were 1/3:1/3:1/3, 1/6:1/6:2/3, 2/3:1/6:1/6, and 1/6:2/3:1/6 mole percent quinoline:m-cresol:tetralin. The measurement temperatures ranged from 291 to 669 K, and pressures from 0.2 to 10.3 MPa. Liquid, vapor, and two phase enthalpy data were obtained within an error of +/- 1.0 percent.

Enthalpy predictions calculated from the Soave-Redlich-Kwong equation of state and a recent modification for polar fluids using five different mixing rules, were generated to compare with the experimental enthalpy. Two density dependent and three simple mixing rules were investigated with the equations of state. The modified equation predicted enthalpies with its modification for polar fluids better than the Soave-Redlich-Kwong. None of the mixing rules would predict both the vapor and liquid phase enthalpies along with the two phase transition. The density dependent mixing rules did not work as well as expected, and new mixing rules should be investigated for enthalpy predictions.

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ACKNOWLEDGMENTS

The author gratefully acknowledges the financial support of the United States Department of Energy, Office of Fossil Energy, through grant #DE-FG22-84PC70006. This research has been supported by the Department of the Interior's Mineral Institutes program administered by the Bureau of Mines under allotment grant number G1164108.

The author would like to thank Dr. Yesavage for his guidance and technical support during the time I spent working on this project. Thanks must also go to Drs. Kidnay and Miller for serving as members of my committee.

The author would also like to express thanks to his parents for their support, and the people who helped in the laboratory and provided technical support: Steve DiGiacinto, Trent Brown, John Flanigan, David Flanigan and Jamal Sandarusi.

## INTRODUCTION

Thermodynamic measurements are very important for the design and implementation of engineering process equipment. Energy balances are required to size and design process equipment in the fields of heat transfer, fluid flow, mass transfer, and reaction kinetics. Energy balances require enthalpy data or correlations to properly define the heat load, so that equipment can be sized correctly and economically. Also, enthalpy data or correlations must be reasonably accurate so that an engineer can be confident in the equipment design. If the information is inaccurate, then the equipment could be designed to be economically inefficient, or could experience process and mechanical failures.

In recent times there has been much research and exploration activity in alternate sources of energy and fuel. At the present time gasoline prices are at their lowest levels since the early eighties, so at this time it does not seem very economical to explore new sources of energy supplements such as coal liquids. However, it is very important to continue supporting research in these fields because they may eventually be an important source of fuel and energy. It is the author's opinion that research and exploration should continue in the

implementation of alternate fuel sources. The main interest in this report is the thermodynamic research on a ternary mixture that will be used to model coal derived liquids.

Previously enthalpy measurements for coal liquids were obtained on the calorimeter apparatus (Kidnay et. al. (1984), Sharma et. al. (1984)). After investigating enthalpies of coal derived liquids it seemed very advantageous to try to model these compounds. A reference ternary system consisting of quinoline, m-cresol, and tetralin was chosen to model coal liquids. Cerise (1980) and Flanigan (1983) and (1986) generated enthalpy data for the pure compounds and the constituent binary mixtures with Flanigan generating almost all of this data. The ternary data of quinoline, m-cresol, and tetralin generated in this investigation completes the investigation of the reference system.

The objective of this research was to study the enthalpy of a reference ternary system that will be used to model the enthalpy of coal liquids. The compounds chosen were m-cresol, quinoline, and tetralin. This ternary system is composed of a phenolic oxygen group, a basic nitrogen group, and an aromatic compound. The chemical structures of these compounds are commonly found in coal derived liquids, and the interactions from this ternary

system are anticipated to represent interactions that take place in coal derived liquids.

The first phase of the research was to generate enthalpy data for this ternary system by using a reference fluid boil-off calorimeter. The calorimetric equipment is a refined apparatus that generates precise data (+/- 1.0 percent) and has been modified over the years to a high level of sophistication. Once the data were measured another goal was to continue the work of Flanigan (1986) and predict ternary enthalpy from the binary enthalpy data. Previously, binary enthalpy data were obtained for compounds making up the ternary system. Binary interaction parameters for two equations of state and five mixing rules were extracted from this data using a maximum likelihood method. These interaction parameters were used to predict ternary enthalpy data for the different systems. The Soave equation and an equation incorporating a modification for polar fluids (Yesavage (1986)) of the Soave equation were used in the predictions of ternary data along with three simple and two density dependent mixing rules.

Ternary enthalpy data are no more difficult to obtain in the laboratory than binary enthalpy data, but it was an important objective to determine whether binary data would be able to predict ternary enthalpy with reasonable

accuracy. The elimination of gathering ternary enthalpy in the lab should save time and money. In the long run, it is very important to predict multicomponent enthalpy with the minimum amount of experimental enthalpy data.

Ternary data were obtained for four different ternary systems, 1/3:1/3:1/3, 2/3:1/6:1/6, 1/6:2/3:1/6, 1/6:1/6:2/3, mole percent m-cresol, quinoline, and tetralin by using a reference fluid boil-off calorimeter. Freon-11 was used as the reference fluid. Temperatures ranged from 291 to 669 K, and pressures from 0.2 to 10.3 MPa. Liquid, vapor and two phase enthalpy data were obtained with a maximum error of +/- 1.0 percent. The calorimeter apparatus was received in excellent working order and no modifications were required for the system.

After ternary data was measured the next step was to compare the measured data to the predicted ternary data. The two equations of state used mixing rules incorporating modifications to the attractive "a" term, while the repulsive "b" term was not modified. The density dependent mixing rules are presented by Holder et. al. (1986), and Luedecke et. al. (1985).

## PROCESS DESCRIPTION

The process flow diagram for the enthalpy apparatus is shown in Figure 1. Figure 2 shows a detailed schematic of the boil-off calorimeter. The process flow is comprised of two circuits. The first circuit consists of the sample fluid circuit and the second circuit consists of the reference fluid system.

Enthalpy measurements are made on the sample fluids flowing through the sample fluid circuit. The sample fluid is pumped from a surge tank to a fluidized sand bath preheater to gain its initial heat input. The fluid enters the fluidized bed and circulates through a coil and is heated to a temperature approaching the desired value. Immediately after the fluid exits the fluidized bed it is heated to its final temperature using a final heater and controller. As soon as the sample is heated to the final temperature, it enters the reference fluid boil-off calorimeter through a coil that is submerged in a bath of Freon-11. The heat from the sample fluid is then transferred to the reference fluid and the Freon-11 boils off. The sample fluid exits the calorimeter at temperatures approaching 65 °F, and the pressure is set by a nitrogen back pressure regulator. The sample then enters a three way valve where it is either diverted to a sample flask for



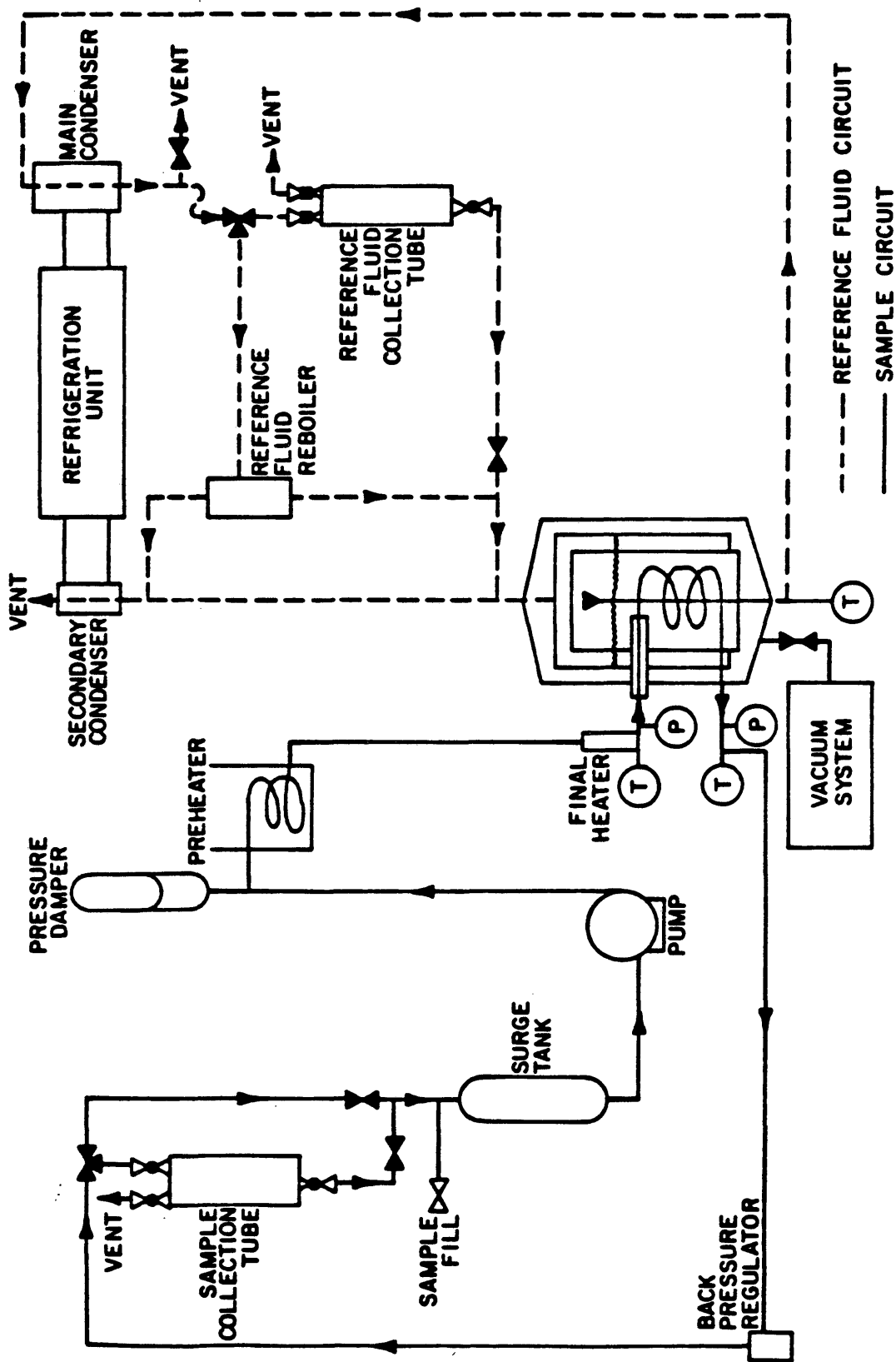
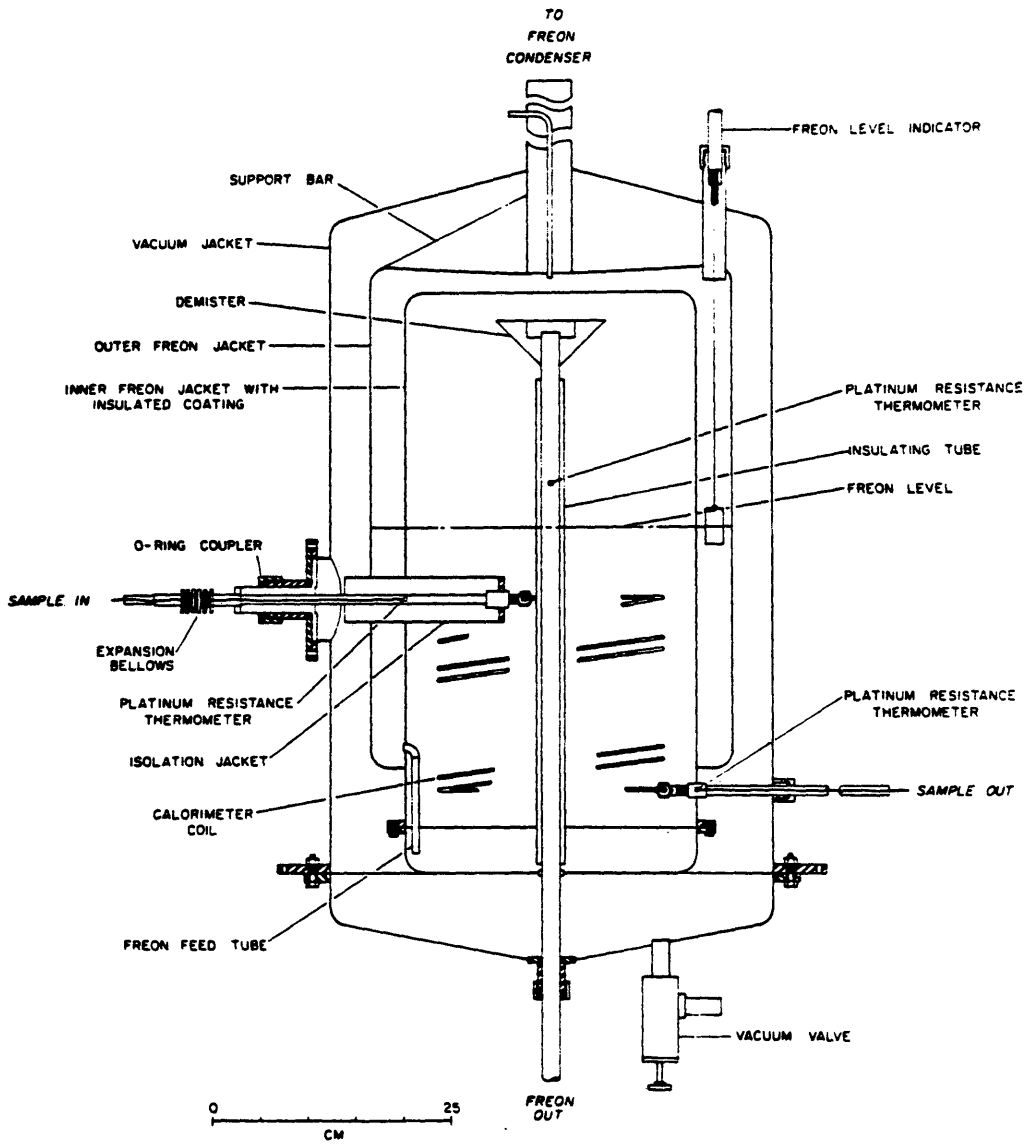


Figure 1 Calorimeter System Flow Diagram

Figure 2

FLOW CALORIMETER



collection or back to the surge tank where it is recirculated through the system. Before the sample is charged back to the surge tank it runs through a molecular sieve filter to help eliminate any water that might be in the sample.

Freon-11 is the reference fluid and it is kept at its boiling point ( 65 °F for Golden, Colorado) inside the calorimeter. The heat from the sample is transferred to the Freon, which boils off and exits the calorimeter. As the reference fluid exits the calorimeter the Freon is superheated to make sure all the boiled off Freon does not recondense. After the Freon is superheated it runs through a condenser and is cooled well below its boiling point. The liquid reference fluid then enters a three way valve where it is either diverted to a sample flask and collected, if a run is being initiated, or it is sent back to the calorimeter. If the Freon is being collected, it is very important that the collection flask is well chilled so that the collected Freon does not vaporize to the atmosphere as it enters the collection flask. Before the Freon returns to the calorimeter it enters a reboiler and is heated to its boiling point, and then is charged back to the calorimeter. This is to make sure no subcooled Freon is put back into the calorimeter ruining the enthalpy measurements. The

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calorimeter has a vacuum jacket and an inside Freon jacket to prevent any heat from penetrating into the reference fluid calorimeter producing erroneous measurements. The Freon system is vented to the atmosphere and a secondary condenser is connected to the vent to prevent any Freon from boiling off to the atmosphere. The vent is also connected to drierite capsules to prevent any water from getting into the Freon side of the calorimeter.

### Process Theory

The enthalpy measurements are generated using a reference fluid boil-off calorimeter, and Freon-11 is used as the reference fluid. The sample fluid is heated and pumped to its desired temperature and pressure where it enters the calorimeter. As it flows through the calorimeter, the heat from the sample fluid is transferred to the reference fluid.

The experimental enthalpy is obtained by applying the first law of thermodynamics to a flow system (Smith and Van Ness 1975), and the first law application to the flow calorimeter yields the following equation.

$$M_S * ( \Delta H + \Delta V^2 / 2g_c + g/g_c * \Delta Z ) = Q - W_S \quad (1)$$

where,  $\Delta H = H(T_{in}, P_{in}) - H(T_{out}, P_{out})$

$Q$  = heat removed from sample fluid

$M_S$  = mass flow rate of sample

$W_S$  = shaft work done by sample fluid

$\Delta V^2 / 2g_c$  = kinetic energy term

$\Delta Z * g / g_c$  = potential energy term

$T_{in}$  = inlet calorimeter temperature

$P_{in}$  = inlet calorimeter pressure

$T_{out}$  = outlet calorimeter temperature

$P_{out}$  = outlet calorimeter pressure

This equation assumes that no external heat gradients

are transmitted into the calorimeter. This phenomena has been studied by Mohr (1980), who determined that heat leaks can be neglected as long as a sufficient sample flow can be maintained by the pump.

The kinetic energy term  $\Delta V^2/2g_c$  and the potential energy term  $\Delta Z \cdot g/g_c$  are neglected, and no shaft work is done by the fluid, so the equation can be simplified to the following form.

$$\Delta H = Q/M_s \quad (2)$$

where,  $Q = h_f \cdot M_f$

$h_f$  = latent heat of vaporization Freon

$M_f$  = mass flow of Freon-11

Thus, the heat balance equation reduces to the following form.

$$\Delta H = h_f \cdot M_f / M_s \quad (3)$$

The outlet calorimeter temperature of the sample is a direct function of the atmospheric pressure, since the Freon-11 boiling point varies with the atmospheric pressure. The Freon boiling point is approximately 65°F in Golden, and it doesn't deviate much from this value. The reference temperature is 65°F and the reference pressure is chosen as 1 atm. The experimental data is then corrected for the reference temperatures and pressures. The tabulated experimental enthalpy is based on  $h=0$  at 65°F and the actual

outlet pressure of the calorimeter. The expression for the experimental enthalpy corrected for temperature is shown below:

$$\Delta H_{\text{exp}} = h_f * M_f / M_s + M_s * C_{p65} * (T_{\text{out}} - 65) \quad (4)$$

$C_{p65}$  = sample heat capacity at 65°F

$T_{\text{out}}$  = outlet calorimeter temperature (°F)

The enthalpy is then corrected for pressure. The pressure correction is based on an enthalpy departure using the method of calculation as outlined by Lee and Kesler, 1975. The corrected enthalpy is based on  $h=0$  at 65°F and an outlet pressure of 1 atm. The expression for the enthalpy corrected for temperature and pressure is as follows:

$$\Delta H_{\text{corr}} = h_f * M_f / M_s + M_s * C_{p65} * (T_{\text{out}} - 65) + H(T_{\text{ref}}, P_{\text{ref}}) \quad (5)$$

$H(T_{\text{ref}}, P_{\text{ref}})$  = Enthalpy pressure correction from Lee-Kesler correlation

The values for  $\Delta H_{\text{exp}}$  and  $\Delta H_{\text{corr}}$  are shown in tabulated form in the enthalpy measurement section of this document.

## EXPERIMENTAL OPERATION

The reference fluid boil-off calorimeter is a reliable apparatus for an experimental operation. This section will explain the start-up and shut-down procedures, and explain the experimental operation required to generate enthalpy data.

Start-up Procedure

- 1.) Turn on the refrigeration unit and wait until the water outlet temperature reaches approximately 40 °F (this usually takes 25 minutes).
- 2.) Turn on vacuum pump.
- 3.) Zero Heise gauges, and then close the gauges.
- 4.) Turn on air to fluidized bed ( make sure an air flow of 150 SCFH is obtained).
- 5.) Turn on thermocouple and PRT indicators.
- 6.) Open all vents to the Freon system.
- 7.) Open vent to surge tank.
- 8.) Turn on pump and start circulating sample fluid.
- 9.) Open Heise gauges slowly to read system pressure.
- 10.) Turn on diffusion pump.
- 11.) Dial temperature on fluidized bed and then turn on the power to start heating up the sample fluid.
- 12.) Set system pressure using the nitrogen back pressure regulator.



13.) Turn on power to final heater and slowly set system temperature.

14.) Wait until the temperature and pressure get to their desired level before starting an experimental run.

Figure 1 shows a pressure damper in the process flow diagram. The pressure damper system is not required anymore since the installation of the low pulse HPLC sample pump. The damper system was not used during this project.

#### Shut-down Procedure

- 1.) Turn off power to final heater controller and the fluidized bed.
- 2.) Turn on water to fluidized bed cooling coil.
- 3.) Vent nitrogen pressure from back pressure regulator. Make sure the sample fluid is in the liquid region before the nitrogen back pressure is vented.
- 4.) Turn off diffusion pump.
- 5.) Wait until sample fluid temperature is below 140 °F and then turn off sample fluid pump.
- 6.) Close vents to the Freon system.
- 7.) Turn off thermocouple and PRT indicators.
- 8.) Turn off water to the fluidized bed and turn off the air flow to the fluidized bed.
- 9.) Close vent to the surge tank.
- 10.) Turn off the vacuum pump.

11.) Turn off the refrigeration unit.

#### Experimental Procedure

An experimental run cannot be initiated until the calorimeter apparatus has been started-up, and the sample pressure and temperature are close to the desired levels. The following steps will illustrate how an experimental run is taken.

- 1.) Fine tune pressure and temperature to their desired levels, using the back pressure regulator and the final heater controller.
- 2.) Wait until temperatures and pressures are stable (a suitable steady state is achieved).
- 3.) Record barometric pressure.
- 4.) Get two sample flasks ready. One will be used for the sample fluid and the other will be used for the reference fluid (the reference fluid flask must be cold).
- 5.) Open three way valves to divert sample and reference fluids to the collection flasks. The fluids will be collected for about five minutes.
- 6.) Record inlet and outlet pressure at the beginning and end of the run.
- 7.) Record Freon system temperatures at the beginning of the run.
- 8.) Record outlet sample temperature and Freon bath

temperature at the midpoint of the experimental run.

9.) Record sample inlet temperature every 30 seconds throughout the run.

10.) Halt the collection of fluids after five minutes by adjusting the three way valves to their recirculation position.

11.) Weigh sample flasks and determine sample and reference weights.

12.) Calculate experimental enthalpy.

#### Experimental Verification

The experimental apparatus has been used extensively during the past two years, and numerous data have been obtained from the equipment. The gauges had been recently calibrated before the author took over the equipment. The equipment was working well, so calibrations were not repeated during this investigation. A gauge had to be replaced during the last system because it was not working properly, but it was replaced with another Heise gauge that had been calibrated earlier. The pressure measurement can always be checked because there are three inlet pressure gauges which can be checked against each other.

Before the experimental work was initiated on this thesis, familiarity was obtained with the equipment by

checking the operation by measuring the enthalpy of n-heptane. This fluid has been used extensively in the past to check if the equipment is working properly. The n-heptane enthalpy was reproduced within the accuracy of the equipment for the 1061.5 (154 psia) isobar.

The n-heptane data generated for the calorimeter check is shown in Table 1. Figure 3 shows the n-heptane data along with other n-heptane data generated by Flanigan (1986). The agreement between the two sets of n-heptane data assures that the equipment is running properly, and that no major modifications were required for the apparatus.

#### Composition Analysis

During the experimental enthalpy determination the sample fluid is subjected to high temperatures and high pressures. During earlier investigations, it had been noticed that some of the pure components and the binary systems of the fluids of interest had broken down under the high temperatures and pressures. Tetralin was one of these compounds that had undergone degradation. The thermal breakdown cannot be avoided, but the samples were analyzed on a gas chromatograph to check if the compounds composition had actually changed. The gas chromatograph checks were applied to the compounds after the sample fluids were subjected to high temperatures, which occur at the high end

Table 1

Specific enthalpy measurements for the pure component				
n-Heptane				
			$\Delta H / (\text{kJ} \cdot \text{kg}^{-1})$	
T(in)/K	P(in)/kPa	P(out)/kPa	expt.	corr.
1061.5 kPa				
366.4	1061.7	1027.2	171.6	172.4
389.8	1065.1	1034.1	230.9	231.7
410.8	1068.5	1040.9	287.8	288.6
436.0	1068.5	1034.0	360.5	361.4
454.9	1061.6	1040.9	418.2	419.0
468.9	1065.0	1047.8	461.1	462.0
477.3	1061.6	1040.9	550.3	551.1
477.9	1061.6	1047.8	658.7	659.5
487.1	1061.6	1040.9	730.4	731.2
495.3	1061.6	1040.9	753.6	754.4
507.5	1061.6	1040.9	788.3	789.1
522.2	1061.6	1047.8	828.2	829.0
533.6	1065.0	1044.3	861.3	862.1

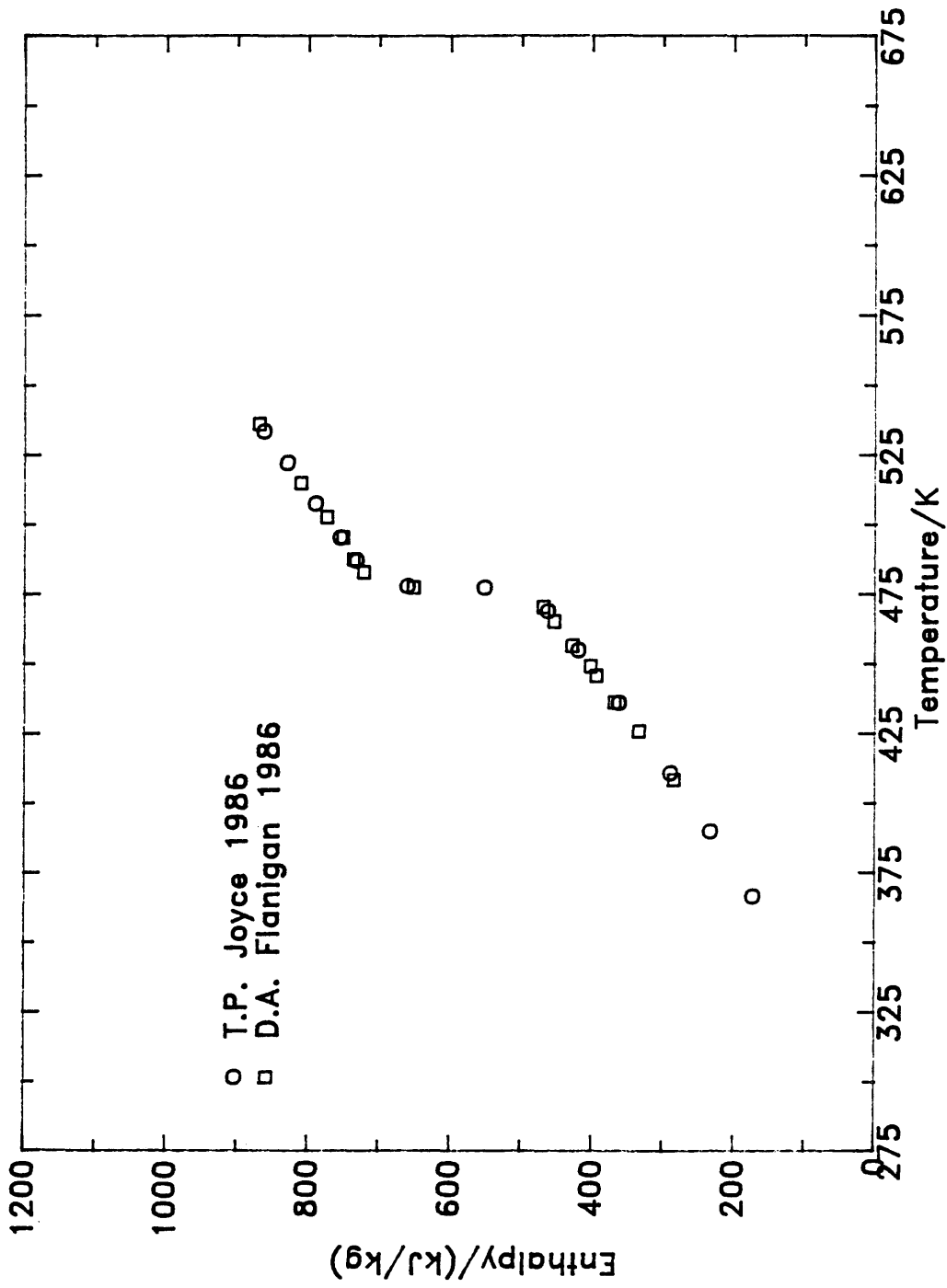


Figure 3 Enthalpy of n-Heptane

of the vapor phase region. The gas chromatograph showed that the composition of the sample fluids did not change during the experimental operation.

The low pressure enthalpy in the liquid region was generated first because the sample does not have a history of decomposing in this region. The two-phase and vapor phase data were then obtained, and the sample composition was checked intermittently for decomposition or cracking. The last data taken were the high pressure liquid phase data. These were taken last because the system was being operated at high pressures and pump failures are a major concern. There is a great need for concentration when operating at high pressure (10340 kPa) due to the potential safety problems.

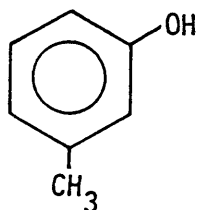
The sample loop had been modified a year ago, and it was isolated from the atmosphere. This prevents the sample fluid from obtaining water from the atmosphere. The modification worked very well, and the sample fluids were checked for water contamination by using a Hewlett Packard gas chromatograph with a thermoconductivity detector (TCD). The TCD detector can determine water contamination. No water contamination was witnessed during this investigation by the gas chromatograph.

## MODELING COMPOUNDS

The three modeling compounds chosen for the ternary system were m-cresol, quinoline, and tetralin. These compounds are very representative of the type of chemical compounds that are found in coal derived liquids.

m-Cresol

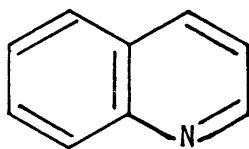
m-Cresol is an acidic type compound and its chemical structure is shown below.



The physical and critical data used for this compound are shown in Table 2. The compound was purchased from the Sigma chemical company with a purity of 99+ mole percent.

Quinoline

Quinoline is a basic nitrogen compound that is commonly found in coal derived liquids and its chemical structure is shown below.



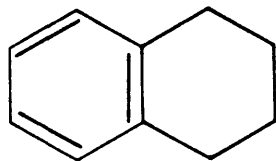
The physical and critical data used for this compound are tabulated in Table 2. The compound was purchased from



the J.T. Baker chemical company with a 99+ mole percent purity.

### Tetralin

Tetralin is a hydroaromatic compound and its chemical structure is shown below.



The physical and critical data for the compound are also presented in Table 2. Tetralin was purchased from the Aldrich chemical company at a purity of 99+ mole percent.

Each of the three compounds described were further purified to +99.9 mole percent using a spinning band distillation column. The distillation column was able to remove water and other impurities in a very simple manner, and no problems were encountered with the distillation.

The ternary systems were composed by measuring the correct weights of each chemical to give the desired mole percent. The weights were measured using a Mettler balance, which can measure to 0.01 grams.

Table 2  
Critical and Physical Property  
of Pure Compounds

	<u>Quinoline</u> <sup>a</sup>	<u>m-Cresol</u> <sup>b</sup>	<u>Tetralin</u> <sup>c</sup>
Critical Temperature (K)	800.2	705.8	719.2
Critical Pressure (MPa)	5.774	4.558	3.514
Acentric Factor	0.318	0.464	0.303
Average Molecular Weight	129.16	108.14	132.21

<sup>a</sup>(Glaser et. al. 1957)

<sup>b</sup>(Reid et. al. 1977)

<sup>c</sup>(Lin et. al. 1980, Reid et. al 1977)

## MATHEMATICAL MODELING

In addition to generating experimental enthalpy, a proposed set of mathematical models were used to test the data. During the investigation by Flanigan (1986), binary interaction parameters were generated for the Soave-Redlich-Kwong equation of state, and an equation that modifies the SRK for polar fluids for five different mixing rules. The modeling in this thesis is a continuation of Flanigan's work. The equations of state will be used for both the liquid and vapor phase fugacities, and no activity coefficient models were investigated. The goal is to use the binary interaction parameters to predict the ternary enthalpy that was obtained during the experimental program. This requires the derivation of the fugacity coefficients and enthalpy departures from the two equations of state and five mixing rules.

### Equations of State

The two investigated equations of state in this thesis are the Soave-Redlich-Kwong (1972) SRK and the modified Soave-Redlich-Kwong for polar fluids by Yesavage YSRK. These two equations were investigated by Flanigan (1986). The work he initiated is continued in this thesis. The SRK equation was chosen for its simplicity and its ability to model nonpolar fluids. The YSRK equation was investigated

because it attempts to separate the effects of shape and polarities of the compound. The YSRK equation has not been used that extensively in the past and this gives us the opportunity to check if the equation will be useful for polar compounds. The SRK equation for a single compound is presented as follows.

$$P = RT/(v-b) - a(T)/v(v+b) \quad (6)$$

where,  $b = 0.08664RT_c/P_c$   
 $a(T_c) = 0.42747R^2T_c^2/P_c$   
 $\alpha = (1 + m(1-(T_r)^{0.5}))^2$   
 $a(T) = a(T_c)*\alpha$   
 $m = 0.48 + 1.574\omega - 0.176\omega^2$

$\omega$  = acentric factor of the compound

$T_c$  = critical temperature

$P_c$  = critical pressure of compound

$T_r = T/T_c$

The YSRK equation is very similar to the SRK equation. The YSRK is a modification of the SRK equation for polar fluids. The modification attempts to separate polar effects from size effects in the " $\alpha$ " portion of the equation. The " $\alpha$ " term in the SRK equation is replaced by " $\alpha_p*\alpha_n$ ". A much more detailed description of this equation is given in Yesavage (1986). The YSRK equation is given as:

$$P = RT/(v-b) - a(T)/v(v+b) \quad (7)$$

where,  $b = 0.08664RT_c/P_c$   
 $a(T_c) = 0.42747R^2T_c^2/P_c$   
 $\alpha_n = (1 + m(1-(T_r)^{0.5}))^2$   
 $\alpha_p = 1 + Rp*\exp(-Rp)^e - Rp*\exp(-(Rp/Tr)^e)$   
 $m = 0.48 + 1.574\omega_n - 0.176\omega_n^2$

$$a(T) = a(T_c)*\alpha_n*\alpha_p$$

$T_c$  = critical temperature

$P_c$  = critical pressure of compound

$$T_r = T/T_c$$

$R_p$  = Polar parameter fit to VP data of polar parameter.

$$e = 0.45$$

$\omega_n$  = acentric factor for nonpolar homomorph

The Yesavage modification of the SRK equation reduces to the SRK equation when  $R_p=0$ .

