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VAPOR LIQUID EQUILIBRIA MEASUREMENTS FOR THE
CONSTITUENT TERNARY MIXTURE OF
M-CRESOL/QUINOLINE/TETRALIN

by

Stephen S. DiGiacinto

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

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ABSTRACT

Vapor-liquid equilibria data were measured for the ternary system of m-cresol, tetralin, and quinoline. These ternary systems were generated at four isotherms: 250, 275, 300, and 325°C. At each isotherm three distinct isobars at elevated pressures were examined. The m-cresol, tetralin, quinoline system was studied due to its non-ideal behavior. These three compounds are accepted model compounds for coal liquids.

The experimental data produced the same general trends at all four isotherms. The lowest isobar measured was obtained at the highest concentrations of quinoline. Since quinoline has the lowest vapor pressure, this result was expected. Also, the general shape of the two phase region shifted between the lowest and middle isobars measured.

Once VLE data for the m-cresol, tetralin, quinoline system were measured a ternary flash program was written to generate predictions based on parameters determined from binary data for the same temperatures and pressures. The flash program used a feed composition based on the assumption that the liquid to feed ratio was 50%. The flash program generated predictions for the ternary system using two equations of state, five mixing rules, and binary interaction parameters.

The Soave-Redlich-Kwong and a modification of it developed by Yesavage were the equations of state studied. The mixing rules examined vary from two simple density independent mixing rules to three complicated density dependent mixing rules. The binary interaction parameters used in these mixing rules were generated by Niesen using a maximum likelihood method on binary VLE data for the three binary systems.

The prediction results in general were not very favorable for any of the mixing rules examined. Over the temperature and pressure range examined, the density independent mixing rules produced the best results. Further work should address the possibilities of different binary interaction parameters used in the expressions for k_{ij} . Other interaction parameters may produce better predictions of the ternary data.

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INTRODUCTION

The primary goal of this research was to further strengthen the understanding of phase behavior for mixtures of non-ideal liquids at elevated temperatures and pressures. Industry will benefit as a result of better modeling techniques for the design of flash tanks, distillation columns, and synthetic fuels processes. The use of m-cresol, tetralin, quinoline was selected since this system is highly non-ideal with interactions due to polar effects and size differences. These same interactions are exhibited in coal liquids, making the chosen system an accepted model for coal liquids.

The first part of this research was to generate ternary vapor-liquid equilibria (VLE) data for the system involving m-cresol, tetralin, quinoline. Once the data were measured, predictions were generated for the temperatures and pressures in question using a flash program. This flash program incorporates the Soave-Redlich-Kwong (SRK) and a recent modification for polar fluids developed by Yesavage, 1986 (YSRK). Five mixing rules were also investigated. These mixing rules vary from two density independent to three density dependent mixing rules. The binary interaction parameters needed for the equations of state and mixing rules were determined by Niesen, 1986 using a maximum

likelihood technique on the binary VLE data.

The hope of this investigator was that the ternary data could be predicted accurately with the binary interaction parameters. Ternary data, due to the extra degree of freedom, are considerably more difficult to obtain than binary data. It would be much less complicated and time consuming if one could accurately predict ternary data using the binary interaction parameters.

Ternary vapor-liquid equilibria data were generated on a flow system capable of temperatures to 350°C and pressures to 10 MPa. The flow system had the advantages of constant flushing of decomposed products from the cell along with the capability of sampling without disturbing the equilibria in the cell. The equipment was inherited from the previous student in excellent working condition. A detailed description of the apparatus is presented by Niesen, 1986. Only the micrometering valve in the constant air bath needed to be made operable to account for the third degree of freedom accompanying the ternary system. The operation of this micrometering valve provided another source for controlling the flowrates leaving the cell.

Besides the generation of the data, techniques for sample composition determination had to be developed. This technique was performed by gas chromatography.

Once these problems were resolved, vapor-liquid equilibria data were generated for the ternary system of m-cresol, tetralin, and quinoline at four isotherms, 250, 275, 300, and 325°C. Three isobars were measured at each isotherm. For the 250°C isotherm the isobars measured were 150.0, 200.0, and 275.0 kPa; for the 275°C isotherm the isobars measured were 250.0, 325.0, and 425.0 kPa; for the 300°C isotherm the isobars measured were 400.0, 480.0, and 650.0 kPa; and for the 325°C isotherm the isobars measured were 600.0, 725.0, and 950.0 kPa.

After the ternary data were measured the next step was to compare the measured data to the predicted ternary data. The predicted data were generated using binary interaction parameters from Niesen (1986), two cubic equations of state, and five mixing rules. The two equations of state (EOS) chosen were the Soave-Redlich-Kwong (SRK) as a base case and a recently proposed modification to the SRK (Yesavage, 1986). This modification attempts to extend the SRK to more polar compounds. The five mixing rules modify only the geometric mean mixing rule for the attractive "a" term, while the arithmetic mean mixing rule for the repulsive "b" term was not modified. The mixing rules vary from a simple interaction parameter to a newly proposed mixing rules which considers density dependency, Holder et. al. (1986) and

Luedecke et al. (1985).

LITERATURE REVIEW

A literature search was performed in December 1986 for articles pertaining to m-cresol, quinoline, and tetralin. This review's objective was to reveal previous material related to the work accomplished in this thesis. More specifically, locate previous work on the ternary mixture for the three compounds mentioned. No information was revealed concerning previous work on the m-cresol, quinoline, tetralin ternary system.

Previous VLE (Niesen, 1986) and enthalpy (Flanigan, 1986) work on the binary systems was performed. The binary interaction parameters needed for the SRK and YSRK were generated by Niesen (1986) from the binary data that she had generated. The research on the ternary system is a natural continuation of the binary research accomplished by Niesen and Flanigan. The ability to take ternary data and to make predictions using the binary interaction parameters generated by Niesen justifies the time and effort invested in these research projects.

The first compound involved was m-cresol which is a polar compound capable of hydrogen bonding through the hydroxyl group. Based on titration calorimetry data and apparent molecular weight determinations, it has been proposed that m-cresol associates with itself in the dimer

and trimer form (Eatough, 1984 and Sandarusi, 1984). A six membered ring of oxygen and hydrogen make up the trimer form. This compound is extremely hydroscopic due to its hydrogen bonding capabilities.

Quinoline was the second compound studied in this investigation. It is polar and capable of hydrogen bonding due to the pair of unbonded electrons present on the nitrogen. Unlike m-cresol, quinoline molecules do not significantly associate with themselves because of the nonacidic nature of the hydrogens present. These hydrogens are not acidic enough to interact with the nitrogen. However, quinoline is hydroscopic due to its capability to form hydrogen bonds with water.

Tetralin was the final compound used in the ternary VLE mixture. The IUPAC name given to tetralin is 1,2,3,4 tetrahydronaphthalene. Tetralin differs from the other two compounds in that it is relatively nonpolar and nonhydroscopic. Therefore, tetralin does not associate with other tetralin molecules.

The three binary systems, investigated by Niesen, involving these compounds produce three distinctively different interactions. The tetralin/quinoline binary system is the most ideal mixture of the three because no hydrogen bonding can occur. The tetralin molecule has no

hydrogens available to bond with the nitrogen on the quinoline molecule. The m-cresol/tetralin binary system involves a highly polar compound with a nonpolar compound. Although the tetralin molecule does not possess hydrogens acidic enough to interact with m-cresol, interactions due to hydrogen bonding will occur between m-cresol molecules. A minimum boiling azeotrope was observed for this binary system. The final binary system, m-cresol/quinoline, provides the opportunity to evaluate a system which involves a polar-polar interaction. Hydrogen bonding will occur between m-cresol and quinoline as well as between m-cresol molecules. A maximum boiling azeotrope may have been observed at low m-cresol concentrations for the 250°C isotherm. This azeotrope was not present for the other isotherms investigated.

EXPERIMENTAL WORK

The ultimate goal of the experimental work was to generate ternary VLE data for the system in question. These data were successfully obtained using a flash vaporization flow system constructed by Niesen (1986). Small variations in operating techniques were required for the measuring of the ternary system. These operating procedures will be discussed in detail later in this thesis.

The measurements were generated on a flow system with "equilibrium conditions" being maintained for approximately 30 minutes. This allowed the system's entire volume to be circulated five to six times. During these "equilibrium conditions" the temperature was maintained to within +/- 0.1 K and the pressure maintained to within the stated accuracy of the gages at flowrates of 100 cm³/min. Reproduction of previous binary data confirmed the ability of this operator to run the apparatus under the required conditions.

The generation of good ternary data was dependent upon two major aspects besides the correct operation of the VLE apparatus. These areas of concern were sample purity and an analytical method for determination of sample compositions. Initial sample purity of > 99.9% was achieved by the use of a spinning band distillation column. This purity was maintained for the mixture throughout its lifetime in the

system by constant monitoring using gas chromatography.

Analytical determination of the sample's composition was also achieved with the use of gas chromatography methods. The gas chromatography methods utilized differed from those used for the binary system and will be discussed in greater detail.

VAPOR LIQUID EQUILIBRIA APPARATUS

An equilibrium flash vaporization flow system has been developed which can generate vapor-liquid equilibrium data at temperatures to 350°C and pressures to 10 MPa (Niesen (1986)). This system was designed to study the phase behavior of coal derived liquids.

A flow vaporization system was chosen for its many advantages over a batch system. Working at such extreme conditions cause decomposition of the chemicals. In the flow system the decomposition products are constantly flushed from the cell. Also, coke particles are flushed from the cell through the liquid line and collected in two filters. One of these filters is located above the surge tank and the other is located below the surge tank before the diaphragm pump. These filters are cleaned randomly to maintain flow. A flow system allows the sample to be degassed as it heats, since any noncondensable gas which exits in the vapor stream, accumulates in the vapor line condenser, and is not recirculated.

Figure 1 is a presentation of the overall flow diagram for the flash vaporization flow apparatus. The apparatus was designed to operate with a sample volume of approximately one liter.

Figure 2 is a diagram of the cell which seals up to 10

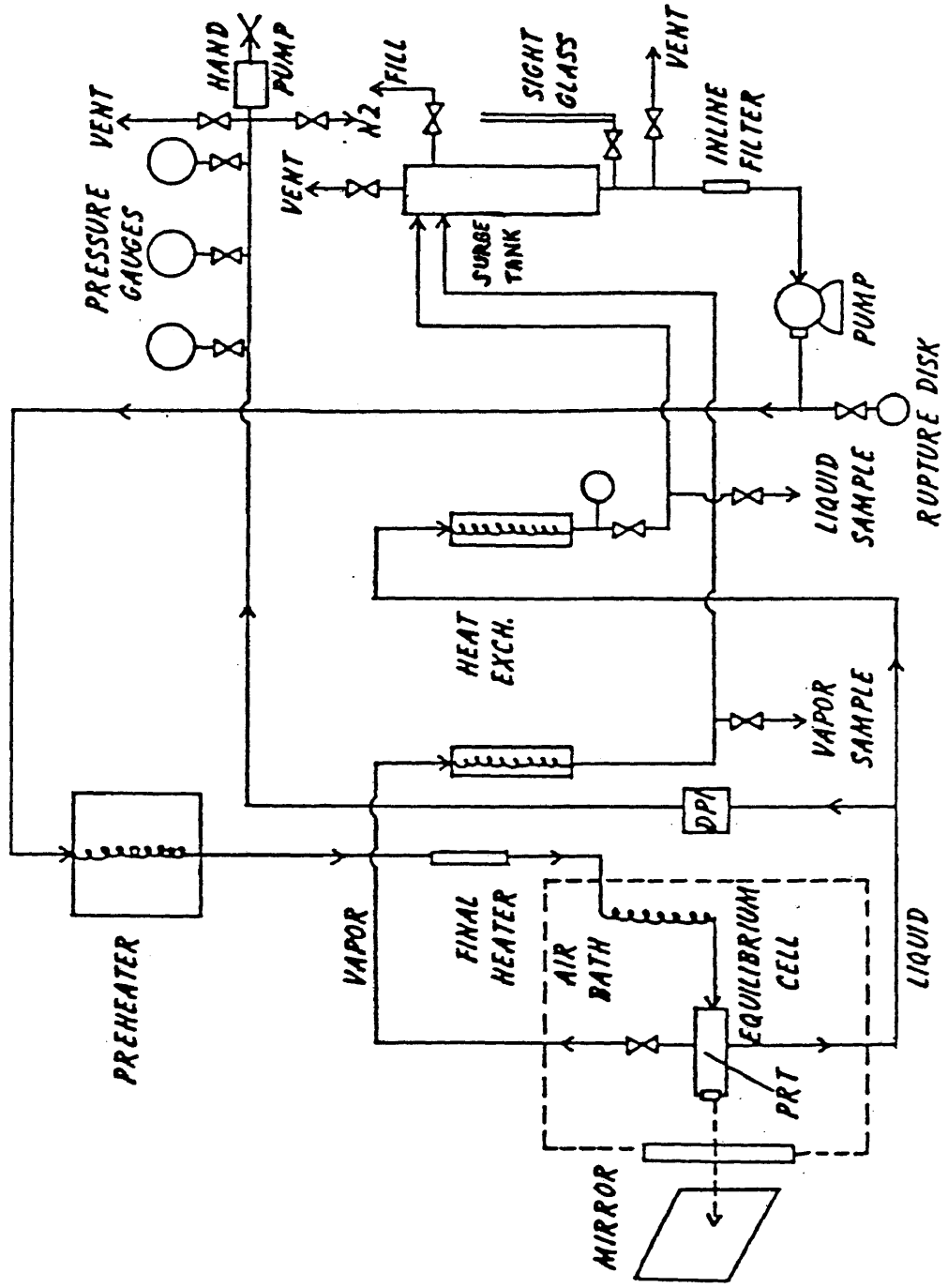


Figure 1: Vapor Liquid Equilibria Apparatus

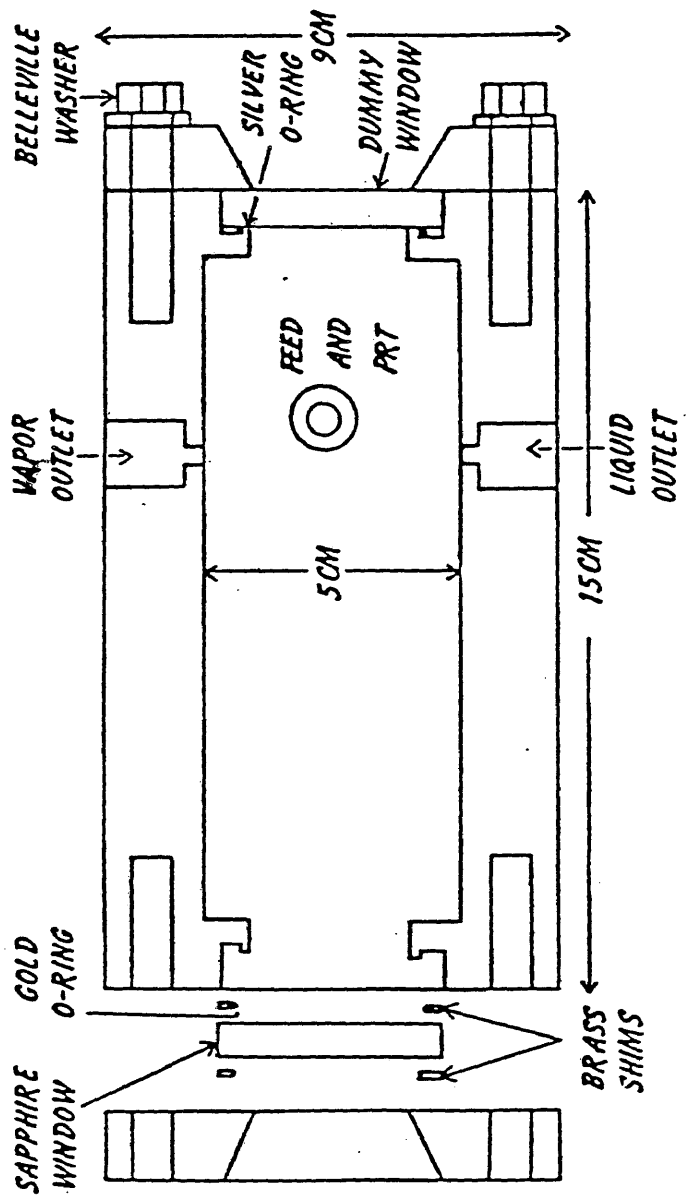


Figure 2: Equilibrium Cell

MPa, showing the location of its major elements. The cell body and end caps were constructed of 316 stainless steel. One end of the cell contains a sapphire window sealed with a 24 K gold o-ring. The other end of the cell contains a dummy window made of stainless steel and sealed with a 99.9% silver o-ring.

A Ruska differential pressure indicator (DPI), null indicator, and a series of bourdon tube gauges made up the pressure sensing system. This arrangement has four major advantages of operation. First, the corrosive compounds were never in contact with the Heise gauges, eliminating the cleaning of the gauges. Second, the liquid's temperature could exceed the maximum temperature for which the gauges are rated without causing erroneous pressure readings. Third, the DPI cell eliminated the need for a long static line in which compositional changes could have occurred while running to the gauges. Fourth, since the DPI cell was at the same height as the cell in the oven, there was no need for a pressure correction due to a height difference.

Temperature control was achieved through the use of three heating devices. An Omega Model D921 controller with a solid state relay was used for controlling the fluidized sand bath. The in-line bayonet heater, located directly before the oven, was controlled by a Bayley Model 124

controller. Finally, the fluid passed through a coil located in the oven. The utilization of these three temperature controlling units allowed the temperature control of the system to within $\pm 0.1^{\circ}\text{C}$.

A detailed description of the apparatus is presented by Niesen, 1986. Appendix A contains a detailed step-by-step description of the operating and shutdown procedures for a ternary system. These operating procedures are different than the operating procedures used for the binary systems (Niesen, 1986).

Maintenance of Equipment

Regular maintenance of the equipment was required to obtain optimal operating conditions. When the equipment was first inherited the circulating pump was operating poorly. This was remedied by changing the oil and cleaning the check valves and diaphragm. Other maintenance performed included the cleaning of the filter located in the liquid line and the filter located directly below the surge tank to remove solid particles which were trapped in these filters. This assured an unrestricted flowrate through the filters. The only other maintenance performed on a routine basis was the cleaning of the micrometering valve on the vapor line located in the oven. The valve was exposed to continual temperature fluctuations causing the valve to freeze, but was remedied with routine cleaning. Because a ternary system was evaluated, the constant operation of this valve was a necessity.

The ternary system presents three degrees of freedom and this third degree of freedom was accounted for by the adjustment of the liquid and vapor flowrates leaving the cell. The micrometering valve controlled the flowrate of the vapor line. By adjusting this valve, one was able to control the amount of vapor that would leave the cell. This in turn would change the height of the liquid level present

in the cell. As the liquid level would change heights, the pressure of the system would change.

Troubleshooting Procedures

The only major problems incurred during the operating of the equipment were the pump periodically losing its prime and the freezing of the micrometering valve on the vapor line located in the oven.

If the pump begins to lose its prime during equipment operations then the operator must try to maintain flow. To aid in repriming, the operator is encouraged to increase the pump stroke setting until the pump has reprimed itself. After the pump has reprimed itself, the stroke setting should be returned to its original setting. If the pump continues to lose its prime shut down the equipment as soon as possible while trying to maintain flow. Before operating the equipment again please consult the pump manual for repriming instructions. If the repriming instructions fail, then consult the manual for instructions to clean the check valves.

The freezing of the vapor line micrometering valve must be handled in two steps. Since the freezing usually takes place while the equipment is operating, the operator is forced to finish taking the point with pressure adjustment being accomplished entirely by the liquid line micrometering valve.

Once the system has cooled down, the vapor line

micrometering valve needs to be removed, cleaned, and returned to the vapor line before further operation of the equipment.

Many other solutions to problems that this operator did not encounter are presented by Niesen (1986).

SAMPLE COMPOSITION ANALYSIS

The determination of the sample composition posed the biggest problem for this investigation. The gas chromatography method used and described by Niesen (1986) was not a practical method for the ternary mixture. This method was used on a flame ionized detector (FID) and required the sample to be bounded by standards. The FID was not able to produce a linear response over the entire compositional range for the samples. Therefore, the samples were bounded by standards having compositions extremely close to that of the sample. A linear relationship was assumed between the standards and a response factor was calculated from this relation. From these response factors, the samples' composition was determined. This method was not feasible for the ternary samples. The limiting factor being the immense size of the standard bank required to bracket the various compositions. For this reason other techniques were investigated for their possible use.

The standard addition method was the first to be investigated. This method required the spiking of the sample with a known amount (mass) of the pure components. The response factor was directly proportional to the amount of pure component added. This technique required repetition for all three components to determine the sample

composition. The standard addition method was dismissed as a viable solution to the problem for two reasons. First, the sample size required from the VLE apparatus was approximately 15 - 20 mls, causing a problem when the sample flowrates were extremely slow. Secondly, one had to be careful not to change the matrix of the solution when the pure component was added. This was especially difficult when spiking the sample with the pure component which was present in small amounts.

The method finally chosen employed the use of a thermal conductivity detector (TCD). This method was incorporated on a Hewlett Packard gas chromatograph (GC), model 5890. As previously mentioned, a thermal conductivity detector (TCD) was used. The column that was used in this GC was a wide-bore 15 meter JW Scientific methyl polysiloxane column. The operating conditions for the GC were:

Injection Port Temperature	= 300°C
Detector Temperature	= 300°C
Oven Temperature	= 110°C
Oven Ramp	= 30°C/min
Final Temperature	= 140°C

This method took advantage of the fact that the response factors were linear. If a response factor shifted from one day to another the other two response factors will shift in the same manner. Initially, just a simple response factor was investigated. This technique was not used

because of the need to inject the same amount of sample to the GC for each determination. The simple response factor is related to the amount of sample that is injected into the GC. This technique works extremely well when one is able to reproduce the sample injection volume, such as injecting a gas with an injection sample loop with a fixed volume. For this research, the physical state of the sample was that of a liquid, and the sample was to be injected with a syringe. These complications made it impossible to reproduce the sample injection volume, therefore, making it impossible to use a simple response factor.

In an effort to eliminate the dependency of the injection volume size, the technique of a relative response factor was investigated. In this technique, the response factor for all three compounds are determined relative to one of the components contained in the mixture. This was accomplished by dividing the response factors of m-cresol, quinoline, and tetralin by the response factor of m-cresol. By doing this, all response factors were made relative to m-cresol. The dependency of volume size injection was also eliminated.

The relative response factor method was employed on six standard mixtures of m-cresol, quinoline, and tetralin. The relative response factors for each compound in each mixture were determined. These relative response factors which are

presented in Table 1 were averaged to determine the three relative response factors that would be used in the determination of the samples' composition. The composition of the samples was determined to within +/- 0.005 mole fraction using the average value for the six relative response factors presented in Table 1.

TABLE 1

Relative Response Factors (RRF)

<u>Standard</u>	<u>RRF (m-Cresol)</u>	<u>RRF (Tetralin)</u>	<u>RRF (Quinoline)</u>
1	1.00000	0.87767	0.91893
2	1.00000	0.86456	0.90218
3	1.00000	0.84399	0.89555
4	1.00000	0.86031	0.92050
5	1.00000	0.86691	0.92296
6	1.00000	0.83670	0.90139
AVERAGE	1.00000	0.85836	0.91025

SAMPLE PURITY

The purity of the sample was important for two reasons. Before adequate data could be taken, one had to be sure that the system was being charged only with a mixture of m-cresol, quinoline, and tetralin. Also, measures needed to be taken to guarantee the integrity of the mixture's purity during its lifetime in the system.

The initial purity of the pure components was achieved using a spinning band distillation column. Once the desired purity of the pure components was achieved (99.9%), the distilled pure components were stored in tightly sealed bottles to lessen the chance of contamination particularly from moisture contained in the atmosphere.

To maintain the integrity of the purity of the mixture the systems, atmospheric vents were connected to a chamber of drierite. These chambers were constantly monitored so that the drierite could be recharged when needed. Once a sample was taken from the system, it was never reintroduced to the system until it was checked for water content and products of decomposition. This was determined directly by gas chromatograph using a TCD detector.

EXPERIMENTAL RESULTS

The work in this research is a direct extension to previous work performed by Niesen (1986) on the binary systems of m-cresol, tetralin, and quinoline. Niesen measured the binary systems at the same four isotherms investigated in this thesis. From this data, she generated binary interaction parameters used in the predictions for the ternary system. The binary diagrams from her research are reproduced in Figures 3 - 8 to give the reader some idea of the different interactions encountered in the binary systems.