### Mixing Rules

A total of five different types of mixing rules for the attractive "a" term were investigated in this study. The mixing rule chosen for the repulsive "b" term was a simple arithmetic type shown below.

$$b = \sum x_i b_i$$

The mixing rules for the "a" term are shown below in Table 3.

Table 3

Mixing Rules for the Attractive "a" Term

- 1.) 
$$a = \frac{\sum_{ij} x_i x_j (a_i a_j)^{0.5}}{\sum_{ij} x_i x_j}$$
- 2.) 
$$a = \frac{\sum_{ij} x_i x_j (a_i a_j)^{0.5} (1 - k_{ij})}{\sum_{ij} x_i x_j}$$
- 3.) 
$$a = \frac{\sum_{ij} x_i x_j (a_i a_j)^{0.5} (1 - (A + B/T))}{\sum_{ij} x_i x_j}$$
- 4.) 
$$a = \frac{\sum_{ij} x_i x_j (a_i a_j)^{0.5} (1 - k_{ij} + B(ij)/(vRT))}{\sum_{ij} x_i x_j}$$
- 5.) 
$$a = \frac{\sum_{ij} x_i x_j (a_i a_j)^{0.5} (1 - k_{ij})}{\sum_{ij} x_i x_j} + \frac{1}{(vRT)} \sum_{ij} x_i x_j (x_i c_i(j) + x_j c_j(i))$$

The first three mixing rules are very simple. Mixing rule one assumes  $k_{ij}$  is equal to zero; mixing rule two incorporates a simple  $k_{ij}$ ; and the third assumes that the  $k_{ij}$  term is dependent on temperature. Mixing rules four and five are density dependent. The fourth mixing rule is a modification of the Holder et. al. (1986) mixing rule, and the fifth was proposed by Luedecke et. al. (1985); both are density dependent.

Binary Interaction Parameters

The binary interaction parameters were generated by

Flanigan (1986). This document uses his parameters to do the enthalpy predictions. The parameters were generated using a maximum likelihood method, and are summarized in Table 4. The SRK equation did not do a good job predicting the pure component m-cresol enthalpy (Flanigan (1986)) so only two mixing rules were investigated for the SRK equation.

Table 4  
Binary Interaction Parameters  
for  
(1)-Quinoline, (2)-m-Cresol, (3)-Tetralin

<u>Mixing Rule</u>	<u>Interaction Parameters</u>	<u>Equation State</u>
1.	$k_{12}=0.0$ $k_{13}=0.0$ $k_{23}=0.0$	SRK
2.	$k_{12}=-5.9E-2$ $k_{13}=-1.66E-2$ $k_{23}=2.84E-2$	SRK
1.	$k_{12}=0.0$ $k_{13}=0.0$ $k_{23}=0.0$	YSRK
2.	$k_{12}=-6.10E-2$ $k_{13}=-2.17E-2$ $k_{23}=3.65E-2$	YSRK
3.	$k_{12}=5.49E-2$ , $B(12)=-34.89$ $k_{13}=-1.842E-3$ , $B(13)=-11.46$ $k_{23}=1.21E-2$ , $B(23)=-37.3$ $B(ij)=B(ji)$	YSRK
4.	$k_{12}=-8.87E-2$ , $B(12)=-5.04E7$ $k_{13}=-3.22E-2$ , $B(13)=-1.68E7$ $k_{23}=-5.88E-2$ , $B(23)=-5.75E7$ $B(ij)=B(ji)$	YSRK
5.	$k_{12}=6.57E-2$ , $c(12)=5.94E-2^*$ $k_{13}=7.01E-3$ , $c(13)=6.31E-3$ $k_{23}=0.155$ , $c(23)=8.92E-2$ $c(21)=8.60E-2$ $c(31)=1.91E-2$ $c(32)=5.57E-2$	YSRK

\*The values of  $c$  are normalized by  $a_i(T_c)^2$



### Derived Thermodynamic Quantities

The derived quantities required for the enthalpy predictions consist of the vapor and liquid fugacity coefficients along with the enthalpy departures. Flanigan (1986) derived these expressions for a multicomponent system using the first three mixing rules and both equations of state, and the exercise is not repeated in this document. The derivations in this investigation had to be completed for mixing rules four and five and the YSRK equation for systems containing three components. These mixing rules were not studied for the the SRK equation since the SRK equation does not do a good job predicting the enthalpy of m-cresol. The fugacity coefficient for mixing rule four and the YSRK equation are shown below.

$$\begin{aligned} \ln \phi_i = & \left( \frac{b_i}{v-b} \right) + \ln \left( \frac{v}{v-b} \right) + \left[ \frac{b_i * A_{mix}}{R*T} \right] * \left[ \left( \frac{1.}{b^2} \right) \ln \left( \frac{b+v}{v} \right) - \left( \frac{1.}{b*(b+v)} \right) \right] \\ & - \left[ \frac{A_{pr}(i)}{b*R*T} \right] * \ln \left( \frac{b+v}{v} \right) + \left[ \frac{b_i * \text{Beta}}{(R*T)^2} \right] * \left[ \frac{b_i + 2*v}{v*b^2*(b+v)} + \left( \frac{2.}{b^3} \right) * \ln \left( \frac{v}{v+b} \right) \right] \\ & - \left[ \frac{\text{Beta} + C_{pr}(i)}{(R*T)^2} \right] * \left[ \left( \frac{1.}{b*v} \right) + \left( \frac{1.}{b^2} \right) * \ln \left( \frac{v}{v+b} \right) \right] - \ln Z \quad (8) \end{aligned}$$

$$\text{where, } b = \sum_i x_i b_i$$

$$A_{mix} = \sum_{ij} x_i x_j (a_i a_j)^{1/2} (1 - k_{ij})$$

$$C_{mix} = \sum_{ij} x_i x_j (a_i a_j)^{1/2} (B_{ij})$$

$$A_{pr}(i) = 2 \sum_j x_j (a_i a_j)^{1/2} (1 - k_{ij})$$

$$C_{apr}(i) = 2 \sum_j x_j (a_i a_j)^{1/2} (B_{ij})$$

$$Z = (P \cdot v) / (R \cdot T)$$

The enthalpy departure for this mixing rule and the YSRK equation is listed below.

$$(H-H^*) = R \cdot T \cdot (Z-1) - \left[ \frac{A_{prime} \cdot T - A_{eos}}{b} \right] * \ln \left( \frac{Z}{Z+B} \right) + \left( \frac{1}{R \cdot b^2} \right) * \left[ D_{beta} - \left( \frac{2 \cdot Beta}{T} \right) \right] * \left[ \left( \frac{B}{Z} \right) + \ln \left( \frac{Z}{Z+B} \right) \right] \quad (9)$$

where,  $b = \sum_i x_i b_i$

$$B = (P \cdot b) / (R \cdot T)$$

$$A_{eos} = \sum_{ij} x_i x_j (a_i a_j)^{1/2} (1 - k_{ij})$$

$$Beta = \sum_{ij} x_i x_j (a_i a_j)^{1/2} B_{ij}$$

$$A_{prime} = \sum_{ij} (1/2) x_i x_j (a_i a_j)^{-1/2} (a_i \cdot A_{pr}(j) + a_j \cdot A_{pr}(i)) * (1 - k_{ij})$$

$$D_{beta} = \sum_{ij} (1/2) x_i x_j (a_i a_j)^{-1/2} (a_i \cdot A_{pr}(j) + a_j \cdot A_{pr}(i)) * B_{ij}$$

$$A_{pr}(i) = -a T_c(i) * (((R_p(i) / T_r(i)) ** e) * \alpha(i)$$

$$* e * R_p(i) / T) * \exp(-(R_p(i) / T_r(i)) ** e) + m(i) * \alpha_p(i)$$

$$* (1.0 + m(i) * (1.0 - T_r(i) ** .5)) / ((T * T_c(i)) ** .5))$$

The fifth mixing rule is somewhat more complicated than the previous mixing rules and the fugacity coefficient is given as:

$$\begin{aligned} \ln \phi_i = & \left( \frac{b_i}{v-b} \right) + \ln \left( \frac{v}{v-b} \right) + \left[ \frac{b_i * A_{mix}}{R * T} \right] * \left[ \left( \frac{1.}{b^2} \right) \ln \left( \frac{b+v}{v} \right) - \left( \frac{1.}{b * (b+v)} \right) \right] \\ & - \left[ \frac{A_{pr}(i)}{b * R * T} \right] * \ln \left( \frac{b+v}{v} \right) + \left[ \frac{b_i * C_{mix}}{(R * T)^2} \right] * \left[ \frac{b_i + 2 * v}{v * b^2 * (b+v)} + \left( \frac{2.}{b^3} \right) * \ln \left( \frac{v}{v+b} \right) \right] \\ & - \left[ \frac{C_{apr}(i)}{(R * T)^2} \right] * \left[ \left( \frac{1.}{b * v} \right) + \left( \frac{1.}{b^2} \right) * \ln \left( \frac{v}{v+b} \right) \right] - \ln Z \quad (10) \end{aligned}$$

where,  $b = \sum_i x_i b_i$

$$A_{mix} = \sum_{ij} x_i x_j (a_i a_j)^{1/2} (1 - k_{ij})$$

$$C_{mix} = \sum_{ij} (x_i^2 x_j c_i(j) + x_i x_j^2 c_j(i))$$

$$A_{pr}(i) = 2 \sum_j x_j (a_i a_j)^{1/2} (1 - k_{ij})$$

$$C_{apr}(i) = 2 \sum_j (2 x_j x_j c_i(j) + x_j^2 c_j(i))$$

$$Z = (P * v) / (R * T)$$

The enthalpy departure for this mixing rule and the YSRK equation is presented below.

$$\begin{aligned}
(H-H^*) = & R^*T^*(Z-1) - \left[ \frac{\text{Aprime}^*T - \text{Aeos}}{b} \right] * \ln \left( \frac{Z}{Z+B} \right) \\
& + \left( \frac{1.}{R^*b^2} \right) * \left[ - \left( \frac{2^*Beta}{T} \right) \right] * \left[ \left( \frac{B}{Z} \right) + \ln \left( \frac{Z}{Z+B} \right) \right] \quad (11)
\end{aligned}$$

where,  $b = \sum_i x_i b_i$

$$B = (P*b)/(R*T)$$

$$\text{Aeos} = \sum_{ij} x_i x_j (a_i a_j)^{1/2} (1 - k_{ij})$$

$$\text{Beta} = \sum_{ij} (x_i^2 x_j c_{ij} + x_i x_j^2 c_{ji})$$

$$\text{Aprime} = \sum_{ij} (1/2) x_i x_j (a_i a_j)^{-1/2} (a_i * \text{apr}(j) + a_j * \text{Apr}(i)) * (1 - k_{ij})$$

$$\text{Apr}(i) = -a T_c(i) * (((Rp(i)/T_r(i)) ** e) * \alpha(i))$$

$$* e * Rp(i)/T * \exp(-(Rp(i)/T_r(i)) ** e) + m(i) * \alpha_p(i)$$

$$* (1.0 + m(i) * (1.0 - T_r(i) ** .5)) / ((T * T_c(i)) ** .5))$$

## ENTHALPY MEASUREMENTS ON THE TERNARY SYSTEM OF M-CRESOL, QUINOLINE, AND TETRALIN

The objective of the experimental portion of this project was to obtain enthalpy measurements for the ternary reference system containing quinoline, m-cresol, and tetralin. This specific system will help to understand the thermodynamics of coal derived liquids.

Four ternary systems of m-cresol, quinoline, and tetralin were generated during the work of this project. The ternary systems are referred by the mole percent quinoline, m-cresol, and tetralin present in each mixture. The enthalpy data are presented in tabular form (Tables 6-9) and they are also shown in enthalpy plots (Figures 4-7). The value labeled  $\Delta H_{\text{exp}}$  is corrected for an outlet calorimeter temperature of 65°F. The value labeled  $\Delta H_{\text{corr}}$  is corrected for the reference temperature of 65°F and an outlet calorimeter reference pressure of 1 atm.

The data for the ternary mixtures were taken over a temperature range of 291 to 669 K, and commonly over the following isobars, 206.8, 413.7, 689.5, 1034, and 10340 kPa. It was not possible to obtain data for the 206.8 kPa isobar during the 1/6:2/3:1/6 quinoline:m-cresol:tetralin system because of the fluid viscosity; instead enthalpy was generated for a 275.7 kPa isobar. The 1034 kPa isobar was obtained only for the 1/3:1/3:1/3 quinoline:m-

cresol:tetralin system and was not repeated for any other system.

Pseudo critical parameters for each ternary mixture had to be determined to correct the experimental enthalpy for temperature and pressure. The pure component constants that were presented in Table 2 were used to calculate the critical parameters for the ternary system, and these values are given in Table 5.

The enthalpy data generated for the 1/3:1/3:1/3, 1/6:1/6:2/3, 2/3:1/6:1/6, 1/6:2/3:1/6 mole percent quinoline:m-cresol:tetralin are presented in Figures 4, 5, 6 and 7, and the data is tabulated in Tables 6, 7, 8, and 9 respectively.

Table 5  
Ternary Mixture Critical Parameters

<u>Mixture of Quinoline:m-Cresol: Tetralin</u>	<u>Critical Temperature (K)</u>	<u>Critical Pressure (MPa)</u>	<u>Acentric Factor</u>	<u>Average Molecular Weight</u>
1/3:1/3:1/3	739.32	4.470	0.3617	123.17
1/6:1/6:2/3	728.66	3.943	0.3323	127.69
2/3:1/6:1/6	768.21	5.063	0.3398	126.17
1/6:2/3:1/6	722.8	4.514	0.4128	115.66

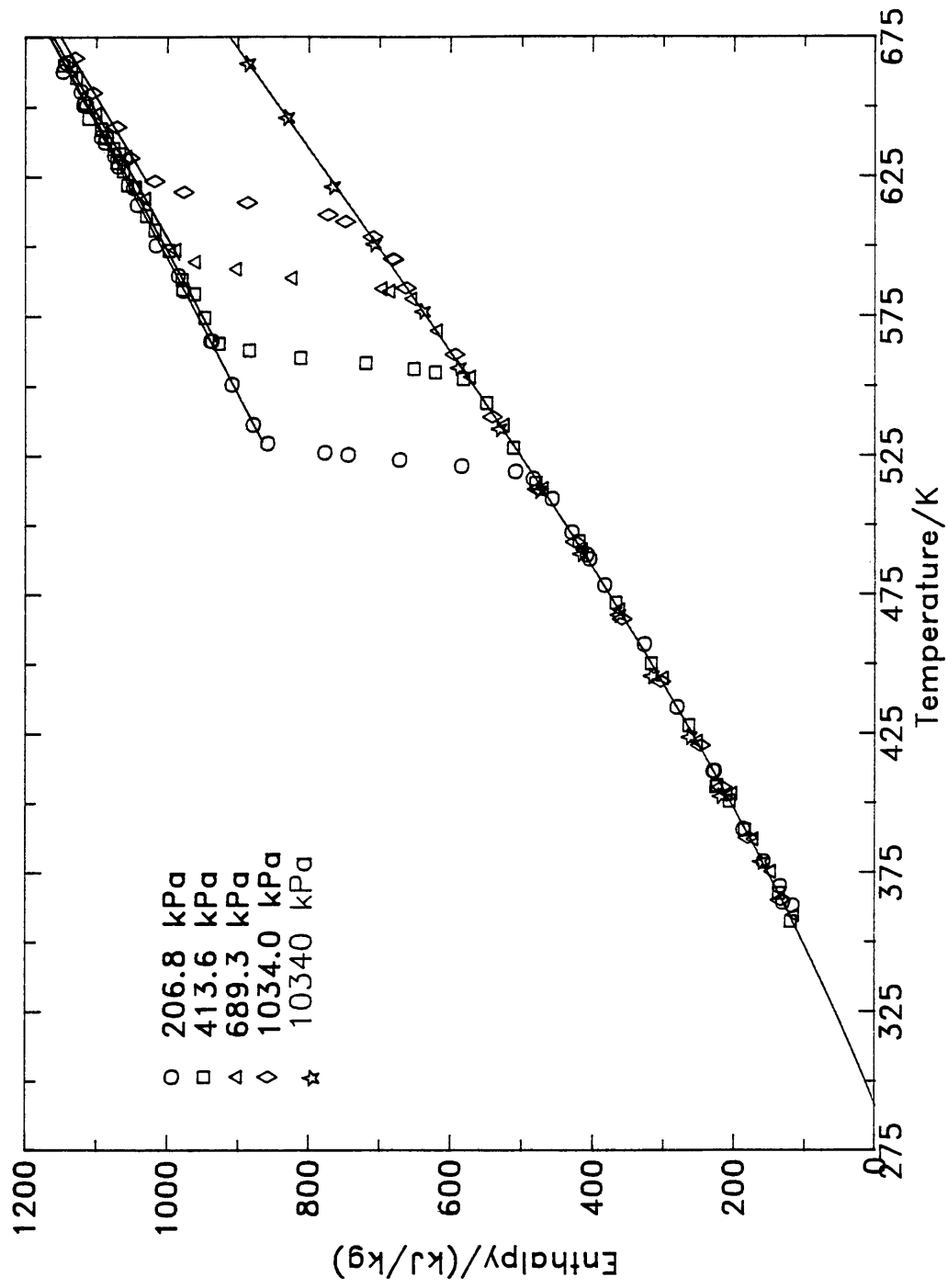


Figure 4 Enthalpy of 1/3:1/3:1/3 Quinoline:m-Cresol:Tetralin



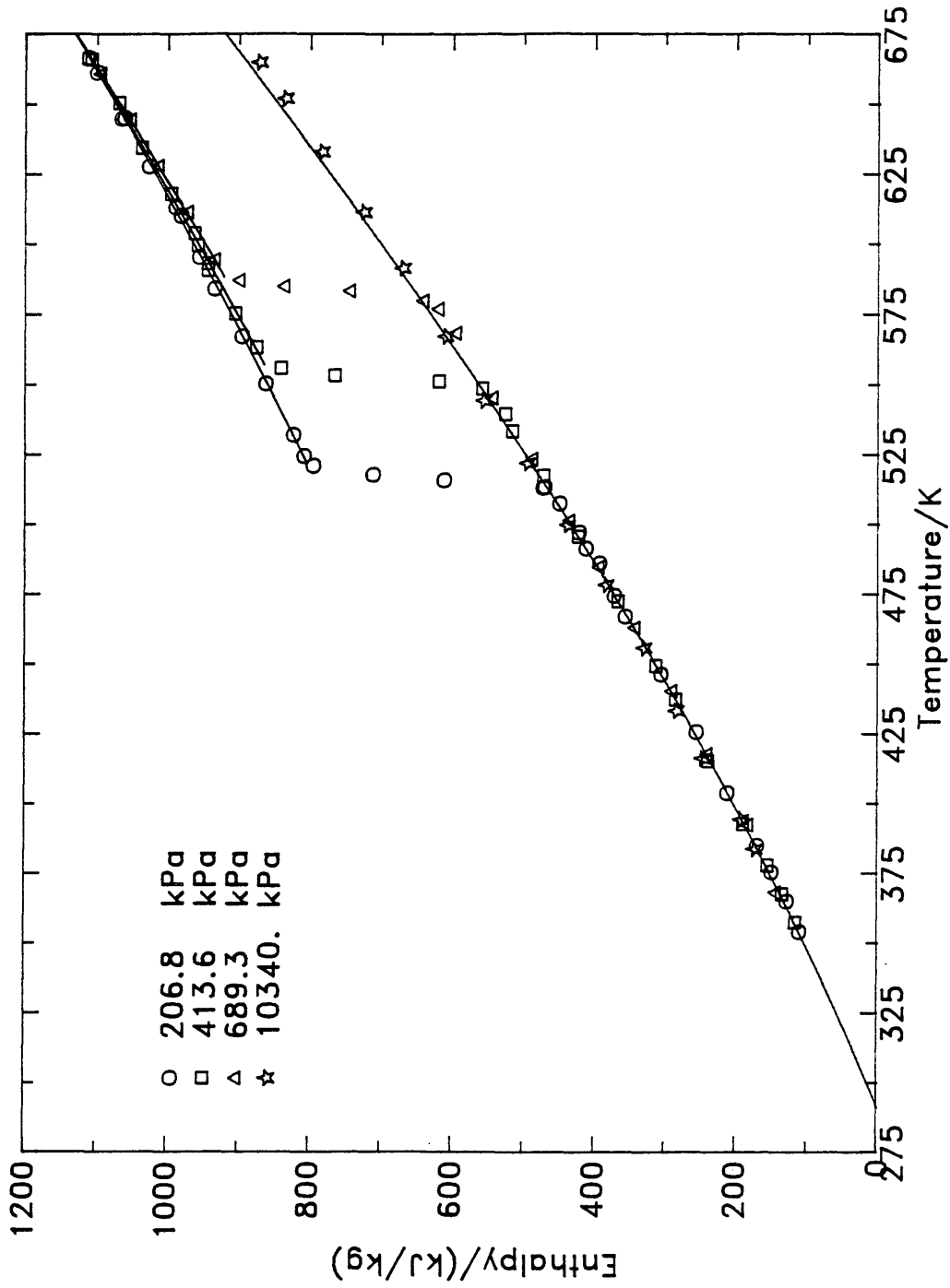


Figure 5 Enthalpy of 1/6:1/6:2/3 Quinoline:m-Cresol:Tetralin

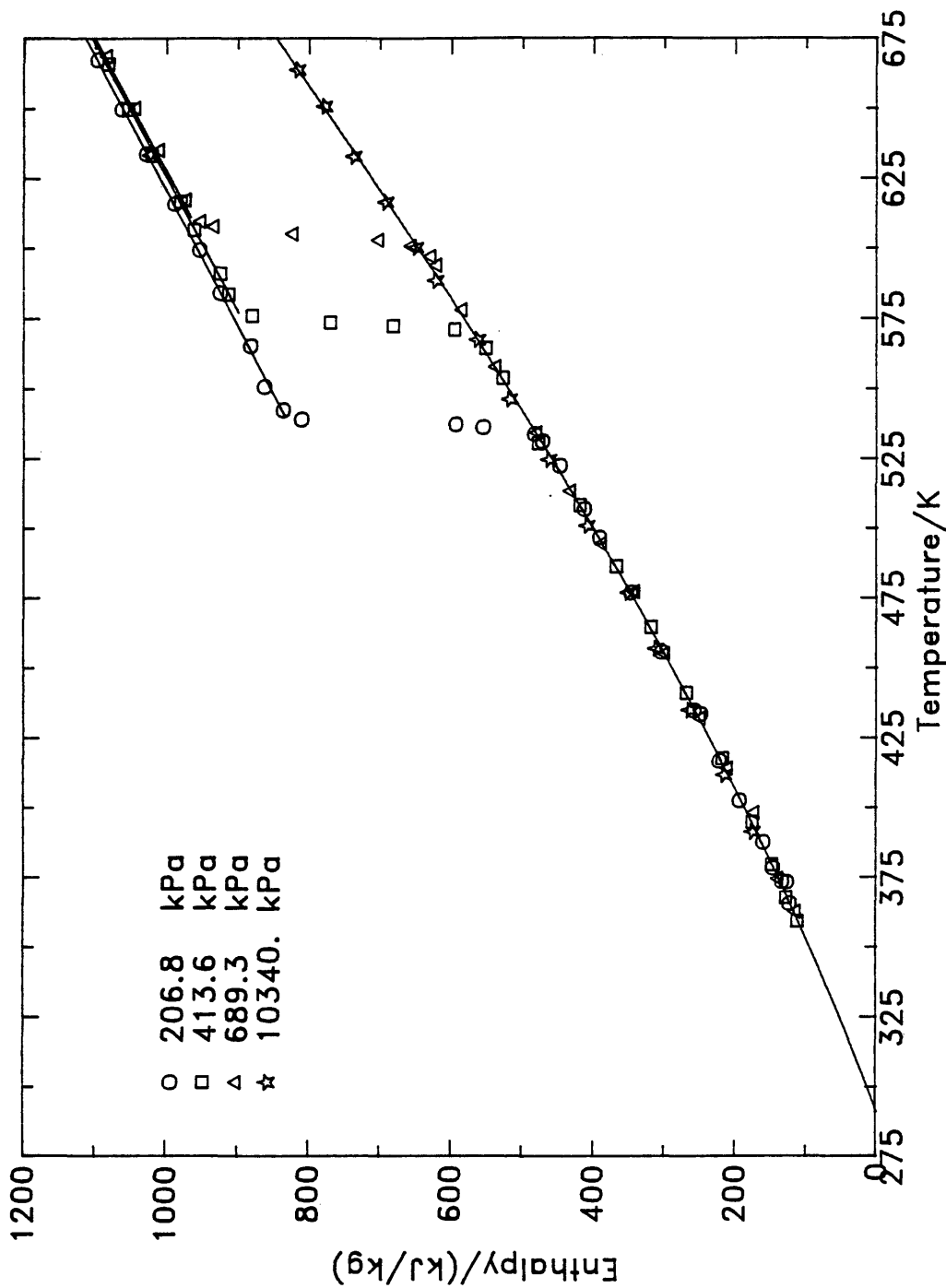


Figure 6 Enthalpy of 2/3:1/6:1/6 Quinoline:m-Cresol:Tetralin

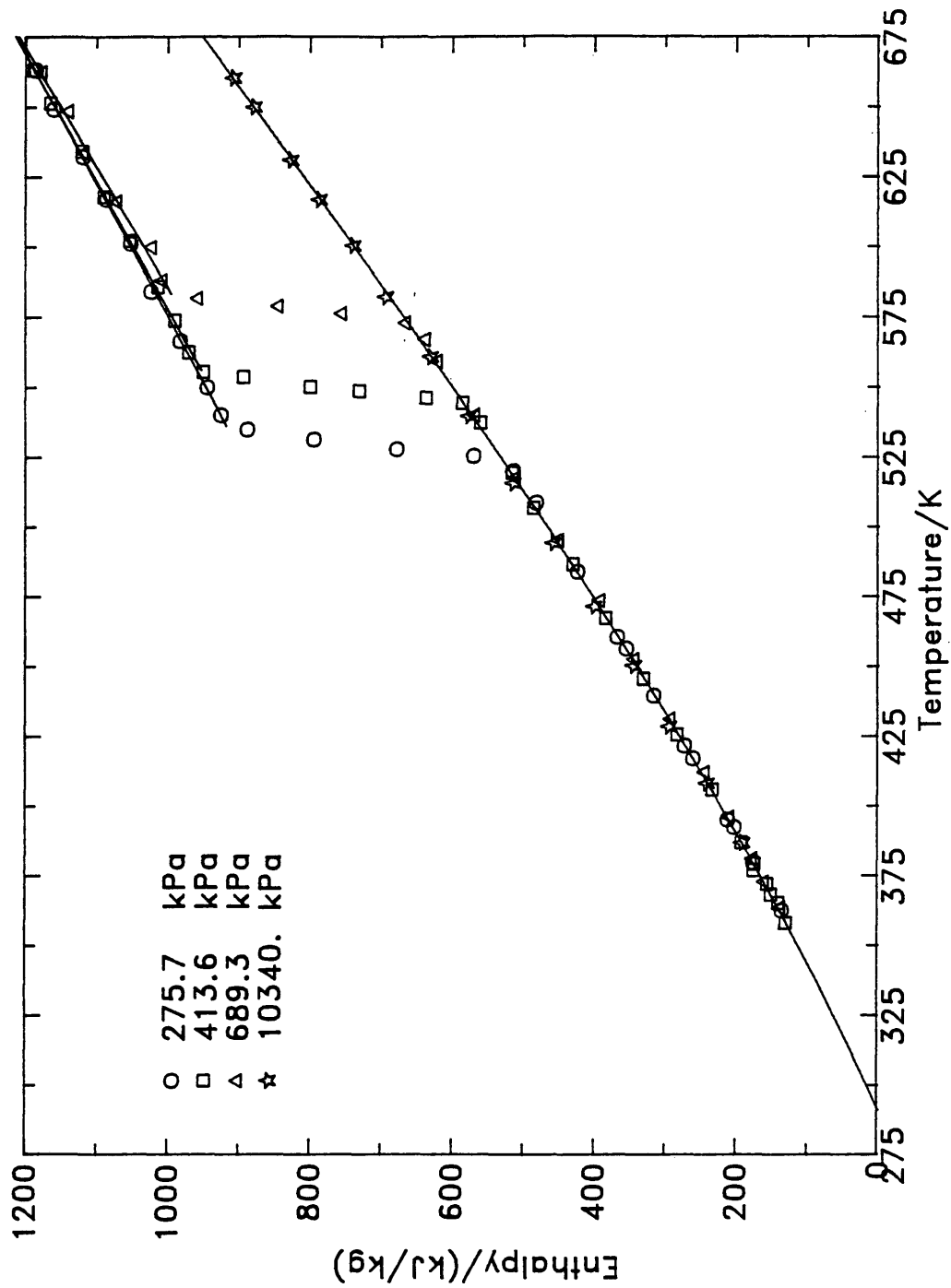


Figure 7 Enthalpy of 1/6:2/3:1/6 Quinoline:m-Cresol:Tetralin

Table 6

Specific enthalpy measurements for a ternary mixture of quinoline, m-cresol and tetralin				
Mole fractions; m-cresol 0.3333, quinoline 0.3333, and tetralin 0.3333.				
$\Delta H / (\text{kJ} \cdot \text{kg}^{-1})$				
T(in)/K	P(in)/kPa	P(out)/kPa	expt.	corr.
206.8 kPa isosbar				
363.0	213.9	159.3	116.3	116.4
364.1	212.0	159.1	130.2	130.2
369.9	205.9	159.3	134.4	134.4
378.9	212.4	159.1	157.9	158.0
390.5	209.3	159.2	186.5	186.6
411.4	207.2	159.1	227.3	227.3
411.5	213.7	159.1	229.3	229.4
434.5	206.8	159.1	280.2	280.2
457.0	207.2	159.1	326.5	326.6
478.2	206.2	159.1	383.0	383.1
487.7	208.9	159.1	403.9	403.9
489.2	209.9	151.5	407.9	407.9
497.3	207.4	151.4	429.4	429.4
509.3	208.2	137.6	457.1	457.2
516.6	208.3	137.1	484.1	484.1
519.2	207.6	137.1	508.7	508.7
521.2	206.4	137.3	584.1	584.2
523.4	206.0	137.3	671.5	671.5
525.3	205.7	137.3	744.3	744.4
526.1	205.1	137.4	777.2	777.2
529.5	206.9	137.1	857.9	857.9
536.2	206.8	130.1	878.3	878.4
550.6	207.7	130.1	908.4	908.4
566.1	207.5	137.0	936.4	936.4
566.3	209.0	151.2	938.4	938.4
584.1	204.7	137.0	976.7	976.7
589.5	206.3	151.2	984.2	984.3
600.4	206.8	137.0	1015.3	1015.3
614.8	207.6	151.1	1041.8	1041.8
621.0	207.9	123.7	1047.3	1047.3
628.7	208.2	123.8	1068.5	1068.6
632.6	208.2	151.1	1074.1	1074.1
637.3	207.3	157.9	1087.4	1087.5
639.1	207.1	123.8	1085.7	1085.7
639.2	207.6	123.7	1092.7	1092.8
650.5	207.7	123.8	1113.6	1113.6

## 206.8 kPa isobar

650.7	206.3	151.0	1117.9	1118.0
655.5	206.3	151.0	1121.4	1121.5
662.8	207.9	123.7	1146.7	1146.7
665.8	205.3	164.8	1141.6	1141.6

## 413.6 kPa isobar

357.2	414.0	316.1	119.1	119.2
367.4	408.0	364.5	135.9	136.1
390.3	415.8	295.5	184.3	184.5
400.7	414.4	315.8	206.0	206.1
405.9	415.5	364.5	225.2	225.3
406.3	414.8	330.3	223.7	223.8
427.9	413.4	357.6	263.4	263.6
450.1	414.3	357.4	316.6	316.7
472.0	416.0	371.2	366.7	366.9
494.0	416.7	364.3	419.0	419.2
515.2	415.8	329.6	480.0	480.2
527.8	413.0	329.6	511.2	511.3
544.0	413.3	329.5	549.2	549.4
552.5	412.7	329.6	581.5	581.6
554.9	415.5	329.6	621.1	621.2
556.2	413.9	329.4	651.0	651.2
558.3	416.7	329.5	719.3	719.4
560.3	412.2	329.4	810.8	811.0
562.9	412.5	329.4	883.7	883.8
565.4	411.5	330.1	926.4	926.6
574.6	413.2	330.1	946.7	946.9
583.1	412.4	337.2	961.0	961.2
584.7	411.0	330.0	977.9	978.1
588.1	413.0	329.9	979.0	979.2
598.6	414.4	330.0	997.1	997.2
605.9	414.3	337.1	1016.6	1016.7
611.0	413.3	329.8	1028.9	1029.0
621.3	412.3	316.8	1044.7	1044.8
622.0	413.8	329.7	1055.4	1055.6
627.2	414.3	337.1	1061.4	1061.6
630.1	415.8	329.6	1071.1	1071.3
633.2	413.1	330.3	1066.8	1066.9
635.2	413.5	329.8	1075.0	1075.1
642.1	414.0	337.1	1092.1	1092.3
642.2	416.0	337.1	1093.1	1093.3
646.0	413.2	329.8	1110.0	1110.1
651.5	413.0	357.8	1116.9	1117.1
660.6	414.9	329.7	1127.9	1128.0
665.0	413.0	357.8	1145.4	1145.6

## 689.5 kPa isobar

359.5	688.4	591.2	115.6	116.0
375.2	687.0	591.2	148.4	148.8
386.9	695.6	591.2	173.4	173.7
403.3	690.2	598.2	210.2	210.5
403.3	688.5	598.2	203.4	203.7
422.1	690.1	605.1	252.6	253.0
444.9	689.1	605.4	300.9	301.2
469.3	690.0	605.6	362.9	363.2
490.9	689.8	605.7	415.6	415.9
513.1	689.9	605.8	471.1	471.5
535.9	689.3	605.8	525.7	526.1
553.2	688.0	592.5	573.1	573.5
569.7	689.0	592.5	619.6	620.0
581.1	691.0	599.3	655.5	655.9
583.9	687.5	592.4	686.4	686.8
584.8	688.9	592.4	697.6	697.9
588.6	686.2	592.4	824.7	825.0
591.9	691.3	592.4	903.3	903.7
594.4	687.2	592.4	961.4	961.7
598.7	690.6	592.4	989.0	989.3
617.0	688.6	599.3	1031.3	1031.7
632.2	688.6	599.3	1057.6	1058.0
647.6	688.9	599.3	1100.5	1100.9

## 1034.0 kPa isobar

364.8	1033.5	964.5	132.4	133.0
387.4	1033.5	964.5	178.6	179.3
405.6	1036.9	964.5	216.2	216.8
420.6	1026.8	926.8	246.4	247.0
443.6	1037.5	930.6	302.7	303.3
466.0	1034.0	937.5	357.3	357.9
493.8	1034.0	937.5	423.7	424.3
512.8	1033.1	937.5	477.4	478.0
538.9	1034.1	944.4	540.3	540.9
561.3	1034.1	944.4	592.9	593.5
585.0	1034.1	951.3	661.6	662.2
595.3	1036.6	964.2	679.2	679.8
595.5	1033.2	964.2	680.1	680.7
603.4	1029.7	957.3	708.4	709.0
608.9	1028.0	957.3	747.4	748.0
611.2	1029.7	957.3	771.5	772.1
615.7	1026.3	964.2	886.1	886.7
619.5	1033.7	964.7	975.6	976.2
623.4	1037.1	964.7	1016.4	1017.0
631.7	1037.0	964.6	1051.6	1052.2

## 1034.0 kPa isobar

642.9	1037.0	964.6	1070.4	1071.0
655.1	1037.0	964.6	1104.3	1104.9
667.5	1037.0	964.6	1129.4	1130.0

## 10340. kPa isobar

378.6	10338.5	10242.0	153.7	160.9
402.3	10341.9	10245.3	212.2	219.4
423.5	10348.7	10252.2	255.8	263.1
445.5	10341.8	10245.3	309.6	316.8
467.5	10334.8	10238.3	357.0	364.2
489.4	10334.8	10238.3	409.7	416.9
512.1	10341.7	10245.2	469.6	476.8
534.5	10341.7	10245.3	524.7	531.9
556.5	10341.7	10245.2	581.6	588.9
576.5	10327.9	10231.4	632.1	639.4
600.7	10330.8	10234.2	701.2	708.5
621.3	10341.0	10244.5	759.3	766.5
646.1	10341.0	10242.0	824.1	831.4
665.3	10341.0	10244.4	879.2	886.5

Table 7

Specific enthalpy measurements for a ternary mixture of  
 quinoline, m-cresol and tetralin

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Mole fractions; m-cresol 0.1667, quinoline 0.1667,  
 and tetralin 0.6667.

$\Delta H / (\text{kJ} \cdot \text{kg}^{-1})$

T(in)/K	P(in)/kPa	P(out)/kPa	expt.	corr.
206.8 kPa isosbar				
353.8	210.6	123.6	109.4	109.4
364.9	212.3	123.6	127.5	127.5
375.3	208.9	123.6	148.8	148.8
384.8	209.9	137.3	169.5	169.5
403.8	215.3	137.3	210.9	210.9
425.6	208.8	137.3	254.5	254.5
446.2	210.5	137.3	304.9	304.9
466.9	206.9	137.1	355.7	355.7
474.3	207.5	137.0	371.4	371.4
486.0	209.0	137.1	392.6	392.6
491.3	208.8	136.9	411.8	411.8
497.0	207.7	136.9	421.4	421.5
507.4	209.9	124.0	448.9	448.9
513.1	207.7	136.9	472.1	472.1
513.4	210.6	124.0	469.7	469.7
515.8	207.4	136.9	611.0	611.0
517.8	206.7	123.8	710.4	710.4
521.0	207.4	136.9	794.3	794.4
524.5	207.3	123.8	807.8	807.8
532.0	206.6	123.7	822.6	822.6
550.4	207.5	123.6	861.8	861.8
567.2	206.8	123.6	894.9	894.9
584.2	208.2	123.6	933.5	933.5
595.4	207.6	123.7	955.3	955.3
610.0	207.4	123.5	980.4	980.5
610.1	208.4	123.5	981.3	981.3
613.1	208.6	123.6	988.2	988.2
627.8	207.7	123.6	1026.0	1026.1
644.9	207.3	123.6	1065.0	1065.0
645.1	207.7	123.6	1060.5	1060.5
661.3	207.4	123.5	1099.2	1099.3
666.5	207.4	123.5	1111.5	1111.5
413.6 kPa isobar				
357.3	415.3	337.4	114.9	115.1



## 413.6 kPa isobar

367.5	415.8	330.6	133.5	133.7
377.9	416.1	330.6	154.1	154.2
392.7	415.3	330.5	188.8	189.0
415.3	416.7	330.5	238.7	238.9
437.3	414.9	330.5	284.3	284.5
449.3	416.0	330.5	311.8	312.0
472.4	416.0	337.4	365.7	365.8
495.7	416.7	337.4	422.3	422.4
517.5	414.9	337.4	471.2	471.4
533.5	414.4	330.3	515.4	515.6
539.6	415.8	330.1	525.2	525.4
548.7	414.9	330.1	558.0	558.2
551.3	415.1	330.3	618.4	618.5
553.4	413.8	330.3	764.5	764.7
556.0	414.1	330.3	840.0	840.1
563.4	415.1	330.3	874.4	874.6
575.5	412.4	330.2	904.5	904.7
590.9	414.3	330.2	942.9	943.1
593.3	413.5	336.7	942.7	942.9
599.7	410.9	329.5	957.2	957.4
604.0	414.0	329.8	961.7	961.9
618.0	412.9	329.5	994.9	995.1
634.5	414.0	329.5	1035.9	1036.1
650.6	415.1	336.5	1068.3	1068.5
666.0	409.6	329.6	1107.5	1107.7
666.2	413.8	336.5	1112.1	1112.2

## 689.5 kPa isobar

367.9	694.0	592.6	143.4	143.8
392.3	697.0	606.3	183.0	183.4
417.6	695.2	613.2	240.6	241.0
440.2	690.7	613.2	290.6	291.0
462.8	691.7	613.1	343.2	343.6
484.6	691.0	620.0	394.4	394.7
501.3	690.9	613.0	436.2	436.6
523.4	693.0	619.9	488.4	488.8
545.3	690.9	619.9	544.4	544.8
568.4	688.2	619.9	595.7	596.1
576.9	689.8	606.7	620.2	620.6
579.7	686.0	606.7	641.9	642.3
583.3	688.5	613.7	744.2	744.6
584.9	687.4	613.5	836.6	837.0
587.1	686.9	606.6	899.5	899.9
594.4	687.7	613.4	934.3	934.7
611.5	688.6	620.3	971.8	972.2

## 689.5 kPa isobar

627.9	688.6	613.4	1013.2	1013.6
644.3	689.6	613.4	1053.2	1053.6

## 10340. kPa isobar

383.6	10369.4	10341.8	164.5	172.4
394.3	10258.9	10176.2	184.0	191.7
416.1	10327.8	10245.1	238.4	246.2
433.2	10331.2	10251.9	275.9	283.6
455.7	10327.7	10251.9	321.5	329.3
478.2	10334.6	10251.8	375.5	383.3
499.8	10341.4	10258.7	430.5	438.3
522.1	10340.4	10264.6	486.7	494.5
544.4	10336.9	10271.4	547.7	555.5
567.2	10340.2	10271.3	601.5	609.3
591.4	10333.3	10264.4	661.7	669.5
611.4	10340.1	10271.1	716.4	724.1
633.0	10340.0	10271.1	775.6	783.3
652.0	10336.6	10271.1	826.7	834.5
664.8	10333.1	10271.1	863.7	871.5

Table 8

Specific enthalpy measurements for a ternary mixture of quinoline, m-cresol and tetralin				
Mole fractions; m-cresol 0.1667, quinoline 0.6667, and tetralin 0.1667.				
$\Delta H / (\text{kJ} \cdot \text{kg}^{-1})$				
T(in)/K	P(in)/kPa	P(out)/kPa	expt.	corr.
206.8 kPa isobar				
365.4	209.2	143.5	121.9	122.0
373.1	212.1	123.7	126.3	126.3
373.3	210.1	123.8	132.8	132.8
378.2	211.6	136.7	145.8	145.8
387.4	213.5	123.7	159.6	159.6
402.5	213.0	123.7	193.0	193.0
416.7	210.0	137.5	221.7	221.8
433.4	210.4	137.6	248.2	248.2
434.7	207.5	148.0	257.5	257.5
455.5	209.5	151.4	302.9	302.9
476.8	211.9	146.7	346.5	346.5
496.6	209.4	151.3	390.8	390.9
506.9	210.6	151.2	412.1	412.1
522.5	211.0	144.3	446.9	446.9
531.2	207.5	137.1	471.6	471.6
533.8	209.7	130.2	482.6	482.6
536.3	210.8	151.2	554.5	554.5
537.3	209.6	123.3	593.0	593.1
539.1	205.5	137.1	809.5	809.5
542.4	209.5	123.2	835.3	835.3
550.8	206.7	123.1	861.9	861.9
565.3	206.7	123.1	881.1	881.1
584.2	207.7	123.1	924.2	924.2
599.4	206.2	150.2	953.2	953.2
616.0	208.6	150.0	987.8	987.8
633.8	210.4	150.0	1027.8	1027.8
649.7	209.9	150.0	1061.8	1061.8
667.3	207.8	149.9	1096.2	1096.2
413.6 kPa isobar				
359.0	413.0	385.4	110.5	110.6
367.6	413.7	316.5	127.1	127.2
379.5	415.0	316.4	147.3	147.4
394.8	415.5	316.3	174.9	175.1
417.7	414.4	316.2	217.2	217.3

## 413.6 kPa isobar

441.1	414.7	316.1	268.1	268.3
464.5	416.1	316.1	317.5	317.7
486.3	414.0	316.1	366.9	367.0
508.3	414.0	316.1	418.4	418.5
530.6	414.0	316.1	477.2	477.4
554.0	414.7	316.1	526.7	526.8
564.5	413.7	316.5	550.6	550.8
571.2	414.4	323.4	595.1	595.3
572.4	413.1	316.5	680.7	680.9
573.6	412.9	323.3	769.3	769.4
576.1	413.3	316.4	879.2	879.3
583.7	414.3	316.4	912.2	912.3
591.2	413.3	323.3	923.8	923.9
606.6	411.6	323.4	960.0	960.2
616.7	415.5	343.8	979.4	979.6
633.2	416.0	343.6	1019.7	1019.8
649.8	416.0	343.6	1052.8	1053.0
665.9	417.0	343.6	1080.5	1080.7

## 689.5 kPa isobar

362.5	692.4	592.1	114.5	114.9
374.3	690.3	592.1	139.8	140.1
398.1	691.2	591.9	173.8	174.1
414.0	691.1	585.0	211.4	211.7
432.0	692.8	591.8	250.6	250.9
455.0	694.2	591.8	300.1	300.5
477.2	694.4	591.7	342.8	343.1
494.3	694.4	591.7	389.3	389.6
513.3	689.4	599.1	433.2	433.5
534.4	690.7	599.0	480.7	481.0
557.8	692.8	599.0	538.1	538.4
578.0	689.1	606.0	585.9	586.2
594.0	693.0	606.1	621.6	622.0
597.1	687.3	590.8	630.0	630.3
600.8	687.0	606.0	657.0	657.3
603.0	688.2	599.2	702.7	703.0
605.2	686.9	599.1	823.4	823.7
607.9	687.8	606.0	934.5	934.8
609.7	687.4	599.2	952.9	953.2
617.4	693.5	619.2	973.6	973.9
633.3	687.8	605.4	1024.0	1024.3
635.2	694.0	605.4	1010.8	1011.1
650.2	694.6	612.3	1044.3	1044.6
668.6	690.9	612.3	1084.5	1084.9

## 10340. kPa isobar

391.1	10341.6	10127.8	168.1	174.6
411.6	10341.6	10148.5	208.5	215.0
434.9	10334.6	10162.3	258.0	264.5
456.8	10334.6	10169.1	304.4	310.9
476.8	10341.4	10176.0	344.2	350.8
500.9	10341.4	10182.8	402.2	408.7
524.7	10327.6	10189.7	456.2	462.8
546.2	10341.4	10196.6	511.3	517.9
567.5	10341.4	10203.6	556.5	563.1
588.5	10337.9	10203.5	615.1	621.7
600.3	10341.4	10203.5	642.7	649.2
616.5	10340.2	10229.9	685.0	691.6
632.9	10340.2	10243.7	730.0	736.6
650.7	10340.1	10243.6	771.0	777.6
663.7	10340.1	10243.5	809.0	815.6

Table 9

Specific enthalpy measurements for a ternary mixture of quinoline, m-cresol and tetralin				
Mole fractions; m-cresol 0.6667, quinoline 0.1667, and tetralin 0.1667.				
$\Delta H / (\text{kJ} \cdot \text{kg}^{-1})$				
T(in)/K	P(in)/kPa	P(out)/kPa	expt.	corr.
275.7 kPa isobar				
362.3	277.2	123.3	135.1	135.1
379.6	280.6	123.2	175.0	175.1
392.3	277.5	164.2	201.8	201.9
395.0	281.3	123.2	211.1	211.1
416.9	278.1	123.1	260.0	260.0
421.5	280.9	164.2	272.0	272.1
439.5	278.1	123.1	315.7	315.7
456.2	277.0	164.1	354.4	354.5
460.4	277.7	123.0	367.2	367.2
483.8	279.0	123.0	423.7	423.7
508.6	279.0	122.9	481.8	481.9
520.0	277.7	130.0	513.9	513.9
525.4	278.4	123.1	570.2	570.2
527.8	277.0	130.0	678.0	678.0
531.4	277.0	130.0	794.2	794.2
535.0	277.4	130.0	887.7	887.8
540.1	278.1	136.9	924.6	924.6
550.0	274.6	130.0	944.1	944.1
566.5	276.3	136.9	982.0	982.1
584.0	277.3	123.3	1023.4	1023.4
601.1	279.0	123.3	1051.9	1051.9
616.9	276.5	130.2	1086.6	1086.6
632.1	277.2	130.2	1119.0	1119.0
649.2	280.0	130.2	1160.1	1160.1
663.1	281.0	130.2	1185.2	1185.2
413.6 kPa isobar				
357.8	415.8	344.4	129.2	129.4
365.1	417.4	131.3	139.9	139.9
368.2	417.1	351.3	150.1	150.3
371.9	417.8	111.0	155.5	155.5
376.9	419.1	131.2	174.4	174.4
379.2	417.5	351.4	173.3	173.5
386.9	413.8	138.0	191.8	191.8
405.9	417.2	138.0	232.8	232.8

## 413.6 kPa isobar

425.6	413.8	138.0	282.1	282.2
445.6	417.2	138.0	329.5	329.5
467.3	417.2	138.0	383.2	383.2
486.6	417.1	137.9	429.7	429.8
506.9	417.1	137.9	485.1	485.2
519.5	413.1	220.1	515.0	515.1
537.5	415.8	220.1	559.8	559.9
544.5	415.7	233.7	585.0	585.1
546.3	413.8	233.7	636.7	636.8
548.7	416.4	233.7	730.4	730.5
550.2	413.0	226.8	799.1	799.2
553.8	416.7	226.9	893.1	893.2
555.6	413.0	226.8	949.3	949.4
562.5	416.7	233.7	969.8	969.9
573.9	413.5	233.6	989.9	990.0
585.8	413.9	233.6	1013.4	1013.5
602.2	414.9	233.6	1053.2	1053.3
617.9	414.2	240.4	1089.6	1089.7
634.1	415.5	240.4	1120.3	1120.4
651.4	413.8	240.4	1164.4	1164.5
663.3	414.2	240.4	1188.3	1188.4

## 689.5 kPa isobar

363.5	688.8	399.2	138.6	138.8
372.6	689.8	385.5	161.3	161.5
381.0	688.8	385.4	178.0	178.2
395.9	690.5	399.2	209.9	210.2
412.1	692.2	399.2	245.7	245.9
431.0	694.0	399.2	293.8	294.0
452.4	692.6	427.2	345.2	345.5
473.5	690.9	427.2	393.2	393.5
495.1	691.8	434.1	451.7	451.9
517.5	689.1	434.0	512.6	512.9
540.1	689.1	440.9	569.6	569.9
559.3	691.7	440.9	622.3	622.5
567.1	690.7	413.0	639.4	639.6
572.8	690.9	413.0	667.1	667.3
576.2	689.8	413.0	757.1	757.3
578.9	690.5	413.0	845.9	846.2
581.6	687.4	440.9	958.9	959.1
588.0	692.2	412.9	1009.1	1009.3
599.8	693.2	412.9	1024.1	1024.3
616.2	689.6	419.8	1073.4	1073.7
633.7	689.8	426.8	1119.1	1119.4
648.4	691.2	426.8	1141.1	1141.3

## 689.5 kPa isobar

662.3	688.4	426.8	1178.7	1178.9
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## 10340. kPa isobar

386.7	10338.6	9680.1	183.7	190.7
408.1	10314.3	9721.4	234.3	241.3
428.5	10328.1	9735.1	287.4	294.4
450.2	10313.5	9735.1	336.9	343.9
471.4	10341.8	9679.9	392.9	399.9
494.1	10314.1	9679.8	450.8	457.8
515.7	10314.1	9679.8	507.4	514.4
539.8	10314.1	9679.8	569.8	576.7
560.9	10323.3	9899.3	623.4	630.5
582.2	10340.4	9857.8	686.3	693.4
600.3	10326.7	9871.6	732.5	739.7
616.8	10319.7	9871.6	780.0	787.1
631.0	10340.4	9871.6	819.7	826.9
650.0	10333.4	9878.4	871.6	878.8
660.3	10312.8	9878.4	900.5	907.6



Also included on the plots of the experimental data are curves generated by fitting the vapor and liquid phase enthalpies to polynomial expressions. The experimental vapor and liquid phase enthalpies were fit to polynomial expressions, and the fits worked well. The polynomial expression for the vapor phase is described by:

$$\Delta h/(\text{kJ/kg}) = C1 + C2(T/K)^2 + C3(T/K) + C4(T/K)(P/\text{kPa}) + C5(P/\text{kPa}) + C6(P/\text{kPa})^2. \quad (12)$$

The liquid phase enthalpy was fit to the following expression:

$$\Delta h/(\text{kJ/kg}) = C7*[(T-291.48)/K] + C8*[(T-291.48)/K]^2 + C9*[(T-291.48)/K]^3. \quad (13)$$

An expression for liquid heat capacity can be obtained by taking the derivative of equation 13 with respect to temperature at constant pressure. Ideal gas enthalpies can be obtained by setting  $p=0$  in equation (12). An error measurement was defined to show how the experimental data deviates from the polynomial fits. This expression is simple and is given below:

$$\text{ERR} = (\Delta H_{\text{corr}} - \Delta H_{\text{pf}})/\Delta H_{\text{corr}}*100 \quad (14)$$

where,  $\Delta H_{\text{pf}}$  = Enthalpy prediction by polynomial fit.

ERR = Percent error between experimental and polynomial fit data.

The error was calculated for each experimental data point. The absolute value of the errors was summed throughout the

data base, and an average absolute deviation (AAPD) was determined. The AAPD for each system is reported with the constants of the polynomial fits for the vapor and liquid phases. The constants to the polynomial expressions along with the AAPD are presented in Table 10.

The plots in Figures 4-7 show that the experimental data are consistent. The polynomial expressions fit the data well and this can be seen in the plots. The AAPD for the liquid phases ranged from 0.570 to 0.889 with the 1/6:1/6:2/3 quinoline:m-cresol:tetralin system the greatest AAPD. The polynomial fit curve deviates minutely at the higher temperatures in the 1/6:1/6:2/3 quinoline:m-cresol:tetralin system, but the fits work extremely well for the other three systems. The AAPD of the polynomial fits of the vapor phases ranged from 0.211 to 0.303. The curves fit the vapor phase enthalpies extremely well and this can easily be seen in the plots. The incorporation of the polynomial fits to the experimental liquid and vapor phase enthalpies show that the data are consistent.

Ideal gas enthalpy differences were generated from Reham and Lee<sup>9</sup> (1985) and compared to ideal gas enthalpy differences extracted from experimental data. Experimental ideal gas enthalpies are calculated from the polynomial expression (equation 12) describing the vapor phase

Table 10

## Constants for Polynomial Fits

## 1/3:1/3:1/3 Quinoline:m-Cresol:Tetralin

<u>Vapor Phase</u>	<u>Liquid Phase</u>
C1 = -51.9	C7 = 1.59307
C2 = 4.024E-4	C8 = 2.9203E-3
C3 = 1.5315	C9 = -2.28E-6
C4 = 2.818E-4	AAPD = 0.659
C5 = -1.8043E-1	
C6 = -2.366E-5	
AAPD = 0.287	

## 1/6:1/6:2/3 Quinoline:m-Cresol:Tetralin

<u>Vapor Phase</u>	<u>Liquid Phase</u>
C1 = 197.1	C7 = 1.62291
C2 = 1.2742E-3	C8 = 2.4026E-3
C3 = 5.218E-1	C9 = -9.9E-7
C4 = 4.208E-4	AAPD = 0.889
C5 = -2.7832E-1	
C6 = 8.05E-6	
AAPD = 0.211	

## 2/3:1/6:1/6 Quinoline:m-Cresol:Tetralin

<u>Vapor Phase</u>	<u>Liquid Phase</u>
C1 = -224.3	C7 = 1.47101
C2 = 1.09E-4	C8 = 2.4230E-3
C3 = 1.931	C9 = -1.32E-6
C4 = 6.66E-5	AAPD = 0.746
C5 = -1.346E-1	
C6 = 7.004E-5	
AAPD = 0.303	

## 1/6:2/3:1/6 Quinoline:m-Cresol:Tetralin

<u>Vapor Phase</u>	<u>Liquid Phase</u>
C1 = -87.5	C7 = 1.77410
C2 = 1.630E-4	C8 = 2.6604E-3
C3 = 1.7994	C9 = -2.14E-6
C4 = 4.819E-4	AAPD = 0.570
C5 = -2.650E-1	
C6 = 7.144E-5	
AAPD = 0.259	

enthalpies. Ideal gas enthalpies are calculated by inserting a specific temperature and zero for the pressure. The comparisons of these ideal gas enthalpies are presented in Table 11 along with an absolute percent deviation (APD) between the two enthalpies.

The ideal gas enthalpy differences between the experimental and the calculated compare very well for the 1/3:1/3:1/3, and 1/6:2/3:1/6 quinoline:m-cresol:tetralin systems. The absolute percent deviation ranges from 0.29 and 3.02 for these two systems. The absolute percent deviation for the 1/6:1/6:2/3 quinoline:m-cresol:tetralin system ranges from 3.82 to 4.14. The vapor phase polynomial fit of this system does not do a very good job distinguishing between isobars at the higher temperatures. The 206.8, 413.6, and 689.3 kPa enthalpy data at the very high temperatures seem to fall on a common line instead of falling on separate lines. This phenomena will effect the polynomial fits and in turn effect the calculation of the experimental ideal gas enthalpies. The vapor phase entahlpies still fall within the experimental error of the apparatus in this region. The absolute percent deviation between the ideal gas enthalpies for the 2/3:1/6:1/6 quinoline:m-cresol:tetralin system range from 1.88 to 4.54. Again, the large deviations can be attributed in the scatter

Table 11

Ideal Gas Enthalpy Difference Comparisons  
Between Experimental and Calculated Values

1/3:1/3:1/3 Quinoline:m-Cresol:Tetralin

	Enthalpy Differences		<u>Percent Deviation</u>
	<u>Experimental</u>	<u>Tabulated</u>	
(h <sub>570K</sub> -h <sub>540K</sub> )*	59.34	58.20	1.92
(h <sub>600K</sub> -h <sub>540K</sub> )*	119.41	118.58	0.70
(h <sub>630K</sub> -h <sub>540K</sub> )*	180.21	181.01	0.44
(h <sub>660K</sub> -h <sub>540K</sub> )*	241.72	245.36	1.50

1/6:1/6:2/3 Quinoline:m-Cresol:Tetralin

	Enthalpy Differences		<u>Percent Deviation</u>
	<u>Experimental</u>	<u>Tabulated</u>	
(h <sub>610K</sub> -h <sub>600K</sub> )*	21.55	20.64	4.23
(h <sub>630K</sub> -h <sub>600K</sub> )*	65.36	62.67	4.11
(h <sub>650K</sub> -h <sub>600K</sub> )*	110.11	105.73	3.98
(h <sub>670K</sub> -h <sub>600K</sub> )*	155.74	149.80	3.82

2/3:1/6:1/6 Quinoline:m-Cresol:Tetralin

	Enthalpy Differences		<u>Percent Deviation</u>
	<u>Experimental</u>	<u>Tabulated</u>	
(h <sub>610K</sub> -h <sub>600K</sub> )*	20.63	19.69	4.54
(h <sub>630K</sub> -h <sub>600K</sub> )*	61.95	59.71	3.62
(h <sub>650K</sub> -h <sub>600K</sub> )*	103.36	100.53	2.73
(h <sub>670K</sub> -h <sub>600K</sub> )*	144.86	142.14	1.88

Table 11

Ideal Gas Enthalpy Difference Comparisons  
Between Experimental and Calculated Values  
(Continued)

1/6:2/3:1/6 Quinoline:m-Cresol:Tetralin

	Enthalpy Differences		<u>Percent Deviation</u>
	<u>Experimental</u>	<u>Tabulated</u>	
$(h_{580K} - h_{550K})^*$	59.51	58.80	1.19
$(h_{610K} - h_{550K})^*$	119.31	119.65	0.29
$(h_{640K} - h_{550K})^*$	179.40	182.43	1.69
$(h_{670K} - h_{550K})^*$	239.79	247.03	3.02

\* Ideal gas enthalpy differences

APD: Absolute percent deviation

$$: (h_{\text{experimental}} - h_{\text{calculated}}) / (h_{\text{experimental}}) * 100.$$

of the vapor phase enthalpies at the higher temperatures for the 413.6 and 689.3 kPa isobars.

The comparisons of the ideal gas enthalpy differences show that the experimental data are consistent. Two of the systems had rather large percent deviations between the experimental and calculated values, but they fall well within the accuracy of the apparatus (+/- 1.0 percent).

Flanigan (1983) and (1986) also converted the experimental binary data to a pure fluid datum by adding on a value for the the excess enthalpy. This could not be achieved in this investigation because excess enthalpies could not be obtained for the ternary mixtures.

ENTHALPY PREDICTIONS FOR THE TERNARY SYSTEM OF QUINOLINE,  
m-CRESOL, AND TETRALIN

A set of computer programs were generated to predict the enthalpy of the ternary system containing quinoline, m-cresol, and tetralin. The programs incorporating mixing rules one to three were developed by Flanigan (1986). The ternary system prediction programs for the two density dependent mixing rules (mixing rules four and five) were developed during this project. The programs involving the two density dependent mixing rules were a modification of Flanigan's binary enthalpy prediction programs.

Enthalpy predictions are generated with two equations of state and five mixing rules. The predictions are plotted on a graph that also contains the experimental data. This will help to visually see how good the predictions actually work. Only two mixing rules were investigated for the Soave-Redlich-Kwong equation of state and they consist of the simple  $k_{ij}$  and  $k_{ij}=0$ . Flanigan had observed that the SRK equation did a poor job predicting the enthalpies of m-Cresol, so binary interaction parameters were not generated for the other three mixing rules. The main emphasis in this investigation was the YSRK equation of state.

In order to do the enthalpy predictions for the YSRK equation, the nonpolar homomorph must be defined along with its respective acentric factor. The polar parameter  $R_p$  must



also be defined. This information is tabulated in Table 12.

Table 12  
Nonpolar Homomorph Acentric Factors and  
Polar Parameters for Ternary System

Compound	Homomorph	$\omega_n$	$R_p$
m-Cresol	m-Xylene	0.326	0.909
Quinoline	Naphthalene	0.303	0.02679
Tetralin	Tetralin	0.327	0.0

During the analysis it was determined that the binary interaction parameters determined by Flanigan for the density dependent mixing rule  $k_{ij}=A-B/vRT$  are in error due to a mistake in the derivation of the enthalpy departure. The corrected enthalpy departure was used in the ternary enthalpy predictions, so the enthalpy predictions for this mixing rule will not be consistent. The objective for this investigation was to predict the ternary enthalpies from Flanigan's binary interaction parameters.