After the analytical and operating techniques for the ternary mixture were determined, experimental data were generated for the ternary mixture of m-cresol, tetralin, and quinoline. This ternary mixture was evaluated at four isotherms, 250, 275, 300, 325°C, all of which are below the critical temperature for the three compounds investigated. Two of the compounds studied were polar and exhibit some type of association among themselves. A literature search conducted produced no published material on these three compounds involved as a ternary mixture. The selected compounds for this work have been generally accepted as "model" compounds for coal liquids, Yesavage (1984). Therefore, the data generated from this thesis can be used

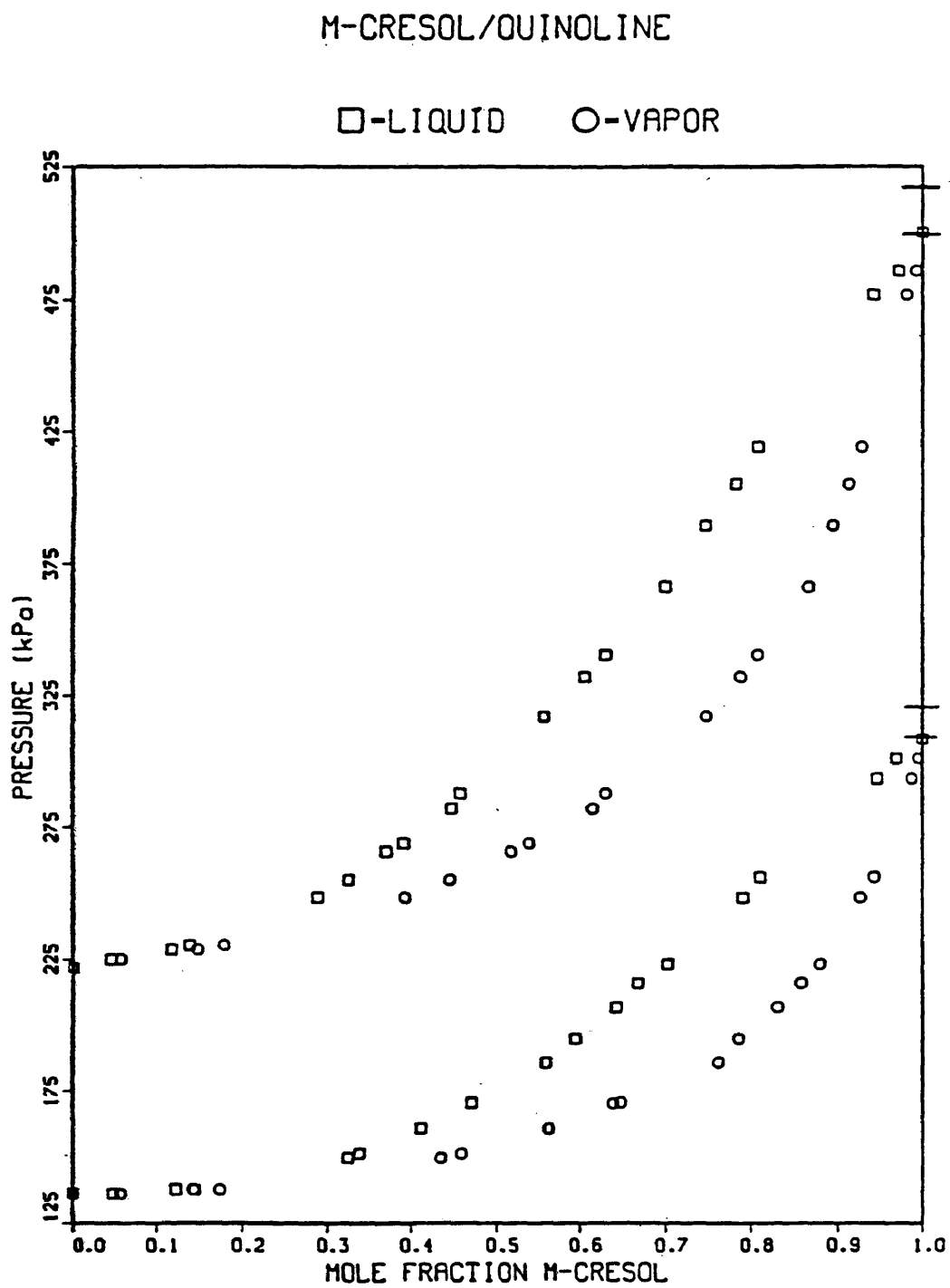


Figure 3: MC/Q Binary Data (250-275°C)

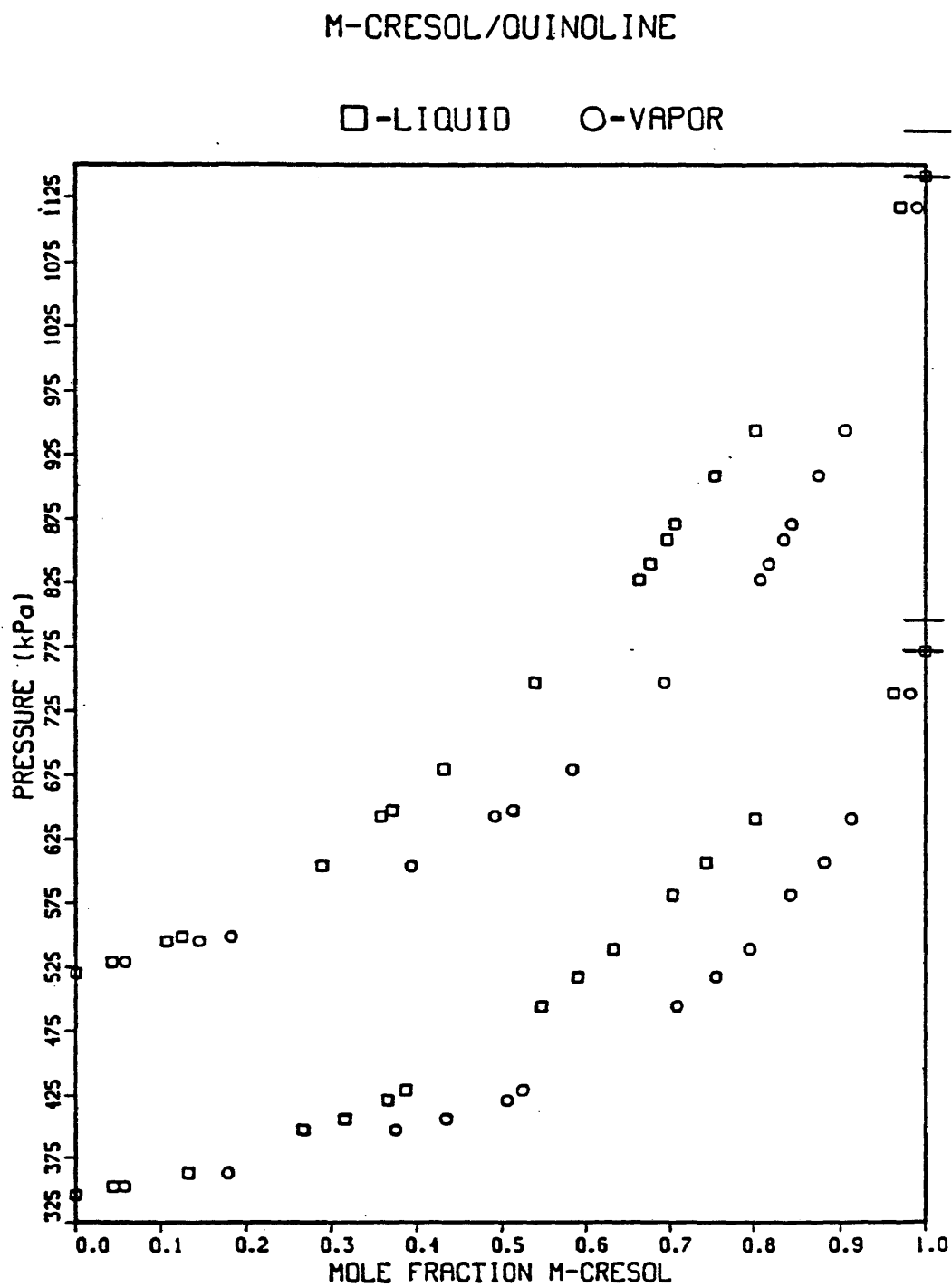


Figure 4: MC/Q Binary Data (300-325°C)

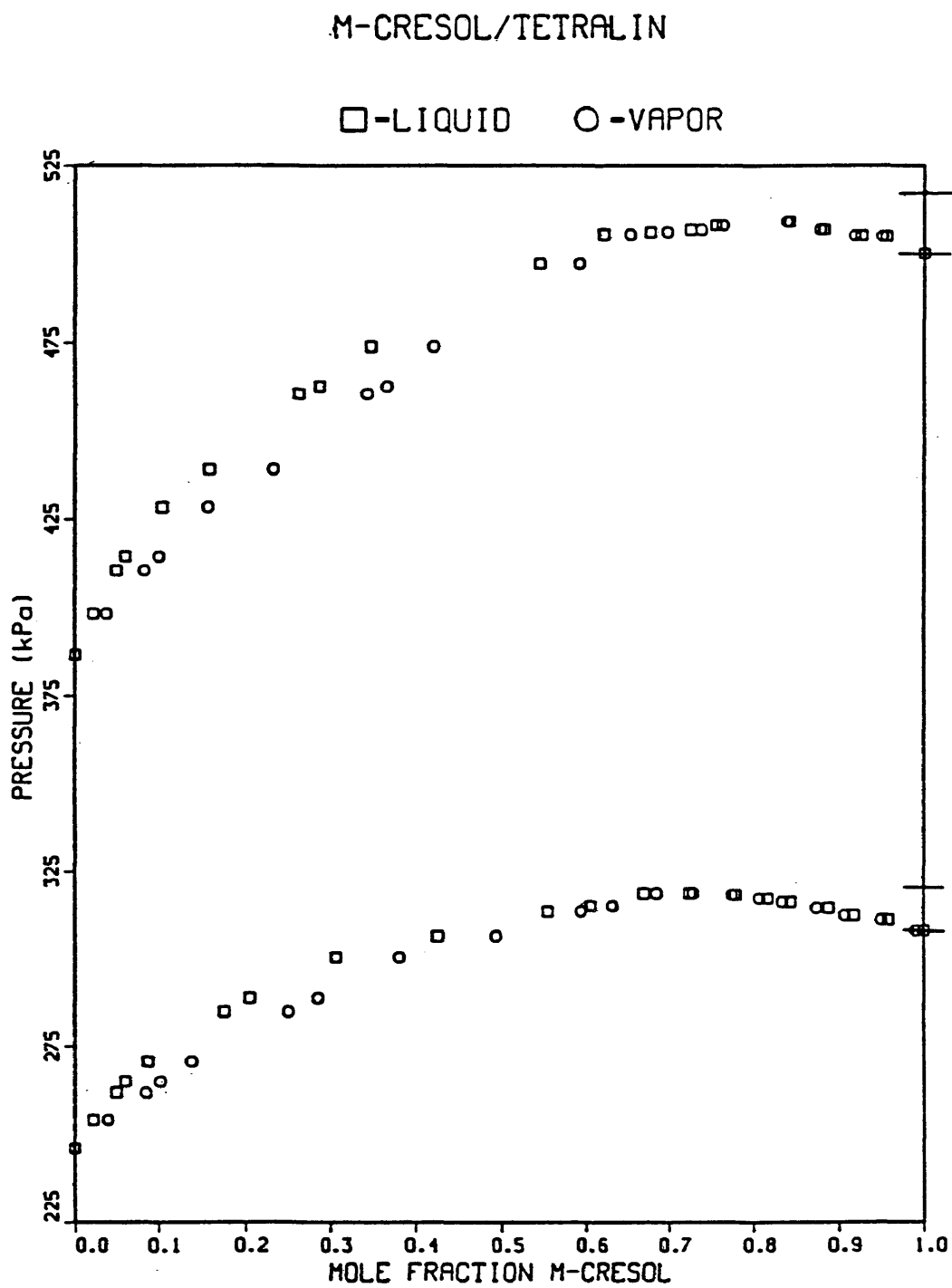


Figure 5: MC/T Binary Data (250-275°C)

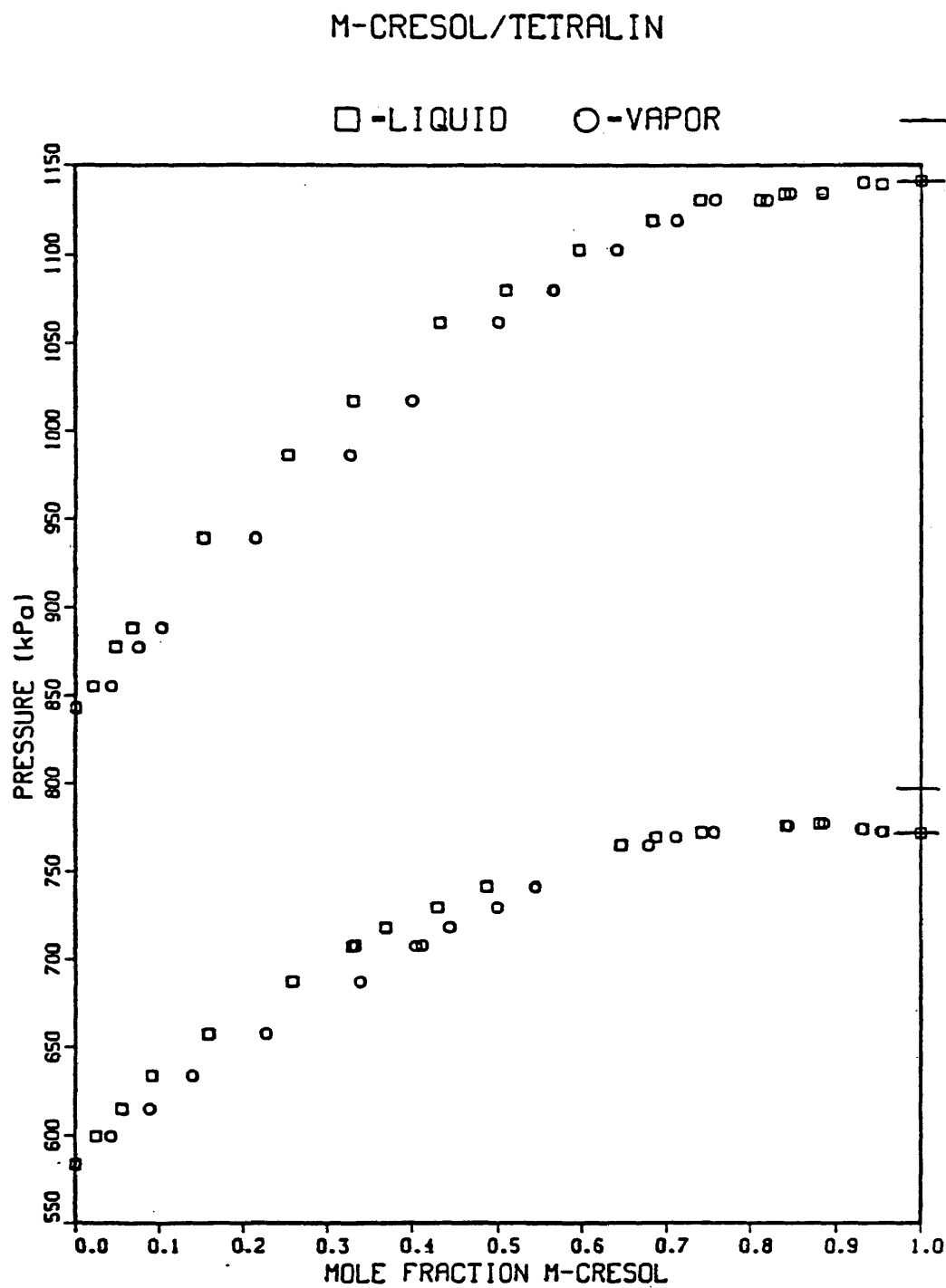


Figure 6: MC/T Binary Data (300-325°C)

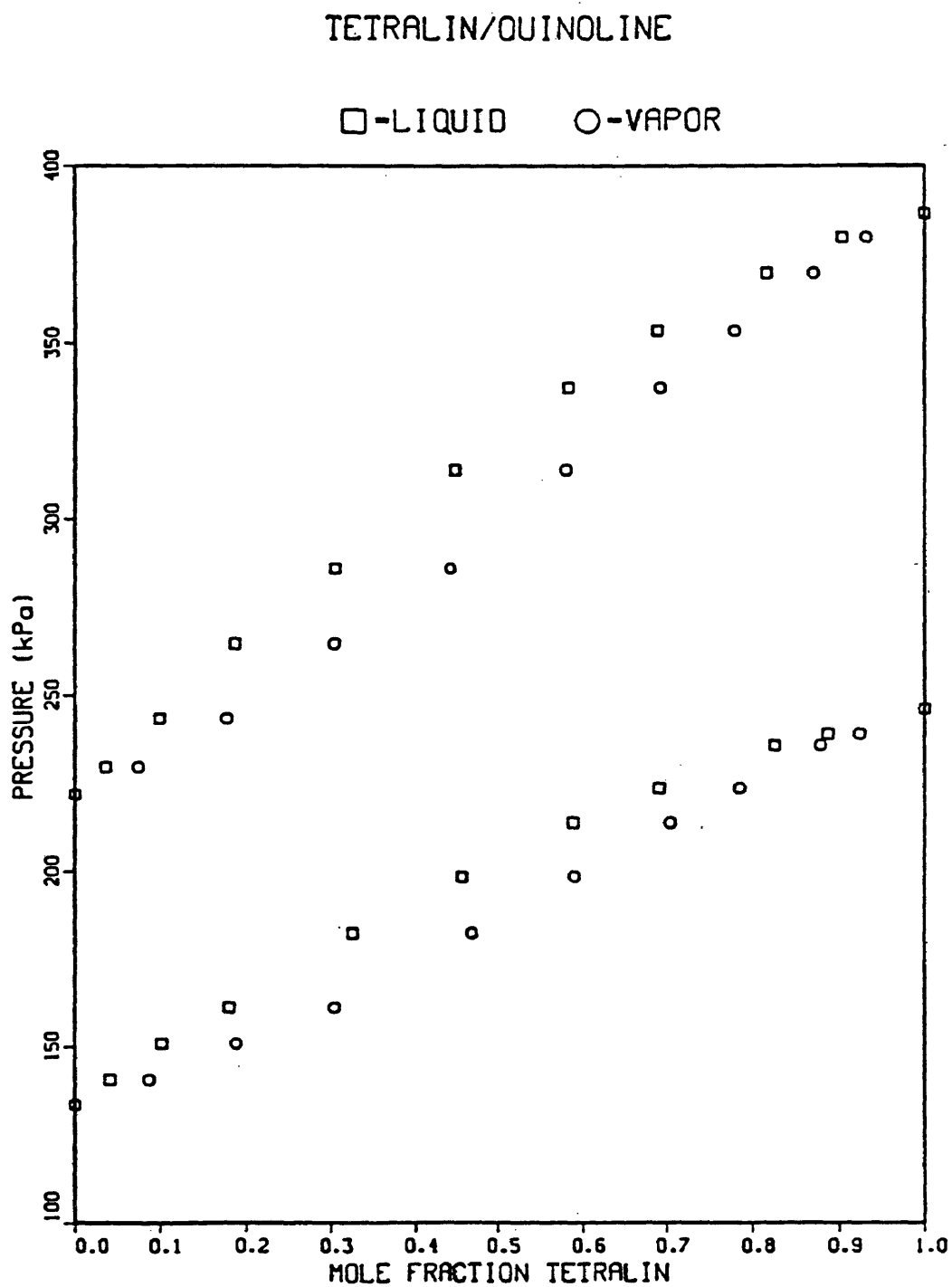


Figure 7: T/Q Binary Data (250-275°C)

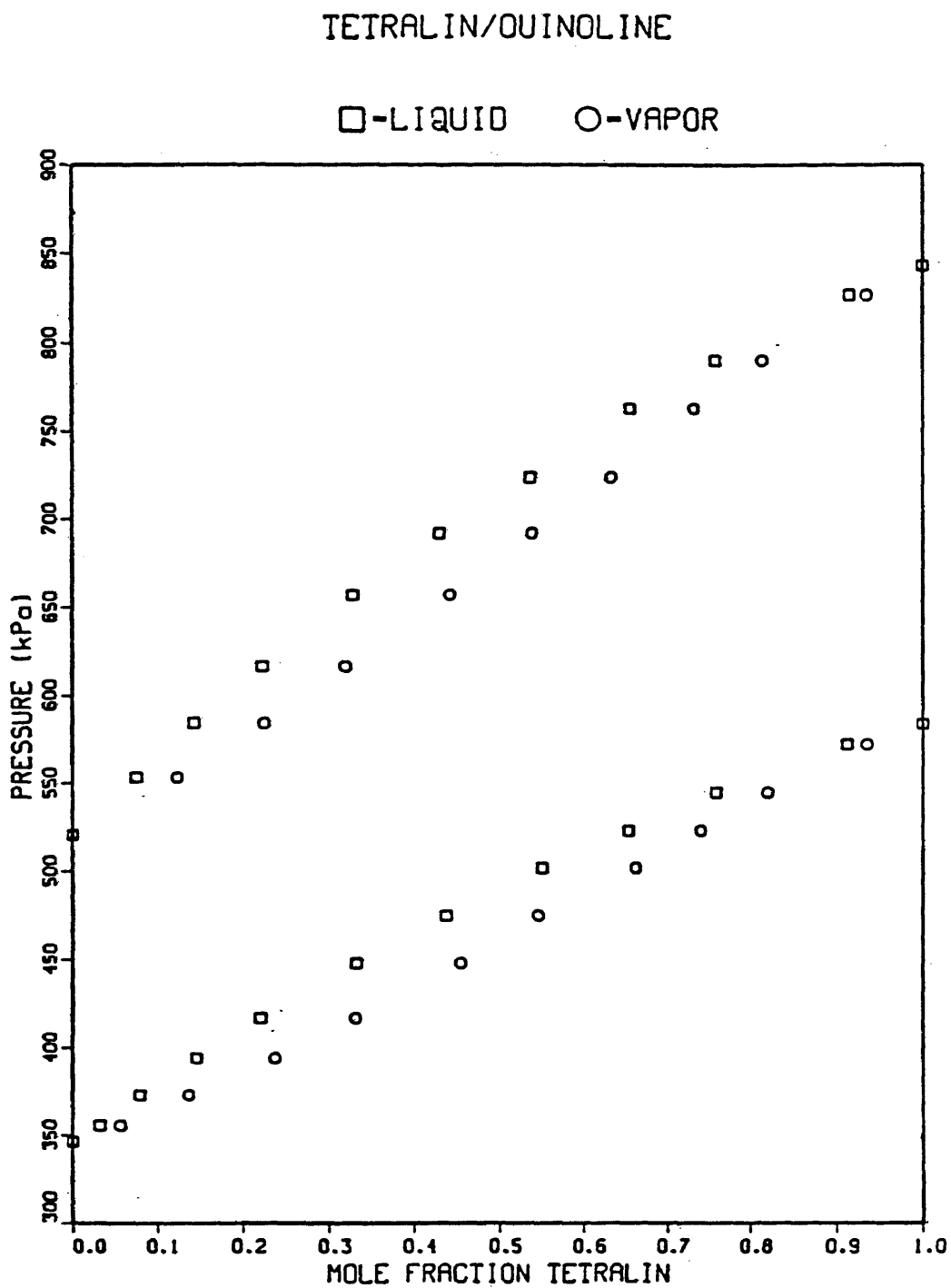


Figure 8: T/Q Binary Data (300-325°C)

for basic thermodynamic research and practical application.

The VLE data generated for the 250°C isotherm are presented in Table 2. Similarly, the VLE data for the 275°C isotherm are contained in Table 3. Table 4 contains the VLE data for the 300°C isotherm. Finally, the 325°C isotherm VLE data are represented in Table 5. The MC, T, and Q are abbreviations for m-cresol, tetralin, and quinoline respectively. Also, the X's are for liquid mole fraction and the Y's for vapor mole fraction. Figures 9, 10, 11, and 12 contain the ternary diagrams for the temperatures investigated.

Three distinct isobars were measured at each isotherm to demonstrate the varying degrees of interaction amongst the compounds. The following VLE data exemplifies these various interactions.

As can be seen in the ternary diagrams for the data (Figures 9-12), the same general trends are seen at all four isotherms. In these four figures, the solid symbols represent the vapor data and the open symbols represent the liquid data. As the pressure increases the composition of quinoline present in the mixture decreases. This seems to follow logic, since the vapor pressure of quinoline is the lowest of the three compounds. Therefore, as the quinoline concentration decreases one would expect the systems

pressure to increase. A second general trend that is noticed in the four figures is the shape of the two phase regions. At the lowest pressure investigated at the four isotherms, the two phase region curves to the right, but at the two other pressures the two phase region curves to the left. This shift in the shape of the two phase region takes place between the lowest and middle pressures investigated. The fact that the two phase region changes shape suggests that there are different interactions between the three compounds. These various interactions also appear to be related to the concentration of quinoline present in the mixture. The shape of the two phase region changes as the concentration of quinoline decreases.

Table 2

VLE Measurements for MC/Q/T

T = 250°C P = 150.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.0000	0.0987	0.9013	0.0000	0.1850	0.8150
0.0770	0.0930	0.8299	0.0857	0.1796	0.7347
0.1650	0.0667	0.7683	0.1942	0.1373	0.6686
0.2196	0.0456	0.7375	0.2589	0.1094	0.6318
0.3210	0.0000	0.6790	0.4305	0.0000	0.5695

T = 250°C P = 200.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.0000	0.4638	0.5362	0.0000	0.6000	0.4000
0.0940	0.3638	0.5422	0.1105	0.4888	0.4007
0.2788	0.2103	0.5109	0.3252	0.3247	0.3500
0.4596	0.0943	0.4556	0.5438	0.1552	0.3010
0.6170	0.0000	0.3830	0.8100	0.0000	0.1900

T = 250°C P = 275.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.1117	0.8883	0.0000	0.1701	0.8299	0.0000
0.2091	0.6813	0.1096	0.3136	0.6357	0.0507
0.3216	0.5335	0.1413	0.4087	0.5303	0.0610
0.4153	0.4299	0.1553	0.4912	0.4574	0.0514
0.4888	0.3489	0.1623	0.5437	0.3974	0.0590

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.6425	0.1859	0.1716	0.7078	0.2344	0.0578
0.7765	0.0759	0.1476	0.8483	0.1027	0.0489
0.8849	0.0000	0.1151	0.9650	0.0000	0.0350

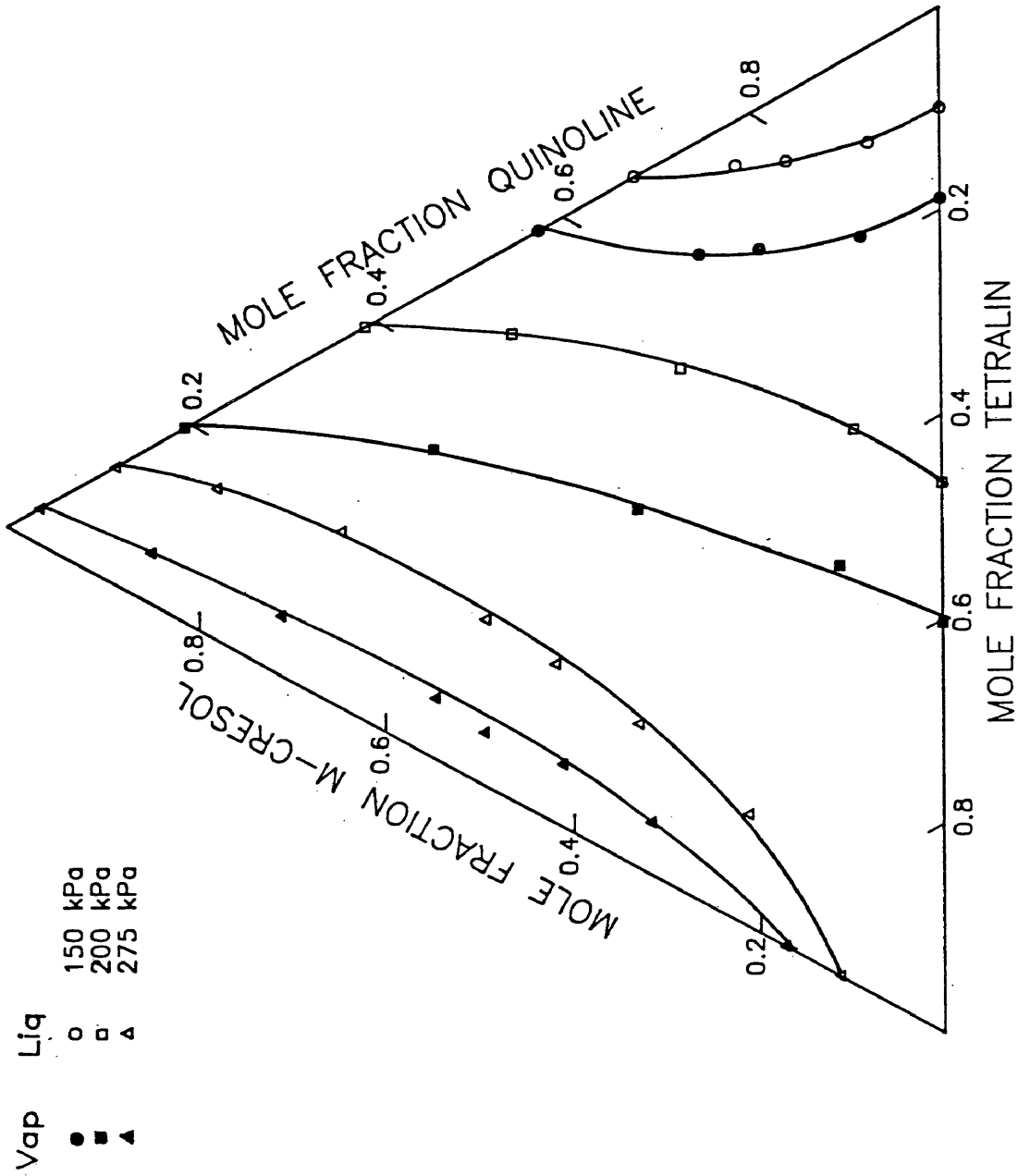


Figure 9: MC/Q/T Ternary Data T = 250°C

Table 3

VLE Measurements for MC/Q/T

T = 275°C P = 250.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.0000	0.1253	0.8747	0.0000	0.2175	0.7825
0.0846	0.0955	0.8198	0.1056	0.1651	0.7293
0.1926	0.0532	0.7542	0.2469	0.1051	0.6480
0.2999	0.0000	0.7001	0.4100	0.0000	0.5900

T = 275°C P = 325.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.0000	0.5099	0.4901	0.0000	0.6310	0.3690
0.0956	0.3912	0.5132	0.1311	0.5016	0.3673
0.2889	0.2059	0.5052	0.3574	0.3123	0.3303
0.3393	0.1596	0.5012	0.4228	0.2529	0.3242
0.3793	0.1250	0.4957	0.4771	0.2049	0.3179
0.5807	0.0000	0.4193	0.7700	0.0000	0.2300

T = 275°C P = 425.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.0925	0.9075	0.0000	0.1419	0.8581	0.0000
0.1933	0.6781	0.1287	0.2825	0.6450	0.0724
0.3250	0.4950	0.1800	0.4081	0.5009	0.0910
0.4135	0.3907	0.1958	0.4842	0.4285	0.0873
0.4620	0.3412	0.1969	0.5309	0.3840	0.0851

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.6350	0.1579	0.2071	0.7170	0.2068	0.0762
0.8268	0.0000	0.1732	0.9373	0.0000	0.0627

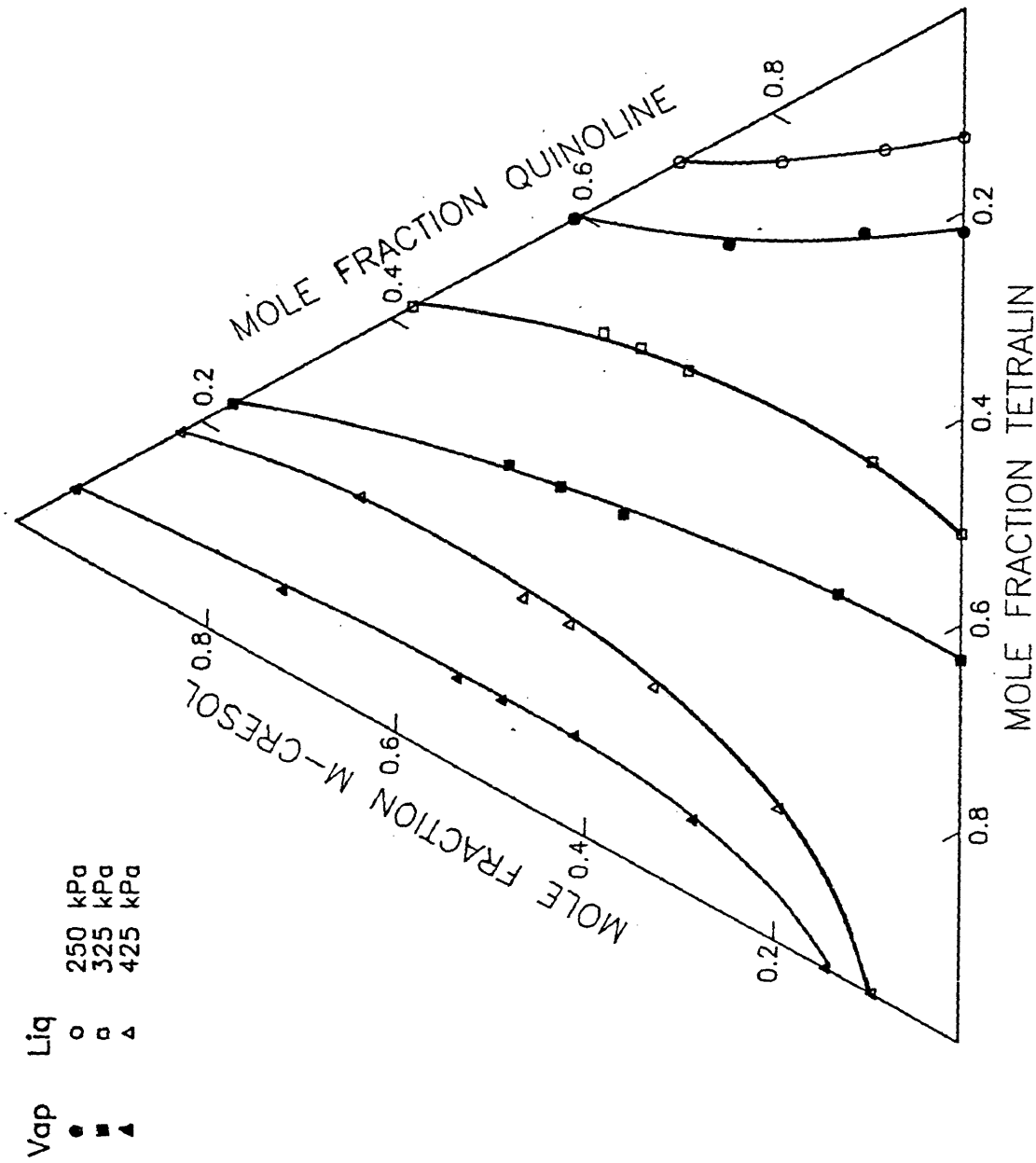


Figure 10: MC/Q/T Ternary Data T = 275°C

Table 4

VLE Measurements for MC/Q/T

T = 300°C P = 400.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.0000	0.1611	0.8389	0.0000	0.2609	0.7391
0.0794	0.1167	0.8038	0.1025	0.2039	0.6935
0.2122	0.0483	0.7395	0.2865	0.0908	0.6227
0.2845	0.0000	0.7155	0.4000	0.0000	0.6000

T = 300°C P = 480.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.0000	0.4607	0.5393	0.0000	0.5724	0.4276
0.0999	0.3318	0.5682	0.1256	0.4418	0.4326
0.2460	0.1972	0.5567	0.2960	0.2849	0.4190
0.3464	0.1162	0.5373	0.4215	0.1900	0.3885
0.5155	0.0000	0.4845	0.6800	0.0000	0.3200

T = 300°C P = 650.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.1387	0.8613	0.0000	0.2000	0.8000	0.0000
0.2446	0.6541	0.1113	0.3271	0.6185	0.0543
0.3315	0.5028	0.1657	0.4082	0.5047	0.0871
0.4161	0.3940	0.1900	0.4882	0.4205	0.0913
0.5429	0.2400	0.2170	0.6230	0.2732	0.1038
0.6194	0.1749	0.2057	0.6851	0.2130	0.1019

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.8151	0.0000	0.1849	0.9200	0.0000	0.0800

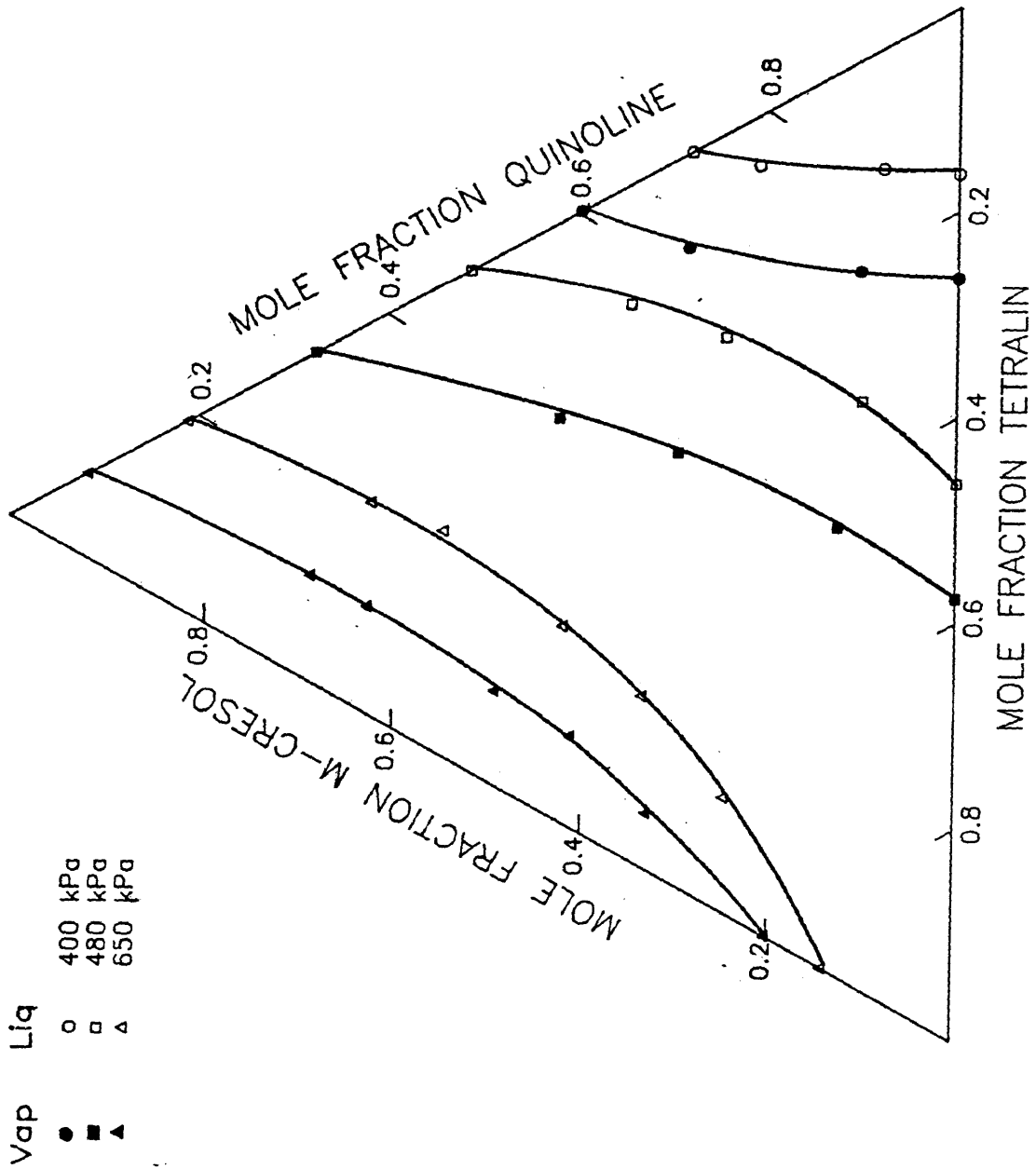


Figure 11: MC/Q/T Ternary Data T = 300°C

Table 5

VLE Measurements for MC/Q/T

T = 325°C P = 600.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.0000	0.1810	0.8190	0.0000	0.2704	0.7296
0.0767	0.1268	0.7965	0.1010	0.2022	0.6968
0.1951	0.0420	0.7629	0.2678	0.0704	0.6618
0.1953	0.0435	0.7612	0.2646	0.0685	0.6669
0.2758	0.0000	0.7242	0.3800	0.0000	0.6200

T = 325°C P = 725.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.0000	0.5400	0.4600	0.0000	0.6325	0.3675
0.0929	0.3905	0.5165	0.1201	0.4749	0.4049
0.2296	0.2193	0.5511	0.2749	0.3183	0.4067
0.3108	0.1450	0.5464	0.3909	0.2158	0.3955
0.3166	0.1441	0.5393	0.3963	0.2161	0.3875
0.3544	0.1097	0.5359	0.4575	0.1663	0.3762
0.5089	0.0000	0.4911	0.6600	0.0000	0.3400

T = 325°C P = 950.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.1770	0.8230	0.0000	0.2401	0.7599	0.0000
0.2520	0.6396	0.1083	0.3399	0.6059	0.0542
0.3473	0.4812	0.1715	0.4169	0.4828	0.1002

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.3872	0.4205	0.1923	0.4536	0.4377	0.1088
0.4891	0.2913	0.2196	0.5632	0.3148	0.1220
0.6172	0.1707	0.2121	0.6857	0.2013	0.1139
0.8071	0.0000	0.1929	0.9100	0.0000	0.0900

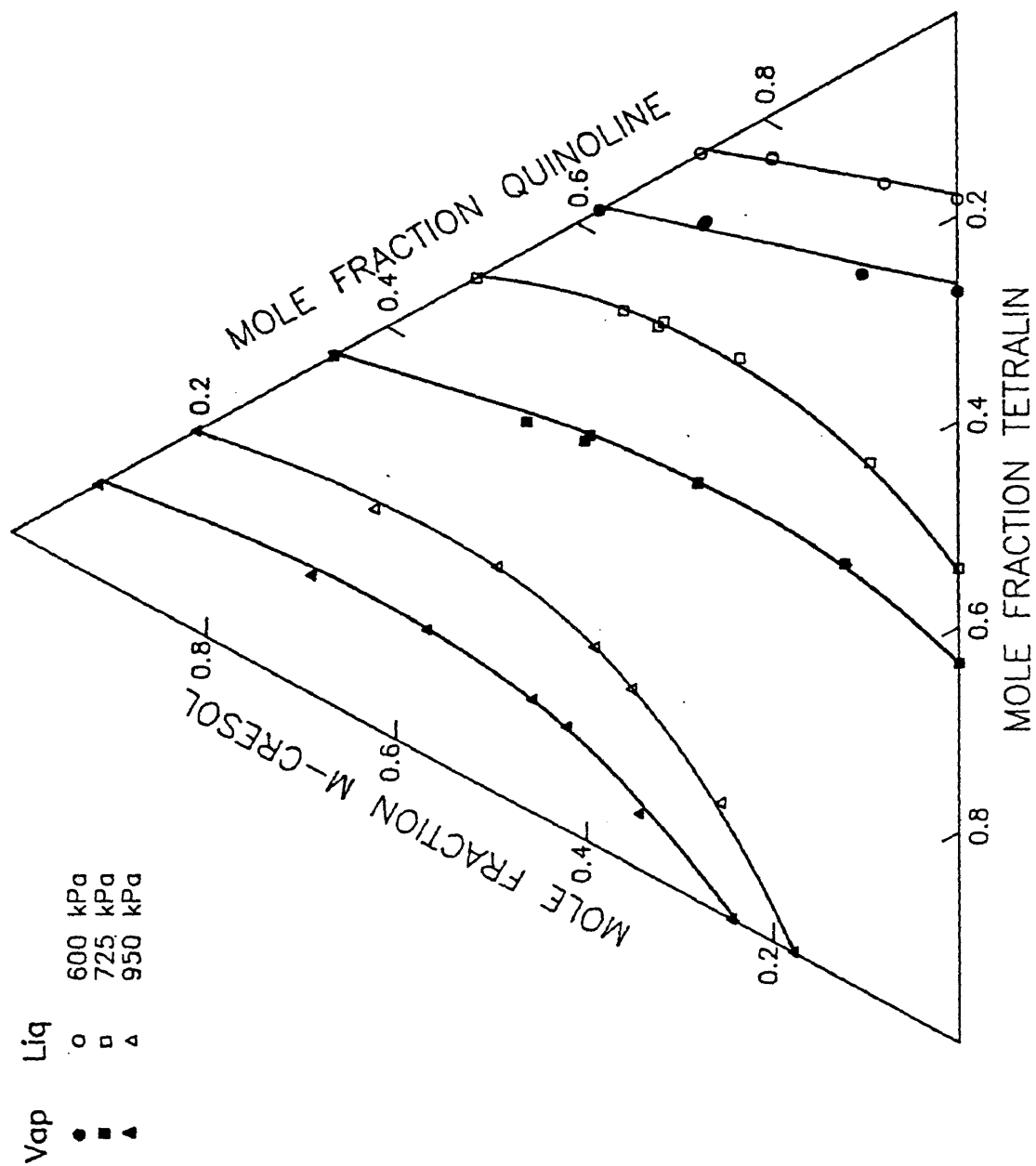


Figure 12: MC/Q/T Ternary Data T = 325°C

CORRELATION METHODS

The purpose of the correlation work was to see how well ternary data could be predicted using the binary interaction parameters generated from binary data. Two equations of state and five mixing rules were investigated in this correlation work.

Equations of State

The three parameter cubic equations of state (EOS) were studied in this investigation. These equations of state model asymmetric, nonpolar compounds well, however, lack the ability to model polar compounds. To model polar compounds, the acentric factor must be able to account for strong polar forces as well as forces due to symmetry.

The first equation of state studied is the Soave-Redlich-Kwong (SRK) equation as described by Soave (1971). The SRK equation was chosen because it performs well for nonpolar compounds while remaining a simple, three parameter, cubic EOS. The SRK equation for a pure compound is given as:

$$P = RT/(v-b) - a(T)/(v(v+b)) \quad (1)$$

where

$$b = 0.08664 RT_c/P_c$$

$$a = 0.42747 R^2 T_c^2 / P_c (1 + m(1 - (T_r)^{0.5}))^2$$

$$m = 0.48 + 1.574\omega - 0.176\omega^2$$

ω = acentric factor of the compound
 T_c = critical temperature of the compound
 P_c = critical pressure of the compound
 T_r = reduced temperature (T/T_c)

For a mixture mixing rules must be chosen to combine with the "a" and "b" parameters. The SRK will assume different forms depending upon the mixing rule chosen.

As previously mentioned, this type of equation does not predict extremely well for polar compounds (Yesavage, 1986). Therefore, attempts have been made to modify the SRK, so that predictions for polar compounds can be performed with reasonable accuracy. In this research the modification studied is that proposed by Yesavage (1986). Yesavage attempts to modify the SRK while still using only three parameters.

Yesavage's modification to the SRK (YSRK) is given as:

$$P = RT/(v-b) - a(T_c)\alpha_n\alpha_p/(v(v+b)) \quad (2)$$

where

$$b = 0.08664 RT_c/P_c$$

$$a(T_c) = 0.42747 R^2 T_c^2 / P_c$$

$$\alpha_n = (1.0 + m(1 - T_r^{0.5}))^2$$

$$\alpha_p = 1 + R_p \exp(-R_p^e) - R_p \exp(-(R_p/T_r)^e)$$

$$m = 0.480 + 1.574\omega_n - 0.176\omega_n^2$$

R_p = polar parameter fit to VP data

T_c = critical temperature of polar compound

P_c = critical pressure of polar compound

$$e = 0.45$$

ω_n = acentric factor for nonpolar homomorph

Yesavage's modification to the SRK attempts to separate the effects due to shape from the effects due to polarity. Yesavage divides the "a" component of the SRK into three pieces. The $a(T_c)$ is obtained from the critical conditions of the compound, and it models the forces due to symmetry that are present in simple molecules. To account for the intermolecular forces due to asymmetry, the α_n term was developed. This term uses the acentric factor of a nonpolar homomorph to approximate the shape of the polar compound. The third term, α_p , is an addition that attempts to account for the polar forces due to hydrogen bonding, dipole or quadrupole moments, etc. This third term is obtained from the effective intermolecular attractive potential and includes a new polar parameter, R_p , which is determined from vapor pressure data. When $R_p = 0.0$, which indicates no polarity effects, the modified equation reduces to the SRK equation. Table 6 contains the values for the nonpolar homomorph, its acentric factor, and R_p .

Table 6

Homomorph Acentric Factors/Polar Parameters

<u>Compound</u>	<u>Nonpolar Homomorph</u>	<u>ω_n</u>	<u>R_p</u>
m-Cresol	m-Xylene	0.326	0.909
Quinoline	Tetralin	0.303	0.02679
Tetralin	Tetralin	0.303	0.0

Mixing Rules

Originally, mixing rules for mixtures were simple arithmetic or geometric means of the parameters "a" and "b" as shown below.

$$b = \sum x_i b_i \quad (3)$$

$$a = \sum \sum x_i x_j a_{ij} \quad (4)$$

$$\text{where } a_{ij} = (a_i a_j)^{0.5} (1.0 - k_{ij})$$

In this research, the "b" parameter was not changed; however, five variations to the geometric mean mixing rule for the attractive "a" parameter were examined. All variations in the "a" parameter were different expressions for the interaction parameter k_{ij} . The interaction parameters used in the different expressions for k_{ij} in the SRK and YSRK were generated from m-cresol, quinoline, tetralin binary data by Niesen (1986), and are presented in Table 7, 8, and 9.

The first mixing rule (Model 1) was a single, simple interaction parameter, k_{ij} .

The second mixing rule examined is a slight variation to Model 1. As temperature rises the kinetic energy of the molecules exceed the energies of association; therefore, the number intermolecular interactions will increase. This being the case, one would assume the contribution from the attractive term would decrease while that of the repulsive

term would increase as temperature increases. The second mixing rule (Model 2) examined addressed this theory. The form of this mixing rule is $k_{ij} = A + B/T$.