Enthalpy Predictions for the 1/3:1/3:1/3 Quinoline:m-Cresol:Tetralin Mixture

The enthalpy predictions for the SRK equation of state are shown in Figures 8 and 9. Figure 8 does not incorporate any interaction parameters. Figure 9 generates the

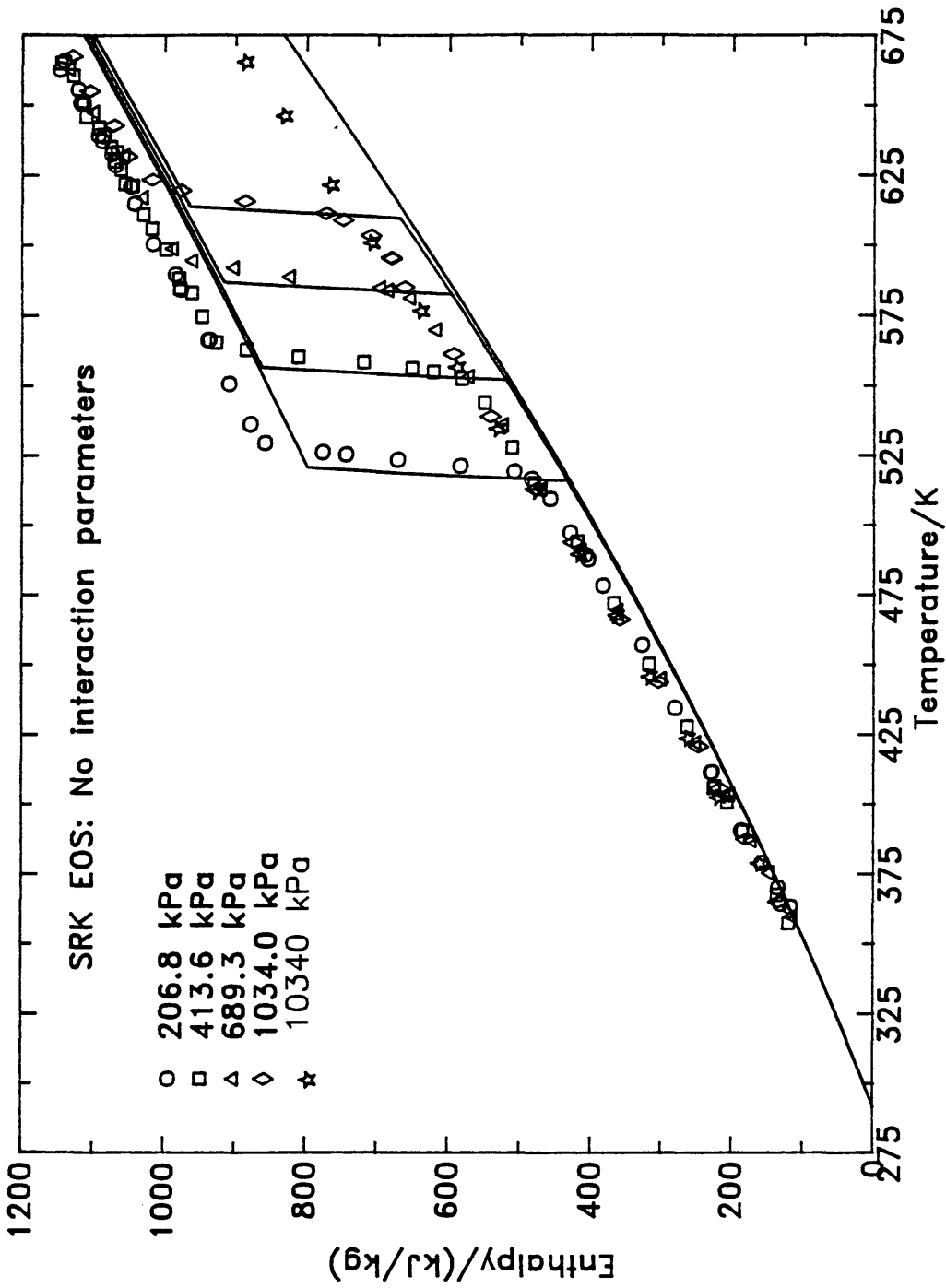


Figure 8 Enthalpy Predictions of 1/3:1/3:1/3 Quinoline:m-Cresol:Tetralin  
 SRK: Mixing Rule  $k_{ij} = 0$

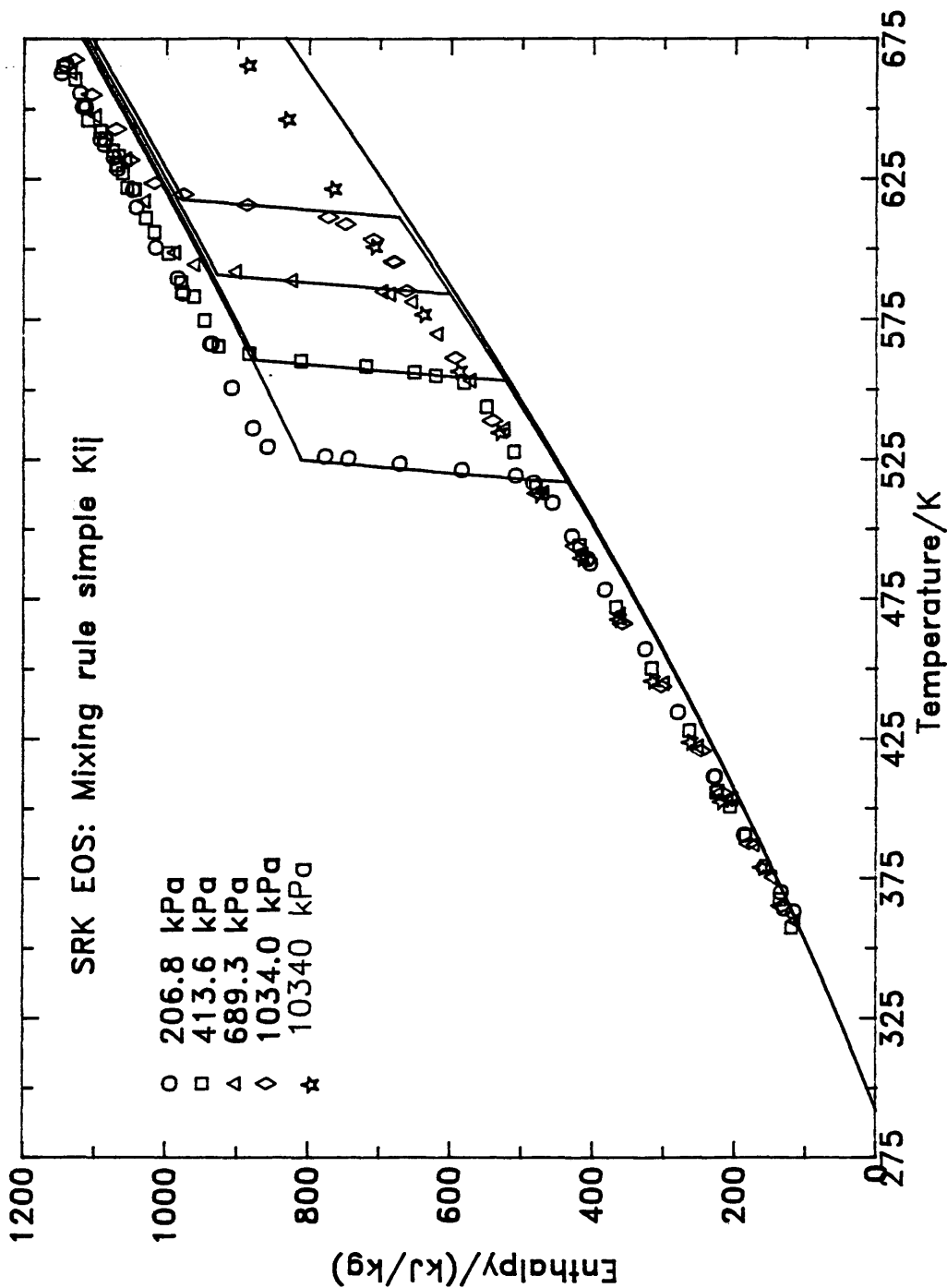


Figure 9 Enthalpy Predictions of 1/3:1/3:1/3 Quinoline:m-Cresol:Tetralin  
SRK: Mixing Rule  $k_{ij}$

predictions with the simple  $k_{ij}$  mixing rule. With both mixing rules, the liquid and vapor phase enthalpies are predicted low. Also, both predict the boiling point of the fluid to be lower than the experimental value. The  $k_{ij}$  mixing rule predicts the two phase region better than the mixing rule  $k_{ij}=0$ .

The enthalpy predictions for the YSRK equation of state are shown in Figures 10 to 14. Figure 10 incorporates the mixing rule  $k_{ij}=0$ , Figure 11 uses the simple  $k_{ij}$  mixing rule, and Figure 12 incorporates the mixing rule  $k_{ij}=A+B/T$ . Again the mixing rules  $k_{ij}$  and  $k_{ij}=0$  both predict the liquid and vapor phase enthalpies to be low. The simple  $k_{ij}$  mixing rule predicts the two phase region much better than the mixing rule  $k_{ij}=0$ . The mixing rule  $k_{ij}=A+B/T$  predicts the liquid phase and vapor phase enthalpies better than the other mixing rules, but falters predicting the two phase region. Figures 13 and 14 incorporate the density dependent mixing rules  $k_{ij}=A-B/vRT$  and  $A+C$  respectively. The mixing rule  $k_{ij}=A-B/vRT$  does not work very well due to the error in Flanigan's equation. Mixing rule  $A+C$  predicts the liquid phase well at the lower temperatures, but it seems to falter at the higher temperatures. This mixing rule predicts the vapor enthalpies to be lower than the experimental values, and it misses the two phase transition region.

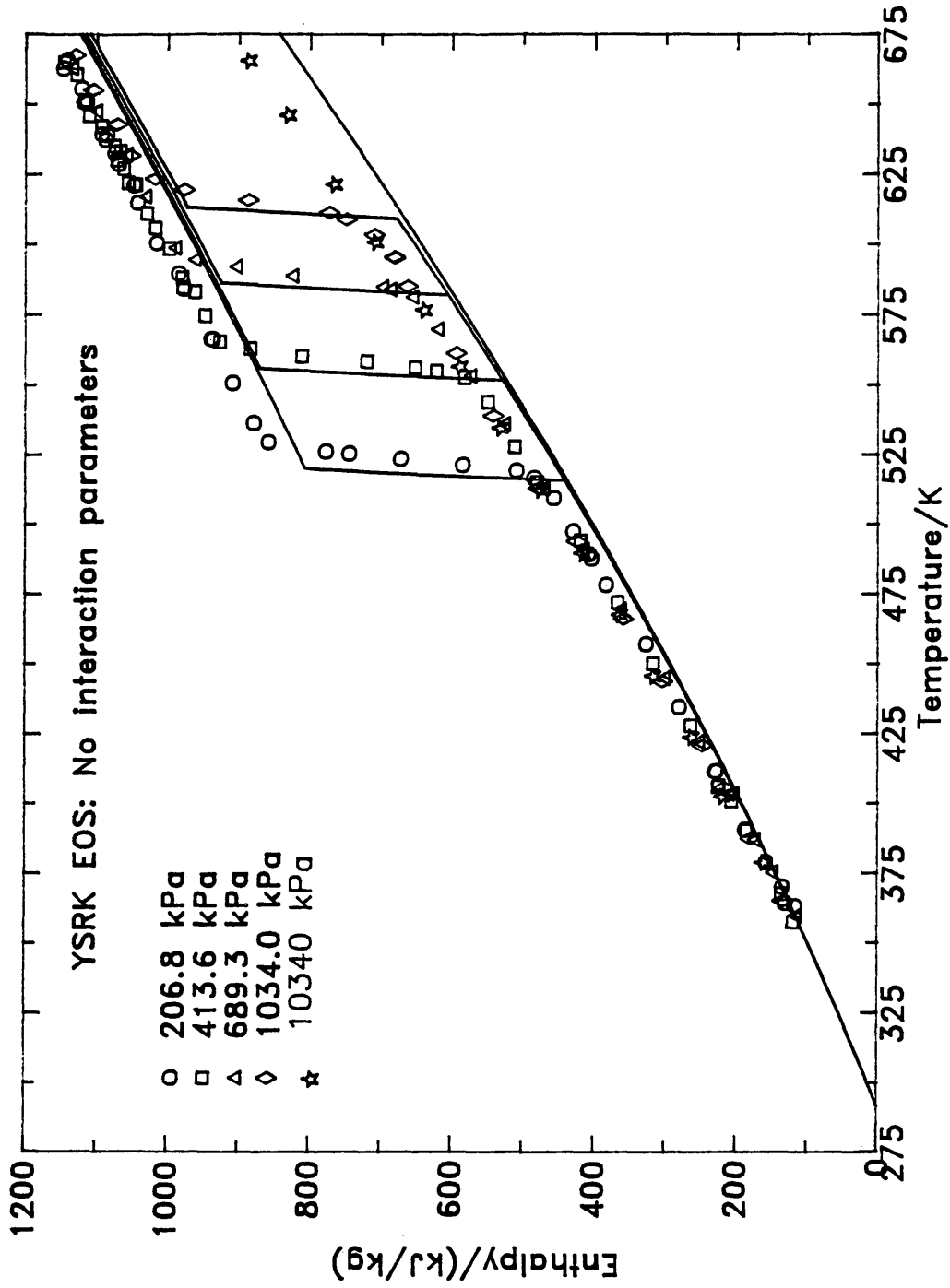


Figure 10 Enthalpy Predictions of 1/3:1/3:1/3 Quinoline:m-Cresol:Tetralin  
YSRK: Mixing Rule  $k_{ij} = 0$

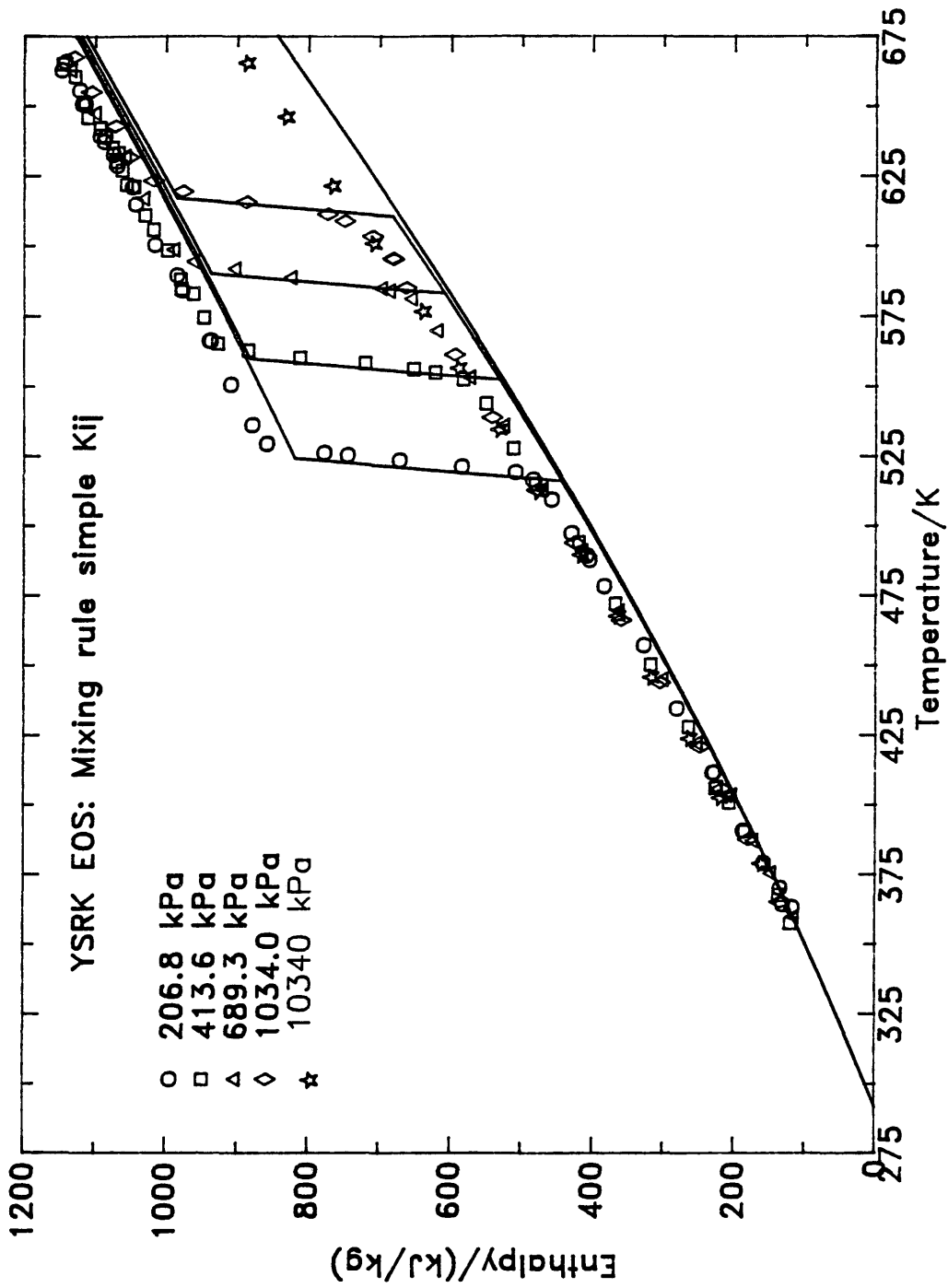


Figure 11 Enthalpy Predictions of 1/3:1/3:1/3 Quinoline:m-Cresol:Tetralin  
 YSRK: Mixing Rule  $k_{ij}$

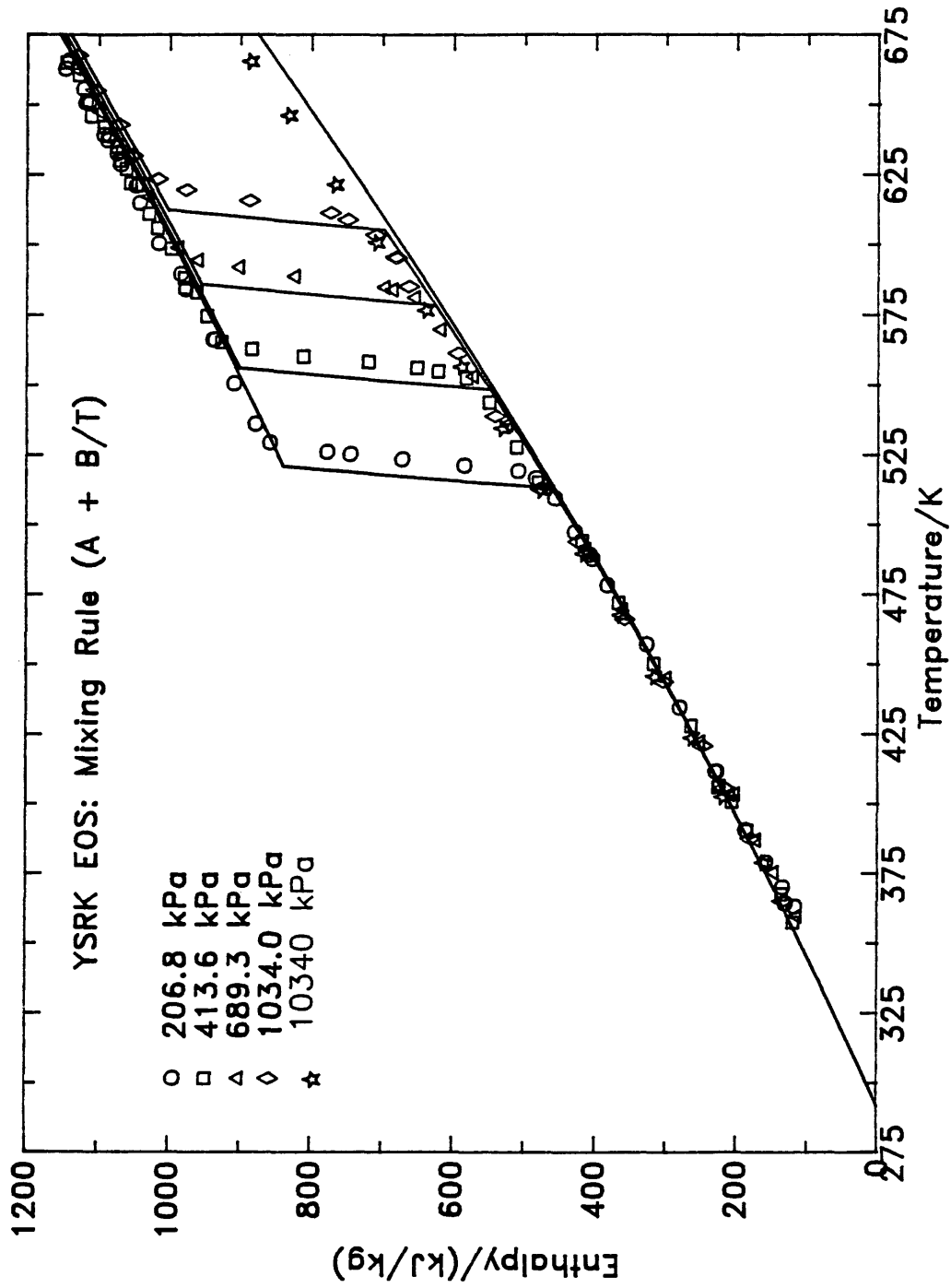


Figure 12 Enthalpy Predictions of 1/3:1/3:1/3 Quinoline:m-Cresol:Tetralin  
 YSRK: Mixing Rule  $k_{ij} = A+B/T$

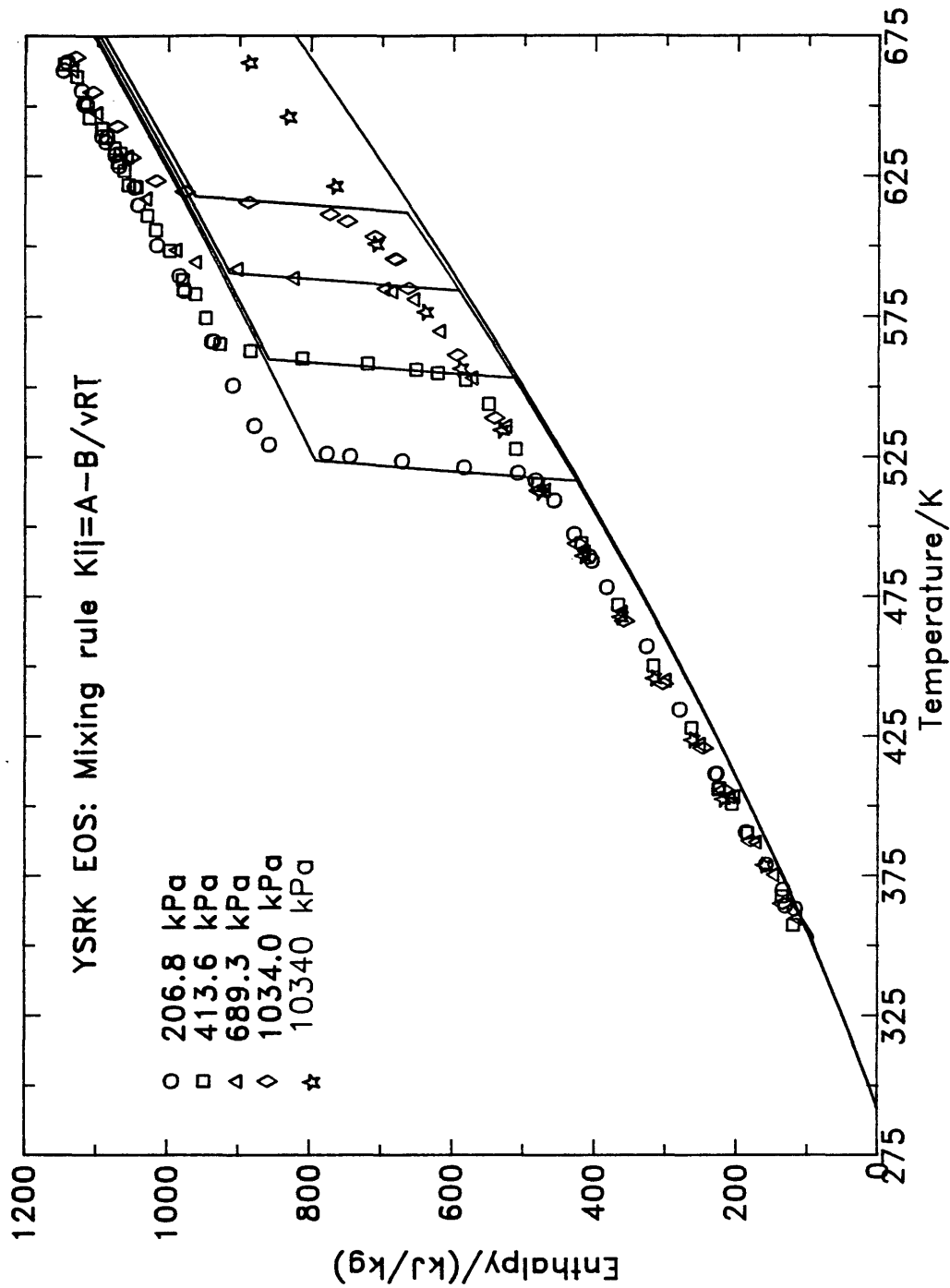


Figure 13 Enthalpy Predictions of 1/3:1/3:1/3 Quinoline:m-Cresol:Tetralin  
 YSRK: Mixing Rule  $k_{ij} = A - B/vRT$



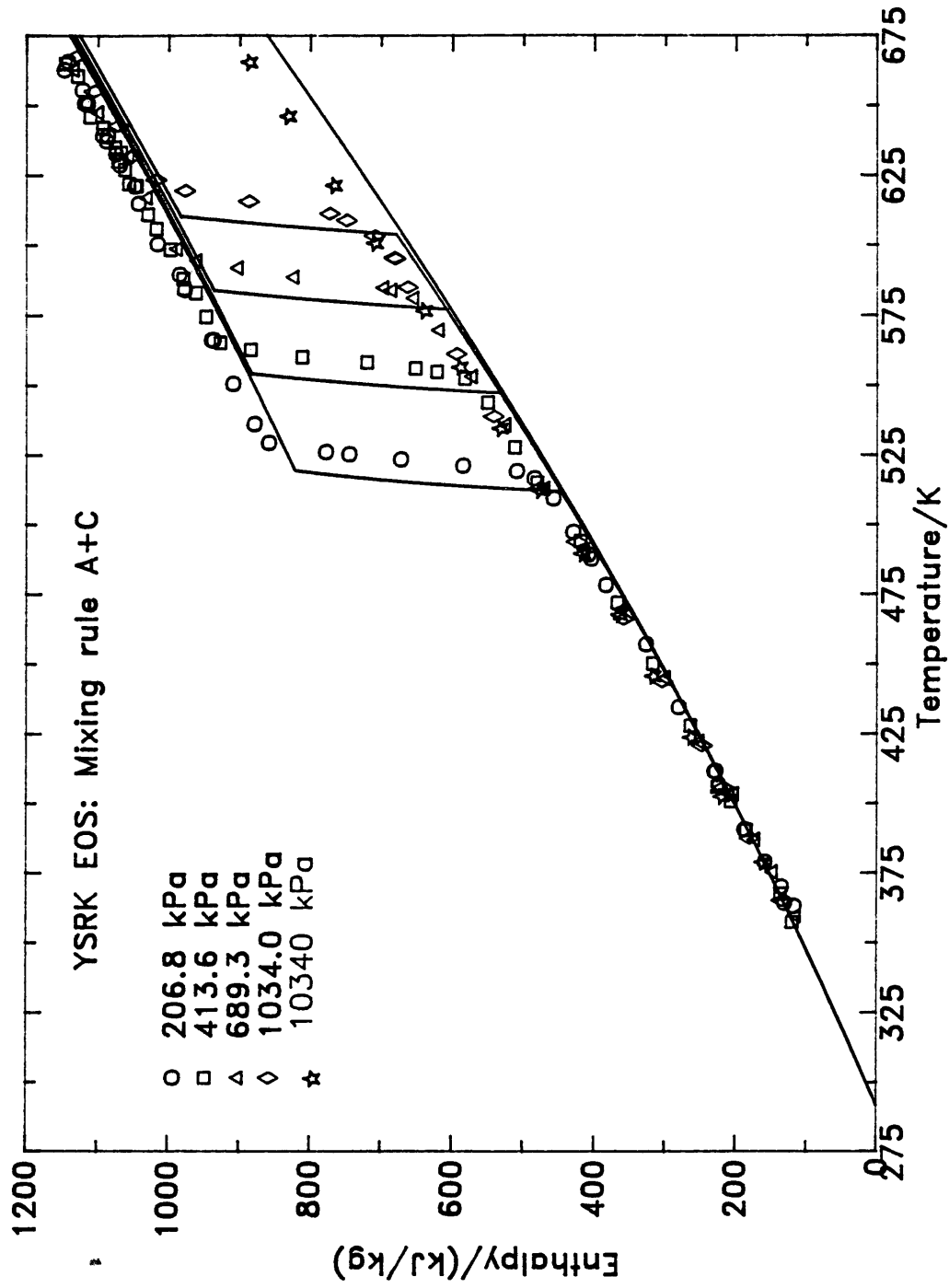


Figure 14 Enthalpy Predictions of 1/3:1/3:1/3 Quinoline:m-Cresol:Tetralin  
YSRK: Mixing Rule A+C

### Enthalpy Predictions for the 1/6:1/6:2/3 Quinoline:m-Cresol:Tetralin Mixture

Figures 15 and 16 show the enthalpy predictions for the SRK equation of state. Both of these mixing rules do a good job predicting the experimental enthalpy. The liquid and vapor phase predictions are a little low, but they do predict the two phase region well. There is no noticeable difference between the two mixing rules.

The enthalpy predictions for the YSRK equation of state are shown in Figures 17 to 21. The simple nondensity mixing rules are presented in figures 17 to 19, and they work fairly well mapping the experimental data. Figure 19 uses the mixing rule  $k_{ij}=A+B/T$ , which predicts both enthalpy phases and the two phase region well. Mixing rules  $k_{ij}$  and  $k_{ij}=0$  map the two phase region well, but predict the vapor and liquid phase enthalpies low. They do about the same job as the mixing rules applied to the SRK equation of state, and there is no noticeable difference. The mixing rule  $k_{ij}=A+B/T$  does actually predict the vapor and liquid phase enthalpies better than the other mixing rules, but the predictions for the two phase region are not as good as the simple  $k_{ij}$  and  $k_{ij}=0$ . Figure 20 incorporates the mixing rules  $K_{ij}=A-B/vRT$  and Figure 21 uses the mixing rule  $A+C$ . The mixing rule  $A+C$  predicts the vapor and liquid phase enthalpies quite well, but it is off somewhat predicting the

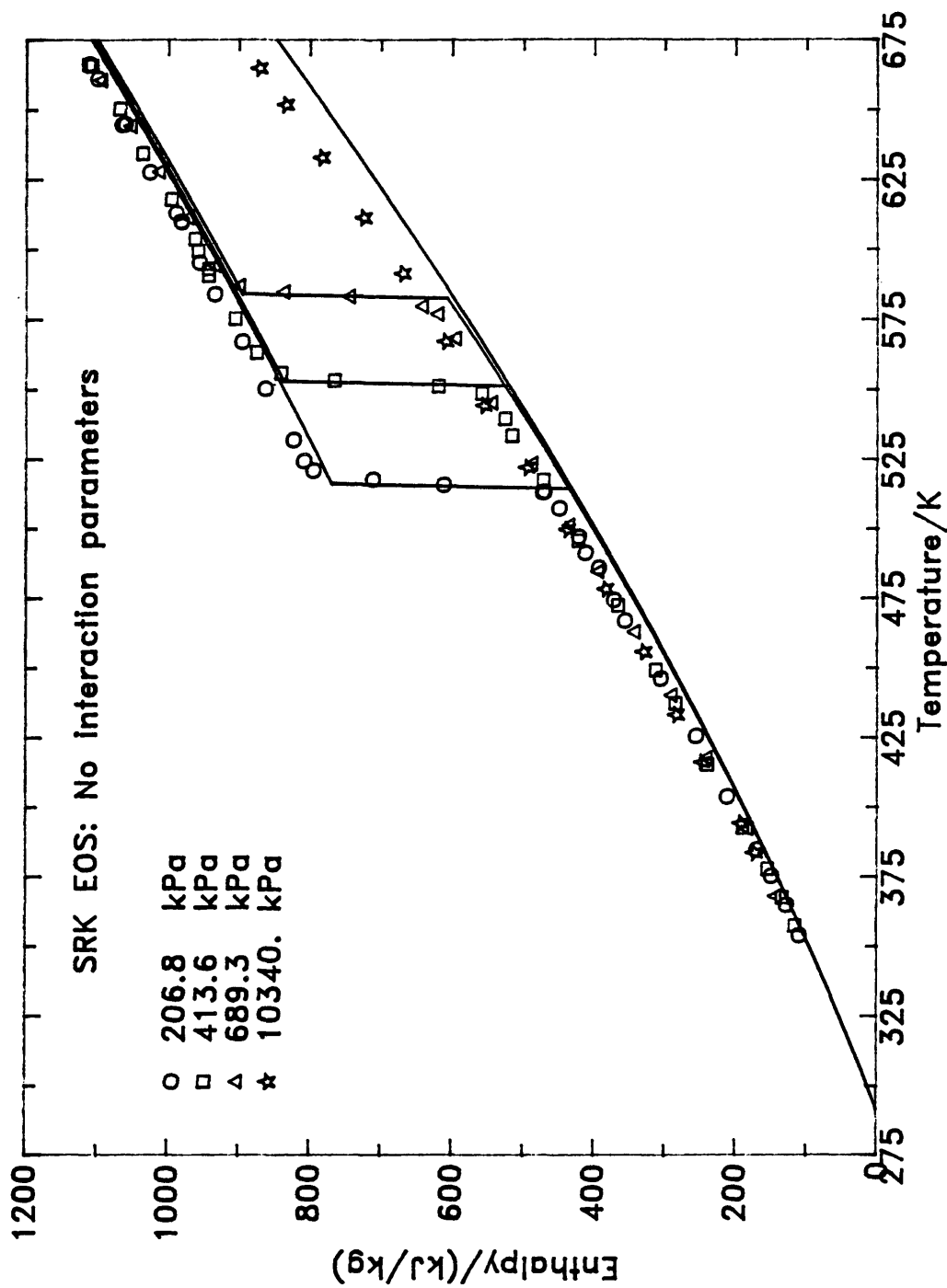


Figure 15 Enthalpy Predictions of 1/6:1/6:2/3 Quinoline:m-Cresol:Tetralin  
 SRK: Mixing Rule  $k_{ij} = 0$

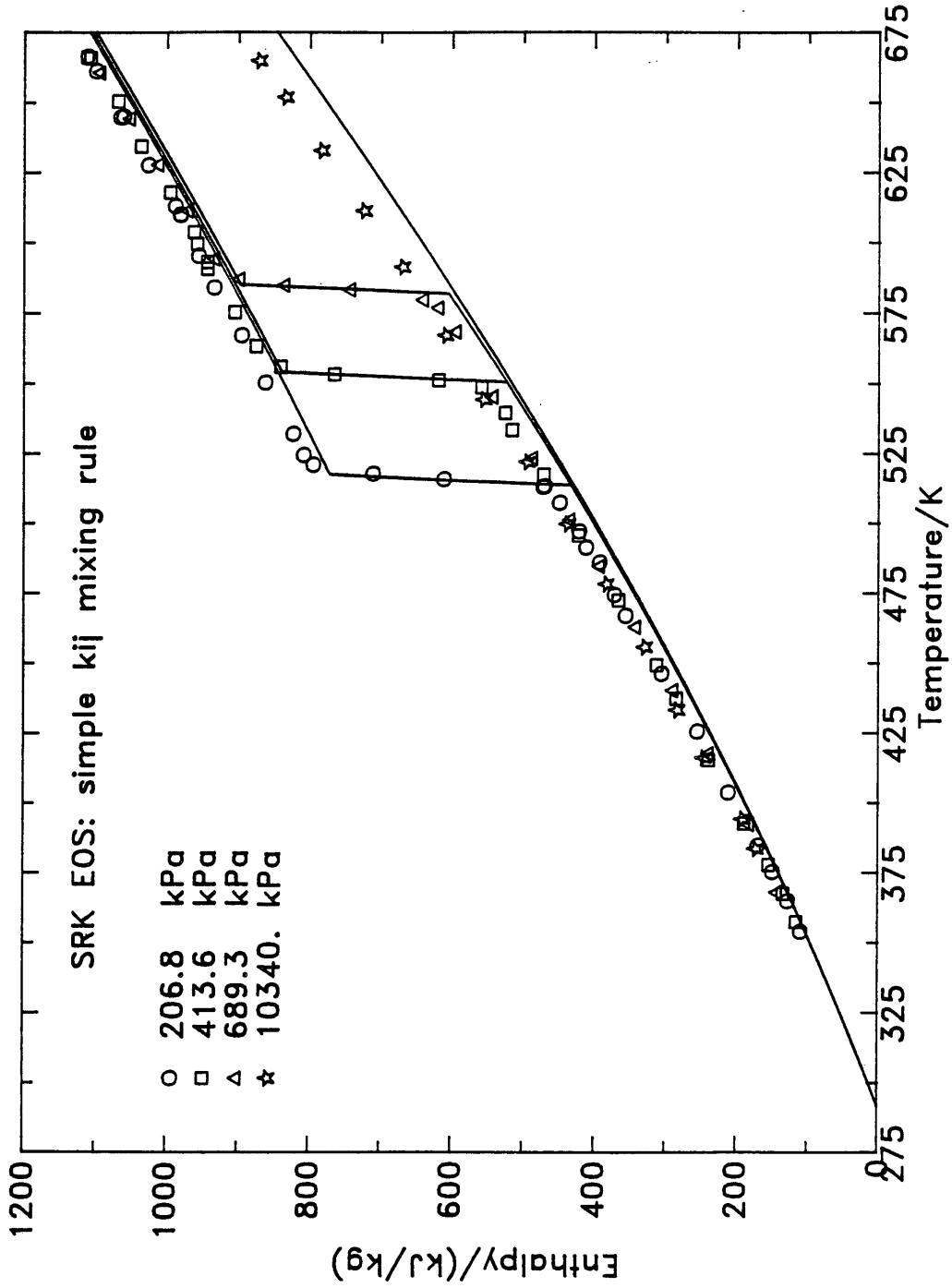


Figure 16 Enthalpy Predictions of 1/6:1/6:2/3 Quinoline:m-Cresol:Tetralin  
SRK: Mixing Rule  $k_{ij}$

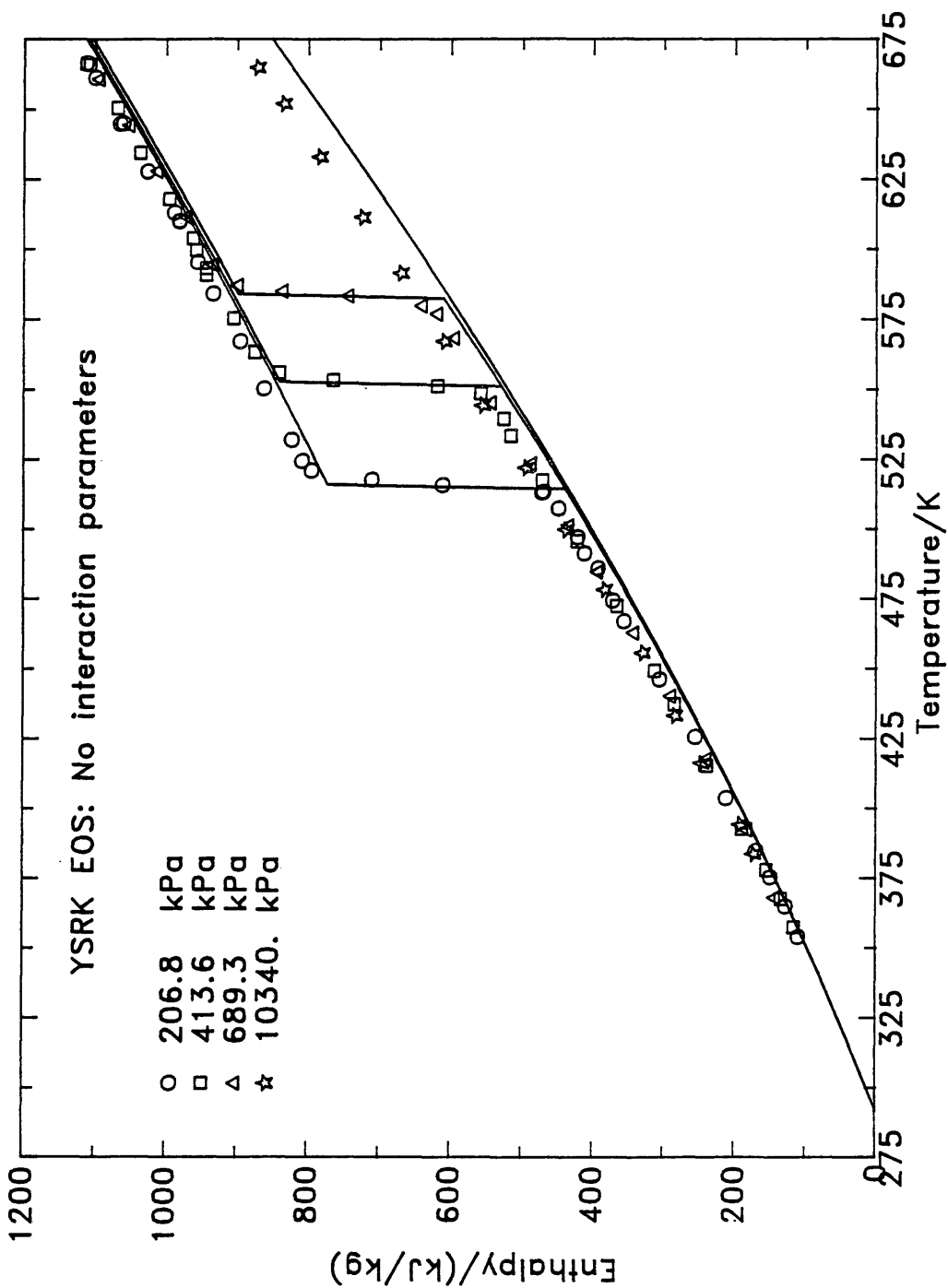


Figure 17 Enthalpy Predictions of 1/6:1/6:2/3 Quinoline:m-Cresol:Tetralin  
 YSRK: Mixing Rule  $k_{ij} = 0$

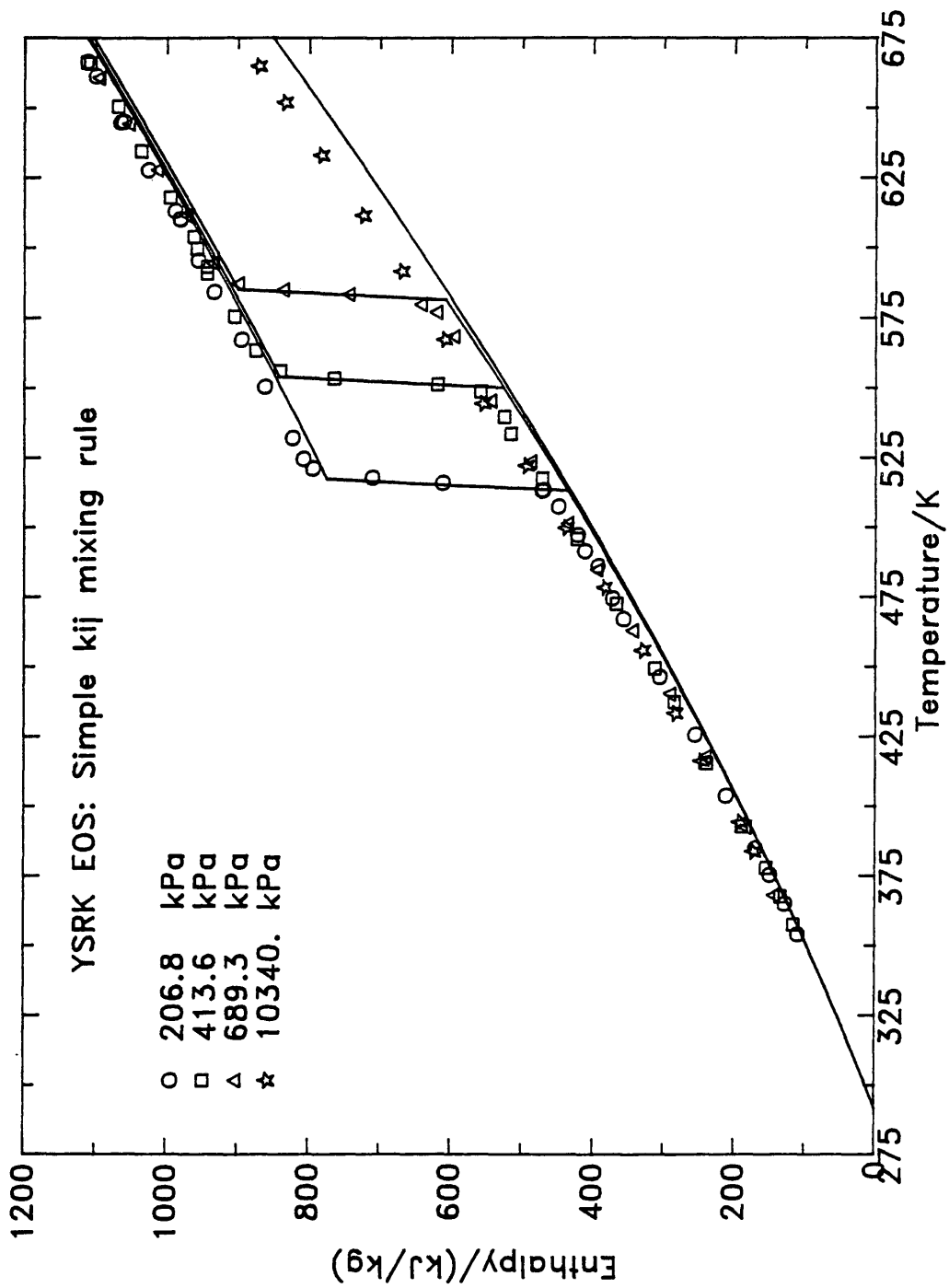


Figure 18 Enthalpy Predictions of 1/6:1/6:2/3 Quinoline:m-Cresol:Tetralin  
 YSRK: Mixing Rule  $k_{ij}$

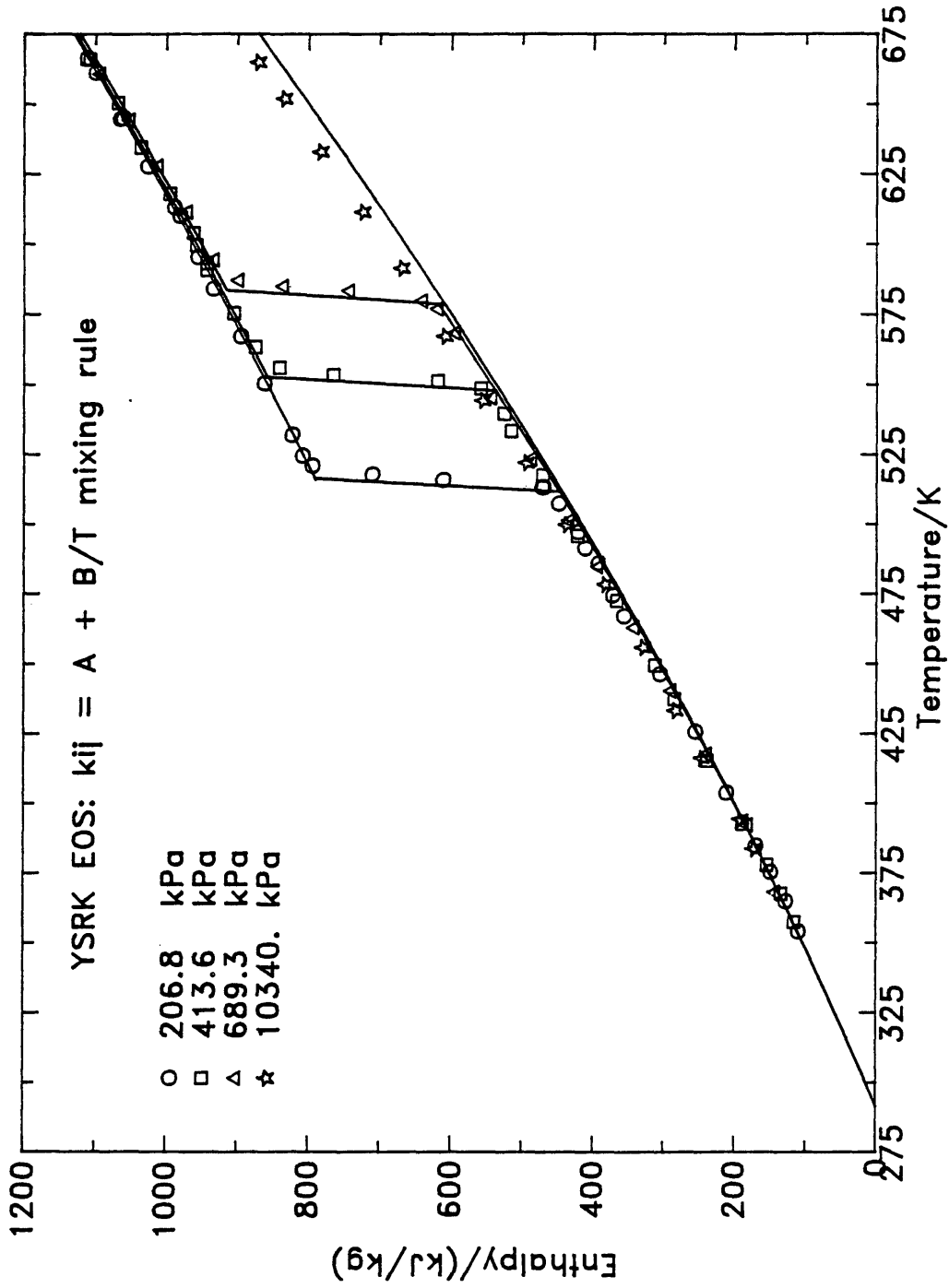


Figure 19 Enthalpy Predictions of 1/6:1/6:2/3 Quinoline:m-Cresol:Tetralin  
 YSRK: Mixing Rule  $k_{ij} = A+B/T$

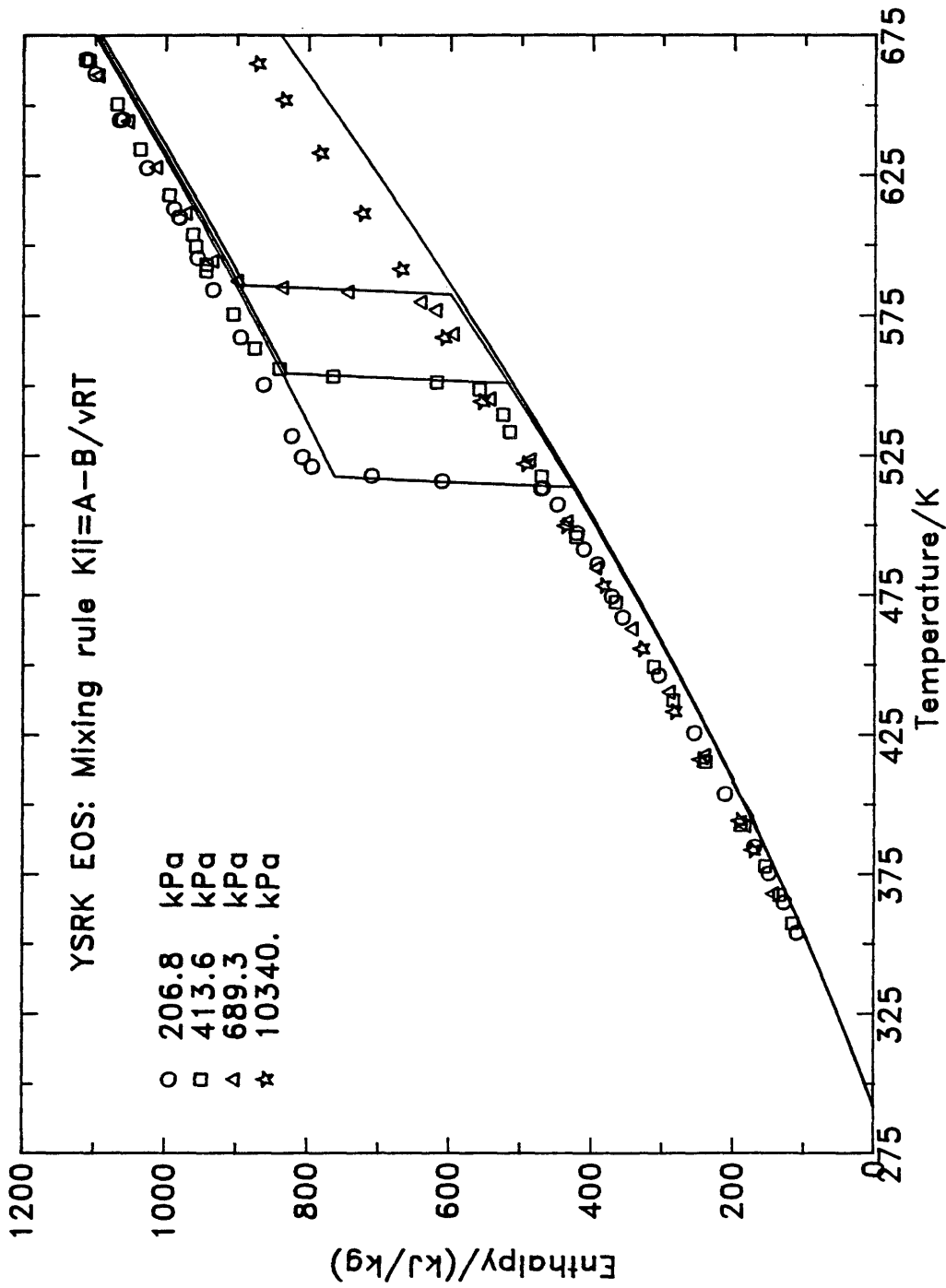


Figure 20 Enthalpy Predictions of 1/6:1/6:2/3 Quinoline:m-Cresol:Tetralin  
 YSRK: Mixing Rule  $k_{ij} = A - B/vRT$



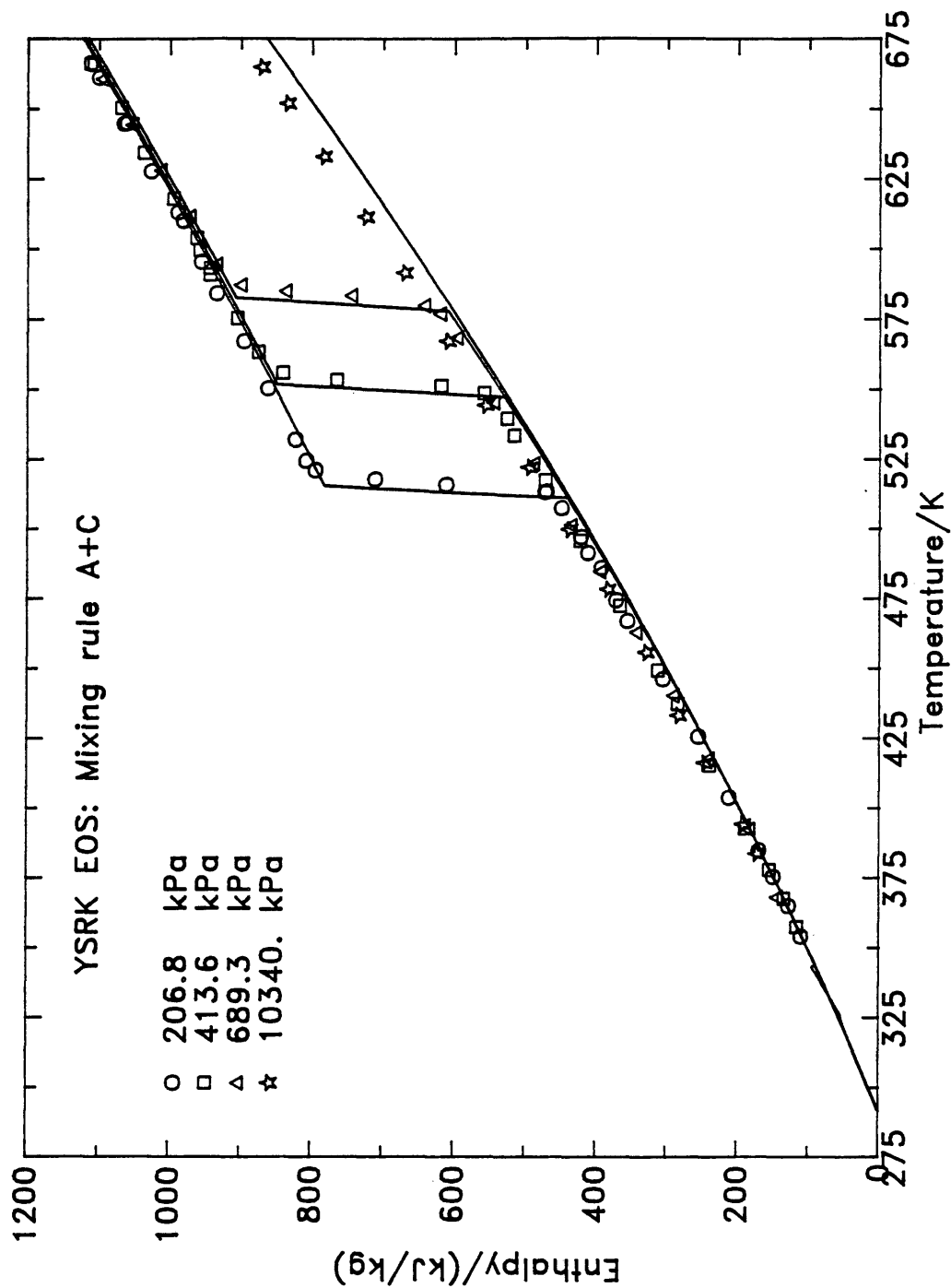


Figure 21 Enthalpy Predictions of 1/6:1/6:2/3 Quinoline:m-Cresol:Tetralin  
YSRK: Mixing Rule A+C

two phase region. The vapor and liquid phase enthalpies are predicted low by the density dependent mixing rule  $k_{ij}=A-B/vRT$ , but the two phase region is defined well.

The predictions worked very well for this system. One reason for the success was the greater mole fraction of tetralin. Since tetralin is nonpolar, the polar interactions are not as strong in this system. Thus, the enthalpy predictions should work very well for this mixture.

#### Enthalpy Predictions for the 2/3:1/6:1/6 Quinoline:m-Cresol:Tetralin Mixture

The enthalpy predictions for the SRK equation of state are shown in Figures 22 and 23. The mixing rule incorporating  $k_{ij}$  predicts the enthalpies fairly well, but they are a little low, and it does not map the two phase region as well as expected. The mixing rule  $k_{ij}=0$  does not work nearly as well as the simple  $k_{ij}$  mixing rule.

Figures 24 to 28 show the enthalpy predictions for the YSRK equation of state. Again mixing rules  $k_{ij}$  and  $k_{ij}=0$  predict the vapor and liquid phase enthalpies low, but the  $k_{ij}$  mixing rule predicts the two phase region much better than  $k_{ij}=0$ . The mixing rule  $k_{ij}=A+B/T$  falters on the two phase transition, but predicts the liquid and vapor phase enthalpies much better than the previous mixing rules. Figure 27 and 28 incorporates the density dependent mixing

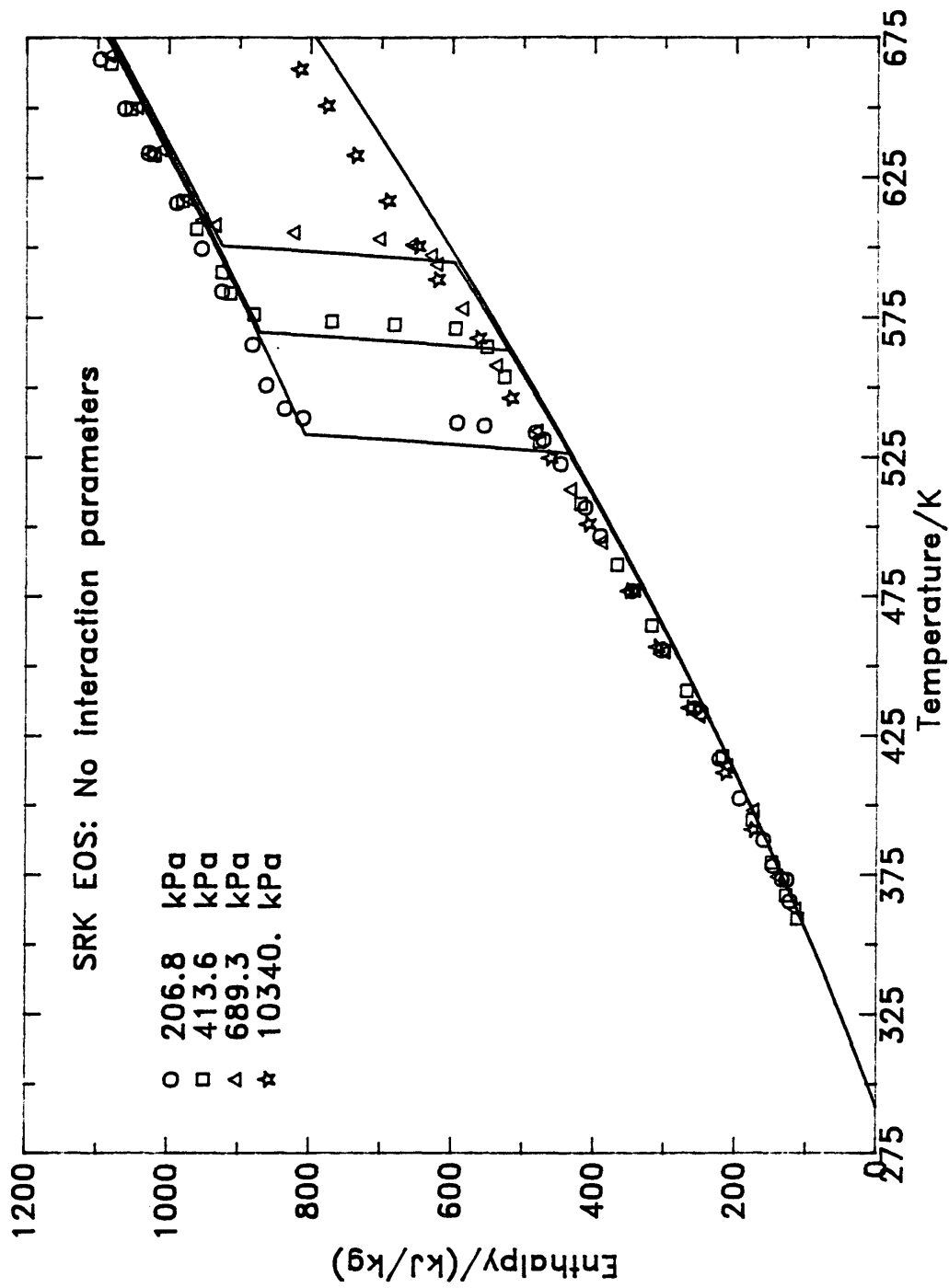


Figure 22 Enthalpy Predictions of 2/3:1/6:1/6 Quinoline:m-Cresol:Tetralin  
 SRK: Mixing Rule  $k_{ij} = 0$

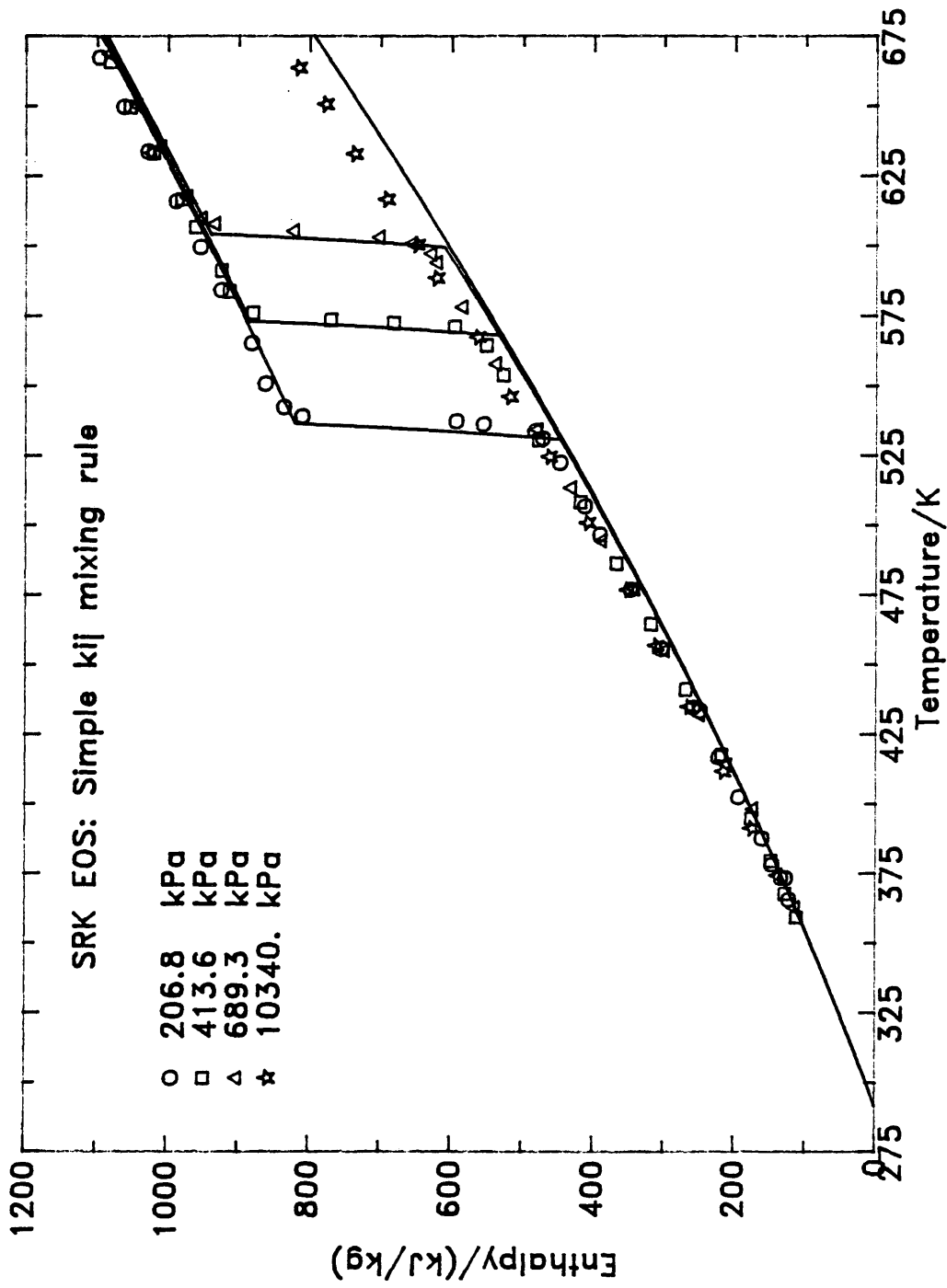


Figure 23 Enthalpy Predictions of 2/3:1/6:1/6 Quinoline:m-Cresol:Tetralin  
SRK: Mixing Rule kij

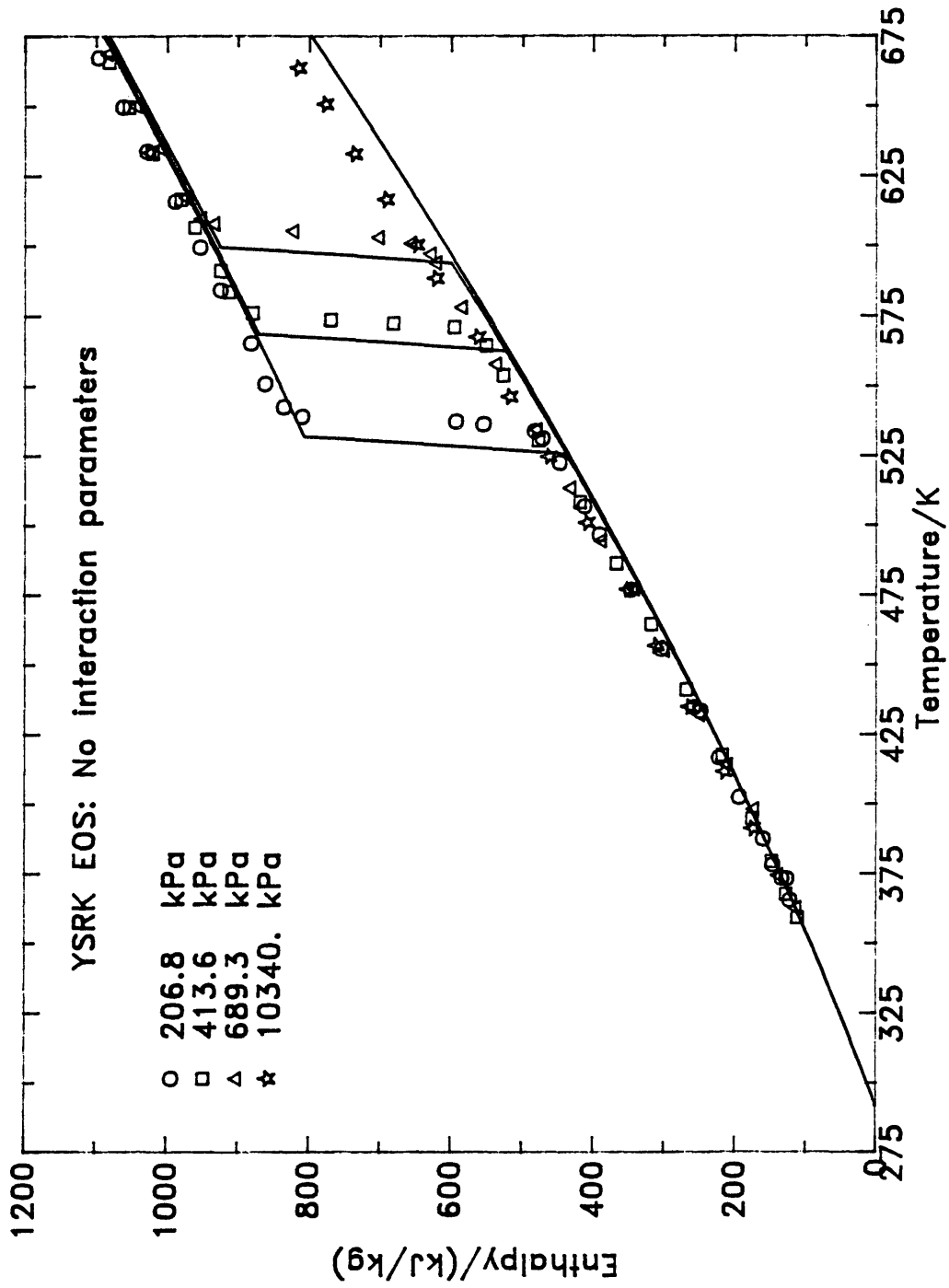


Figure 24 Enthalpy Predictions of 2/3:1/6:1/6 Quinoline:m-Cresol:Tetralin  
 YSRK: Mixing Rule  $k_{ij} = 0$