The remaining mixing rules examined were different forms of density dependent interaction parameters. The interaction between molecules should be quite different between the liquid and vapor phase. This is primarily due to the difference in spacing between the molecules. When the volume is incorporated into the mixing rule; temperature, pressure, and compositional dependencies are changed because the volume is actually a function of these. The density dependence was only evaluated as a first order contribution, as any other order leads to an equation of state which cannot be solved explicitly.

This density dependence makes the EOS quartic in volume, and requires extra computation in the solving of the quartic equation with a quartic solver (Flanigan, 1986). The quartic solver actually solves a resultant cubic equation. The appropriate roots are chosen in the same manner as for a cubic equation solver.

Three forms of density dependent mixing rules were evaluated. The first of these was a function of only the density. This mixing rule was proposed by Holder et al. (1986) and is given the form, $k_{ij} = A - B/v$ (Model 3).

A modification to Holder's mixing rule was the second density dependent mixing rule studied. This mixing rule (Model 4) incorporates a temperature function as well as the density function. The form of the interaction parameter for this mixing rule is $k_{ij} = A - B/(vRT)$.

The final density dependent mixing rule evaluated was proposed by Luedecke et al. (1985). This mixing rule (Model 5) is different from the other density dependent mixing rules in that it has a cubic compositional dependency with three parameters and is written as:

$$\sum_i \sum_j x_i x_j (a_i a_j)^{0.5} (1.0 - k_{ij}) + 1.0 / (vRT) \sum_i \sum_j x_i x_j (x_i C_{ij} + x_j C_{ji}),$$

where i does not equal j for the second double summation term. To conserve on space, this mixing rule will be expressed as A+C's.

Table 7
Interaction Parameters*
m-Cresol/Quinoline

EOS	Model	Parameters		
SRK ¹	k_{ij}	$k_{ij} = -8.00E-2$		
SRK ²	A+B/T	$A = -5.58E-2$	$B = -13.652$	
SRK ³	A-B/v	$A = -0.1389$	$B = -18.516$	
SRK ⁴	A-B/vRT	$A = -9.68E-2$	$B = -24613426$	
SRK ⁵	A+C's	$A = -7.57E-2$	$C_{12} = 7.09E-3$	$C_{21} = -2.16E-3$
YSRK ⁵	A+C's	$A = -0.1063$	$C_{12} = -1.15E-2$	$C_{21} = -1.17E-2$

1 = simple interaction parameter

2 = temperature dependent mixing rule

3 = density dependent mixing rule (Holder et al., 1986)

4 = modification of Holder mixing rule

5 = density dependent mixing rule (Luedecke et al., 1985)

* Note: Parameters generated by Niesen, (1986).

Table 8
 Interacton Parameters*
 m-Cresol/Tetralin

EOS	Model	Parameters		
SRK ¹	k_{ij}	$k_{ij} = 3.83E-2$		
SRK ²	A+B/T	A = -1.99E-2	B = 31.973	
SRK ³	A-B/v	A = 8.59E-2	B = 18.475	
SRK ⁴	A-B/vRT	A = 5.36E-2	B = 27259270	
SRK ⁵	A+C'S	A = -5.17E-2	$C_{13} = -5.71E-2$	$C_{31} = -5.29E-2$
YSRK ⁵	A+C's	A = -7.28E-2	$C_{13} = -7.03E-2$	$C_{31} = -6.37E-2$

- 1 = simple interaction parameter
 2 = temperature dependent mixing rule
 3 = density dependent mixing rule (Holder et al., 1986)
 4 = modification of Holder mixing rule
 5 = density dependent mixing rule (Luedecke et al., 1985)

* Note: Parameters generated by Niesen, (1986).

Table 9
Interaction Parameters*
Tetralin/Quinoline

EOS	Model	Parameters		
SRK ¹	k_{ij}	$k_{ij} = -1.52E-2$		
SRK ²	A+B/T	A = -0.1355	B = 67.791	
SRK ³	A-B/v	A = 2.53E-2	B = 14.657	
SRK ⁴	A-B/vRT	A = 3.13E-2	B = 31083465	
SRK ⁵	A+C's	A = -0.1356	$C_{32} = -7.18E-2$	$C_{23} = -6.66E-2$
YSRK ⁵	A+C's	A = -0.1331	$C_{32} = -7.08E-2$	$C_{23} = -5.69E-2$

- 1 = simple interaction parameter
- 2 = temperature dependent mixing rule
- 3 = density dependent mixing rule (Holder et al., 1986)
- 4 = modification of Holder mixing rule
- 5 = density dependent mixing rule (Luedecke et al., 1985)

* Note: Parameters generated by Niesen, (1986).

PREDICTION RESULTS

Before any conclusions could be drawn from the experimental data, predictions needed to be generated using the two EOS and five mixing rules. An isothermal flash program was written incorporating the SRK and YSRK equations of state, the five mixing rules, and the respective interaction parameters for each mixing rule and the corresponding equation of state. The binary interaction parameters were determined by Niesen (1986) from the binary data that she had generated. A maximum likelihood method developed by Anderson et al. (1978) was employed by Niesen (1986) to determine these interaction parameters. This flash program predicts ternary VLE data at 250, 275, 300, and 325°C at their measured pressures. The isothermal flash program used to generate the predicted results assumed a liquid to feed ratio of 50% with the actual data points as the initial guess for most of the predicted points. In some cases these initial guesses would predict a single phase point. When this occurred, initial guesses were input by hand along the same tie line as the actual point. This was continued until a two phase point was predicted from the flash program. It should be noted that isothermal flash programs may be written making different assumptions which will produce different results than those presented in this

thesis.

The results for the first mixing rule together with the experimental data at 250°C and 150, 200, and 275 kPa are presented in Table 11 and shown graphically in Figure 13. Likewise, the results for the second, third, fourth, and fifth mixing rules at 250°C and the same three pressures are presented in Tables 12 - 16. These six tables are presented in Appendix A. These results are also graphically presented in Figures 14 - 18.

For the 275°C isotherm using the first mixing rule at the pressures of 250, 325, and 425 kPa, the results are presented in Table 17. A ternary plot comparing the predicted results with the actual data is shown in Figure 19. Similarly the results for the 275°C isotherm for the other four mixing rules are presented in Tables 18 - 22 which are presented in Appendix A. The ternary diagrams occupying Figures 20 - 24 are the plots for the predicted data.

Table 23 contains the predicted values for the first mixing rule for the 300°C isotherm at its corresponding pressures. Tables 24 - 28 contain the predicted results for the four other mixing rules at 300°C. All six tables are presented in Appendix A. Figures 25 - 30 are the ternary diagrams which compare the actual data to the predicted

results.

For the 325°C isotherm, the predicted results for the first mixing rule are contained in Table 29. Similarly, the computer generated predictions for the other four mixing rules at this isotherm are presented in Tables 30 - 34. These six tables are also presented in Appendix A. The predicted results for these five mixing rules are presented in Figures 31 - 36 as ternary VLE diagrams. The actual data are also shown on these figures.

Once predicted data had been generated from the flash program, comparisons were made with the actual data measured on the VLE apparatus. A simple percent difference expressed as:

$$\text{ABSOLUTE VALUE (ACTUAL - PREDICTED)} * 100$$

was used to compare the actual data with the predicted data. This was performed for every point on each isotherm and then averaged together allowing comparisons of the five mixing rules. The results of these comparisons are presented in Table 10. While some of the results of these comparisons were expected, others were quite unexpected.

First of all, it appears that the Luedecke mixing rule (Model 5, A+C's) predicts the binary points the best over the temperature and pressure ranges investigated. This same result was noticed for the prediction of the binary data