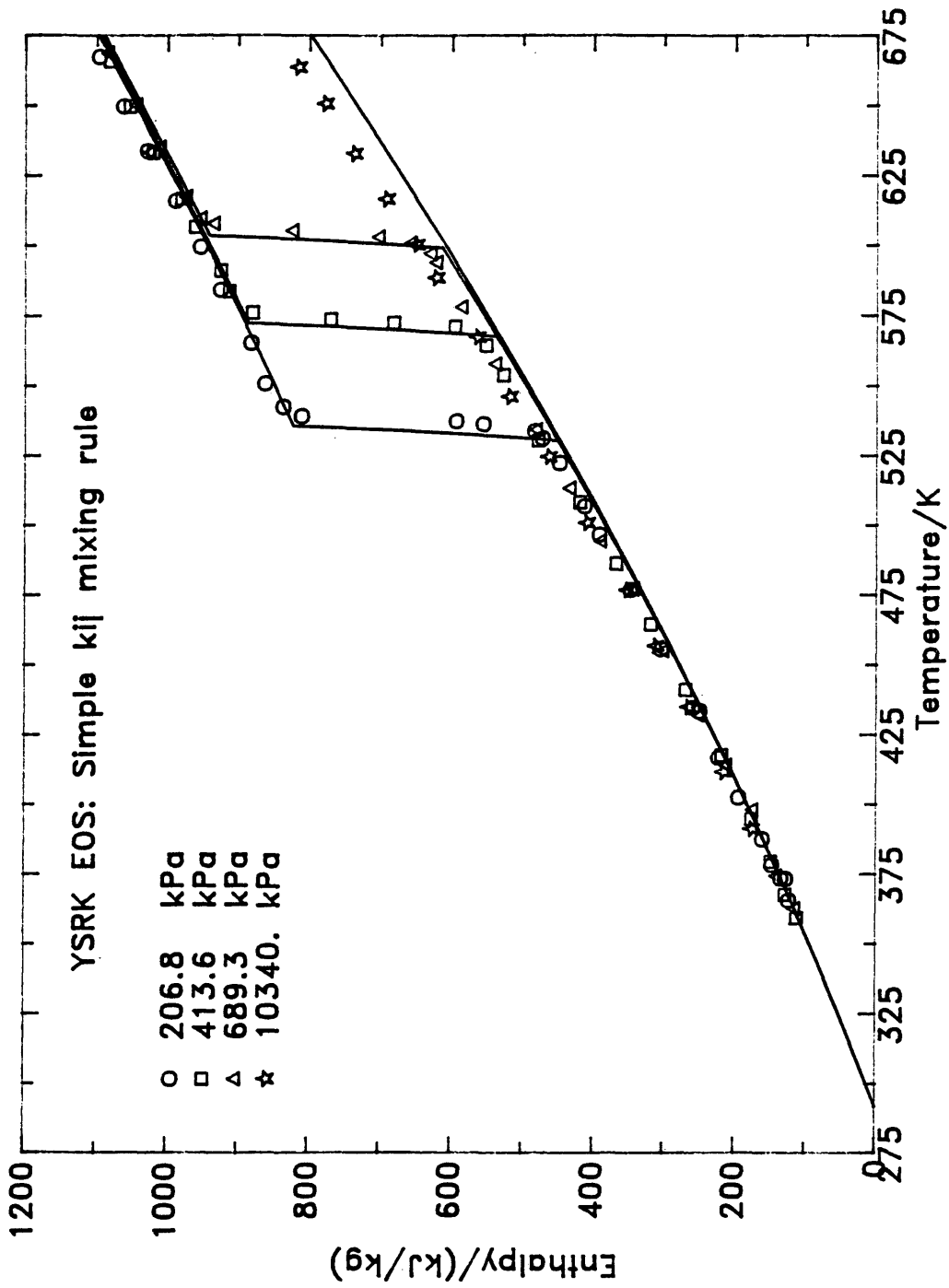


Figure 25 Enthalpy Predictions of 2/3:1/6:1/6 Quinoline:m-Cresol:Tetralin  
 YSRK: Mixing Rule  $k_{ij}$

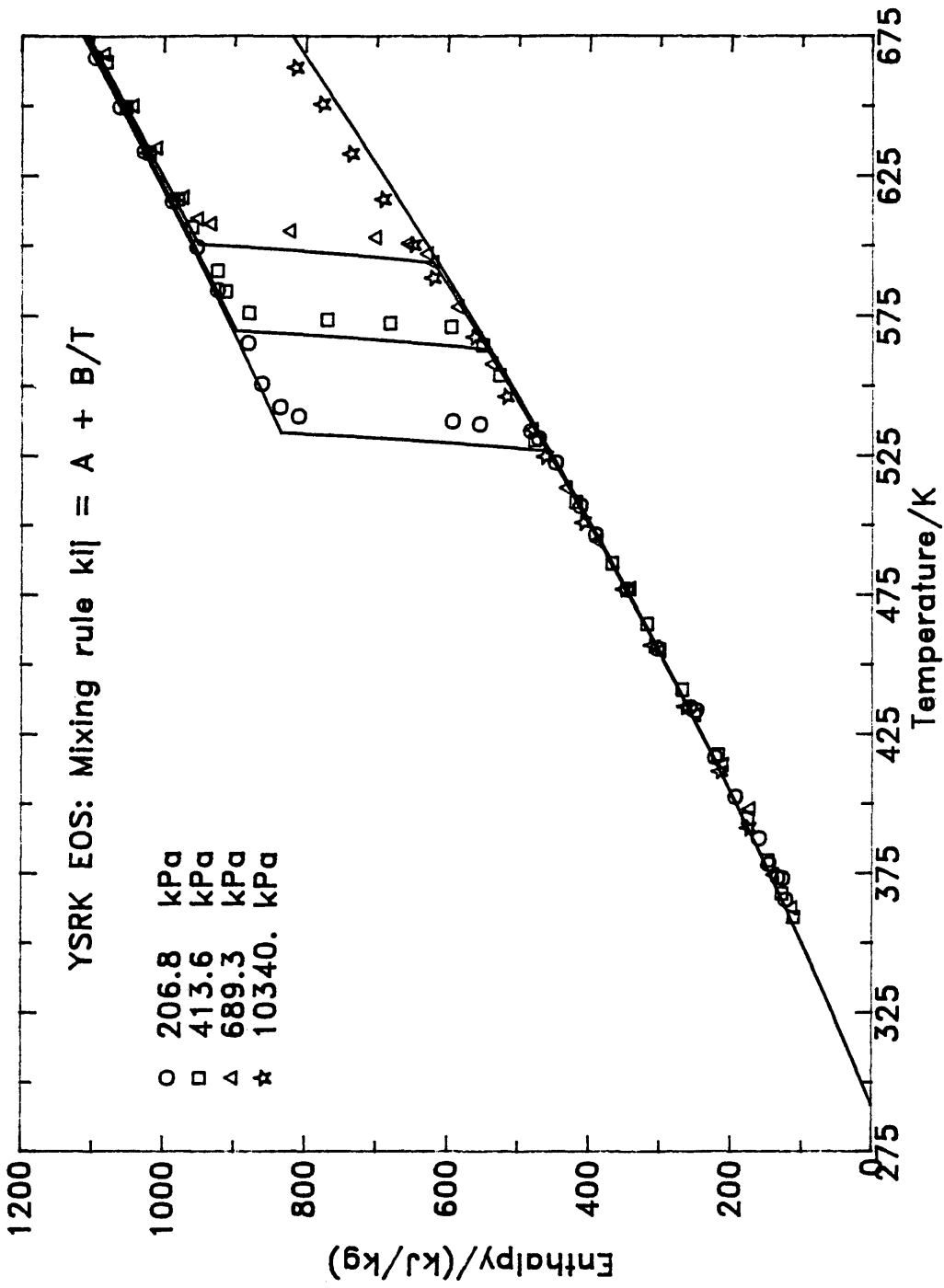


Figure 26 Enthalpy Predictions of 2/3:1/6:1/6 Quinoline:m-Cresol:Tetralin  
 YSRK: Mixing Rule  $k_{ij} = A+B/T$

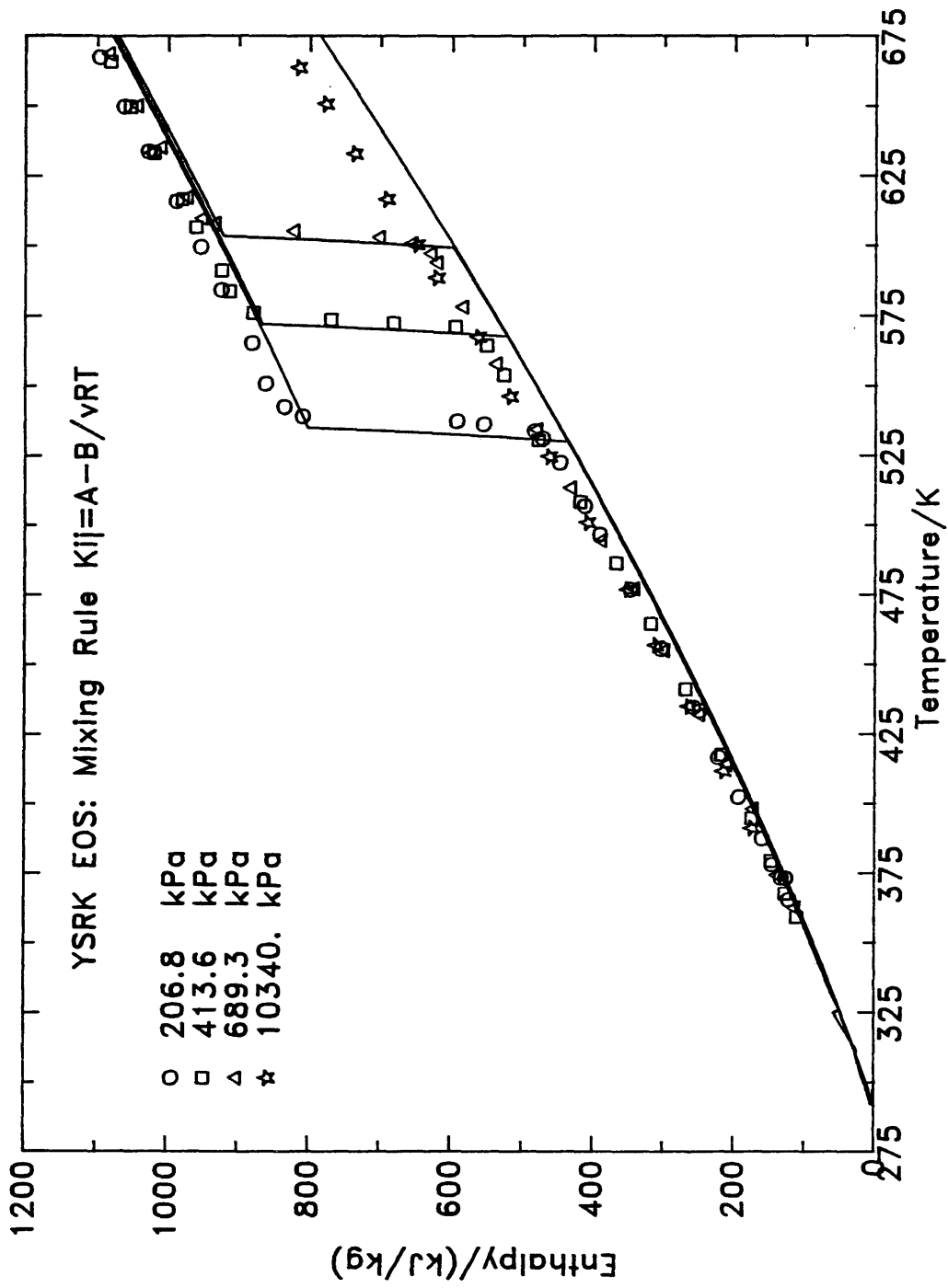


Figure 27 Enthalpy Predictions of 2/3:1/6:1/6 Quinoline:m-Cresol:Tetralin  
 YSRK: Mixing Rule  $k_{ij} = A - B/vRT$



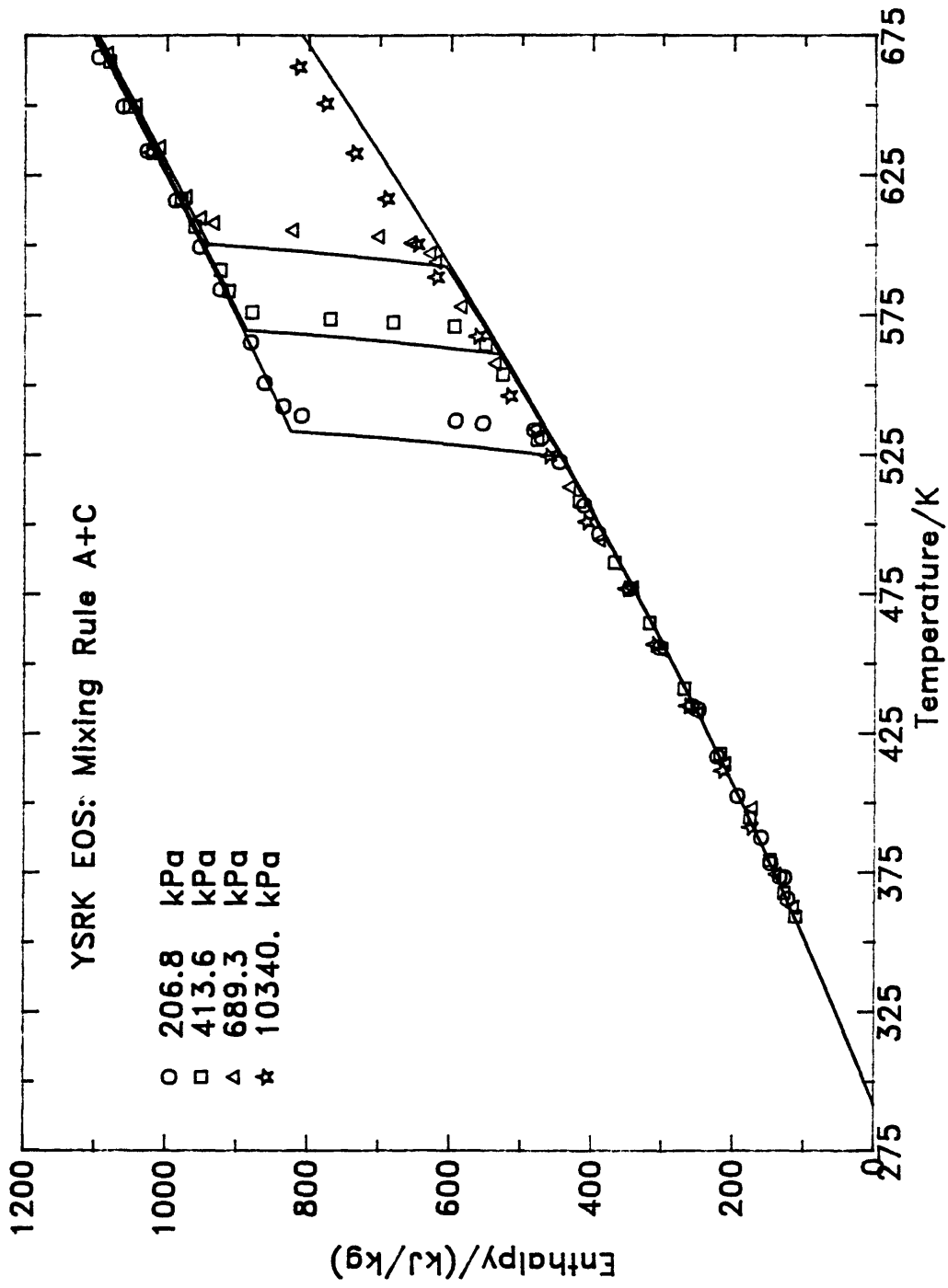


Figure 28 Enthalpy Predictions of 2/3:1/6:1/6 Quinoline:m-Cresol:Tetralin  
YSRK: Mixing Rule A+C

rules  $k_{ij}=A-B/vRT$  and  $A+C$  respectively. Mixing rule  $k_{ij}=A-B/vRT$  predicts both enthalpy phases poorly, but it does predict the two phase region well. The mixing rule  $A+C$  does a fairly good job with the liquid phase region, but does better at the lower temperatures than the higher temperatures. The mixing rule does fine predicting the vapor phase enthalpy, but falters predicting the two phase region.

#### Enthalpy Predictions for the 1/6:2/3:1/6 Quinoline:m-Cresol:Tetralin Mixture

Figures 29 and 30 show enthalpy predictions for the SRK equation of state incorporating the mixing rules  $k_{ij}$  and  $k_{ij}=0$  respectively. Both mixing rules do a poor job predicting the enthalpies. The vapor and liquid phase are predicted low, and the two phase transition prediction is far off for  $k_{ij}=0$  and better for the mixing rule  $k_{ij}$ .

The enthalpy predictions for the YSRK equation of state using the simple nondensity dependent mixing rules are shown in Figures 31 to 35. Again mixing rules  $k_{ij}$  and  $k_{ij}=0$  predict the vapor and liquid phase low, but the predictions are better than the SRK equation of state. Mixing rule  $k_{ij}$  predicts the two phase transition better than  $k_{ij}=0$  and  $k_{ij}=A+B/T$ . The mixing rule  $k_{ij}=A+B/T$  does a very good job in the prediction of the vapor and liquid phase enthalpies, and falters on the prediction of the two phase transition

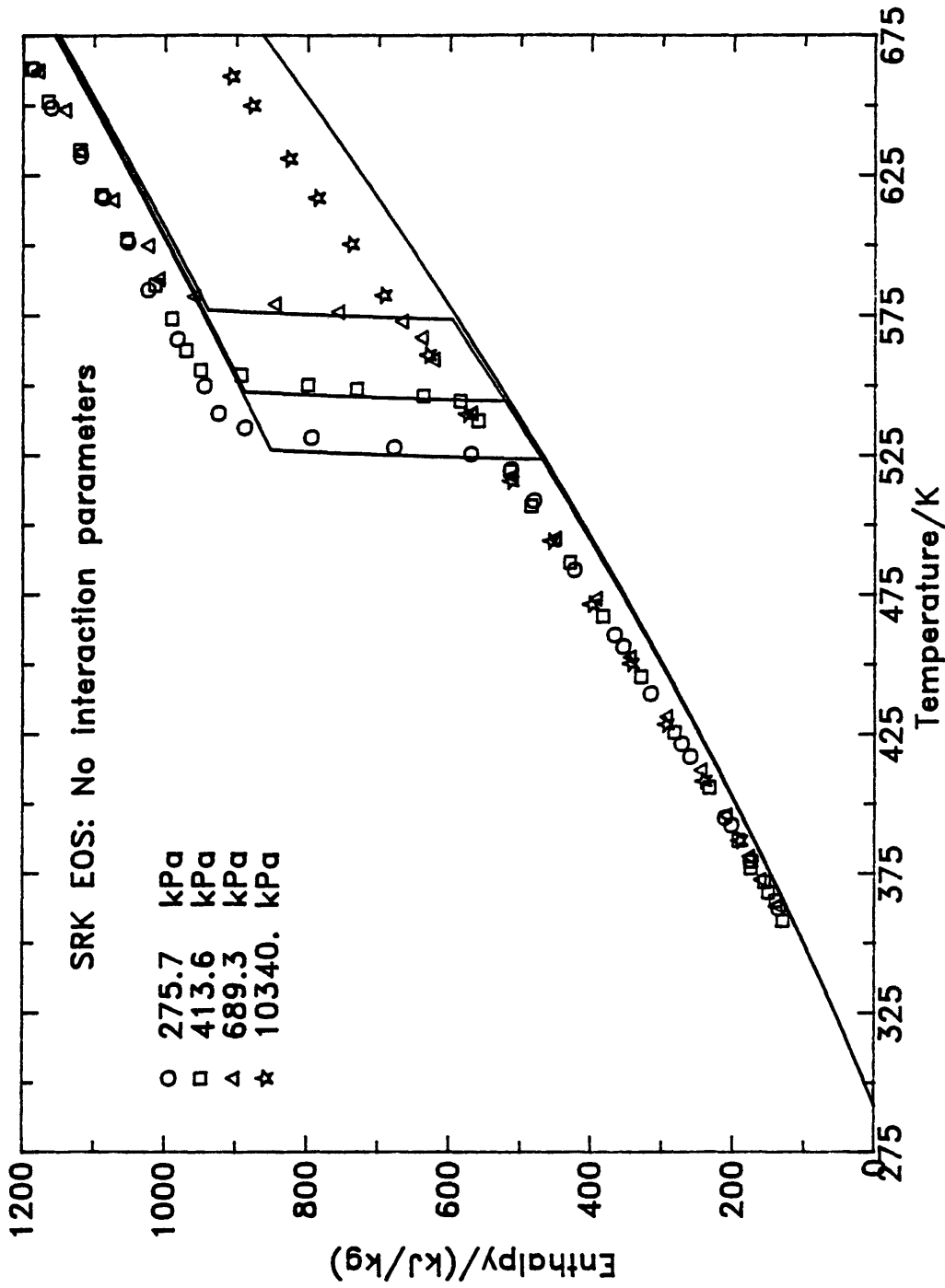


Figure 29 Enthalpy Predictions of 1/6:2/3:1/6 Quinoline:m-Cresol:Tetralin  
 SRK: Mixing Rule  $k_{ij} = 0$

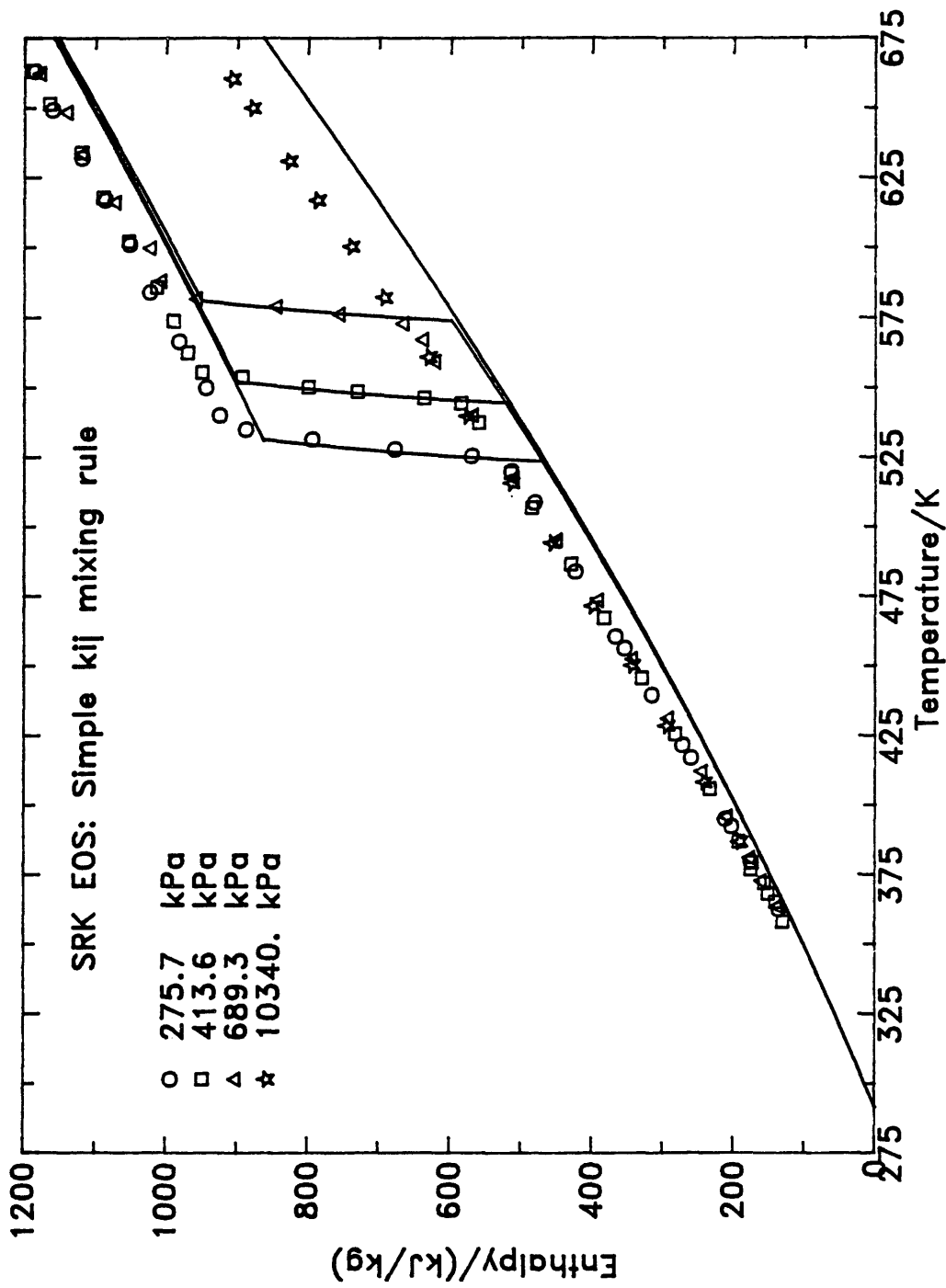


Figure 30 Enthalpy Predictions of 1/6:2/3:1/6 Quinoline:m-Cresol:Tetralin  
 SRK: Mixing Rule  $k_{ij}$

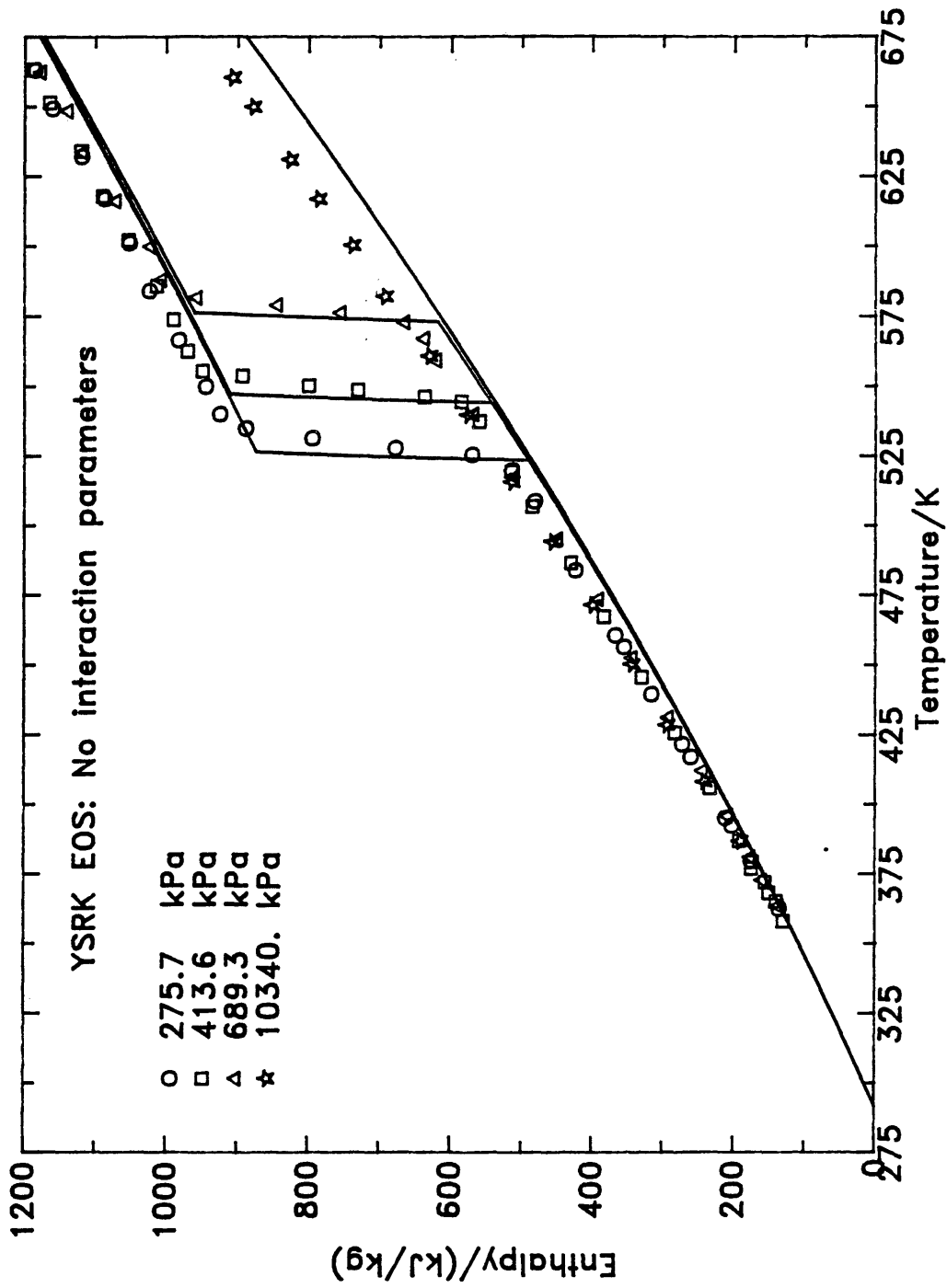


Figure 31 Enthalpy Predictions of 1/6:2/3:1/6 Quinoline:m-Cresol:Tetralin  
 YSRK: Mixing Rule  $k_{ij} = 0$

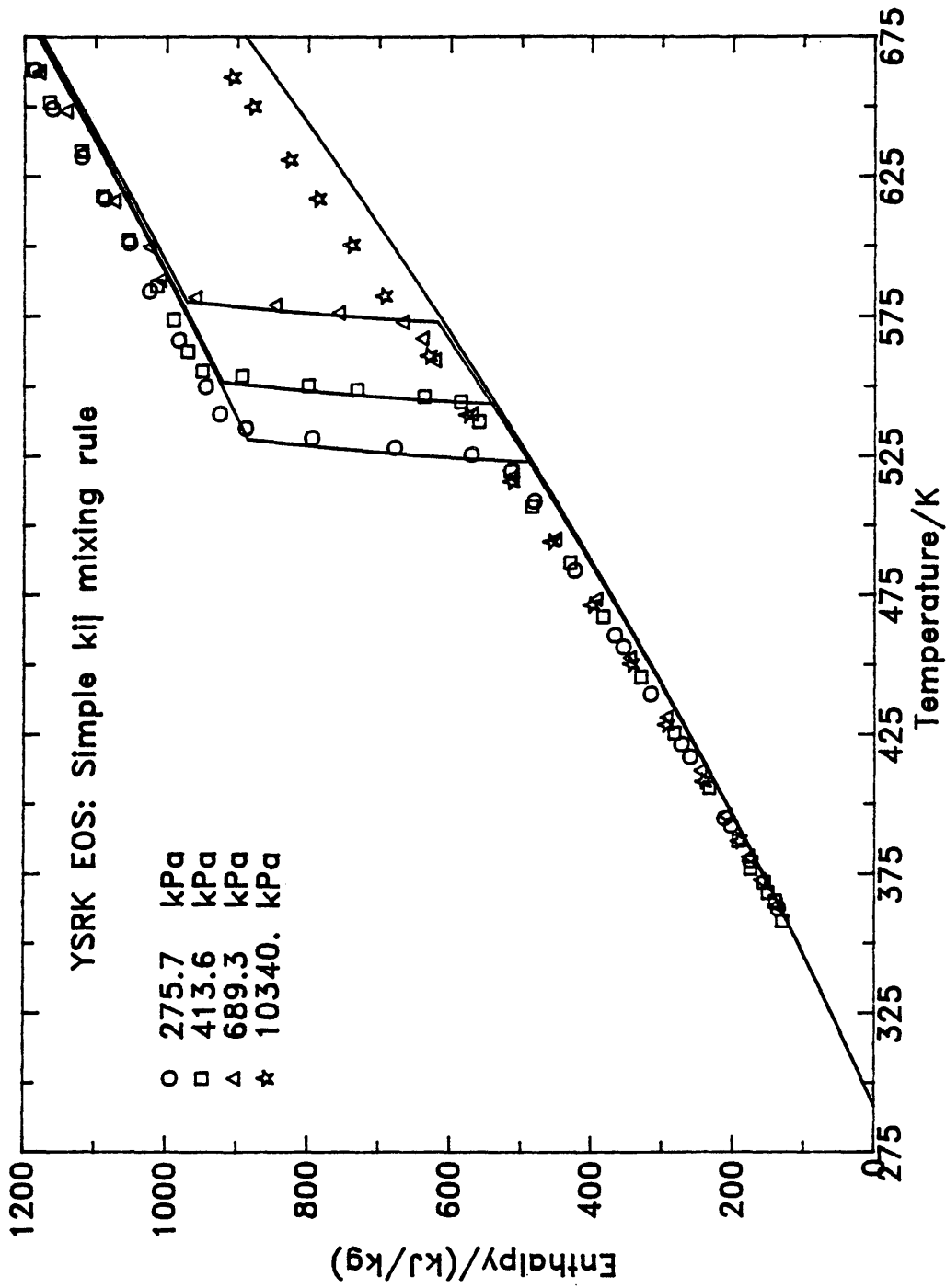


Figure 32 Enthalpy Predictions of 1/6:2/3:1/6 Quinoline:m-Cresol:Tetralin  
 YSRK: Mixing Rule  $k_{ij}$