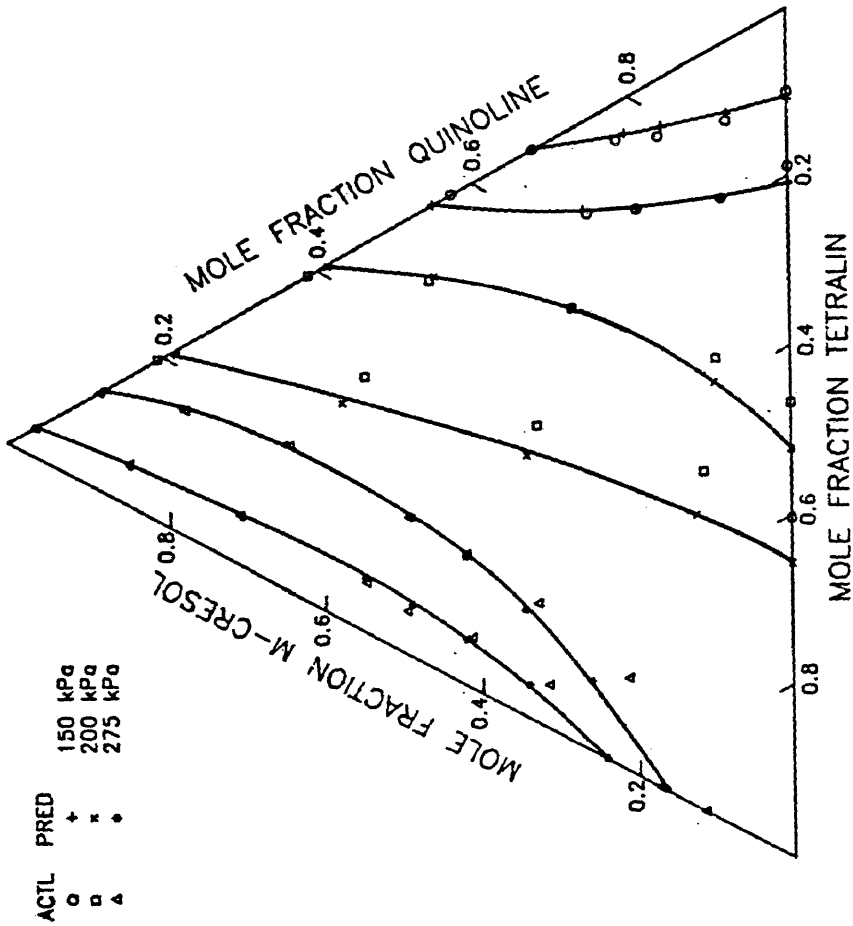


Figure 13: MC/Q/T Predictions T = 250°C
SRK Model 1

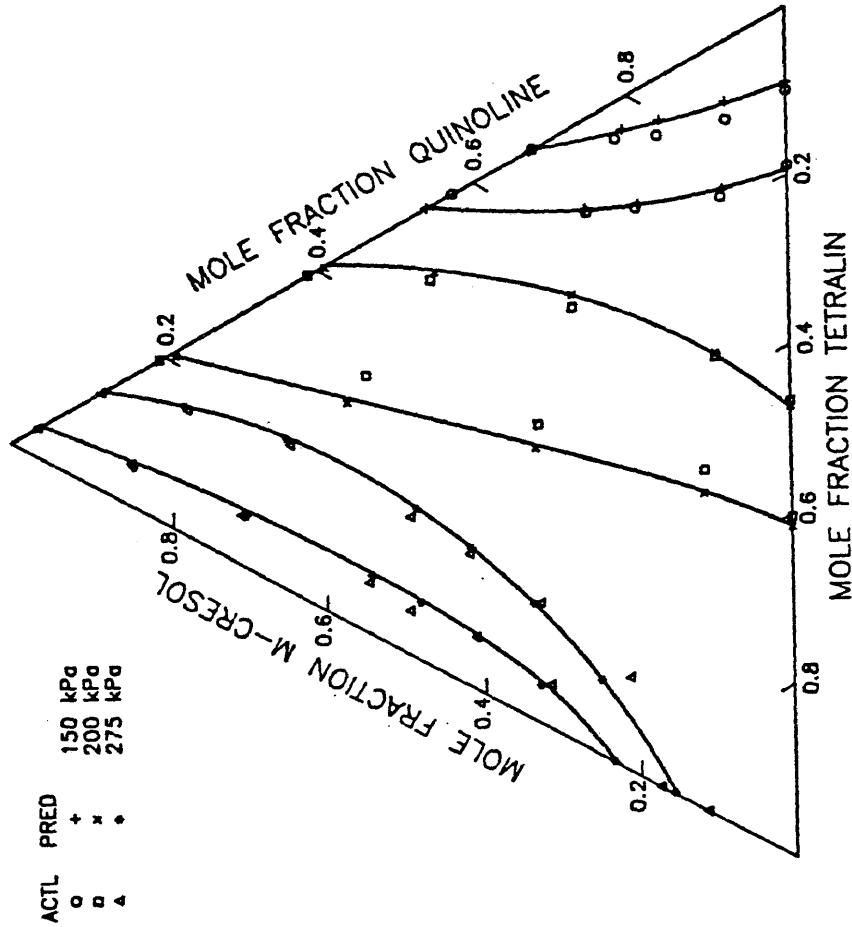


Figure 14: MC/Q/T Predictions T = 250°C
SRK Model 2

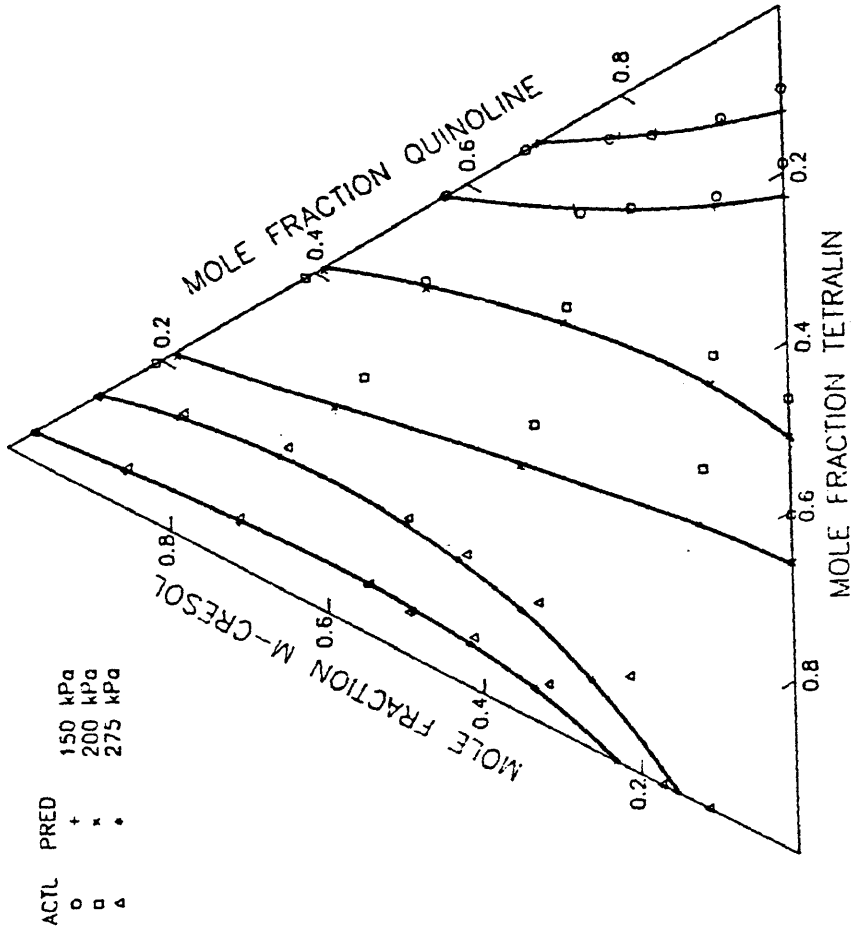


Figure 15: MC/Q/T Predictions T = 250°C
Model 3
SRK

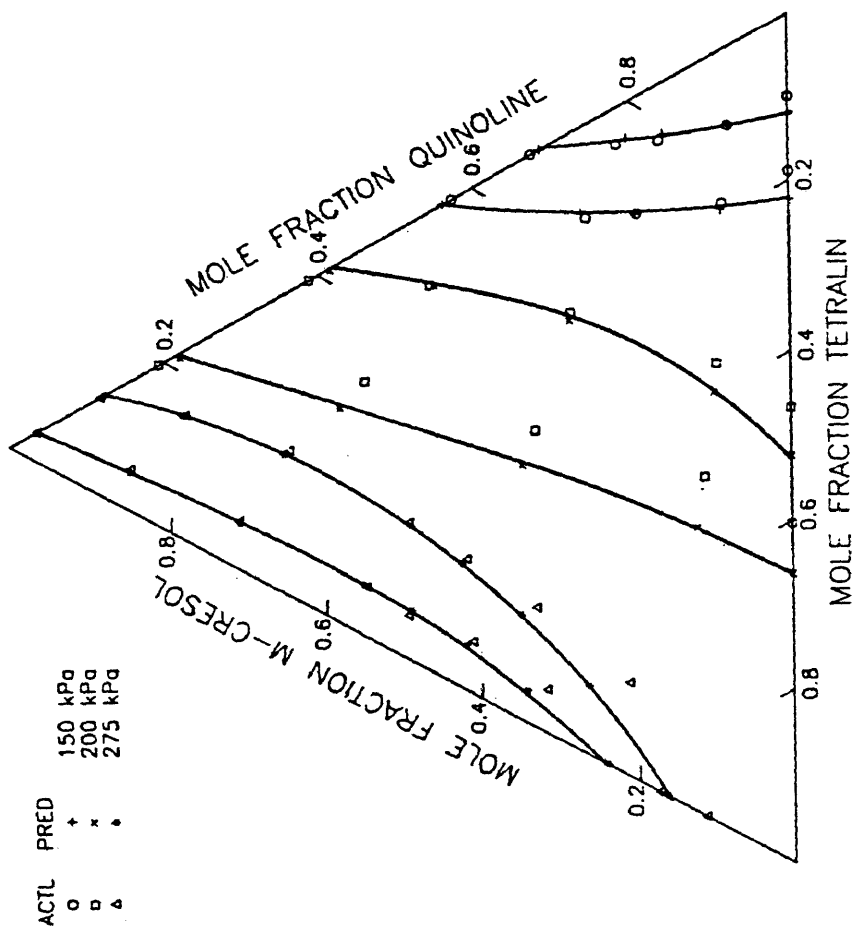


Figure 16: MC/Q/T Predictions
SRK
T = 250°C
Model 4

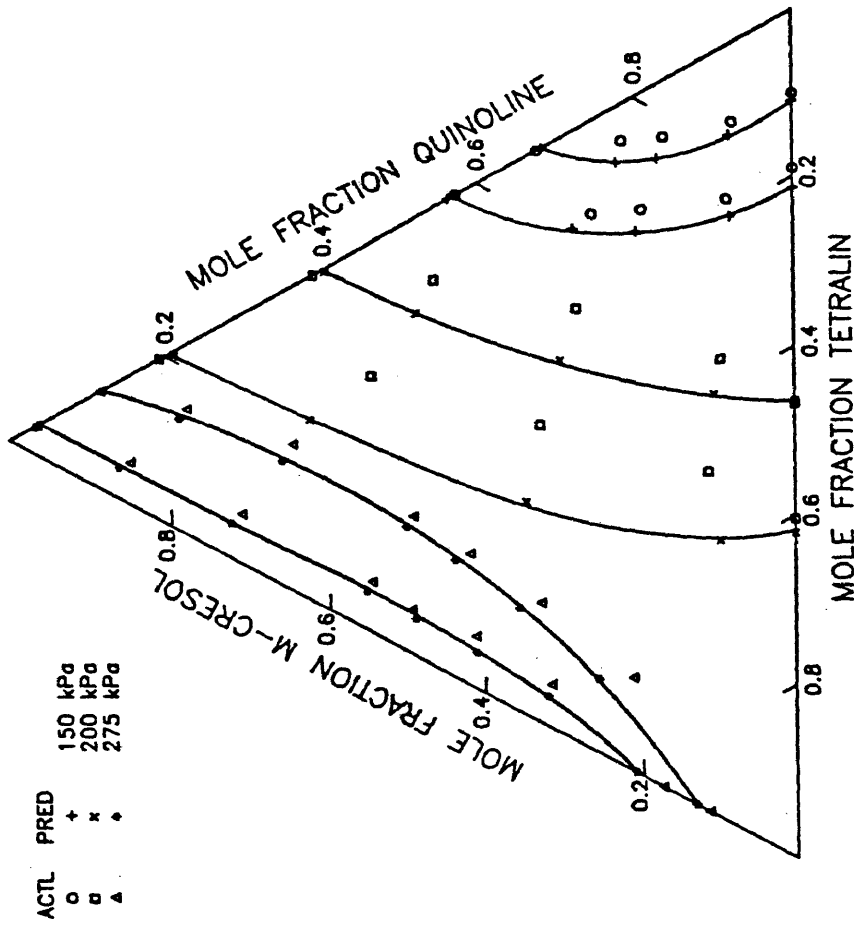


Figure 17: MC/Q/T Predictions T = 250°C
SRK Model 5

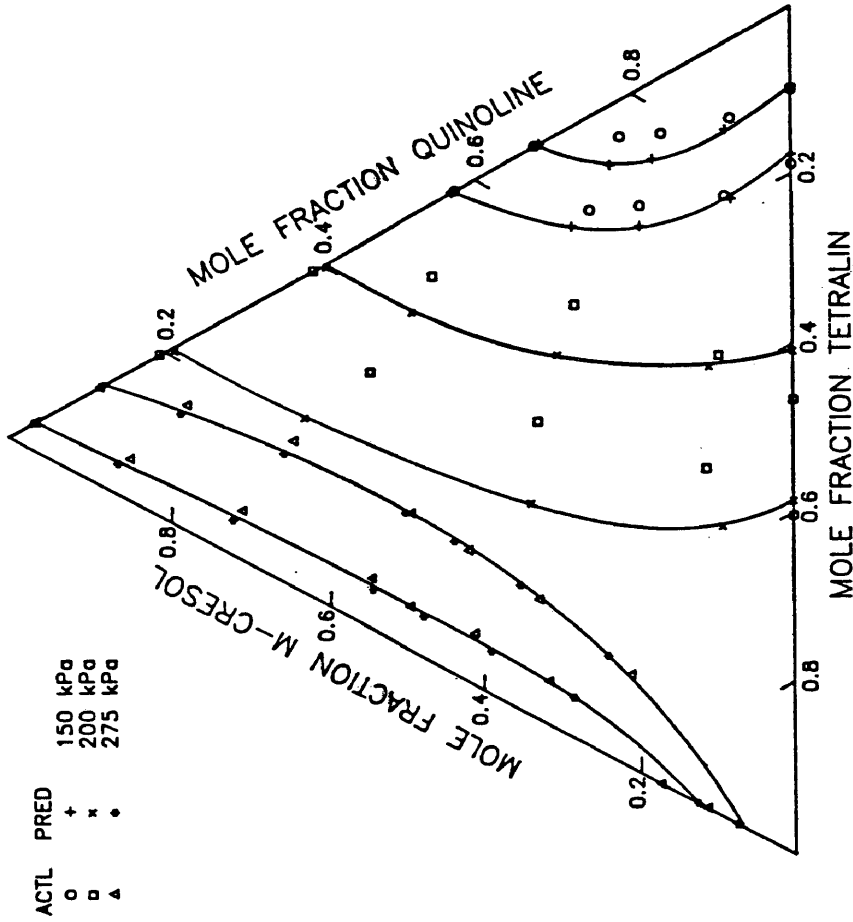


Figure 18: MC/Q/T Predictions T = 250°C
 YSRK Model 5

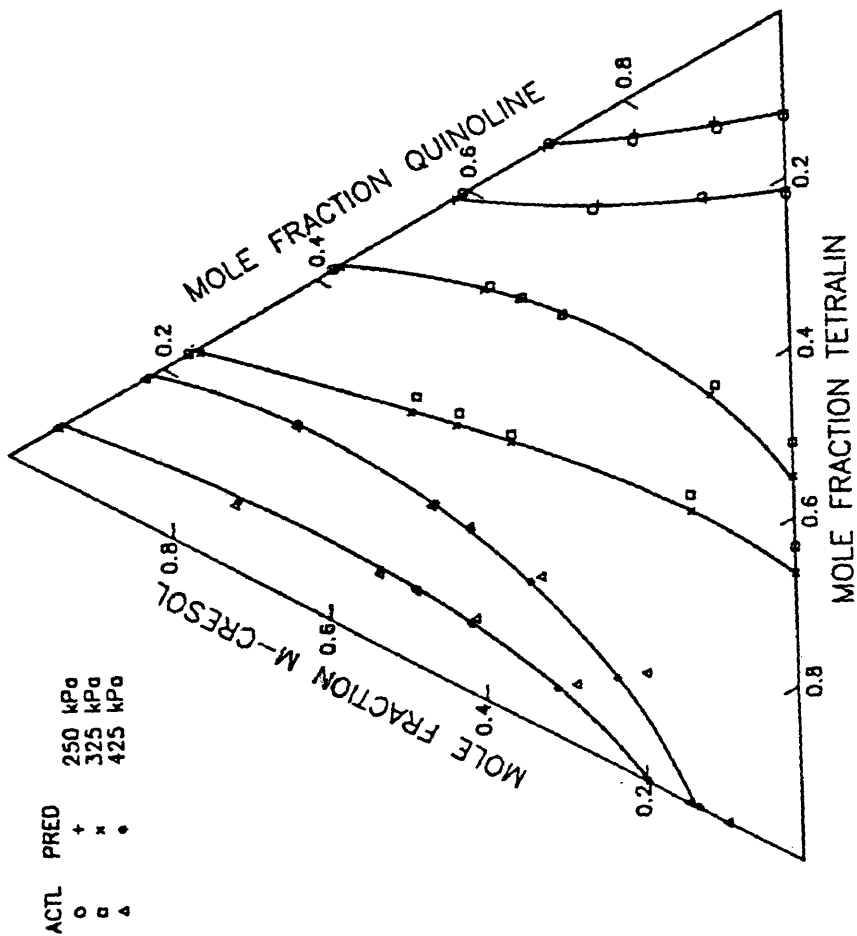


Figure 19: MC/Q/T Predictions
SRK
T = 275°C
Model 1

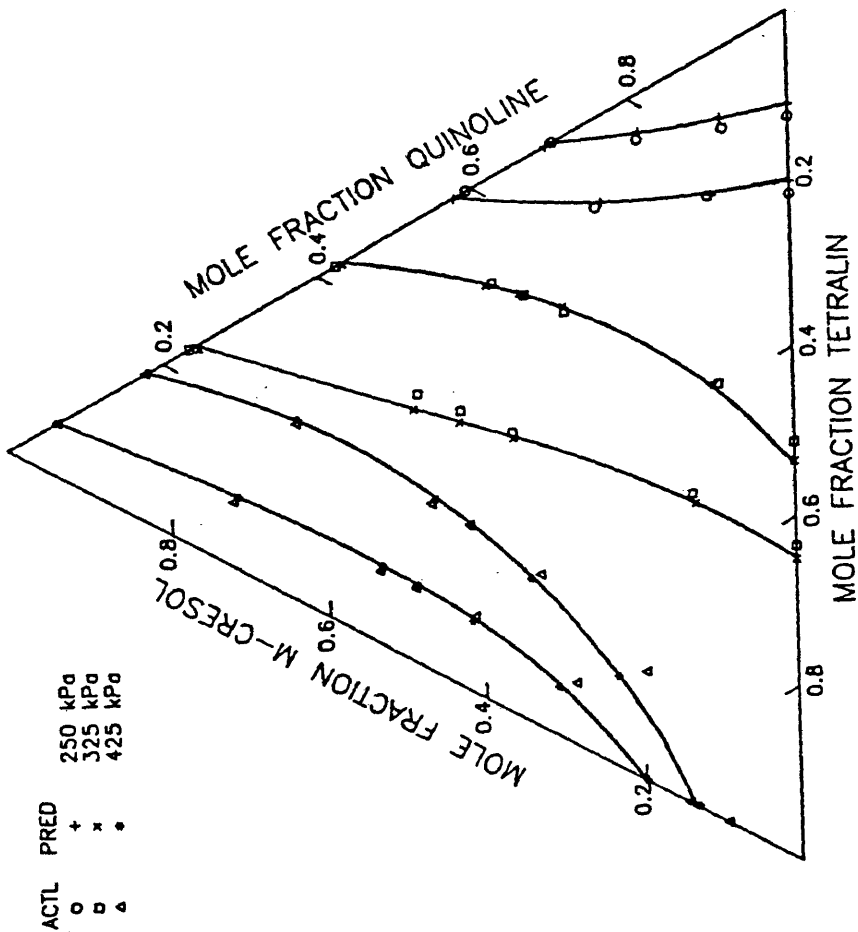


Figure 20: MC/Q/T Predictions
 SRK
 T = 275°C
 Model 2

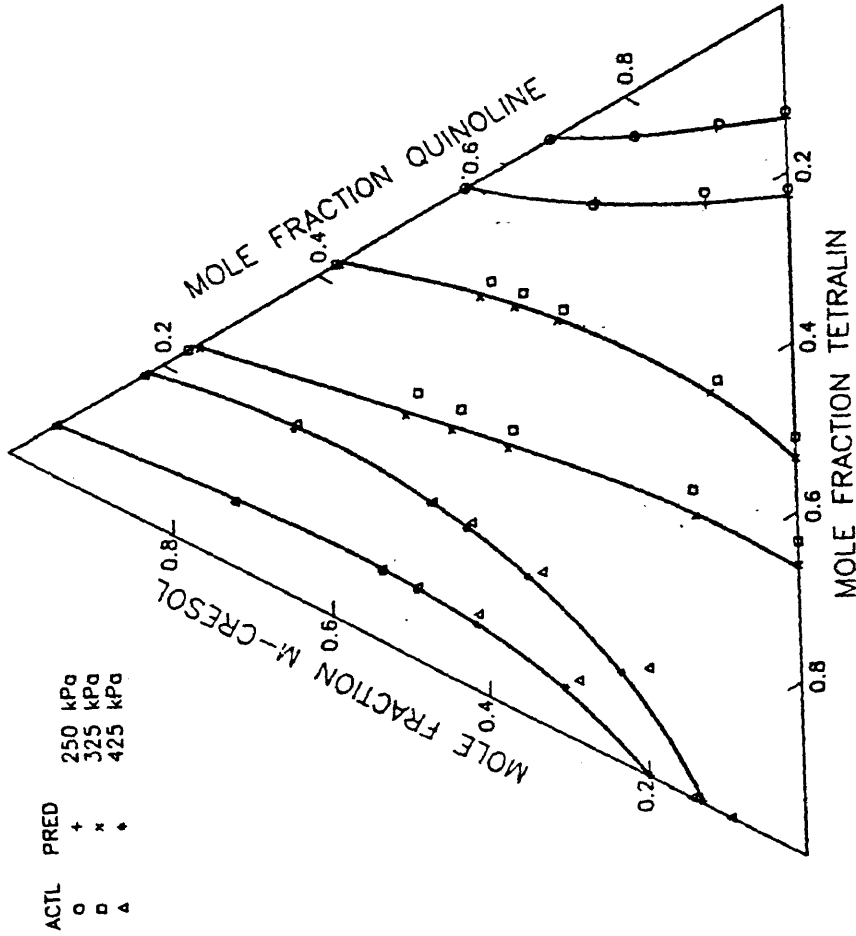


Figure 21: MC/Q/T Predictions T = 275°C
SRK Model 3

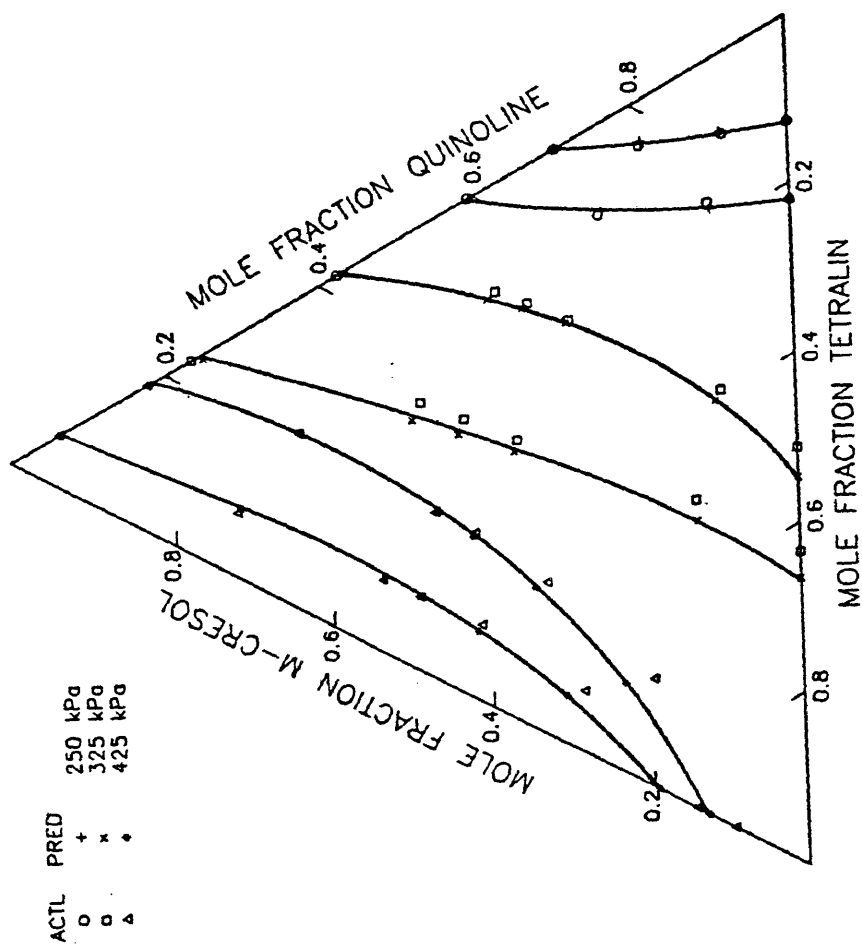


Figure 22: MC/Q/T Predictions T = 275°C
SRK Model 4

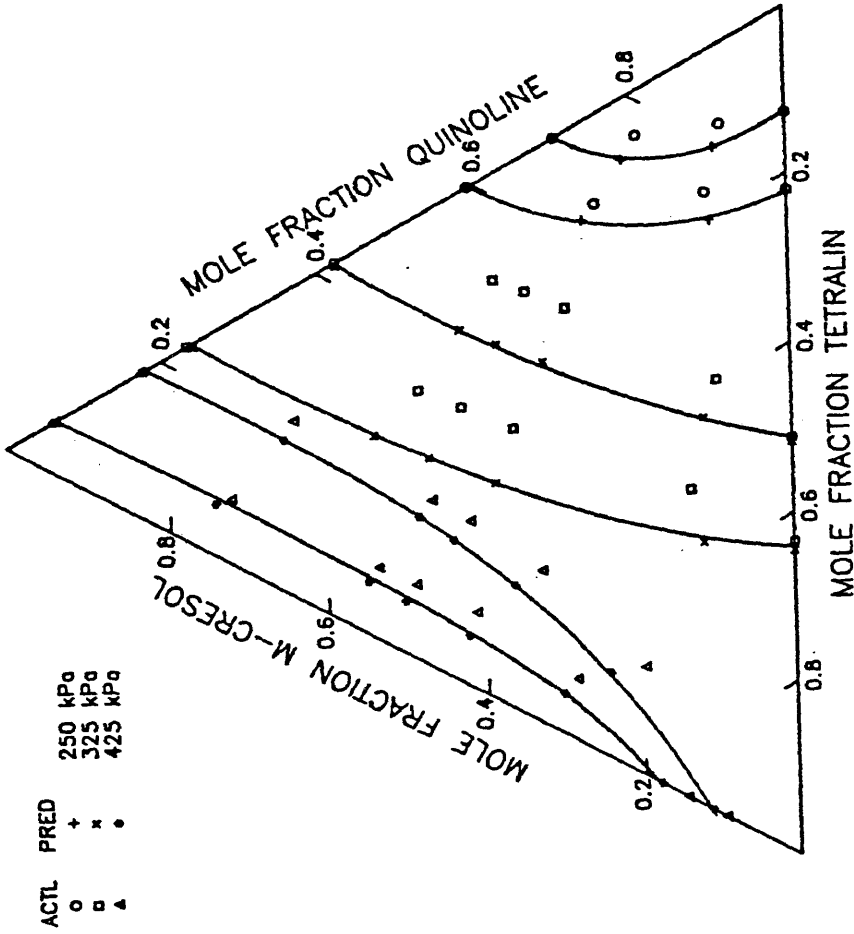
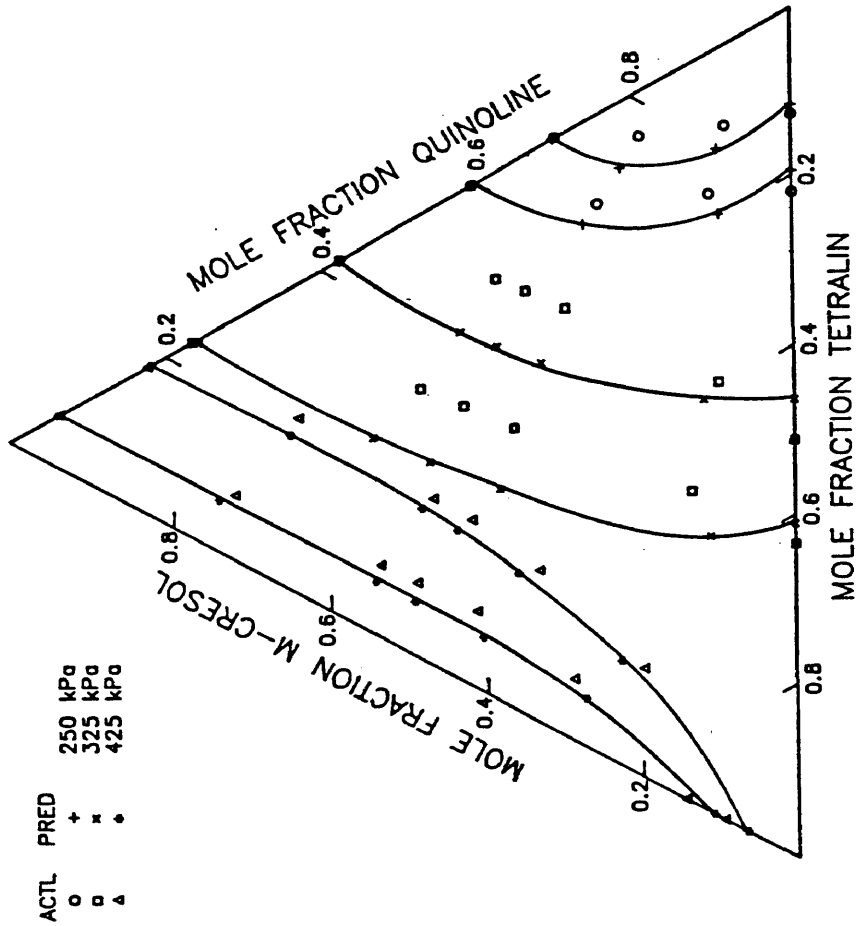


Figure 23: MC/Q/T Predictions T = 275°C
SRK Model 5



ACTL	PRED	250 kPa
○	+	325 kPa
□	x	425 kPa
△	•	

Figure 24: MC/Q/T Predictions T = 275°C
 YSRK Model 5

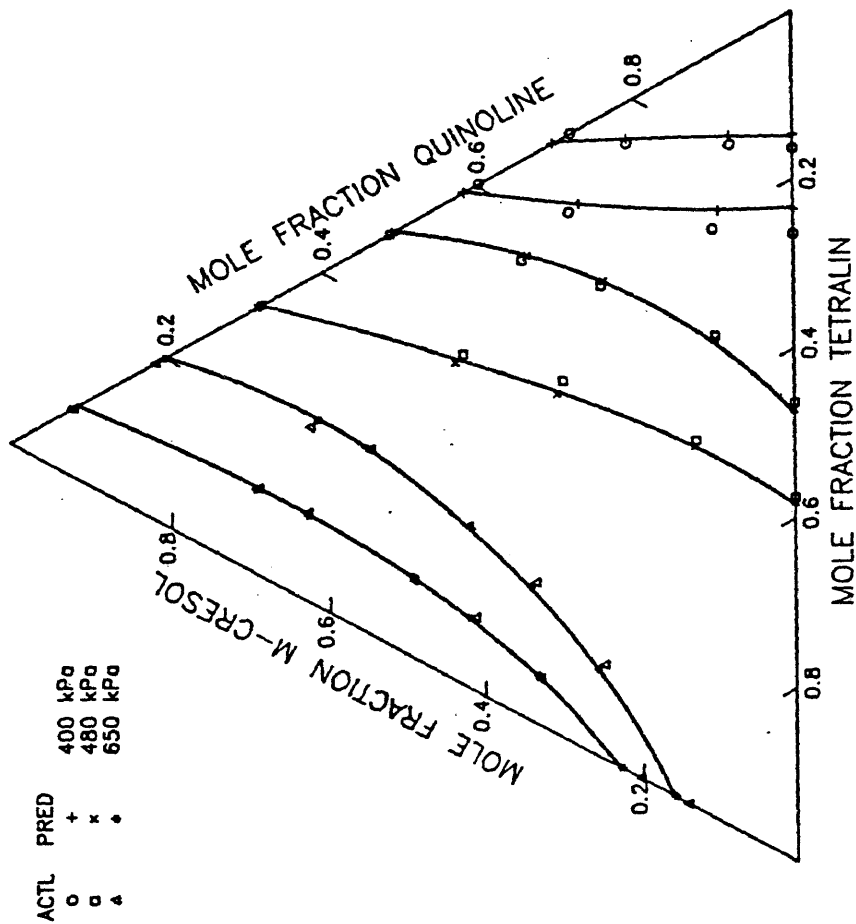


Figure 25: MC/Q/T Predictions T = 300°C
SRK Model 1

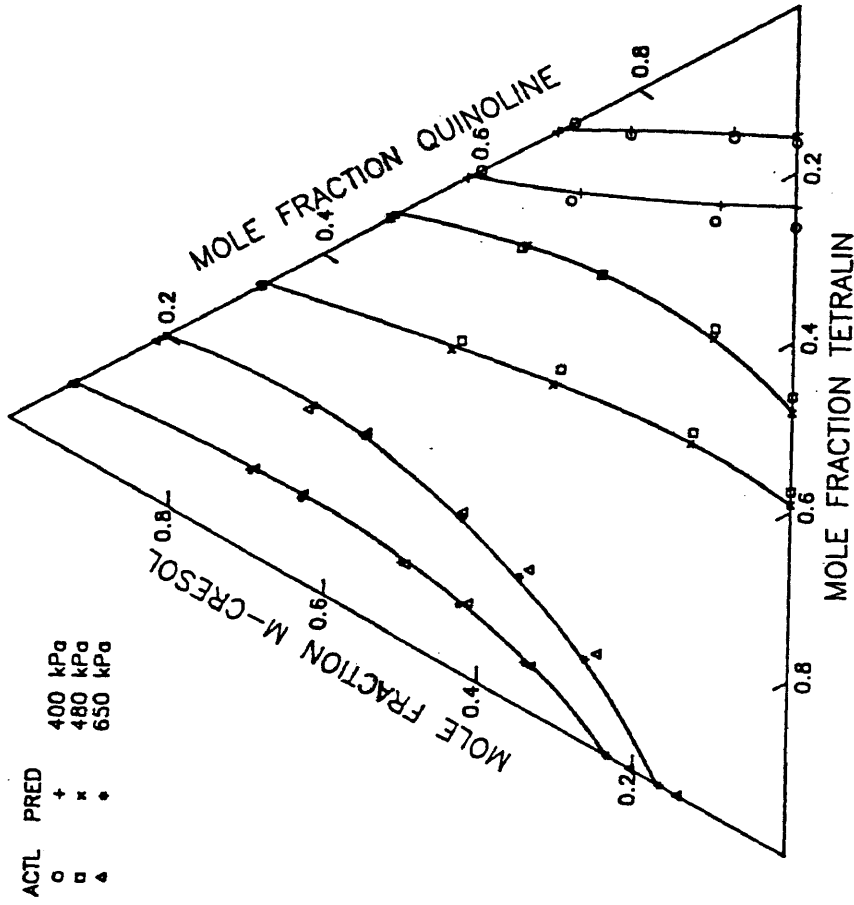


Figure 26: MC/Q/T Predictions T = 300°C
SRK Model 2

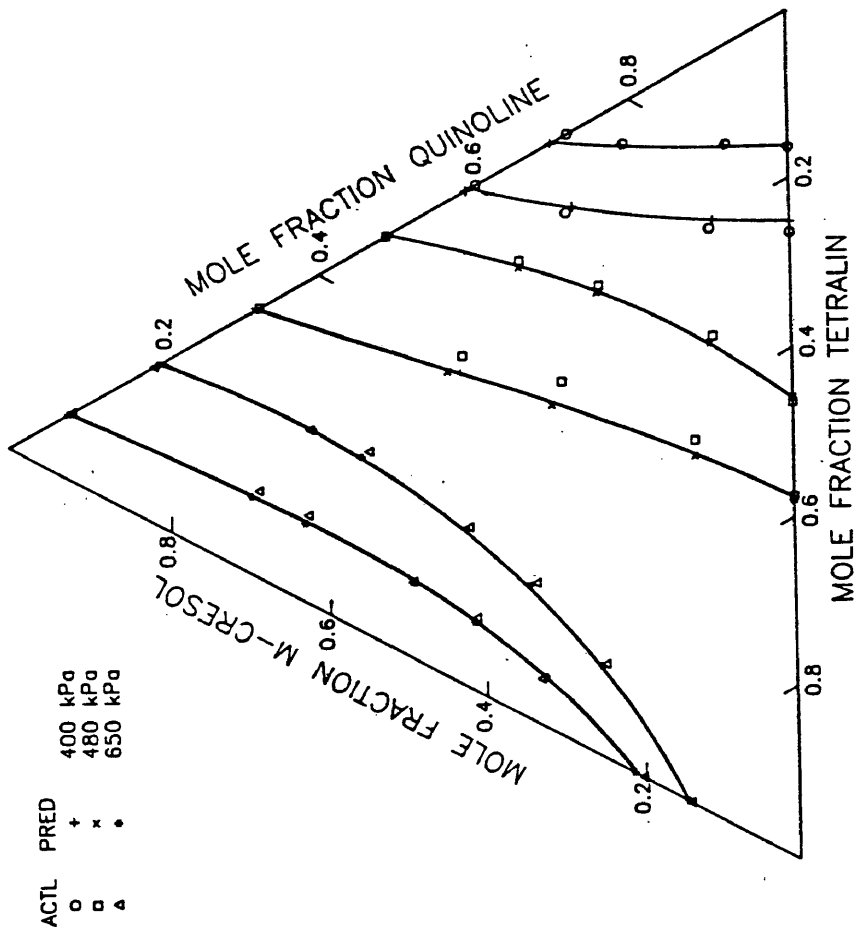


Figure 27: MC/Q/T Predictions
SRK
T = 300°C
Model 3

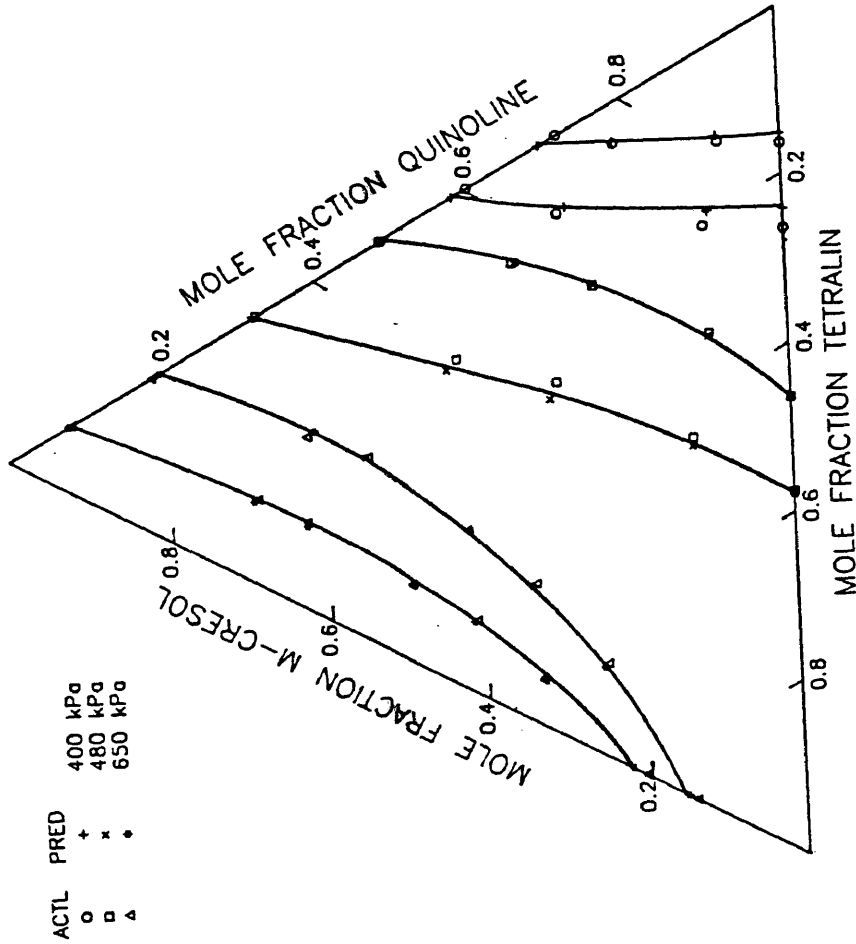


Figure 28: MC/Q/T Predictions
SRK
T = 300°C
Model 4

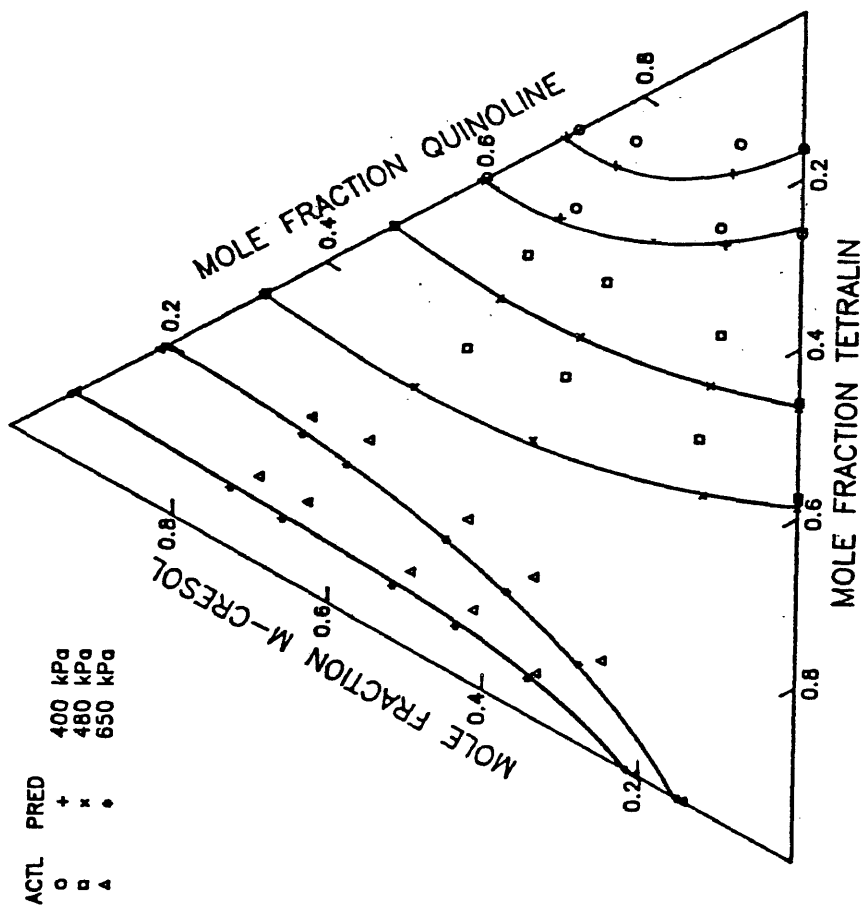


Figure 29: MC/Q/T Predictions T = 300°C
 SRK Model 5

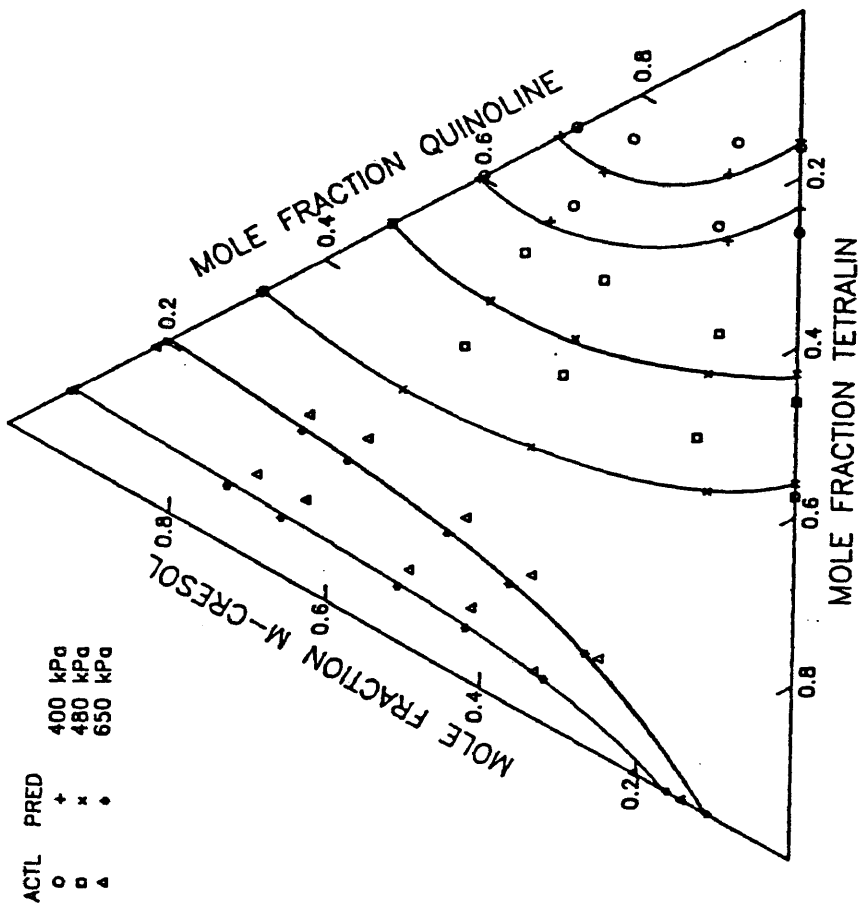


Figure 30: MC/Q/T Predictions T = 300°C
 YSRK Model 5

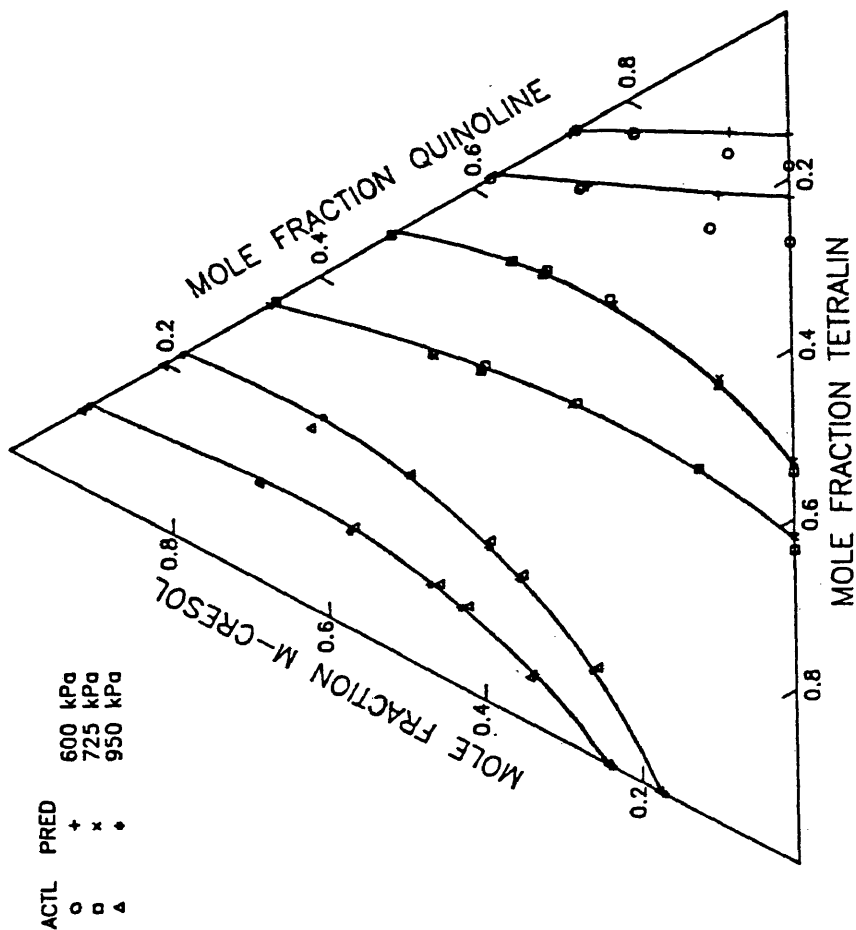


Figure 31: MC/Q/T Predictions T = 325°C
SRK Model 1

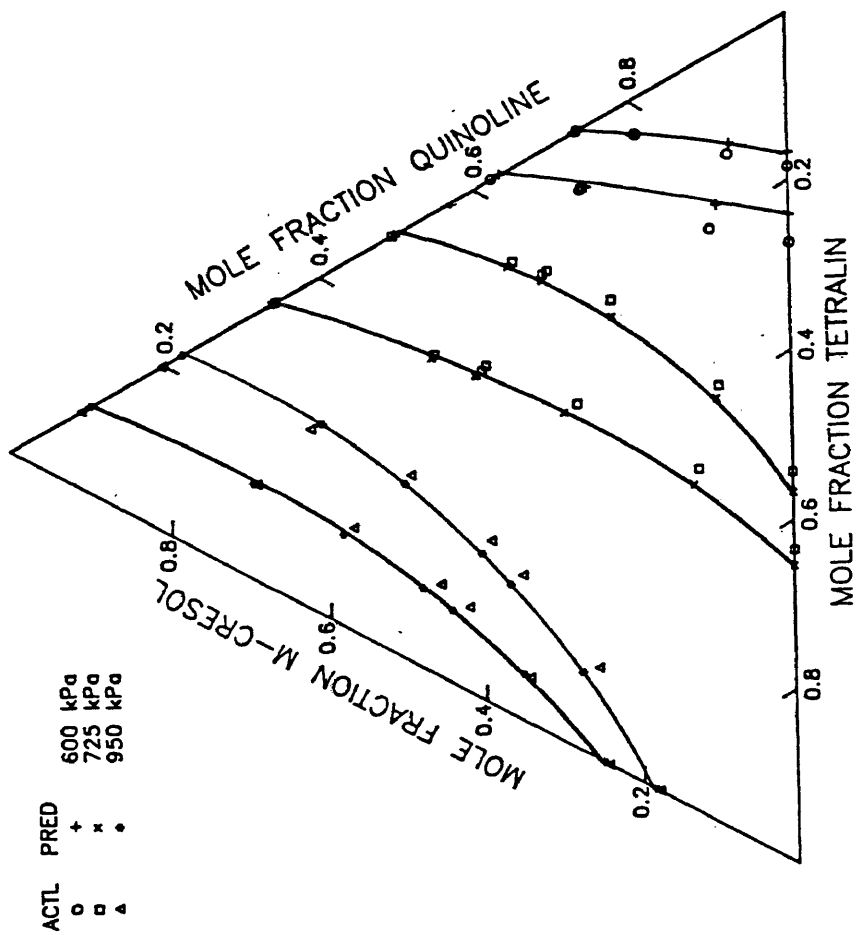


Figure 32: MC/Q/T Predictions
SRK
T = 325°C
Model 2

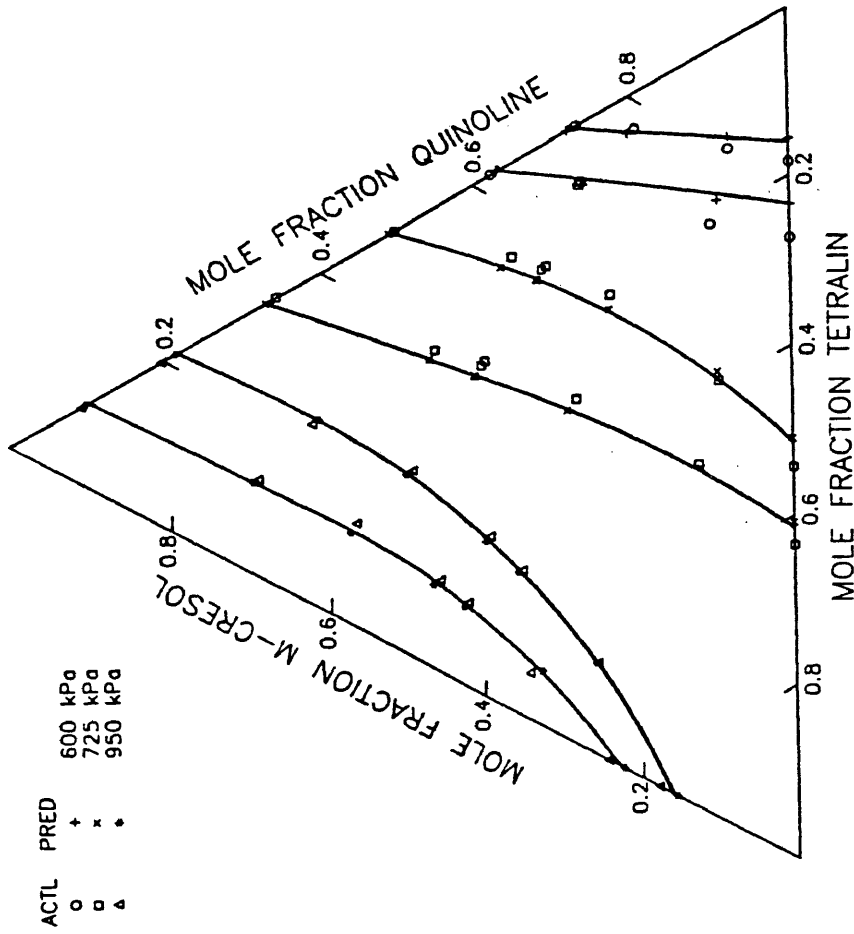
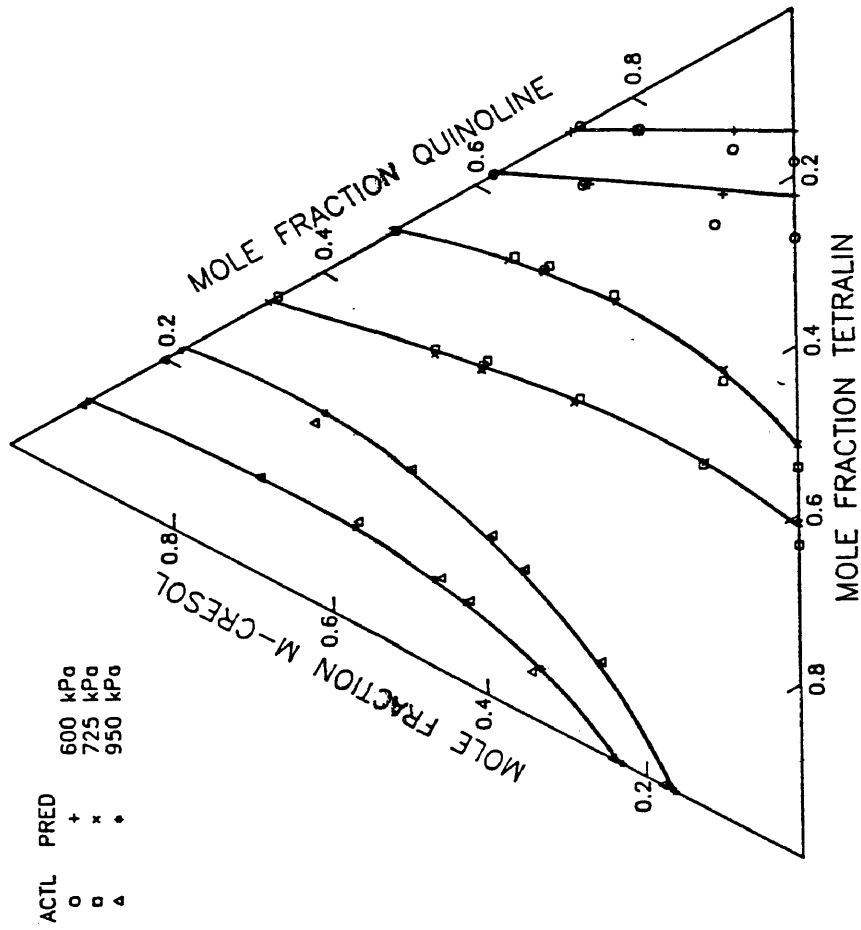


Figure 33: MC/Q/T Predictions T = 325°C
SRK Model 3



ACTL	PRED	600 kPa
○	+	725 kPa
□	x	950 kPa
△	•	

Figure 34: MC/Q/T Predictions T = 325°C
SRK Model 4

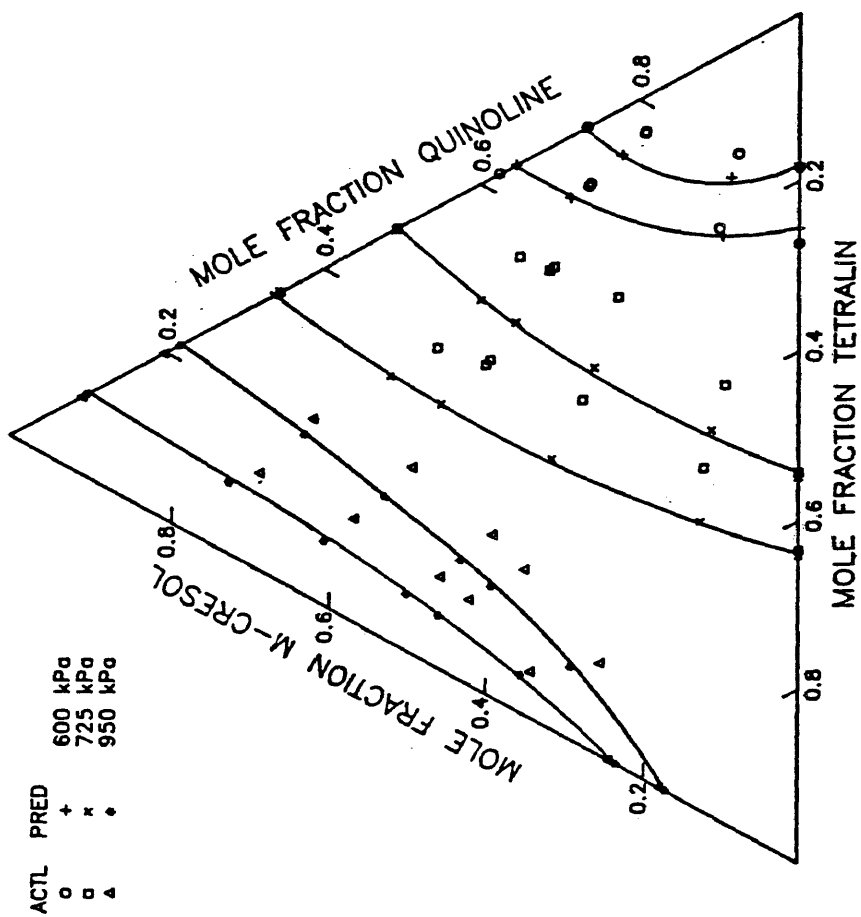


Figure 35: MC/Q/T Predictions T = 325°C
SRK Model 5

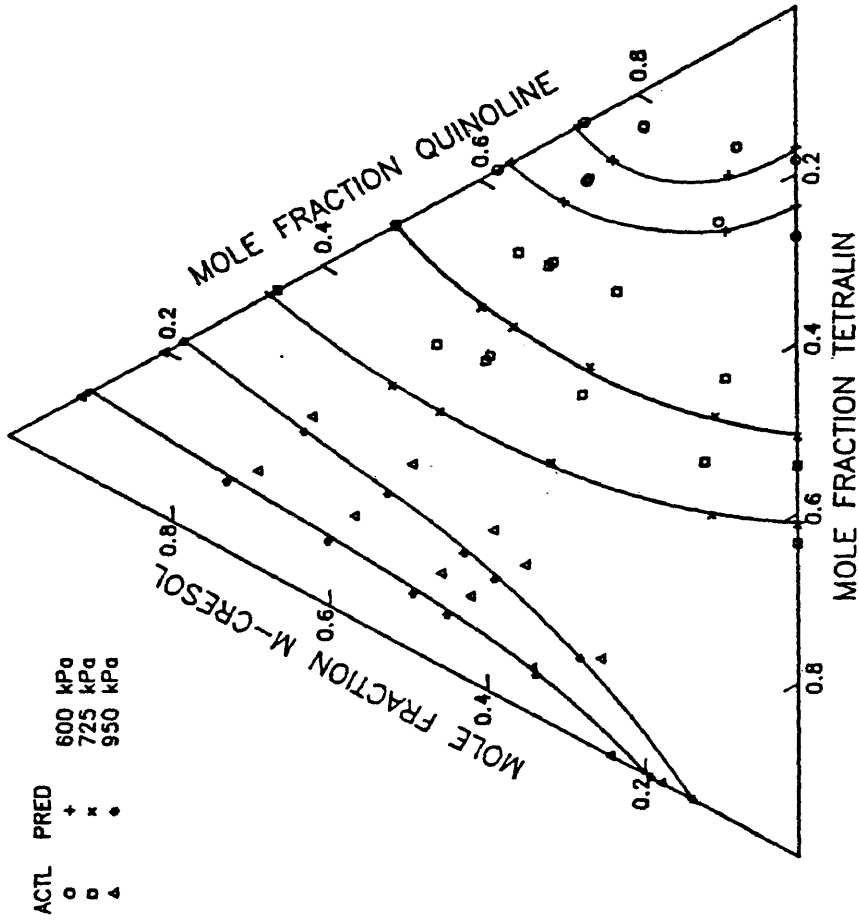


Figure 36: MC/Q/T Predictions T = 325°C
YSRK Model 5

Table 10

Percent Difference for MC/Q/T

<u>EOS</u>	<u>MR</u>	<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
SRK	1	0.819	1.485	1.844	0.996	1.741	1.816
SRK	2	0.859	1.342	1.760	1.073	1.603	1.733
SRK	3	0.895	1.299	1.814	1.011	1.847	2.071
SRK	4	0.841	1.353	1.696	1.615	2.260	1.978
SRK	5	1.834	2.132	3.701	1.970	2.291	3.441
YSRK	5	1.994	2.610	3.966	2.154	2.841	3.612

(Niesen, 1986). One would expect the mixing rule with the most fitting parameters to predict the data better. However, this same mixing rule does not predict the ternary data very well for the middle isobar investigated at the four isotherms. While the other mixing rules predict the correct shape for the two phase region at these pressures, the Luedecke mixing rule predicts the wrong shape of the entire curve.

None of the mixing rules examined in this thesis predicted the actual data very well. One would expect the density dependent mixing rules would predict better since they take into account the different interactions between the liquid and vapor phase. Unfortunately, the density dependent mixing rules did not predict better than the density independent mixing rules. The density dependent mixing rules seem to rely more upon curve fitting than the density independent mixing rules. This effect is most evident for the Luedecke mixing rules. Therefore, they will not predict as well when extrapolated into regions outside of which the interaction parameters were generated.

Another possible cause for the poor performance of the mixing rules could be the binary interaction parameters that were used in the mixing rules. These interaction parameters were generated using a maximum likelihood technique. The

method provided the most likely set of interaction parameters within a range of values. It might be of considerable interest to evaluate these mixing rules with other binary interaction parameters chosen from within the range of values provided by the maximum likelihood technique.

No general comparisons could be made between the SRK and the modified SRK (YSRK). Only the interaction parameters for the Luedecke mixing rule were available for both equations of state.

CONCLUSIONS

VLE data were generated for the m-cresol, quinoline, tetralin system. This was accomplished with a few minor alterations to the operating procedures for the binary system. The data was measured at four isotherms, 250, 275, 300, and 325°C. At each isotherm investigated, three isobars were measured for the ternary mixtures. Before a liquid and vapor sample could be taken, the temperature and pressure had to be maintained at equilibrium conditions for at least 30 minutes. Equilibrium conditions consisted of temperature control of +/- 0.1°C and pressure control to within the stated accuracy of the gages.

A ternary flash program was developed and debugged. The flash program used in this thesis assumed that the liquid to feed ratio was 50% based on the experimental compositions. After the flash program was operating properly, predictions were generated for the four isotherms, and comparisons were made.

Percent difference comparisons were first made to determine which mixing rule most accurately predicted the ternary data over the entire temperature and pressure ranges investigated. One would believe the most complex mixing rule would produce the best prediction. However, this was not the case. The two density independent mixing rules

predicted the actual data better than the density dependent mixing rules over the temperature range evaluated in this work.

Overall, Luedecke's mixing rule (Model 5, A+C's) produced the most discouraging results. This mixing rule predicts the binary data points very well; yet, can not be extended to the ternary two phase region. The fact that it fits the binary points well is not surprising, as the parameters for this mixing rule, as well as the others, were generated from actual binary data. However, one cannot extend this mixing rule to areas outside of which the parameters were generated, as evidenced by the mixing rule's inability to predict the shape of the two phase region for the middle isobar at each isotherm investigated. Although the density independent mixing rules predicted the best, they did not predict very well in some areas.

This inability to predict the data could be caused by the binary interaction parameters. The interaction parameters were chosen from a range of possible values that was determined by a maximum likelihood method. These were the most likely values for the interaction parameters. Perhaps the mixing rules would predict better if different binary interaction parameters were chosen from the range of possible values.

A comparison between the SRK and the modified SRK (YSRK) equations of state was not performed. Interaction parameters for the Luedecke mixing rule were the only parameters available for both equations of state. To make a justifiable comparison, interaction parameters for the other four mixing rules are needed for the YSRK.

RECOMMENDATIONS

More experimental work is needed to fully evaluate the mixing rules examined in this research. The data generated in this research was obtained on equipment that was only able to achieve a maximum temperature of 350°C. The mixing rules should be evaluated over broader temperature ranges, therefore, VLE data needs to be generated over a broader temperature range.

Different binary interaction parameters should be evaluated for the mixing rules. The inability to predict the actual data may not be due to the mixing rules. This inability may be due to the incorrect interaction parameters used in the mixing rules. The maximum likelihood method, which was used to generate the interaction parameters, produces a range of possible values. From within this range, the most likely binary interaction parameters were chosen. Therefore, the interaction parameters used in this research are just one of many possible interaction parameters that could be used in the mixing rules. It would be useful to see if other interaction parameters were chosen how well the mixing rules would predict the actual data.

Measures need to be taken to separate the effects due to polarity and size. This can be accomplished by examining ternary mixtures which incorporate one or the other but not

both of them. Experimental work like this would hopefully separate and clearly define the effects of either size or polarity differences between compounds.