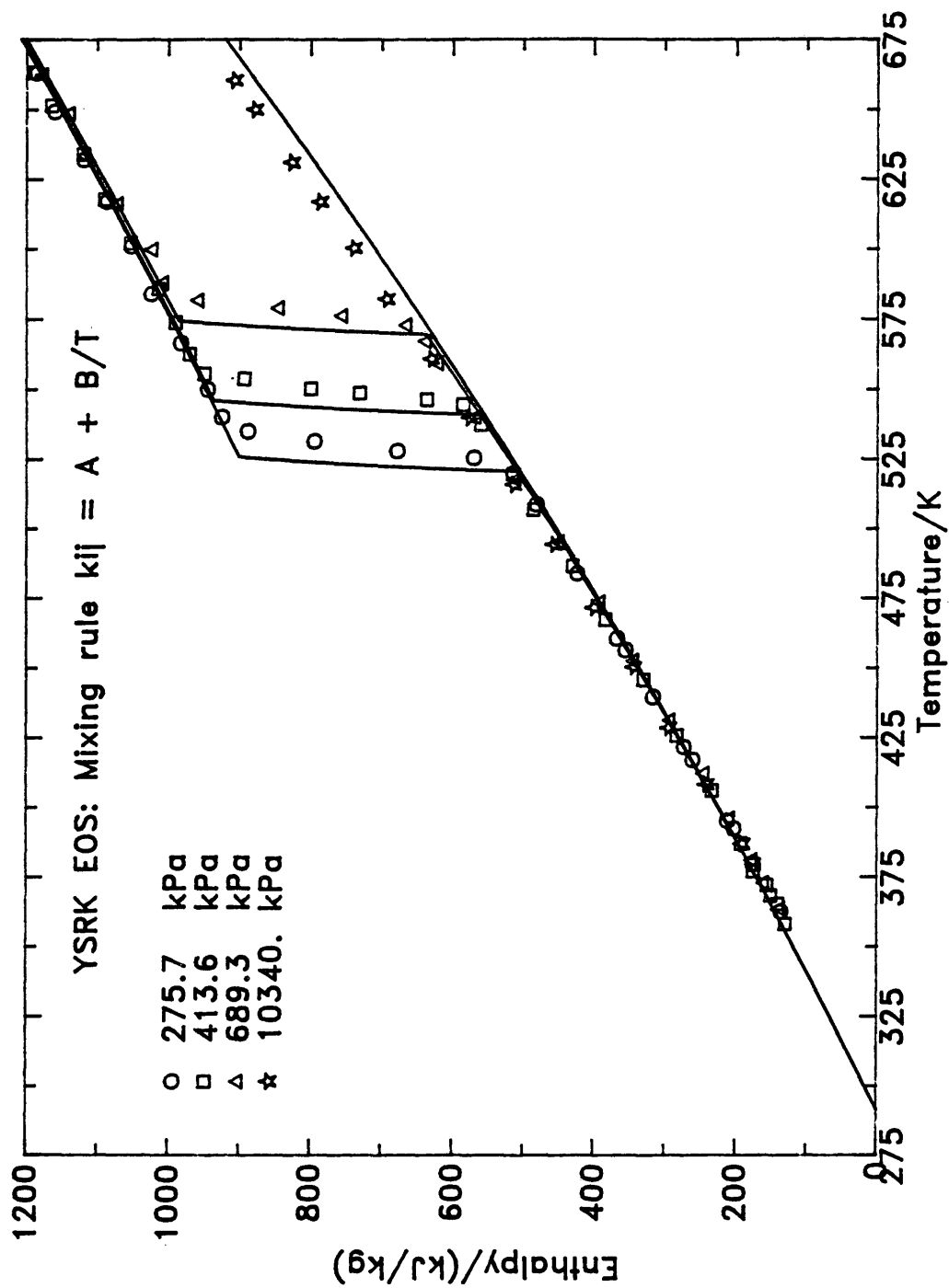


Figure 33 Enthalpy Predictions of 1/6:2/3:1/6 Quinoline:m-Cresol:Tetralin  
 YSRK: Mixing Rule  $k_{ij} = A+B/T$

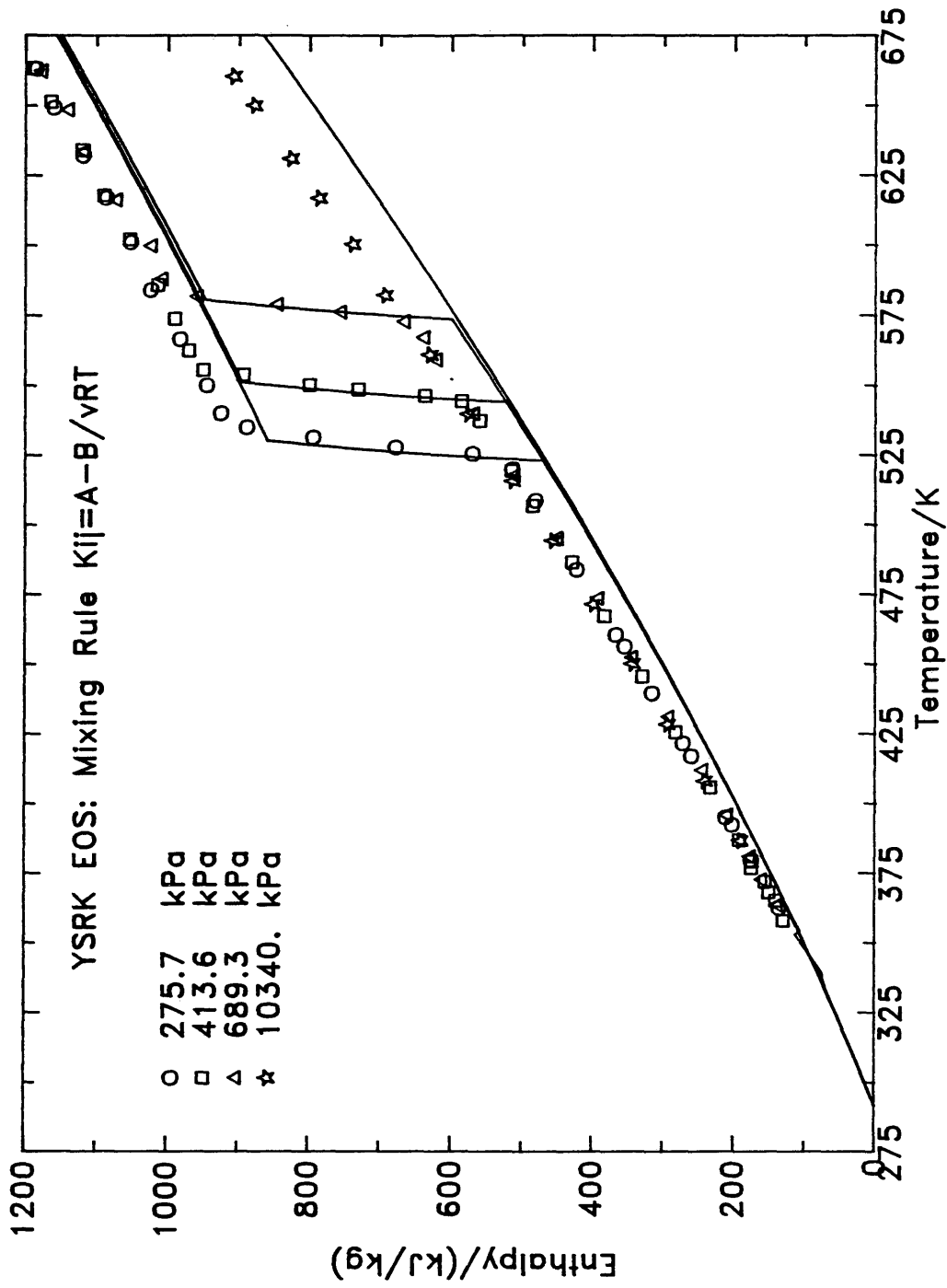


Figure 34 Enthalpy Predictions of 1/6:2/3:1/6 Quinoline:m-Cresol:Tetralin  
 YSRK: Mixing Rule  $k_{ij} = A-B/vRT$



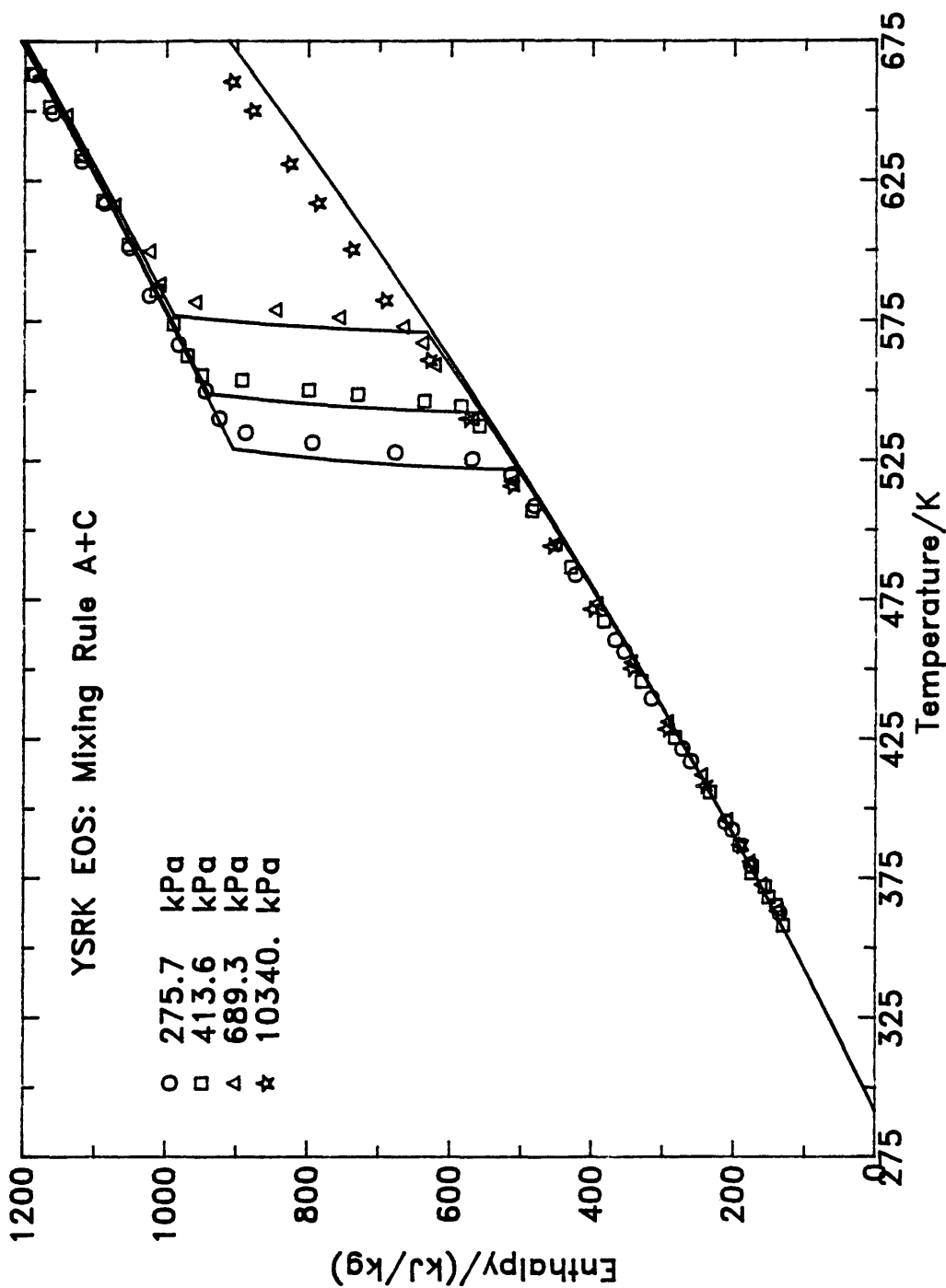


Figure 35 Enthalpy Predictions of 1/6:2/3:1/6 Quinoline:m-Cresol:Tetralin  
 YSRK: Mixing Rule A+C

region. The enthalpy predictions incorporating the density dependent mixing rules are shown in Figure 34 to 35. The mixing rule  $k_{ij}=A-B/vRT$  does not work very well predicting the enthalpies, but it does find the two phase transition fine. The A+C mixing rule does a satisfactory job predicting the liquid and vapor phase enthalpies, but again it falters predicting the two phase transition region.

The two parameter ( $k_{ij}=A+B/T$ ) and the density dependent (A+C) mixing rules generally do a better job predicting enthalpy for this mixture than the other mixing rules, but they do not do a satisfactory job predicting the two phase transition. The polar interactions are very strong in this system due to the high concentration of m-cresol, which is one reason why the SRK equation of state does not work as well as the YSRK equation.

The enthalpy predictions in this investigation are similar to the results of Flanigan's (1986) investigation. Flanigan was able to fit the binary enthalpy well using the YSRK equation and the appropriate mixing rules. The two parameter mixing rule ( $k_{ij}=A+B/T$ ) was shown to work better than the three parameter density dependent (A+C) mixing rule. These mixing rules worked better than the other three. In this investigation the same two mixing rules worked the best, but they did not predict the ternary data

as well as they fit the binary data. The three parameter mixing rule shows no significant improvement on the enthalpy predictions over the two parameter mixing rule, and Flanigan observed the same phenomena. The three parameter mixing rule seems to act more as a curve fitting technique that fits the binary enthalpy well but then falters substantially when it predicts the ternary enthalpy. This investigation and Flanigan's both showed that the SRK predictions were poor.

## CONCLUSIONS

The primary goal of this investigation was to generate enthalpy measurements for the ternary system of quinoline, m-cresol, and tetralin. The experimental data were successfully collected with no major problems. The precision of the experimental data as demonstrated by the fitting equations was satisfactory for the liquid as for the vapor. There was no other experimental data to compare with the data generated from this investigation.

A set of trends were observed during the predictions of the experimental data. The following conclusions can be made about the various mixing rules. The mixing rule  $k_{ij}=0$  predicts the vapor and liquid phase enthalpies quite low and misses the two phase transition region. The simple  $k_{ij}$  mixing rule predicts the two phase region very well, but like the mixing rule  $k_{ij}=0$  it predicts the vapor and liquid phase enthalpies low. The mixing rule  $k_{ij}=A+B/T$  predicts the liquid and vapor phase enthalpies very well, but falters predicting the two phase region. The density dependent mixing rule  $A+C$  predict the vapor and liquid phase enthalpies quite well, but it also falters substantially predicting the two phase region. The results for the mixing rule  $k_{ij}=A-B/vRT$  were off due to an error in Flanigan's expression for the enthalpy departure for this rule. The

mixing rule  $k_{ij}=A+B/T$  predicts the vapor and liquid phase enthalpies about as well as the density dependent mixing rules.

The use of the density dependent mixing rules cannot be justified in this investigation. The mixing rule  $k_{ij}=A+B/T$  reasonably duplicates the predictions by the density dependent mixing rules. The density dependent mixing rules are very complicated and use more computer time than the  $k_{ij}=A+B/T$  mixing rule, but do not work significantly better. Thus, the mixing rule  $k_{ij}=A+B/T$  should be used over the density dependent mixing rules because it is simpler and uses less computer time. The simple  $k_{ij}$  mixing rule is the only one that can predict the two phase region well, but it falters substantially in the liquid and vapor phase region. None of the mixing rules studied could predict the two phase region along with the liquid and vapor phase enthalpies satisfactorily. The mixing rules would either predict the two phase region or the vapor and liquid phase enthalpies, but would never do both.

The YSRK equation predicted enthalpies better than the SRK equation of state when the polar interactions were strong as in the 1/3:1/3:1/3, 1/6:2/3:1/6, and 2/3:1/6:1/6 quinoline:m-cresol:tetralin systems. The YSRK equation is superior than the SRK equation because it incorporates the

modification for polar fluids.

None of the currently proposed mixing rules were able to predict ternary enthalpy data using parameters generated from binary data alone. Either an appropriate mixing rule has as yet not been found, or perhaps it will not be possible to reliably predict enthalpy of ternary and also multicomponent mixtures using binary data alone.

## RECOMMENDATIONS

- 1.) The Heise gauge calibrations should be checked before the start of another enthalpy system. The gauges have been used extensively for the past two years and have taken much abuse.
- 2.) It would be very beneficial to the enthalpy apparatus if a differential pressure indicator were installed on the equipment. This would allow the use of nitrogen gas on the side of the gauges and would relieve the gauges from excessive abuse. This would also reduce the volume required to make measurements by reducing the system volume.
- 3.) The sample pump should be thoroughly inspected and checked before another major project is initiated. The pump had problems at the higher pressures (10340 kPa), and it also experienced leaking tendencies at these pressures.
- 4.) There should be more investigation of mixing rules. A mixing rule is desired that will predict the liquid and vapor phase enthalpies as well as the two phase region better than the mixing rules observed in this investigation. It is possible that the density dependent mixing rules from this investigation could be modified to achieve this goal.

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APPENDIX A  
Example Computer Program

```

C      THIS PROGRAM USES THE YSRK EQUATION OF
C      STATE AND A LUEDECKE MIXING RULE TO
C      PREDICT ENTHALPIES.
C      AUTHORS: TIMOTHY P. JOYCE, DAVID A. FLANIGAN
C      LAST MODIFIED: MAY 14, 1987
C      COMPOUNDS: (1) QUINOLINE, (2) M-CRESOL, (3) TETRALIN

C BUBDEW DRIVER.....

      PARAMETER  NC=3
      IMPLICIT REAL*8 (A-H,O-Z)
C NC IS THE NUMBER OF COMPONENTS.
      CHARACTER*20 FILN1,FILN2,FILN3,FILN4

C DIMENSION ARRAYS AND VECTORS.
      REAL*8 MINUS

      REAL*8 AEN(NC),BEN(NC),CEN(NC),DEN(NC),EEN(NC),FEN
2      (NC),GEN(NC),HEN(NC)

      REAL*8 TCRIT(NC),PCRIT(NC),OMEGA(NC),MW(NC),OMEGAN
2      (NC),Rp(NC)

      REAL*8 K(NC,NC),BETA(NC,NC),YBG(NC),YB(NC),ZX(NC),
2      KD(NC)
2      ,B(NC),APR(NC),PHIV(NC),PHIL(NC),A(NC),XD(NC)
2      ,XDG(NC)
2      ,CPR(NC),CAPR(NC),ATC(NC)
C COMMON BLOCK FOR ENTHALPY PARAMETERS .....
      COMMON/IDEAL/AEN,BEN,CEN,DEN,EEN,FEN,GEN,HEN
      COMMON/PAR/TCRIT,PCRIT,OMEGA,MW,OMEGAN,Rp
      COMMON/ENTH/HID,HDEP,HREF
      COMMON/BUB/XD,YB

C SET VALUE FOR REAL -1
      MINUS=-DFLOAT(1)
C *****
C START BY INITIALIZING DATA BASE FOR THE COMPOUNDS OF
C INTEREST.

      E=0.45
      R=8314.41

C ENTER DATA BASE FILES CONTAINING CRITICAL PARAMETERS FOR
C COMPOUNDS.

```

```

DO I=1,NC

    TYPE*, ' FOR COMPONENT ',I
    TYPE*, ' ENTER MOLE FRACTION COMPONENT ',I
    ACCEPT*,ZX(I)
    TYPE*, ' NAME OF THE DATA BASE FILE FOR CRITICAL
2      PARAMETERS'
    READ(5,15)FILN1
15    FORMAT(A20)
        OPEN(UNIT=10, FILE=FILN1, STATUS='OLD')
C
C THE STRUCTURE OF THE DATA FILE IS AS FOLLOWS
C TCRIT/K,PCRIT/kPa,OMEGA,MOLECULAR WEIGHT
C OMEGA HOMOMORPH, POLAR PARAMETER
C CONSTANTS FOR IDEAL GAS ENTHALPY expression a,b,c,d
C E,F,G,H ; A total of FOUR lines.

    READ(10,25)TCRIT(I),PCRIT(I),OMEGA(I),MW(I)
25    FORMAT(4D)
        READ(10,35)OMEGAN(I),Rp(I)
35    FORMAT(2D)
        READ(10,25)AEN(I),BEN(I),CEN(I),DEN(I)
        READ(10,25)EEN(I),FEN(I),GEN(I),HEN(I)
        CLOSE(10)

ENDDO

DO I=1,NC
    ATC(I)=(0.42747*R**2*TCRIT(I)**2)/PCRIT(I)
ENDDO

C***** SET K(I,J) AND BETA(I,J)
K(1,1)=0.0
K(1,2)=6.57E-2
K(1,3)=7.01E-3
K(2,1)=6.57E-2
K(2,2)=0.0
K(2,3)=0.155
K(3,1)=7.01E-3
K(3,2)=0.155
K(3,3)=0.0
BETA(1,1)=0.0
BETA(1,2)=5.94E-2*(ATC(1)**2.)
BETA(1,3)=6.31E-3*(ATC(1)**2.)
BETA(2,1)=8.60E-2*(ATC(2)**2.)
BETA(2,2)=0.0
BETA(2,3)=8.92E-2*(ATC(2)**2.)
BETA(3,1)=1.91E-2*(ATC(3)**2.)

```

```

BETA(3,2)=5.57E-2*(ATC(3)**2.)
BETA(3,3)=0.0

TYPE*, ' ENTER OPERATING PRESSURE/kPa '
ACCEPT*, P
TYPE*, '1-LIQUID ONLY,2-TWO PHASE '
ACCEPT*, KIND
TYPE*, 'ENTER OUTPUT FILE NAME '
READ(5,15)FILN3
OPEN(UNIT=30,FILE=FILN3,STATUS='NEW')
TYPE*, 'ENTER 1-EXP.REF. IE OUTLET PRESS, 2-1ATM
2      STD. REF. '
ACCEPT*, KREFI
IF (KREFI.EQ. 1) THEN
PREF=0.95*P
ELSE
PREF=101.325
ENDIF
IF (KIND.EQ.1) GO TO 499
C START BUBBLE POINT CALCULATION WITH GUESS OF TEMPERATURE
TYPE*, ' ENTER GUESS OF BUB. POINT TEMP./K '
ACCEPT*, TBGUESS
CALL BUBDEW (TBGUESS,P,K,BETA,ZX,TB,TD)
TYPE*, 'BUBBLE POINT/K IS',TB
TYPE*, 'VAPOR PHASE MOLE FRACTIONS ARE:'
DO I=1,NC
    TYPE*, 'Y',I,YB(I)
ENDDO

TYPE*, 'DEW POINT/K ',TD
TYPE*, 'LIQUID MOLE FRACTIONS ARE'
DO I=1,NC
    TYPE*, 'X',I,XD(I)
ENDDO

C ENTER REFERENCE CONDITIONS OUTPUT FILE
T=291.48
CALL DELH (T,ZX,K,BETA,P,PREF,O,HCAL)
WRITE(30,325)T,HCAL
325  FORMAT(1X,F7.3,F7.1)
IF (KIND.EQ.1) GO TO 499
CALL DELH (TB,ZX,K,BETA,P,PREF,O,HCALTB)
TYPE*, 'T/K,ENTHALPY/KJ/KG',TB,HCALTB

CALL DELH (TD,ZX,K,BETA,P,PREF,1,HCALTD)
TYPE*, 'T/K,ENTHALPY/KJ/KG',TD,HCALTD
KTB=INT(TB)
C WRITE LIQUID POINTS TO FILE.....

```

```

DO KTEMP=292,KTB
T=DFLOAT(KTEMP)
CALL DELH (T,ZX,K,BETA,P,PREF,O,HCAL)
WRITE(30,325)T,HCAL
ENDDO
WRITE(30,325)TB,HCALTB

C BEGIN FLASH CALCULATIONS.@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@
C DIVIDE THE TWO-PHASE REGION IN TO NTWO PARTS
TYPE*, 'HOW MANY POINTS DO YOU WISH TO DIVIDE THE TWO
2     PHASE'
ACCEPT*,NTWO
DELT=(TD-TB)/DFLOAT(NTWO)
DO 344 II=1,NTWO-1
    T=DFLOAT(II)*DELT+TB
    CALL DELH (T,ZX,K,BETA,P,PREF,2,HCAL)
C     TYPE*, 'T/K,P,V,H/KJ/KG',T,P,V,HCAL
    WRITE(30,325)T,HCAL
344   CONTINUE
    WRITE(30,325)TD,HCALTD
499   IF (KIND.EQ.1) THEN
C     .....LIQUID
        KTD=292
        KEND=0
        ELSE
C     .....VAPOR
        KEND=1
        KTD=INT(TD+0.5)
        ENDIF
        DO KTEMP=KTD,675
            T=DFLOAT(KTEMP)
            CALL DELH (T,ZX,K,BETA,P,PREF,KEND,HCAL)
            WRITE(30,325)T,HCAL
            ENDDO
        CLOSE(30)
C     .....END OF MAIN PROGRAM.
999   CONTINUE
        STOP
        END

SUBROUTINE BUBDEW (TBGUESS,P,K,BETA,ZX,TB,TD)
PARAMETER NC=3
IMPLICIT REAL*8 (A-H,O-Z)
C NC IS THE NUMBER OF COMPONENTS.

C DIMENSION ARRAYS AND VECTORS.
REAL*8 MINUS

```

```

REAL*8 AEN(NC), BEN(NC), CEN(NC), DEN(NC), EEN(NC), FEN
2  (NC), GEN(NC), HEN(NC)

REAL*8 TCRIT(NC), PCRIT(NC), OMEGA(NC), MW(NC), OMEGAN
2  (NC), Rp(NC)

REAL*8 K(NC,NC), BETA(NC,NC), YBG(NC), YB(NC), ZX(NC),
2  KD(NC)
2  , B(NC), APR(NC), PHIV(NC), PHIL(NC), A(NC), XD
2  (NC), XDG(NC)
2  , CPR(NC), KIJ, CAPR(NC)
C COMMON BLOCK FOR ENTHALPY PARAMETERS .....
COMMON/IDEAL/AEN, BEN, CEN, DEN, EEN, FEN, GEN, HEN
COMMON/PAR/TCRIT, PCRIT, OMEGA, MW, OMEGAN, Rp
COMMON/ENTH/HID, HDEP, HREF
COMMON/BUB/XD, YB
C SET VALUE FOR REAL -1
MINUS=-DFLOAT(1)
C Initialize variables here.
C DEW AND BUBBLE POINT RANGE IN KELVIN.
TLEFT=375.0
TRIGHT=675.0
TBLEFT=TLEFT
TBRIGHT=TRIGHT
TDRIGHT=TRIGHT
ITMAX1=30
ITMAX2=30

C *****

C
E=0.45
R=8314.41
TDGUESS=TBGUESS
C USE RAOULTS LAW TO GET FIRST ESTIMATES OF THE Y'S
C INITIALIZE COUNTER FOR MAXIMUM NUMBER OF ITERATIONS
ICOUNT=0
SUMY=0.0
DO I=1,NC
KD(I)=PCRIT(I)*DEXP(-7.0*(1.0+OMEGA(I))*(TCRIT(I)
1 /TBGUESS
1 -1.0)*DLOG(DFLOAT(10))/3.0 )/P
YBG(I)=KD(I)*ZX(I)
SUMY=SUMY+YBG(I)
ENDDO

C NORMALIZE VAPOR PHASE FRACTION GUESSES
DO I=1,NC

```



```

        YBG(I)=YBG(I)/SUMY
        ENDDO

C SOLVE FOR VAPOR EOS MOLE FRACTIONS AT THIS TEMPERATURE
C AND PRESSURE
C BY SUCESSIVE SUBSTITUTION.
C CALCULATE LIQUID PHASE FUGACITY COEF.'S
      CALL BFUG (TCRIT,PCRIT,R,ZX,B,BEOS,NC)
      CALL AFUG (TBGUESS,TCRIT,PCRIT,OMEGAN,R,Rp,e,K,
2         BETA,
2         ZX,AEOS,CEOS,APR,CPR,NC,CAPR)
      CALL QYSRK (R,AEOS,BEOS,CEOS,TBGUESS,P,COEF1,
1         COEF2,COEF3,
1         COEF4,ANORM,BNORM,CNORM)
      CALL QUAD (COEF1,COEF2,COEF3,COEF4,Z,0,BNORM)
      DO I=1,NC
        CALL FUGACITY (R,TBGUESS,P,Z,B(I),BEOS,BNORM,
2         AEOS,CEOS,
2         APR(I),CPR(I),PHIL(I),CAPR(I))
      ENDDO
C THE LIQUID VALUES STAY THE SAME UNTIL THE TEMPERATURE
C IS CHANGED.

C NOW CALCULATE NEW ESTIMATES OF VAPOR PHASE MOLE FRACTIONS.
C THE VAPOR PHASE FUG. COEF.'S ARE EVALUATED USING THE
C CURRENT
C ESTIMATES OF YB. YB IS THE MOLE FRACTION AT THE BUBBLE
C POINT.

50      CALL BFUG (TCRIT,PCRIT,R,YBG,B,BEOS,NC)
      CALL AFUG (TBGUESS,TCRIT,PCRIT,OMEGAN,R,Rp,e,K,
2         Beta,YBG,AEOS,CEOS,APR,CPR,NC,CAPR)
      CALL QYSRK (R,AEOS,BEOS,CEOS,TBGUESS,P,COEF1,COEF2
1         ,COEF3,
1         COEF4,ANORM,BNORM,CNORM)
      CALL QUAD (COEF1,COEF2,COEF3,COEF4,Z,1,BNORM)
      DO I=1,NC
        CALL FUGACITY (R,TBGUESS,P,Z,B(I),BEOS,BNORM,
2         AEOS,CEOS,
2         APR(I),CPR(I),PHIV(I),CAPR(I))
        YBG(I)=ZX(I)*PHIL(I)/PHIV(I)
      ENDDO

DO II=1,ITMAX1
  SYPERR=0.0
  SUMY=0.0
  CALL BFUG (TCRIT,PCRIT,R,YBG,B,BEOS,NC)

```

```

      CALL AFUG (TBGUESS,TCRIT,PCRIT,OMEGAN,R,Rp,e,K,
2         BETA,
2         YBG,AEOS,CEOS,APR,CPR,NC,CAPR)
      CALL QYSRK (R,AEOS,BEOS,CEOS,TBGUESS,P,COEF1,COEF2
1         ,COEF3,
1         COEF4,ANORM,BNORM,CNORM)
      CALL QUAD (COEF1,COEF2,COEF3,COEF4,Z,1,BNORM)
      DO I=1,NC
        CALL FUGACITY (R,TBGUESS,P,Z,B(I),BEOS,BNORM,
2         AEOS,CEOS,
2         APR(I),CPR(I),PHIV(I),CAPR(I))
        YB(I)=ZX(I)*PHI(I)/PHIV(I)
        SYPERR=DABS( 100.0*(YB(I)-YBG(I))/YB(I) )+SYPERR
        SUMY=SUMY+YB(I)
      ENDDO

      SYPERR=SYPERR/DFLOAT(NC)
      IF ( SYPERR.LE. 0.01 ) THEN

C IF THE VALUES ARE CHANGING BY LESS THAN .01 PER CENT THEN
C WE HAVE CONVERGED TO THE MOLE FRACTIONS AT THESE
c CONDITIONS.
        GO TO 10
      ELSE

C IF NOT THEN RESET MOLE FRACTIONS AND RECALCULATE Y'S
        DO I=1,NC
          YBG(I)=YB(I)
        ENDDO
      ENDIF
    ENDDO

C WE MUST FIND WHERE WE ARE IN RELATION TO THE BUBBLE POINT.

10      IF ( SUMY .LE. 1.0 ) THEN
C TBGUESS IS NOT HIGH ENOUGH. WE ARE TO THE LEFT OF THE
c BUBBLE POINT.
        TLEFT=TBGUESS
C NEED TO INCREASE THE GUESS.....
        IF ( TLEFT .LT. TLEFT ) THEN
C
          OUT OF BOUNDS. ERROR
          TYPE*,'BUBBLE POINT OUT OF RANGE, QUIT'
          GO TO 999
        ENDIF
C UPDATE TGUESS.....
        TBGUESS=(TBRIGHT+TLEFT)/2.0
      ELSE

C TBGEUSS TO HIGH. TO THE RIGHT OF BUBBLE POINT. 2222222222