For continued experimental work on this equipment, the following recommendations are made:

1.) A GC equipped with a thermal conductivity detector (TCD) should be used so that the water content of the samples may be monitored while the samples compositions are being determined.

2.) A visual surge tank would be desirable especially if ternary mixtures are going to be investigated. This would allow the operator to visually monitor the level present in the surge tank when adding and taking out fluid to adjust the composition.

3.) For safety reasons, the controller unit to the in-line bayonet heater should be mounted out of the way. Mounting of this unit would prevent the controller from being accidentally knocked off of the chair.

4.) The heat exchanger on the liquid line should be repaired or replaced with an exchanger that is enclosed so that the cooling water will not overflow, flooding the room.

5.) Replace the pump with one which does not lose its prime. Loss of fluid flow in the system during operation of

equipment could be extremely dangerous.

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APPENDIX A
OPERATING AND SHUTDOWN PROCEDURES

Operating Procedures for VLE Apparatus

The following operating procedure was found to work well for a ternary system and posed no serious safety hazards.

- 1.) Open vents on the surge tank.
- 2.) Fill the surge tank with approximately one liter of fluid through the funnel located on the surge tank. Close the valve after all the fluid has entered the tank.
- 3.) Open the micrometering valve on the vapor line slightly. This will need further adjustment later, to achieve the correct operational conditions.
- 4.) Prime the pump by turning the pump on and opening the valve just beyond the pump outlet. Increase the pump stroke setting to 300. After a short period of time the pump will prime itself. Collect fluid from the purge line until a steady flowrate is achieved. Close the valve. Watch the outlet pressure gauge located near the pump outlet. Once the pressure begins to rise, quickly decrease the pump setting to 100. If the pump is correctly primed the pump stroke will be apparent on the gauge. The pressure on the gauge should not exceed 200 psi (1400 KPa).
- 5.) Allow the pump to run until fluid has filled the equilibrium cell. Purge the DPI cell by allowing fluid to flow through the u-tube located on the lower chamber of the

cell. This should be done until all air bubbles are eliminated.

6.) Open the valves to the Heise pressure gauges located on the front panel. The gauges will then adjust to atmospheric pressure.

7.) Turn on the water to the vapor and liquid heat exchangers. The knobs are located on the wall above the work bench. The liquid line heat exchanger requires a low flowrate, while the vapor line heat exchanger requires a high flowrate.

8.) Turn the on the air flow to the fluidized sand bath. A pressure reading of 20 psi is required on the regulator located on the wall above the work bench to achieve a flowrate of 100 scfh on the rotameter located on the front control panel. A pneumatic safety switch prevents the operation of the fluidized sand bath without adequate air flow.

9.) Turn on the Keithley multimeter located on the front control panel. This should be on for at least one hour before it is used.

10.) Set the oven to the desired temperature. The oven controls are located below the window of the oven.

11.) Set the fluidized sand bath set point temperature with the Omega temperature controller located on the front

panel. The optimal condition, that can be achieved with this set point temperature, is to have the fluid leave the sand bath at a temperature 1 - 2°C below the desired operating temperature.

12.) Once both oven and fluidized sand bath temperatures are set, turn on their respective main power switches located on the righthand side as one faces the front panel.

13.) Partially close the micrometering valve on the liquid line. This will need to be done periodically to keep the fluid in the liquid phase.

14.) Allow the equipment to warm up to the desired temperature. This warm up should take anywhere from 2-4 hours depending upon your desired temperature. If taking longer check the flowrate and the water supply to the cooling coil to the fluidized bed. A low flowrate will lead to a low heat transfer. If the cooling coil is operating the system will never heat up.

15.) During the initial warm up, if a vapor level appears, close the micrometering valve on the liquid line, to increase the pressure in the cell. Do this until the vapor level disappears.

16.) While the equipment is warming up, adjust the Hiese gauge that will be used to read 0 psi. Close the

valves to the other gauges that will not be used.

17.) Once the temperature of the fluid is approximately 5°C above the desired temperature, the liquid line micrometering valve should be opened until two phases can be detected in the equilibrium cell. Opening this valve reduces the pressure in the cell allowing the two phases to form. This also reduces the temperature in the cell due to the heat load of vaporization.

18.) When two phases are present fine adjustment of the liquid micrometering valve will establish a stable phase boundary.

19.) Once a stable phase boundary is established, the Bayley controller for the inline heater should be turned on. To do this, the 10 turn set point adjustment knob on the Bayley should be turned to zero. Turn on the main power switch located on the front of the controller. If the needle on the indicator gauge rapidly peaks to 100% (right) and then back to 0% (left) then the controller is working properly. Increase the setting on the set point adjustment knob until the controller starts to apply power to the heater as indicated by the indicator gauge. This controller should be used only for small inputs of heat to stabilize the temperature at the desired setting.

20.) After temperature control is established, turn on

the null indicator located on the front panel. Increase the nitrogen pressure on the nitrogen tank with the regulator to slightly above the estimated system pressure. Close the vent valve on the front panel and open the nitrogen inlet valves to slowly increase the nitrogen pressure until the Heise gauge reads the desired pressure for the system. If too much nitrogen is added the vent valve can be slowly opened to decrease the pressure until the Heise gauge reads the desired pressure. Fine adjustment of the Heise gauge readings can be accomplished by pushing in the black knob below the hand pump and then using the hand pump. If the null indicator is not at zero, small amounts of one of the pure components will need to be added to adjust the pressure to register on the indicator.

21.) When the pressure in the cell is close enough to the desired pressure that the needle on the null detector gauge begins to oscillate, final fine adjustments can be made by adjusting either the liquid line or vapor line micrometering valve. The valve to adjust will depend on the relative flowrates. It is desirable to keep both the liquid and vapor line flowrates approximately equal to aid in sampling. Remember two levels must always be present through this entire routine.

22.) While the pressure is being set, the Bayley

controller will need to be adjusted to maintain the temperature control.

23.) Equilibrium conditions will have to be controlled for 30 minutes. That is the temperature will have to be within ± 0.1 K, two phases must be maintained, and the desired pressure must be maintained to within the gauge accuracy.

24.) Once the equilibrium conditions have been maintained for the required time record the resistance reading on the Keithley multimeter (temperature) and the set pressure on the Heise gauge (remember the null indicator must read zero). Flush the vapor and liquid sample lines until approximately 15 mls are removed. Collect the samples into small vials. Once again check the resistance and the pressure.

25.) Then raise the temperature to the next isotherm and take a point at that temperature in the manner previously described. Once a point has been taken at all four isotherms at this particular composition pure components are added to the system to change the feed composition of the system. The method described is repeated until the ternary diagram is complete for each isotherm.

26.) When raising the temperature between points make sure to turn off the Bayley controller and return to step 14

and repeat the procedure.

27.) When changing the composition add two of the pure components to increase the composition of these components. Remove approximately the same amount from either the liquid or vapor stream depending on which stream has the highest concentration of the third component (the component that is being decreased). Be careful when adding or removing fluid from the system that you are within the two phase region at the desired temperature and pressure.

Shutdown Procedures

- 1.) Turn off the Bayley controller.
- 2.) Turn off the fluidized sand bath and the oven at their main power switches.
- 3.) Partially close the liquid line micrometering valve to increase the pressure in the cell causing the vapor phase to disappear.
- 4.) Open the oven door to enhance the cooling of the oven.
- 5.) Open the water valve to the cooling coil for the fluidized sand bath.
- 6.) Pull out the black knob beneath the hand pump and open the vent valve to discharge the nitrogen and return the Heise gauges to atmospheric conditions.
- 7.) Close the valve located on the nitrogen tank and

release all pressure in the lines by opening the regulator on the tank.

8.) Turn off the null indicator.

9.) Allow the pump to continue to run until the fluid and the fluidized bath temperatures are below the boiling point of the lowest boiling compound.

10.) Turn off the pump.

11.) Turn off all the main power switches located on the front panel.

12.) Turn off the water to the heat exchangers and close the water valve to the cooling coil for the fluidized bed.

13.) Close vents of the surge tank.

14.) If next scheduled day for running the equipment is two or more days away, shut off the air to the fluidized sand bath.

APPENDIX B
TABULATED PREDICTION RESULTS

Table 11

VLE Predictions for MC/Q/T
SRK EOS k_{ij}

T = 250°C P = 150.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.0000	0.1065	0.8935	0.0000	0.2063	0.7937
0.0769	0.0839	0.8392	0.0851	0.1809	0.7340
0.1608	0.0567	0.7825	0.1940	0.1365	0.6695
0.2084	0.0405	0.7511	0.2631	0.1037	0.6332
0.3244	0.0000	0.6756	0.4541	0.0000	0.5459

T = 250°C P = 200.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.0000	0.5192	0.4808	0.0000	0.6532	0.3468
0.0964	0.3908	0.5128	0.1200	0.5354	0.3446
0.2787	0.2113	0.5100	0.3380	0.3541	0.3079
0.4528	0.0838	0.4634	0.5725	0.1724	0.2551
0.5896	0.0026	0.4078	0.7859	0.0064	0.2077

T = 250°C P = 275.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.1624	0.8365	0.0011	0.2389	0.7605	0.0006
0.2579	0.6600	0.0821	0.3380	0.6235	0.0385
0.3410	0.5332	0.1258	0.4160	0.5294	0.0546

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.4169	0.4317	0.1514	0.4849	0.4535	0.0616
0.4829	0.3521	0.1650	0.5451	0.3913	0.0636
0.6471	0.1829	0.1700	0.7040	0.2382	0.0578
0.7792	0.0723	0.1485	0.8471	0.1071	0.0458
0.8801	0.0004	0.1195	0.9653	0.0006	0.0341

Table 12

VLE Predictions for MC/Q/T
SRK EOS A + B/T

T = 250 °C P = 150.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.0000	0.0880	0.9120	0.0000	0.1898	0.8102
0.0780	0.0716	0.8504	0.0832	0.1720	0.7448
0.1619	0.0502	0.7879	0.1908	0.1345	0.6747
0.2098	0.0368	0.7534	0.2604	0.1045	0.6351
0.3313	0.0000	0.6687	0.4631	0.0000	0.5369

T = 250 °C P = 200.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.0000	0.4704	0.5296	0.0000	0.6115	0.3885
0.0950	0.3587	0.5463	0.1118	0.5154	0.3728
0.2789	0.1956	0.5255	0.3289	0.3512	0.3199
0.4533	0.0791	0.4676	0.5673	0.1754	0.2573
0.5930	0.0026	0.4044	0.7895	0.0066	0.2039

T = 250 °C P = 275.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.1534	0.8455	0.0011	0.2310	0.7684	0.0006
0.2465	0.6650	0.0885	0.3259	0.6301	0.0440
0.3329	0.5309	0.1362	0.4054	0.5330	0.0616
0.4130	0.4240	0.1630	0.4770	0.4548	0.0682

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.4811	0.3430	0.1759	0.5385	0.3923	0.0692
0.6468	0.1765	0.1767	0.7000	0.2397	0.0603
0.7790	0.0700	0.1510	0.8453	0.1085	0.0462
0.8809	0.0004	0.1187	0.9661	0.0006	0.0333

Table 13

VLE Predictions for MC/Q/T
SRK EOS A - B/v

T = 250 °C P = 150.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.0000	0.1241	0.8759	0.0000	0.2260	0.7740
0.0765	0.0982	0.8253	0.0883	0.1910	0.7207
0.1602	0.0660	0.7738	0.1986	0.1372	0.6642
0.2068	0.0466	0.7466	0.2660	0.1004	0.6336
0.3123	0.0000	0.6877	0.4334	0.0000	0.5666

T = 250 °C P = 200.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.0000	0.5086	0.4914	0.0000	0.6561	0.3439
0.0984	0.3951	0.5065	0.1175	0.5506	0.3319
0.2840	0.2261	0.4899	0.3438	0.3638	0.2924
0.4592	0.0937	0.4471	0.5828	0.1702	0.2470
0.5915	0.0031	0.4054	0.7828	0.0062	0.2110

T = 250 °C P = 275.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.1526	0.8473	0.0001	0.2288	0.7711	0.0001
0.2576	0.6599	0.0825	0.3315	0.6311	0.0374
0.3474	0.5300	0.1226	0.4131	0.5363	0.0506
0.4264	0.4298	0.1438	0.4851	0.4595	0.0054

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.4920	0.3543	0.1537	0.5467	0.3970	0.0563
0.6535	0.1914	0.1551	0.7093	0.2398	0.0509
0.7840	0.0779	0.1381	0.8526	0.1055	0.0419
0.8818	0.0004	0.1178	0.9658	0.0006	0.0336

Table 14

VLE Predictions for MC/Q/T
SRK EOS A + B/vRT

T = 250 °C P = 150.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.0000	0.1183	0.8817	0.0000	0.2187	0.7813
0.0763	0.0922	0.8315	0.0871	0.1866	0.7263
0.1597	0.0614	0.7789	0.1965	0.1365	0.6670
0.2065	0.0433	0.7502	0.2645	0.1014	0.6341
0.3161	0.0000	0.6839	0.4418	0.0000	0.5582

T = 250 °C P = 200.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.0000	0.5207	0.4793	0.0000	0.6604	0.3396
0.0974	0.2960	0.5066	0.1208	0.5437	0.3355
0.2801	0.2187	0.5012	0.3422	0.3570	0.3008
0.4538	0.0880	0.4582	0.5768	0.1701	0.2531
0.5878	0.0029	0.4093	0.7824	0.0062	0.2114

T = 250 °C P = 275.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.1611	0.8388	0.0001	0.2371	0.7628	0.0001
0.2602	0.6590	0.0808	0.3379	0.6248	0.0373
0.3449	0.5323	0.1228	0.4168	0.5310	0.0522
0.4212	0.4321	0.1467	0.4864	0.4551	0.0585

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.4867	0.3541	0.1592	0.5469	0.3928	0.0603
0.6492	0.1872	0.1636	0.7066	0.2382	0.0552
0.7806	0.0748	0.1446	0.8492	0.1061	0.0447
0.8801	0.0004	0.1195	0.9650	0.0006	0.0344

Table 15

VLE Predictions for MC/Q/T
SRK EOS A+C's

T = 250°C P = 150.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.0000	0.1065	0.8935	0.0000	0.2095	0.7905
0.0814	0.1062	0.8124	0.0811	0.2024	0.7165
0.1738	0.0867	0.7395	0.2014	0.1594	0.6392
0.2266	0.0649	0.7085	0.2826	0.1150	0.6024
0.3202	0.0000	0.6798	0.4400	0.0000	0.5600

T = 250°C P = 200.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.0000	0.4604	0.5396	0.0000	0.6167	0.3833
0.1032	0.4004	0.4964	0.0964	0.5762	0.3274
0.3000	0.2608	0.4392	0.3432	0.4056	0.2512
0.4833	0.1125	0.4042	0.6208	0.1685	0.2107
0.6004	0.0042	0.3935	0.7921	0.0055	0.2024

T = 250°C P = 275.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.1291	0.8709	0.0000	0.2067	0.7933	0.0000
0.2537	0.6599	0.0864	0.3181	0.6474	0.0345
0.3526	0.5253	0.1221	0.4071	0.5504	0.0425
0.4340	0.4271	0.1389	0.4852	0.4704	0.0444

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.4982	0.3559	0.1459	0.5502	0.4057	0.0441
0.6565	0.1981	0.1454	0.7205	0.2393	0.0402
0.7857	0.0826	0.1317	0.8626	0.1019	0.0355
0.8838	0.0005	0.1157	0.9677	0.0006	0.0317

Table 16

VLE Predictions for MC/Q/T
YSRK EOS A+C's

T = 250°C P = 150.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.0000	0.0929	0.9071	0.0000	0.1749	0.8251
0.0842	0.1025	0.8133	0.0769	0.1882	0.7349
0.1767	0.0910	0.7323	0.1950	0.1608	0.6442
0.2324	0.0697	0.6979	0.2820	0.1170	0.6010
0.3213	0.0000	0.6787	0.4343	0.0000	0.5657

T = 250°C P = 200.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.0000	0.4063	0.5937	0.0000	0.5831	0.4169
0.1071	0.3700	0.5229	0.0899	0.5672	0.3429
0.3002	0.2590	0.4408	0.3347	0.4162	0.2491
0.4862	0.1142	0.3996	0.6279	0.1672	0.2049
0.5984	0.0045	0.3971	0.7915	0.0054	0.2031

T = 250°C P = 275.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.0728	0.9272	0.0000	0.1237	0.8763	0.0000
0.2385	0.6440	0.1175	0.2816	0.6713	0.0471
0.3492	0.5040	0.1468	0.3868	0.5633	0.0499
0.4337	0.4096	0.1567	0.4734	0.4782	0.0484

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.4970	0.3441	0.1589	0.5417	0.4119	0.0464
0.6542	0.1953	0.1505	0.7186	0.2410	0.0404
0.7839	0.0825	0.1336	0.8630	0.1014	0.0356
0.8833	0.0005	0.1162	0.9672	0.0005	0.0323

Table 17

VLE Predictions for MC/Q/T
SRK EOS k_{ij}

T = 275°C P = 250.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.0000	0.1181	0.8819	0.0000	0.2091	0.7909
0.0877	0.0859	0.8264	0.1017	0.1697	0.7286
0.1908	0.0460	0.7632	0.2407	0.1030	0.6563
0.3063	0.0006	0.6931	0.4227	0.0016	0.5757

T = 275°C P = 325.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.0000	0.5492	0.4508	0.0000	0.6620	0.3380
0.1025	0.3992	0.4983	0.1306	0.5211	0.3483
0.2905	0.2031	0.5064	0.3589	0.3205	0.3206
0.3437	0.1586	0.4977	0.4273	0.2652	0.3075
0.3868	0.1251	0.4881	0.4848	0.2195	0.2957
0.5695	0.0031	0.4274	0.7559	0.0065	0.2376

T = 275°C P = 425.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.1300	0.8690	0.0010	0.1955	0.8039	0.0006
0.2312	0.6639	0.1049	0.3078	0.6364	0.0558
0.3383	0.4942	0.1675	0.4142	0.5042	0.0816
0.4125	0.3942	0.1933	0.4857	0.4252	0.0891

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.4564	0.3402	0.2034	0.5285	0.3905	0.0910
0.6327	0.1549	0.2124	0.7109	0.2043	0.0848
0.8227	0.0004	0.1769	0.9366	0.0007	0.0627

Table 18

VLE Predictions for MC/Q/T
SRK EOS A + B/T

T = 275°C P = 250.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.0000	0.1104	0.8896	0.0000	0.2025	0.7979
0.0879	0.0816	0.8305	0.1005	0.1668	0.7327
0.1912	0.0446	0.7642	0.2397	0.1031	0.6572
0.3087	0.0006	0.6907	0.4258	0.0016	0.5726

T = 275°C P = 325.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.0000	0.5319	0.4681	0.0000	0.6465	0.3535
0.1017	0.3894	0.5089	0.1273	0.5148	0.3579
0.2907	0.1990	0.5103	0.3560	0.3199	0.3241
0.3439	0.1557	0.5004	0.4247	0.2656	0.3097
0.3870	0.1231	0.4899	0.4826	0.2203	0.2971
0.5709	0.0030	0.4261	0.7573	0.0066	0.2361

T = 275°C P = 425.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.1303	0.8683	0.0014	0.1958	0.8034	0.0008
0.2296	0.6645	0.1059	0.3052	0.6375	0.0573
0.3374	0.4933	0.1693	0.4116	0.5050	0.0834
0.4122	0.3927	0.1951	0.4836	0.4257	0.0907

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.4566	0.3384	0.2050	0.5267	0.3810	0.0923
0.6331	0.1540	0.2129	0.7101	0.2048	0.0851
0.8231	0.0005	0.1764	0.9371	0.0006	0.0623

Table 19

VLE Predictions for MC/Q/T
SRK EOS A - B/v

T = 275°C P = 250.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.0000	0.1334	0.8666	0.0000	0.2270	0.7730
0.0885	0.0980	0.8135	0.1050	0.1788	0.7162
0.1915	0.0522	0.7563	0.2446	0.1027	0.6527
0.2993	0.0006	0.7001	0.4095	0.0014	0.5891

T = 275°C P = 325.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.0000	0.5335	0.4665	0.0000	0.6587	0.3413
0.1052	0.4001	0.4947	0.1286	0.5333	0.3381
0.2970	0.2150	0.4880	0.3647	0.3296	0.3057
0.3509	0.1703	0.4788	0.4354	0.2709	0.2937
0.3944	0.1357	0.4699	0.4943	0.2222	0.2835
0.5739	0.0035	0.4226	0.7555	0.0062	0.2383

T = 275°C P = 425.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.1303	0.8683	0.0014	0.1958	0.8034	0.0008
0.2296	0.6645	0.1059	0.3052	0.6375	0.0573
0.3374	0.4933	0.1693	0.4116	0.5050	0.0834
0.4122	0.3927	0.1951	0.4836	0.4257	0.0907

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.4566	0.3384	0.2050	0.5267	0.3810	0.0923
0.6331	0.1540	0.2129	0.7101	0.2048	0.0851
0.8231	0.0005	0.1764	0.9371	0.0006	0.0623

Table 20

VLE Predictions for MC/Q/T
SRK EOS A - B/vRT

T = 275°C P = 250.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.0000	0.1264	0.8736	0.0000	0.2184	0.7816
0.0879	0.0916	0.8205	0.1033	0.1742	0.7225
0.1907	0.0486	0.7607	0.2425	0.1029	0.6546
0.3027	0.0006	0.6967	0.4170	0.0014	0.5816

T = 275°C P = 325.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.0000	0.5441	0.4559	0.0000	0.6624	0.3376
0.1034	0.3999	0.4967	0.1304	0.5262	0.3434
0.2923	0.2076	0.5001	0.3615	0.3235	0.3150
0.3496	0.1629	0.4915	0.4306	0.2668	0.3026
0.3887	0.1290	0.4823	0.4884	0.2200	0.2916
0.5700	0.0032	0.4268	0.7548	0.0064	0.2388

T = 275°C P = 425.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.1266	0.8733	0.0001	0.1919	0.8080	0.0001
0.2302	0.6641	0.1057	0.3050	0.6392	0.0558
0.3400	0.4930	0.1670	0.4132	0.5066	0.0802
0.4151	0.3936	0.1913	0.4859	0.4272	0.0869

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.4592	0.3403	0.2005	0.5293	0.3923	0.0884
0.6347	0.1572	0.2081	0.7129	0.2046	0.0825
0.8234	0.0005	0.1761	0.9367	0.0007	0.0626

Table 21

VLE Predictions for MC/Q/T
SRK EOS A+C's

T = 275°C P = 250.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.0000	0.1271	0.8729	0.0000	0.2209	0.7791
0.0942	0.1179	0.7879	0.1001	0.2006	0.6993
0.2114	0.0720	0.7166	0.2639	0.1162	0.6199
0.3009	0.0009	0.6982	0.4093	0.0011	0.5896

T = 275°C P = 325.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.0000	0.5148	0.4852	0.0000	0.6418	0.3582
0.1130	0.4268	0.4602	0.1159	0.5716	0.3125
0.3198	0.2531	0.4271	0.3819	0.3632	0.2549
0.3773	0.2025	0.4202	0.4659	0.2898	0.2443
0.4225	0.1616	0.4159	0.5338	0.2284	0.2378
0.5794	0.0045	0.4161	0.7617	0.0054	0.2329

T = 275°C P = 425.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.1117	0.8883	0.0000	0.1765	0.8235	0.0000
0.2395	0.6605	0.1000	0.3012	0.6531	0.0457
0.3595	0.4946	0.1459	0.4185	0.5231	0.0584
0.4360	0.4013	0.1627	0.4979	0.4409	0.0612

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.4794	0.3516	0.1690	0.5447	0.3935	0.0618
0.6486	0.1735	0.1779	0.7373	0.2019	0.0608
0.8280	0.0005	0.1715	0.9399	0.0006	0.0595

Table 22

VLE Predictions for MC/Q/T
YSRK EOS A+C's

T = 275°C P = 250.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.0000	0.1138	0.8862	0.0000	0.1920	0.8080
0.0954	0.1173	0.7873	0.0939	0.1947	0.7114
0.2181	0.0776	0.7043	0.2652	0.1197	0.6151
0.3033	0.0009	0.6958	0.4060	0.0011	0.5929

T = 275°C P = 325.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.0000	0.4611	0.5389	0.0000	0.6072	0.3928
0.1153	0.4019	0.4828	0.1082	0.5664	0.3254
0.3208	0.2541	0.4251	0.3772	0.3732	0.2496
0.3797	0.2047	0.4156	0.4669	0.2961	0.2370
0.4259	0.1636	0.4105	0.5392	0.2306	0.2302
0.5767	0.0048	0.4185	0.7613	0.0052	0.2335

T = 275°C P = 425.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.0651	0.9349	0.0000	0.1073	0.8927	0.0000
0.2223	0.6542	0.1235	0.2677	0.6756	0.0567
0.3536	0.4838	0.1626	0.4009	0.5355	0.0636
0.4327	0.3929	0.1744	0.4871	0.4492	0.0637