```



```

        SUMX=0.0
        TDLEFT=TB
C ESTIMATE MOLE FRACTIONS IN THE LIQUID PHASE USING
c RAOULTS LAW.
        DO I=1,NC
            XDG(I)=ZX(I)/KD(I)
            SUMX=SUMX+XDG(I)
        ENDDO
C NORMALIZE THE VALUES.
        DO I=1,NC
            XDG(I)=XDG(I)/SUMX
        ENDDO
C SOLVE FOR LIQUID EOS MOLE FRACTIONS AT THIS TEMPERATURE
c AND PRESSURE
C BY SUCESSIVE SUBSTITUTION.
C CALCULATE VAPOR PHASE FUGACITY COEF.'S
        CALL BFUG (TCRIT,PCRIT,R,ZX,B,BEOS,NC)
        CALL AFUG (TDGUESS,TCRIT,PCRIT,OMEGAN,R,Rp,e,K,
2           BETA,
2           ZX,AEOS,CEOS,APR,CPR,NC,CAPR)
        CALL QYSRK (R,AEOS,BEOS,CEOS,TDGUESS,P,COEF1,COEF2
1           ,COEF3,
1           COEF4,ANORM,BNORM,CNORM)
        CALL QUAD (COEF1,COEF2,COEF3,COEF4,Z,1,BNORM)
        DO I=1,NC
            CALL FUGACITY (R,TDGUESS,P,Z,B(I),BEOS,BNORM,
2           AEOS,CEOS,
2           APR(I),CPR(I),PHIV(I),CAPR(I))
        ENDDO
C THE VAPOR VALUES STAY THE SAME UNTIL THE TEMPERATURE IS
C CHANGED.
C NOW CALCULATE NEW ESTIMATES OF LIQUID PHASE MOLE
C FRACTIONS.
C THE LIQUID PHASE FUG. COEF.'S ARE EVALUATED USING THE
C CURRENT
C ESTIMATES OF XD. XD IS THE MOLE FRACTION AT THE DEW POINT.

100        CALL BFUG (TCRIT,PCRIT,R,XDG,B,BEOS,NC)
        CALL AFUG (TDGUESS,TCRIT,PCRIT,OMEGAN,R,Rp,e,K,
2           BETA,
2           XDG,AEOS,CEOS,APR,CPR,NC,CAPR)
        CALL QYSRK (R,AEOS,BEOS,CEOS,TDGUESS,P,COEF1,
2           COEF2,COEF3,
1           COEF4,ANORM,BNORM,CNORM)
        CALL QUAD (COEF1,COEF2,COEF3,COEF4,Z,0,BNORM)
        DO I=1,NC
            CALL FUGACITY (R,TDGUESS,P,Z,B(I),BEOS,BNORM,

```

```

2      AEOS,CEOS,
2      APR(I),CPR(I),PHIL(I),CAPR(I))
      XDG(I)=ZX(I)*PHIV(I)/PHIL(I)
      ENDDO

DO II=1,ITMAX1
  SXPERR=0.0
  SUMX=0.0
  CALL BFUG (TCRIT,PCRIT,R,XDG,B,BEOS,NC)
  CALL AFUG (TDGUESS,TCRIT,PCRIT,OMEGAN,R,Rp,e,K,
2      BETA,
2      XDG,AEOS,CEOS,APR,CPR,NC,CAPR)
  CALL QYSRK (R,AEOS,BEOS,CEOS,TDGUESS,P,COEF1,COEF2
2      ,COEF3,
1      COEF4,ANORM,BNORM,CNORM)
  CALL QUAD (COEF1,COEF2,COEF3,COEF4,Z,0,BNORM)
  DO I=1,NC
    CALL FUGACITY (R,TDGUESS,P,Z,B(I),BEOS,BNORM,
2      AEOS,CEOS,
2      APR(I),CPR(I),PHIL(I),CAPR(I))
    XD(I)=ZX(I)*PHIV(I)/PHIL(I)
    SXPERR=DABS( 100.0*(XD(I)-XDG(I))/XD(I) )+SXPERR
    SUMX=SUMX+XD(I)
  ENDDO

  SXPERR=SXPERR/DFLOAT(NC)
  IF ( SXPERR.LE. 0.001 ) THEN

C IF THE VALUES ARE CHANGING BY LESS THAN .01 PER CENT THEN
C WE HAVE CONVERGED TO THE MOLE FRACTIONS AT THESE
C CONDITIONS.
    GO TO 60
  ELSE

C IF NOT THEN RESET MOLE FRACTIONS AND RECALCULATE X'S
    DO I=1,NC
      XDG(I)=XD(I)
    ENDDO
  ENDIF
ENDDO

C WE MUST FIND WHERE WE ARE IN RELATION TO THE DEW POINT.

60      IF ( SUMX .GT. 1.0 ) THEN
C TDGUESS IS NOT HIGH ENOUGH. WE ARE TO THE LEFT OF THE
C DEW POINT.
      TDLEFT=TDGUESS
C NEED TO INCREASE THE GUESS.....
      IF ( TDLEFT .LT. TLEFT ) THEN

```

```

C                                     OUT OF BOUNDS. ERROR
      TYPE*, 'DEW POINT OUT OF RANGE, QUIT'
      GO TO 999
      ENDIF
C UPDATE TGUESS.....
      TDGUESS=(TDRIGHT+TDLEFT)/2.0
      ELSE

C TDGEUSS TO HIGH. TO THE RIGHT OF DEW POINT. ****
      TDRIGHT=TDGUESS

      IF ( TDRIGHT.GE.TRIGHT ) THEN
C                                     OUT OF BOUNDS. ERROR
      TYPE*, 'DEW POINT OUT OF RANGE, QUIT'
      GO TO 999
      ENDIF
C UPDATE TBGUESS. ****
      TDGUESS=(TDRIGHT+TDLEFT)/2.0
      ENDIF

C                                     CHECK FOR DEW POINT.+++++

      IF ( (TDRIGHT-TDLEFT).LE. 0.01 ) THEN

          TD=TDGUESS
          GO TO 40

      ELSE
          ICOUNT=ICOUNT+1
          IF (ICOUNT.GT.ITMAX2) THEN
              TYPE*, 'ITMAX2 EXCEEDED END, DEW POINT'
              GO TO 999
          ENDIF
C ITERATE AGAIN
      CALL BFUG (TCRIT,PCRIT,R,ZX,B,BEOS,NC)
      CALL AFUG (TDGUESS,TCRIT,PCRIT,OMEGAN,R,Rp,e,K,
2          BETA,
2          ZX,AEOS,CEOS,APR,CPR,NC,CAPR)
      CALL QYSRK (R,AEOS,BEOS,CEOS,TDGUESS,P,COEF1,COEF2
1          ,COEF3,
1          COEF4,ANORM,BNORM,CNORM)
      CALL QUAD (COEF1,COEF2,COEF3,COEF4,Z,1,BNORM)
      DO I=1,NC
          CALL FUGACITY (R,TDGUESS,P,Z,B(I),BEOS,BNORM,
2          AEOS,CEOS,
2          APR(I),CPR(I),PHIV(I),CAPR(I))
      ENDDO

      GO TO 100

```

```

      ENDIF
40     CONTINUE

C     ***** END OF BUBDEW*****

999    CONTINUE
      RETURN
      END

C HELP
      SUBROUTINE DELH(T,ZX,K,BETA,P,PREF,KPHASE,HCAL)
      PARAMETER NC=3
      IMPLICIT REAL*8 (A-H,O-Z)
C
C THE PURPOSE OF THIS PROGRAM IS CALCULATE SINGLE-PHASE
C TERNARY DELTA H VALUES CORRESPONDING TO THOSE
C OBTAINED IN THE ENTHALPY LAB CALORIMETRY EXPERIMENTS.
C THE EQUATION OF STATE USED IS THE YESAVAGE MODIFICATION
C OF THE SRK EOS. THIS PROGRAM IS WRITTEN IN A WAY TO
C ALLOW IT TO BE USED AS A FUNCTION IN DETERMING MIXING
C RULE PARAMETERS.

      REAL*8 KIJ,MW(NC),CATC(2),CPR(NC),K(NC,NC),
      2 BETA(NC,NC)
      REAL*8 YBG(NC),YB(NC),ZX(NC),KD(NC),CAPR(NC)
      2      ,B(NC),APR(NC),PHIV(NC),PHIL(NC),A(NC),
      2      XD(NC),XDG(NC)
C FLASH CALCULATION VARIABLES.
      REAL*8 XOLD(NC),Y(NC),X(NC),XNEW(NC)

      COMMON/IDEAL/AEN(NC),BEN(NC),CEN(NC),DEN(NC),
      2 EEN(NC),
      2 FEN(NC),
      2 GEN(NC),HEN(NC)
      COMMON/PAR/TCRIT(NC),PCRIT(NC),OMEGA(NC),MW,
      2 OMEGAN(NC),Rp(NC)
      COMMON/ENTH/DELID,HDEP,HDREF
      ITMAX3=40
      ITMAX2=40
      ITMAX=30
C CALCULATE REFERENCE CONDITION VALUES FIRST.
C DEFINE REFERENCE CONDITONS.
      TREF=(65.0+459.67)/1.8
C REFERENCE PRESSURE IS NOT USED TO FIT THE DATA
C INSTEAD THE ACTUAL OUTLET PRESSURE IS USED FOR THIS
C PURPOSE.
      X(1)=ZX(1)

```





```

      V=0.5
      VOLD=0.5
C ESTIMATE DISTRIBUTION COEF.'S USING RAUOLTS LAW

      DO I=1,NC
        KD(I)=PCRIT(I)*DEXP(-7.0*(1.0+OMEGA(I)))*(
1          TCRIT(I)/T
1          -1.0)*DLOG(DFLOAT(10))/3.0 )/P
        ZX(I)=X(I)
      ENDDO
C ESTIMATE MOLE FRACTIONS.
      SUMX=0.0
      DO I=1,NC
        XOLD(I)=ZX(I)/(V*(KD(I)-1.0) +1.0)
        Y(I)=KD(I)*XOLD(I)
      ENDDO

      DO 322 IV=1,ITMAX3
C USE THE EQUATION OF STATE TO CALCULATE KD'S
C LIQUID PHASE FIRST.....
      CALL BFUG (TCRIT,PCRIT,R,XOLD,B,BEOS,NC)
      CALL AFUG (T,TCRIT,PCRIT,OMEGAN,R,Rp,e,K,BETA,
2          XOLD,AEOS,CEOS,APR,CPR,NC,CAPR)
      CALL QYSRK (R,AEOS,BEOS,CEOS,T,P,COEF1,COEF2,
1          COEF3,
1          COEF4,ANORM,BNORM,CNORM)
      CALL QUAD (COEF1,COEF2,COEF3,COEF4,Z,0,BNORM)
      DO I=1,NC
        CALL FUGACITY (R,T,P,Z,B(I),BEOS,BNORM,AEOS,
2          CEOS,
2          APR(I),CPR(I),PHIL(I),CAPR(I))
      ENDDO

C VAPOR PHASE NEXT.....

      CALL BFUG (TCRIT,PCRIT,R,Y,B,BEOS,NC)
      CALL AFUG (T,TCRIT,PCRIT,OMEGAN,R,Rp,e,K,BETA,
2          Y,AEOS,CEOS,APR,CPR,NC,CAPR)
      CALL QYSRK (R,AEOS,BEOS,CEOS,T,P,COEF1,COEF2,
2          COEF3,
1          COEF4,ANORM,BNORM,CNORM)
      CALL QUAD (COEF1,COEF2,COEF3,COEF4,Z,1,BNORM)
      DO I=1,NC
        CALL FUGACITY (R,T,P,Z,B(I),BEOS,BNORM,AEOS,
2          CEOS,
2          APR(I),CPR(I),PHIV(I),CAPR(I))
        KD(I)=PHIL(I)/PHIV(I)
      ENDDO

```

```

C BEGIN ITERATION ON FRACTION VAPORIZED V.
  DO JJ=1,ITMAX2
    GV=0.0
    GVPRIM=0.0
    DO I=1,NC
      GV=GV+(KD(I)-1.0)*ZX(I)/( V*(KD(I)-1.0) +1.0 )
      GVPRIM=GVPRIM+ZX(I)*(KD(I)-1.0)**2/(V*(KD(I)-
2      1.0) +1.0)**2
    ENDDO

C ESTIMATE NEW FRACTION V.
  VNEW=V+GV/GVPRIM
  IF ( DABS(VNEW-V).LT.0.0001 ) GO TO 319
  V=VNEW

C .....COMPLETE JJ LOOP.
  ENDDO
  TYPE*, ' NO CONV. IN V, ITMAX2 EXCEEDED'
  GO TO 344
319  V=VNEW
  SUMX=0.0
  DO I=1,NC
    XNEW(I)=ZX(I)/(V*(KD(I)-1.0) +1.0)
    Y(I)=KD(I)*XNEW(I)
    SUMX=SUMX+DABS(XNEW(I)-XOLD(I))
  ENDDO
C TEST FOR OVER ALL CONVERGENCE HERE ++++++
  XERR=SUMX/DFLOAT(NC)
  IF ( (DABS(V-VOLD)+XERR).LT. 0.0002) THEN
    IF (V.LT.0.000001) THEN
C ASSUME LIQUID .....LLLLLLLLLLLLLLLLLLLLLLLLLLLL
379  KPH=0

          CALL AYSRK(T,TCRIT,PCRIT,OMEGAN, R,Rp,e,K,
2          X,AEOS, APRIME,CEOS,DBETA,BETA)
C .....
  CALL BYSRK(TCRIT,PCRIT,R,X,BEOS)
C .....
  CALL QYSRK(R,AEOS,BEOS,CEOS,T,P,COEF1,COEF2,COEF3
1          ,COEF4,ANORM,BNORM,CNORM)
  CALL QUAD (COEF1,COEF2,COEF3,COEF4,Z,KPH,BNORM)
  CALL IDGAS(T,HID,AEN,BEN,CEN,DEN,EEN,FEN,GEN,HEN,X)

  CALL HD (R,T,Z, APRIME,AEOS,BEOS,BNORM,CEOS,DBETA,
2          HDEP,P)

  GO TO 344
ENDIF

```





END

```

SUBROUTINE HD (R,T,Z,APRIME,AEOS,BEOS,BNORM,BETA,
2          DBETA,HDEP,P)
REAL*8 R,T,Z,APRIME,AEOS,BEOS,BNORM,HDEP,BETA,
2          DBETA,P
TERM1=R*T*(Z-1)
TERM2=((T*APRIME-AEOS)/BEOS)*DLOG(Z/(Z+BNORM))
TERM3=(DBETA-2.*BETA/T)*(BNORM/Z+DLOG(Z/(Z+BNORM)))
2/(R*BEOS**2.)
HDEP=TERM1-TERM2+TERM3
RETURN
END

```

```

SUBROUTINE FUGACITY (R,T,P,Z,BI,BEOS,BNORM,AEOS,
2          CEOS,APR,CPR,FUG,CAPR)
IMPLICIT REAL*8 (A-H,O-Z)
V=Z*R*T/P
TERM1=R*T*BI/(V-BEOS)
TERM2=R*T*DLOG(V/(V-BEOS))
TERM3=BI*AEOS*(1./BEOS**2.*DLOG((BEOS+V)/V)-1.
9/(BEOS*(BEOS+V)))
TERM4=-APR/BEOS*DLOG((BEOS+V)/V)
TERM5=(BI*CEOS/R/T)*((BEOS+2.*V)/(V*BEOS**2.*
$ (BEOS+V))+2./BEOS**3.
$ *DLOG(V/(V+BEOS)))
TERM6=-CAPR/R/T*(1./(V*BEOS)+1./BEOS**2.*
$ DLOG(V/(V+BEOS)))
TERM7=-R*T*DLOG(Z)
RTLNFU=TERM1+TERM2+TERM3+TERM4+TERM5+TERM6+TERM7
ALNFU=RTLNFU/(R*T)
FUG=DEXP(ALNFU)
RETURN
END

```

C THIS SUBROUTINE CALCULATES A IDEAL GAS ENTHALPY,  
C REFERENCE STATE IS H=0 AT T=OK, FROM EXPRESSIONS  
C GIVEN BY REHMAN, Z.U. AND LEE, L.L. FLUID PHASE  
C EQUILIBRIA, 22, (1985) 21-31.

C THE EQUATION IS OF THE FORM:

C  $H^* = A + BT + CT(D/T)COTH(D/T) - ET(F/T)TANH(F/T) +$   
C  $IT(J/T)COTH(J/T)$

C THE UNITS OF H\* ARE CAL/gmol.

```

SUBROUTINE IDGAS(T,HIDMIX,A,B,C,D,E,F,I,J,X)
REAL*8 A(3),B(3),C(3),D(3),E(3),F(3),I(3),J(3),

```

```

      2      T,HIDMIX,HID(3),X(3)
      HIDMIX=0.0
      DO 10 N=1,3

      HID(N)= A(N)+ B(N)*T+ ( C(N)*T*(D(N)/T)/
      2      DTANH(D(N)/T) )
      2      -( E(N)*T*(F(N)/T)*DTANH(F(N)/T) )
      3      +( I(N)*T*(J(N)/T)/DTANH(J(N)/T) )
      HIDMIX=HIDMIX+4.1844*X(N)*HID(N)
10     CONTINUE
C
C CALCULATE MIXTURE PROPERTY AND CONVERT TO UNITS OF J/gmol

      RETURN
      END

C THIS SUBROUTINE CONTAINS THE EQUATION OF STATE.*****

      SUBROUTINE QYSRK(R,AEOS,BEOS,CEOS,T,P,COEF1,
      2      COEF2,COEF3
      2      ,COEF4,AA,BB,CC)
      REAL*8 AEOS,BEOS,CEOS,CC,BB,AA,COEF1,COEF2,COEF3,
      2      COEF4
      2      ,P,T,R
C THE FORM OF THE EOS IS
C  $Z^{**4} - Z^{**3} + (-B^{**2} - B + A)Z^{**2} + (C - AB)Z - BC = 0$ 
C THE DIMENSIONLESS GROUPS ARE DEFINED BELOW
      CC=CEOS*P**2/( (R*T)**4 )
      BB=BEOS*P/(R*T)
      AA=AEOS*P/( (R*T)**2 )
C .....
      COEF1=-1.0
      COEF2=(-BB**2-BB+AA)
      COEF3=( CC -AA*BB )
      COEF4=-BB*CC
      RETURN
      END
C THIS SUBROUTINE CALCULATES THE 'A' AND APRIME FOR YSRK*
C

      SUBROUTINE AYSRK(T,TCRIT,PCRIT,OMEGAN,R,Rp,e,K,
      2      X,AMIX,APRIME,BETA,DBETA,BB)
      REAL*8 TCRIT(3),PCRIT(3),OMEGAN(3),R,Rp(3),e,
      2      ATC(3),M(3),
      2      TR(3),T,A(3),APRIME,ALPHAN(3),POLAR(3),
      2      APR(3),AMIX
      3      ,K(3,3),X(3),BETA,DBETA,EBETA,BB(3,3)

```

```

C 'C' IS THE CONSTANT Bij IN THE DENSITY DEPENDENT
C MIXING RULE

      DO 10 I=1,3

C CALCULATE THE PART OF A THAT IS A FUNCTION OF TCRIT ONLY.
      ATC(I)=0.42747*(R**2.)*(TCRIT(I)**2.)/PCRIT(I)
C THE ACENTRIC FACTOR OF THE HOMOMORPH IS USED HERE.
      M(I)=0.480 + 1.574*OMEGAN(I) - 0.176*OMEGAN(I)**2.
C CALCULATE THE REDUCED TEMPERATURE TR
      TR(I)=T/TCRIT(I)
C ALPHA IS CALCULATE WITH TR OF COMPOUND AND OMEGA OF
C THE HOMOM.
      ALPHAN(I)=(1.0 + M(I)*(1.0 - TR(I)**.5))**2.
C CALCULATE THE EFFECTIVE POLAR GROUP
      POLAR(I)=1.0 + Rp(I)*( DEXP(-Rp(I)**e)
1          - DEXP(-(Rp(I)/TR(I))**e) )
C PUT THE PIECES TOGETHER TO FORM AEOS.
      A(I)=ATC(I)*ALPHAN(I)*POLAR(I)
C NOW CALCULATE THE DERIVATIVE WHILE WE ARE HERE*****
      APR(I)=-ATC(I)*(( ( Rp(I)/TR(I))**e )*)
2      ALPHAN(I)*e*Rp(I)/T )
2      *DEXP(-(Rp(I)/TR(I))**e)
2      + M(I)*POLAR(I)*(1.0 +M(I)*(1.0 -
2      TR(I)**.5) )/
3      ( (T*TCRIT(I))**.5 ) )

10      CONTINUE
C REMEMBER AT THIS POINT WE ARE CONCERNED ONLY WITH TERNARY
C CALCULATIONS.
      DBETA=0.0
      BETA=0.0
      AMIX=0.0
      APRIME=0.0
      DO 3 I=1,3
      DO 4 J=1,3
          AMIX=AMIX+X(I)*X(J)*(A(I)*A(J))**.5*(1.0-K(I,J))
          BETA=BETA+X(I)**2.*X(J)*BB(I,J)+X(I)*X(J)**2.
$          *BB(J,I)
          APRIME=APRIME+0.5*X(I)*X(J)*(1./(A(I)*A(J))**0.5)
$          *(A(I)*APR(J)
$          +A(J)*APR(I))*(1.0-K(I,J))

4      CONTINUE
3      CONTINUE
      RETURN
      END

SUBROUTINE CUB (P,Q,R,ROOT,KROOT)

```

```

C      THIS PROGRAM SOLVES A CUBIC EQUATION OF THE FORM***
C      Y**3+P*Y**2+Q*Y+R
C NOW RIGGED FOR EOS 1-VAPOR, 0-LIQUID; KROOT.
      REAL*8 A,B,AA,BB,DET,X1,X2,X3,R,THETA,P,Q,RAD,PIE
      2      ,ROOT
      A=(DFLOAT(3)*Q-P*P)/DFLOAT(3)
      PIE=3.141592653589793
      B=(DFLOAT(2)*P**3- DFLOAT(9)*P*Q + DFLOAT(27)*R)
      2 /DFLOAT(27)
      DET=(B**2)/DFLOAT(4)+A**3/DFLOAT(27)
      IF( DET ) 100,100,200
100   IF (DABS(B).LT. .00000001) GO TO 50
      THETA=DATAN(DSQRT(-DET)*DFLOAT(2)/(-B))
      IF ( B .GT. 0.0 ) THETA=THETA+PIE
      GO TO 55
50    THETA=PIE/DFLOAT(2)
55    RAD=(B**2./DFLOAT(4)-DET)**.5
      X1=DFLOAT(2)*RAD**(1./3.)*DCOS(THETA/DFLOAT(3))-
      2 P/DFLOAT(3)
      X2=DFLOAT(2)*RAD**(1./3.)*DCOS((THETA+DFLOAT(2)*
      2 PIE)/DFLOAT(3)
      2 )-P/DFLOAT(3)
      X3=DFLOAT(2)*RAD**(1./3.)*DCOS((THETA+DFLOAT(4)*
      2 PIE)/DFLOAT(3)
      2 )-P/DFLOAT(3)
      KFLAG=3
      IF (KROOT .EQ. 0) GO TO 99
      ROOT= DMAX1(X1,X2,X3)
      GO TO 2
99    ROOT= DMIN1(X1,X2,X3)
      GO TO 2
200   AA=-B/DFLOAT(2)+DSQRT(DET)
      BB=-B/DFLOAT(2)-DSQRT(DET)
      IF ( AA ) 210,220,220
210   AA=-((-AA)**(1./3.))
      GO TO 225
220   AA=AA**(1./3.)
225   IF (BB) 230,240,240
230   BB=-((-BB)**(1./3.))
      GO TO 245
240   BB=BB**(1./3.)
245   X1=AA+BB-P/DFLOAT(3)
      KFLAG=1
      X2=0.
      X3=0.
      ROOT=X1
2    CONTINUE
      RETURN

```



END

C THIS ROUTINE CALCULATES BEOS FOR THE SRK TYPE B'S\*\*\*\*\*  
 SUBROUTINE BYSRK(TCRIT,PCRIT,R,X,BEOS)  
 REAL\*8 TCRIT(3),PCRIT(3),R,BEOS,X(3)  
 BEOS=0.0  
 DO 10 I=1,3  
     BEOS= BEOS+X(I)\*0.08664\*R\*TCRIT(I)/PCRIT(I)  
 10 CONTINUE  
 RETURN  
 END

C THIS ROUTINE CALCULATES BEOS FOR THE SRK TYPE B'S\*\*\*\*\*  
 SUBROUTINE BFUG (TCRIT,PCRIT,R,X,B,BEOS,NC)  
 REAL\*8 TCRIT(NC),PCRIT(NC),R,BEOS,X(NC),B(NC)  
 BEOS=0.0  
 DO 10 I=1,NC  
     B(I)=0.08664\*R\*TCRIT(I)/PCRIT(I)  
     BEOS=BEOS+X(I)\*B(I)  
 10 CONTINUE  
 RETURN  
 END

C FUGACITY VERSION.  
 SUBROUTINE AFUG (T,TCRIT,PCRIT,OMEGAN,R,Rp,e,  
 2 ALPHA,BETA,  
 2 X,AMIX,CMIX,APR,CPR,NC,CAPR)  
 REAL\*8 TCRIT(3),PCRIT(3),OMEGAN(3),R,Rp(3),e,  
 2 ATC(3),M(3),  
 2 TR(3),T,A(3),APRIME,ALPHAN(3),POLAR(3),  
 2 APR(3),AMIX  
 3 ,X(3),BETA(3,3),ALPHA(3,3),CPR(3),  
 3 CMIX,CAPR(3)  
 DO 10 I=1,NC

C CALCULATE THE PART OF A THAT IS A FUNCTION OF TCRIT ONLY.

ATC(I)=0.42747\*(R\*\*2.)\*(TCRIT(I)\*\*2.)/PCRIT(I)

C THE ACENTRIC FACTOR OF THE HOMOMORPH IS USED HERE.

M(I)=0.480 + 1.574\*OMEGAN(I) - 0.176\*OMEGAN(I)\*\*2.

C CALCULATE THE REDUCED TEMPERATURE TR

TR(I)=T/TCRIT(I)

C ALPHA IS CALCULATE WITH TR OF COMPOUND AND OMEGA

C OF THE HOMOM.

ALPHAN(I)=(1.0 + M(I)\*(1.0 - TR(I)\*\*.5))\*\*2.

C CALCULATE THE EFFECTIVE POLAR GROUP

POLAR(I)=1.0 + Rp(I)\*( DEXP(-Rp(I)\*\*e)

1 - DEXP(-(Rp(I)/TR(I))\*\*e) )

C PUT THE PIECES TOGETHER TO FORM AEOS.

```

      A(I)=ATC(I)*ALPHAN(I)*POLAR(I)
10    CONTINUE
C    REMEMBER AT THIS POINT WE ARE CONCERNED ONLY WITH BINARY
C    CALCULATIONS.
      AMIX=0.0
      CMIX=0.0
      DO I=1,NC
        DO J=1,NC
          AMIX=AMIX+ X(I)*X(J)*( A(I)*A(J) )**0.5*
2          (1.0-ALPHA(I,J))
          CMIX=CMIX+X(I)**2.*X(J)*BETA(I,J)+X(I)*X(J)**2.
2          *BETA(J,I)
        ENDDO
      ENDDO
C    THE DERIVATIVE WITH RESPECT TO Ni
      DO I=1,NC
        APR(I)=0.0
        CAPR(I)=0.0
        DO J=1,NC
          APR(I)=APR(I)+X(J)*( A(I)*A(J) )**0.5
2          *(1.0-ALPHA(I,J))
          CAPR(I)=CAPR(I)+2.*X(I)*X(J)*BETA(I,J)+
2          X(J)**2.*BETA(J,I)
        ENDDO
        APR(I)=APR(I)*2.0
        CAPR(I)=CAPR(I)*2.0
      ENDDO
      RETURN
      END

```

```

      SUBROUTINE QUAD(A,B,C,D,ROOT,KROOT,ZB)
C    THE PURPOSE OF THIS ROUTINE IS CHECK THE METHOD
C    OUTLINE IN THE CRC MATH HAND BOOK FOR SOLUTIONS OF
C    QUARTIC OR BIQUADRATIC EQUATIONS.
C    THE QUARTIC IS OF THE FORM:
C    X**4 +AX**3 +BX**2 +CX +D =0
      IMPLICIT REAL*8 (A-H,O-Z)
      REAL*8 A,B,C,D,YP,YQ,YR,Y,A1,B1,C1,D1,
2          EE,DD,DET,R,ROOT,X(4),ZB,DET2,XX,XDET
      KFLAG=0
      KEFLAG=0
      KDFLAG=0
C    *****
C    FIRST FIND ROOT OF THE RESOLVENT CUBIC.
C    Y**3 -BY**2 +(AC-4D)Y +(-A**2D +4BD -C**2)

      YP=-B
      YQ=A*C-DFLOAT(4)*D

```

```

      YR=-(A**2)*D +DFLOAT(4)*B*D -C**2
C NEED ANY ROOT OF THE RESOLVENT EQUATION.
C THE ROOT TAKEN WILL MAX REAL.
      CALL CUB (YP,YQ,YR,Y,1)
C*****
C FORM FIRST DETERMINANT.
      DET=( A**2/DFLOAT(4) ) -B +Y
      DET2=DET/DSQRT(A**4/DFLOAT(16)+B**2+Y**2)
C CALCULATE THE PART WHICH IS THE SAME IN BOTH
C SOLUTION FORMS.
      A1=DFLOAT(3)*A**2/DFLOAT(4) -DFLOAT(2)*B
C DETECT WHICH FORM TO USE .....
      IF ( DABS(DET2) .LT. 1.0E-6) THEN
          KFLAG=1
          R=0.0
          B1=DFLOAT(2)*DSQRT(Y**2-DFLOAT(4)*D)
          DD=A1+B1
          EE=A1-B1
      ELSE
          R=DSQRT(DET)
          B1=(DFLOAT(4)*A*B-DFLOAT(8)*C-A**3)/(DFLOAT(4)*R)
          DD=A1+B1-R**2
          EE=A1-B1-R**2
      ENDIF
C CALCULATE ROOTS X1,X2,X3,X4
99      C1=-A/DFLOAT(4) +R/DFLOAT(2)
      D1=-A/DFLOAT(4) -R/DFLOAT(2)
      IF( DD .LT. 0.0 ) THEN
C ROOTS ARE COMPLEX.....
          X(1)=-1.0
          X(2)=-1.0
          KDFLAG=-1
      ELSE
C ROOTS ARE REAL .....
          X(1)=C1+DSQRT(DD)/DFLOAT(2)
          X(2)=C1-DSQRT(DD)/DFLOAT(2)
          IF( (KFLAG.EQ.0).AND.(DABS(DET).LT.1.0E-4) ) THEN
              KFLAG=1
              XX=X(1)
              XDET=XX**4 +A*XX**3 +B*XX**2 +C*XX +D
              IF(DABS(XDET).GT.1.E-2) THEN
                  R=0.0
                  B1=DFLOAT(2)*DSQRT(Y**2-DFLOAT(4)*D)
                  DD=A1+B1
                  EE=A1-B1
                  GO TO 99
              ENDIF
          ENDIF
      ENDIF

```

```

        ENDIF
C DEAL WITH OTHER ROOTS
        IF( EE .LT. 0.0 ) THEN
C ROOTS ARE COMPLEX.....
        X(3)=-1.0
        X(4)=-1.0
        KEFLAG=-1
        ELSE
C ROOTS ARE REAL .....
        X(3)=D1+DSQRT(EE)/DFLOAT(2)
        X(4)=D1-DSQRT(EE)/DFLOAT(2)
        IF( (KFLAG.EQ.0).AND.(DABS(DET).LT.1.0E-4) ) THEN
            KFLAG=1
            XX=X(3)
            XDET=XX**4 +A*XX**3 +B*XX**2 +C*XX +D
            IF(DABS(XDET).GT.1.E-2) THEN
                R=0.0
                B1=DFLOAT(2)*DSQRT(Y**2-DFLOAT(4)*D)
                DD=A1+B1
                EE=A1-B1
                GO TO 99
            ENDIF
        ENDIF
        ENDIF
ENDIF
        IF( (KEFLAG.EQ.-1).AND.(KDFLAG.EQ.-1) ) THEN
            R=0.0
            B1=DFLOAT(2)*DSQRT(Y**2-DFLOAT(4)*D)
            DD=A1+B1
            EE=A1-B1
            KDFLAG=1
            KEFLAG=1
            GO TO 99
        ENDIF

DO 100 I=1,4
100 IF( ( X(I).LT.ZB ).AND.(KROOT.EQ.0) ) X(I)=999999999
CONTINUE
        IF ( KROOT .EQ. 0) THEN
            ROOT=DMIN1(X(1),X(2),X(3),X(4))
        ELSE
            ROOT=DMAX1(X(1),X(2),X(3),X(4))
        ENDIF
RETURN
END

```