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.4768	0.3449	0.1783	0.5373	0.3996	0.0631
0.6458	0.1726	0.1816	0.7376	0.2020	0.0604
0.8232	0.0005	0.1763	0.9379	0.0006	0.0615

Table 23

VLE Predictions for MC/Q/T
SRK EOS k_{ij}

T = 300°C P = 400.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.0000	0.1445	0.8555	0.0000	0.2323	0.7677
0.0808	0.1053	0.8139	0.0957	0.1855	0.7188
0.2127	0.0429	0.7444	0.2741	0.0875	0.6384
0.3067	0.0000	0.6933	0.4196	0.0001	0.5803

T = 300°C P = 480.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.0000	0.4693	0.5307	0.0000	0.5782	0.4218
0.1007	0.3356	0.5637	0.1272	0.4482	0.4246
0.2428	0.1934	0.5638	0.3038	0.2962	0.4000
0.3396	0.1150	0.5454	0.4321	0.1946	0.3733
0.5096	0.0001	0.4903	0.6847	0.0002	0.3151

T = 300°C P = 650.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.1554	0.8446	0.0000	0.2239	0.7761	0.0000
0.2528	0.6453	0.1019	0.3299	0.6128	0.0573
0.3380	0.6128	0.0573	0.4153	0.5018	0.0829
0.4134	0.3981	0.1885	0.4893	0.4159	0.0948

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.5458	0.2380	0.2162	0.6229	0.2766	0.1005
0.6082	0.1725	0.2193	0.6895	0.2120	0.0985
0.8042	0.0000	0.1958	0.9208	0.0000	0.0792

Table 24

VLE Predictions for MC/Q/T
SRK EOS A + B/T

T = 300°C P = 400.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.0000	0.1503	0.8497	0.0000	0.2376	0.7624
0.0809	0.1090	0.8101	0.0964	0.1883	0.7153
0.2128	0.0439	0.7433	0.2750	0.0875	0.6375
0.3054	0.0001	0.6945	0.4180	0.0001	0.5819

T = 300°C P = 480.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.0000	0.4798	0.5202	0.0000	0.5879	0.4121
0.1018	0.3425	0.5557	0.1293	0.4532	0.4175
0.2438	0.1975	0.5587	0.3063	0.2978	0.3959
0.3404	0.1171	0.5425	0.4343	0.1946	0.3711
0.5087	0.0001	0.4912	0.6837	0.0002	0.3161

T = 300°C P = 650.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.1616	0.8384	0.0000	0.2295	0.7705	0.0000
0.2593	0.6429	0.0978	0.3358	0.6097	0.0545
0.3433	0.5057	0.1510	0.4205	0.5002	0.0793
0.4173	0.4005	0.1822	0.4935	0.4153	0.0912
0.5481	0.2407	0.2112	0.6259	0.2761	0.0980

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.6097	0.1750	0.2153	0.6918	0.2116	0.0966
0.8039	0.0000	0.1961	0.9205	0.0000	0.0795

Table 25

VLE Predictions for MC/Q/T
SRK EOS A - B/v

T = 300°C P = 400.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.0000	0.1572	0.8428	0.0000	0.2484	0.7516
0.0822	0.1171	0.8007	0.0983	0.1963	0.7054
0.2157	0.0481	0.7362	0.2785	0.0882	0.6333
0.3052	0.0001	0.6947	0.4132	0.0001	0.5867

T = 300°C P = 480.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.0000	0.4559	0.5441	0.0000	0.5767	0.4233
0.1036	0.3383	0.5581	0.1265	0.4600	0.4135
0.2493	0.2038	0.5469	0.3090	0.3063	0.3847
0.3478	0.1241	0.5281	0.4409	0.1988	0.3603
0.5159	0.0000	0.4841	0.6858	0.0001	0.3141

T = 300°C P = 650.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.1424	0.8576	0.0000	0.2166	0.7884	0.0000
0.2493	0.6437	0.1070	0.3219	0.6191	0.0590
0.3411	0.5009	0.1580	0.4114	0.5080	0.0806
0.4202	0.3949	0.1849	0.4891	0.4216	0.0893
0.5535	0.2407	0.2058	0.6271	0.2805	0.0924

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.6157	0.1767	0.2076	0.6952	0.2143	0.0905
0.8009	0.0000	0.1907	0.9234	0.0000	0.0766

Table 26

VLE Predictions for MC/Q/T
SRK EOS A - B/vRT

T = 300°C P = 400.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.0000	0.1492	0.8505	0.0000	0.2385	0.7615
0.0813	0.1097	0.8090	0.0966	0.1899	0.7135
0.2141	0.0449	0.7410	0.2761	0.0883	0.6356
0.3073	0.0000	0.6927	0.4191	0.0001	0.5808

T = 300°C P = 480.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.0000	0.4614	0.5386	0.0000	0.5757	0.4243
0.1015	0.3346	0.5639	0.1267	0.4516	0.4217
0.2447	0.1961	0.5592	0.3053	0.2997	0.3950
0.3421	0.1177	0.5402	0.4349	0.1962	0.3689
0.5120	0.0001	0.4879	0.6858	0.0001	0.3141

T = 300°C P = 650.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.1499	0.8501	0.0000	0.2187	0.7813	0.0000
0.2499	0.6455	0.1046	0.3255	0.6158	0.0587
0.3376	0.5034	0.1590	0.4125	0.5043	0.0832
0.4147	0.3961	0.1892	0.4881	0.4179	0.0940
0.5478	0.2380	0.2142	0.6235	0.1781	0.0984

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.6102	0.1733	0.2165	0.6908	0.2130	0.0962
0.8059	0.0000	0.1941	0.9218	0.0000	0.0782

Table 27

VLE Predictions for MC/Q/T
SRK EOS A+C's

T = 300°C P = 400.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.0000	0.1647	0.8353	0.0000	0.2551	0.7449
0.0897	0.1468	0.7635	0.0972	0.2265	0.6763
0.2378	0.0647	0.6975	0.3064	0.0933	0.6003
0.3004	0.0001	0.6995	0.4058	0.0001	0.5941

T = 300°C P = 480.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.0000	0.4670	0.5330	0.0000	0.5842	0.4158
0.1126	0.3850	0.5024	0.1203	0.5104	0.3693
0.2778	0.2468	0.4754	0.3357	0.3408	0.3235
0.3803	0.1513	0.4684	0.4869	0.2045	0.3086
0.5158	0.0000	0.4842	0.6848	0.0001	0.3151

T = 300°C P = 650.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.1465	0.8544	0.0000	0.2119	0.7881	0.0000
0.2737	0.6344	0.0919	0.3380	0.6184	0.0436
0.3666	0.5033	0.1301	0.4308	0.5123	0.0569
0.4437	0.4046	0.1517	0.5115	0.4255	0.0630
0.5727	0.2537	0.1736	0.6548	0.2768	0.0684

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.6309	0.1896	0.1795	0.7220	0.2081	0.0699
0.8095	0.0000	0.1905	0.9240	0.0000	0.0760

Table 28

VLE Predictions for MC/Q/T
YSRK EOS A+C's

T = 300°C P = 400.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.0000	0.1523	0.8477	0.0000	0.2330	0.7670
0.0908	0.1483	0.7609	0.0917	0.2262	0.6821
0.2486	0.0693	0.6821	0.3159	0.0952	0.5889
0.3051	0.0001	0.6948	0.4067	0.0001	0.5932

T = 300°C P = 480.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.0000	0.4281	0.5719	0.0000	0.5568	0.4432
0.1128	0.3723	0.5149	0.1121	0.5112	0.3767
0.2818	0.2496	0.4686	0.3349	0.3509	0.3142
0.3891	0.1520	0.4589	0.4995	0.2034	0.2971
0.5150	0.0001	0.4849	0.6858	0.0001	0.3141

T = 300°C P = 650.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.1051	0.8949	0.0000	0.1566	0.8434	0.0000
0.2624	0.6292	0.1084	0.3151	0.6339	0.0510
0.3595	0.4991	0.1414	0.4150	0.5245	0.0605
0.4398	0.4008	0.1594	0.5023	0.4334	0.0643
0.5702	0.2525	0.1773	0.6532	0.2792	0.0676

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.6284	0.1892	0.1824	0.7228	0.2082	0.0690
0.8032	0.0001	0.1967	0.9216	0.0000	0.0784

Table 29

VLE Predictions for MC/Q/T
SRK EOS k_{ij}

T = 325°C P = 600.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.0009	0.1428	0.8563	0.0010	0.2173	0.7817
0.0748	0.1029	0.8223	0.0898	0.1689	0.7413
0.2004	0.0383	0.7613	0.2578	0.0715	0.6707
0.1999	0.0385	0.7616	0.2572	0.0718	0.6710
0.2784	0.0000	0.7216	0.3743	0.0000	0.6257

T = 325°C P = 725.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.0000	0.5286	0.4714	0.0000	0.6164	0.3835
0.0920	0.3830	0.5250	0.1187	0.4744	0.4069
0.2253	0.2278	0.5469	0.2829	0.3155	0.4016
0.3138	0.1452	0.5410	0.3961	0.2184	0.3855
0.3153	0.1439	0.5408	0.3981	0.2167	0.3852
0.3584	0.1079	0.5337	0.4557	0.1694	0.3749
0.5058	0.0000	0.4942	0.6685	0.0001	0.3314

T = 325°C P = 950.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.1692	0.8308	0.0000	0.2358	0.7642	0.0000
0.2598	0.6396	0.1006	0.3343	0.6049	0.0608

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.3516	0.4841	0.1643	0.4277	0.4788	0.0935
0.3899	0.4270	0.1831	0.4660	0.4321	0.1019
0.4915	0.2918	0.2167	0.5690	0.3169	0.1141
0.6013	0.1671	0.2316	0.6861	0.1983	0.1156
0.7812	0.0000	0.2188	0.8993	0.0000	0.1007

Table 30

VLE Predictions for MC/Q/T
SRK EOS A + B/T

T = 325°C P = 600.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.0000	0.1639	0.8361	0.0000	0.2372	0.7628
0.0754	0.1146	0.8100	0.0925	0.1783	0.7292
0.2004	0.0404	0.7592	0.2602	0.0710	0.6688
0.2000	0.0406	0.7594	0.2596	0.0714	0.6690
0.2738	0.0000	0.7262	0.3689	0.0000	0.6311

T = 325°C P = 725.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.0000	0.5642	0.4358	0.0000	0.6501	0.3499
0.0963	0.4038	0.4999	0.1267	0.4899	0.3834
0.2292	0.2390	0.5318	0.2919	0.3199	0.3882
0.3165	0.1517	0.5318	0.4034	0.2188	0.3778
0.3178	0.1505	0.5317	0.4051	0.2173	0.3776
0.3601	0.1125	0.5274	0.4613	0.1687	0.3700
0.5026	0.0000	0.4974	0.6649	0.0000	0.3351

T = 325°C P = 950.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.1813	0.8187	0.0000	0.2468	0.7532	0.0000
0.2734	0.6337	0.0929	0.3478	0.5976	0.0546

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.3629	0.4844	0.1527	0.4400	0.4747	0.0853
0.3998	0.4292	0.1710	0.4775	0.4288	0.0937
0.4978	0.2966	0.2056	0.5778	0.3148	0.1074
0.6041	0.1718	0.2241	0.6912	0.1972	0.1116
0.7799	0.0000	0.2201	0.8980	0.0000	0.1020

Table 31

VLE Predictions for MC/Q/T
SRK EOS A - B/v

T = 325°C P = 600.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.0000	0.1532	0.8468	0.0000	0.2309	0.7691
0.0768	0.1128	0.8104	0.0922	0.1789	0.7289
0.2053	0.0424	0.7523	0.2632	0.0728	0.6640
0.2048	0.0427	0.7525	0.2626	0.0732	0.6642
0.2809	0.0000	0.7191	0.3733	0.0000	0.6267

T = 325°C P = 725.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.0000	0.5066	0.4934	0.0000	0.6052	0.3948
0.0947	0.3792	0.5261	0.1173	0.4814	0.4013
0.2320	0.2350	0.5330	0.2865	0.3261	0.3874
0.3228	0.1534	0.5238	0.4038	0.2252	0.3710
0.3244	0.1520	0.5236	0.4059	0.2234	0.3707
0.3683	0.1152	0.5165	0.4648	0.1738	0.3614
0.5155	0.0000	0.4845	0.6734	0.0001	0.3265

T = 325°C P = 950.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.1537	0.8463	0.0000	0.2214	0.7786	0.0000
0.2536	0.6392	0.1072	0.3245	0.6117	0.0638

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.3532	0.4799	0.1669	0.4231	0.4849	0.0920
0.3935	0.4234	0.1831	0.4633	0.4382	0.0985
0.4984	0.2914	0.2102	0.5711	0.3219	0.1070
0.6092	0.1699	0.2209	0.6920	0.2007	0.1073
0.7882	0.0000	0.2118	0.9036	0.0000	0.0964

Table 32

VLE Predictions for MC/Q/T
SRK EOS A - B/vRT

T = 325°C P = 600.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.0001	0.1446	0.8553	0.0001	0.2205	0.7794
0.0757	0.1053	0.8190	0.0905	0.1720	0.7375
0.2031	0.0399	0.7570	0.2605	0.0730	0.6665
0.2027	0.0401	0.7572	0.2598	0.0734	0.6668
0.2823	0.0001	0.7176	0.3780	0.0000	0.6220

T = 325°C P = 725.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.0000	0.5132	0.4868	0.0000	0.6059	0.3941
0.0923	0.3771	0.5306	0.1171	0.4740	0.4089
0.2271	0.2279	0.5450	0.2829	0.3187	0.3984
0.3166	0.1468	0.5366	0.3978	0.2212	0.3810
0.3182	0.1455	0.5363	0.3999	0.2195	0.3806
0.3618	0.1096	0.5286	0.4582	0.1716	0.3702
0.5160	0.0000	0.4894	0.6723	0.0001	0.3276

T = 325°C P = 950.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.1616	0.8384	0.0000	0.2288	0.7712	0.0000
0.2545	0.6409	0.1046	0.3278	0.6089	0.0633

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.3496	0.4823	0.1681	0.4234	0.4815	0.0951
0.3889	0.4249	0.1862	0.4626	0.4347	0.1027
0.4925	0.2902	0.2173	0.5679	0.3189	0.1132
0.6034	0.1668	0.2298	0.6871	0.1995	0.1134
0.7840	0.0000	0.2160	0.9014	0.0000	0.0986

Table 33

VLE Predictions for MC/Q/T
SRK EOS A+C's

T = 325°C P = 600.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.0000	0.1763	0.8237	0.0000	0.2526	0.7474
0.0864	0.1496	0.7640	0.0968	0.2139	0.6893
0.2251	0.0545	0.7204	0.2904	0.0726	0.6370
0.2697	0.0000	0.7303	0.3592	0.0000	0.6408

T = 325°C P = 725.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.0000	0.5454	0.4546	0.0000	0.6375	0.3625
0.1106	0.4355	0.4539	0.1241	0.5359	0.3400
0.2598	0.2872	0.4530	0.3139	0.3680	0.3181
0.3585	0.1852	0.4563	0.4529	0.2352	0.3119
0.3585	0.1852	0.4563	0.4529	0.2352	0.3119
0.4025	0.1370	0.4605	0.5169	0.1705	0.3126
0.5107	0.0000	0.4893	0.6680	0.0000	0.3320

T = 325°C P = 950.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.1691	0.8309	0.0000	0.2319	0.7681	0.0000
0.2893	0.6251	0.0856	0.3529	0.6033	0.0438
0.3895	0.4809	0.1296	0.4560	0.4820	0.0620

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.4275	0.4301	0.1424	0.4965	0.4367	0.0668
0.5239	0.3081	0.1680	0.6029	0.3213	0.0758
0.6286	0.1833	0.1881	0.7237	0.1929	0.0834
0.7864	0.0000	0.2136	0.9026	0.0000	0.0974

Table 34

VLE Predictions for MC/Q/T
YSRK EOS A+C's

T = 325°C P = 600.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.0000	0.1657	0.8343	0.0000	0.2349	0.7651
0.0881	0.1539	0.7580	0.0924	0.2180	0.6896
0.2348	0.0624	0.7028	0.2975	0.0795	0.6230
0.2773	0.0000	0.7227	0.3634	0.0000	0.6366

T 325°C P = 725.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.0000	0.5062	0.4938	0.0000	0.6094	0.3906
0.1063	0.4286	0.4651	0.1116	0.5416	0.3468
0.2649	0.2900	0.4451	0.3143	0.3783	0.3074
0.3615	0.1941	0.4444	0.4547	0.2471	0.2982
0.3615	0.1941	0.4444	0.4547	0.2471	0.2982
0.4012	0.1506	0.4482	0.5146	0.1865	0.2989
0.5119	0.0000	0.4881	0.6712	0.0001	0.3287

T = 325°C P = 950.0 kPa

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.1371	0.8629	0.0000	0.1899	0.8101	0.0000
0.2794	0.6253	0.0953	0.3348	0.6170	0.0482
0.3864	0.4779	0.1357	0.4472	0.4896	0.0632

<u>X(MC)</u>	<u>X(T)</u>	<u>X(Q)</u>	<u>Y(MC)</u>	<u>Y(T)</u>	<u>Y(Q)</u>
0.4250	0.4282	0.1468	0.4894	0.4437	0.0669
0.5205	0.3104	0.1691	0.5984	0.3276	0.0740
0.6277	0.1834	0.1889	0.7261	0.1924	0.0815
0.7807	0.0000	0.2193	0.9005	0.0000	0.0995

APPENDIX C
COMPUTER PROGRAM

THIS FLASH PROGRAM USES THE SRK AND THE YSRK ALONG WITH FIVE MIXING RULES TO PREDICT TERNARY VLE DATA FOR THE m-CRESOL, QUINOLINE, TETRALIN TERNARY SYSTEM.

```
DIMENSION PCD(11),TCD(11),ZCD(11),WD(11),PARAD(11),
          NCOMP(3),PC(3),TC(3),ZC(3),W(3),WN(3),
          PARA(3),Z(3),X(3),Y(3),XN(3),YN(3),RP(3),
          AV(3,3),BV(3,3),PHIV(3),PHIL(3),AL(3,3),
          CL(3,3)
```

```
REAL K12,K12OLD,K(3),K13,K23,KP(3,3),NINC,INC
INTEGER SIGN
```

```
CHARACTER FILNAM*20,ANSWER*1,ANSW1*1,FILN1*20,AMR*1
```

```
PC(1) = 661.38*0.0068947      ! CRITICAL PRESSURE (MPA)
PC(2) = 837.6*0.0068947
PC(3) = 509.8*0.0068947
```

```
TC(1) = 705.8                ! CRITICAL TEMPERATURE (K)
TC(2) = 800.2
TC(3) = 719.2
```

```
W(1) = 0.452                 ! ACENTRIC FACTOR
W(2) = 0.316
W(3) = 0.327
```

C NON-POLAR HOMOMORPH ACENTRIC FACTOR

```
WN(1) = 0.326               ! (M-XYLENE)
WN(2) = 0.303               ! (TETRALIN)
WN(3) = 0.303               ! (TETRALIN)
```

```
RP(1) = 0.909               ! POLAR PARAMETER
RP(2) = 0.02679
RP(3) = 0.0
```

```
EY = 0.45                   ! CONSTANT FOR YSRK
```

```
30  WRITE (6,*) 'FOLLOWING EOS ARE AVAILABLE:  1-SRK'
     WRITE (6,*) '                               2-YSRK'
     WRITE (6,*) 'ENTER NUMBER OF EQUATION YOU WANT.'
     READ (5,*) NEQ
```

```

WRITE(6,*)
WRITE(6,*) 'HOW DO YOU WANT TO ENTER YOUR DATA?'
WRITE(6,*) '      1 - ENTER DATA VIA TERMINAL'
WRITE(6,*) '      2 - ENTER DATA FROM DATA FILE'
READ(5,*) ED

IF(ED.EQ.2) GOTO 600

IF(ED.EQ.1) THEN
700  WRITE(6,*)
      WRITE(6,*) 'LIQ MOLE FRAC OF M-CRESOL AND QUIN'
      READ(5,*) X(1),X(2)

      WRITE(6,*)
      WRITE(6,*) 'VAP MOLE FRAC OF M-CRESOL AND QUIN'
      READ(5,*) Y(1),Y(2)

      WRITE(6,*)
      WRITE(6,*) 'INPUT TEMP(K) AND PRESS(MPA)'
      READ(5,*) T,P

      GOTO 40
ENDIF

600  WRITE(6,*) 'INPUT NAME OF DATA FILE TO READ FROM'
      READ(5,58) FILN1
58   FORMAT(A20)

60   OPEN(UNIT=13, FILE=FILN1, STATUS='OLD')

      WRITE(6,*)
      WRITE(6,*) 'WHAT IS YOUR OUTPUT FILE?'
      READ(5,5) FILNAM
5   FORMAT(A20)

      OPEN(UNIT = 10,FILE = FILNAM,STATUS = 'NEW')

      READ(13,32) T,P ! READING TEMP(K) AND PRESS(MPA)
32  FORMAT(2D)

40  WRITE(6,*) 'CHOOSE MIXING RULE:  1 - K(IJ)'
      WRITE(6,*) '                        2 - A+B/T'
      WRITE(6,*) '                        3 - A-B/V'
      WRITE(6,*) '                        4 - A-B/VRT'
      WRITE(6,*) '                        5 - A+CS'
      READ(5,*) MR

```

```

IF(MR.LT.1.OR.MR.GT.5) GOTO 40

IF(MR.EQ.1)THEN
  DO 50 I = 1,3
    KP(I,I) = 0.0
50  CONTINUE

    KP(1,3) = 0.0383      ! INTERACTION PARAMETERS
    KP(3,1) = 0.0383

    KP(2,3) = -0.0152
    KP(3,2) = -0.0152

    KP(1,2) = -0.08
    KP(2,1) = -0.08
ENDIF

IF(MR.EQ.2)THEN
  DO 51 I=1,3
    KP(I,I)=0.0
51  CONTINUE

    KP(1,2)=-0.0558-13.652/T      ! INTER PARAMETERS
    KP(2,1)=-0.0558-13.652/T

    KP(1,3)=-0.0199+31.973/T
    KP(3,1)=-0.0199+31.973/T

    KP(2,3)=-0.1355+67.791/T
    KP(3,2)=-0.1355+67.791/T
ENDIF

IF(MR.EQ.3)THEN
  DO 52 I=1,3
    AV(I,I)=0.0
    BV(I,I)=0.0
52  CONTINUE

    AV(1,2)=-0.1389      ! A PARAM FOR A-B/V MIXING RULE
    AV(2,1)=-0.1389

    BV(1,2)=-18.516     ! B PARAM FOR A-B/V MIXING RULE
    BV(2,1)=-18.516

    AV(1,3)=0.0859
    AV(3,1)=0.0859

    BV(1,3)=18.475

```

```

        BV(3,1)=18.475

        AV(2,3)=0.0253
        AV(3,2)=0.0253

        BV(2,3)=14.657
        BV(3,2)=14.657
    ENDIF

    IF(MR.EQ.4)THEN
        DO 65 I=1,N
            AV(I,I)=0.0
            BV(I,I)=0.0
65      CONTINUE

        AV(1,2)=-0.0968          ! INTERACTION PARAMETERS
        AV(2,1)=-0.0968

        BV(1,2)=-24613426./(T*8314.41)
        BV(2,1)=-24613426./(T*8314.41)

        AV(1,3)=0.0536
        AV(3,1)=0.0536

        BV(1,3)=27259270./(T*8314.41)
        BV(3,1)=27259270./(T*8314.41)

        AV(2,3)=0.00313
        AV(3,2)=0.00313

        BV(2,3)=31083465./(T*8314.41)
        BV(3,2)=31083465./(T*8314.41)
    ENDIF

    IF(MR.EQ.5)THEN

        DO 67 I=1,3
            AL(I,I)=0.0
            CL(I,I)=0.0
67      CONTINUE

        IF(NEQ.EQ.1)THEN ! LEUDECKE INTER PARAM FOR SRK
            AL(1,2)=-0.0757
            AL(2,1)=-0.0757
            CL(1,2)= 0.00709
            CL(2,1)=-0.00216

            AL(1,3)=-0.0517

```

```
      AL(3,1)=-0.0517
      CL(1,3)=-0.0571
      CL(3,1)=-0.0529

      AL(2,3)=-0.1356
      AL(3,2)=-0.1356
      CL(2,3)=-0.0666
      CL(3,2)=-0.0718
ENDIF

IF(NEQ.EQ.2)THEN ! LEUDECKE INTER PARAM YSRK
      AL(1,2)=-0.1063
      AL(2,1)=-0.1063
      CL(1,2)=-0.0115
      CL(2,1)=-0.0117

      AL(1,3)=-0.0728
      AL(3,1)=-0.0728
      CL(1,3)=-0.0703
      CL(3,1)=-0.0637

      AL(2,3)=-0.1331
      AL(3,2)=-0.1331
      CL(2,3)=-0.0569
      CL(3,2)=-0.0708
ENDIF
ENDIF

197 IF(ED.EQ.2)THEN ! READ X1(MC),X2(Q),Y1(MC),Y2(Q)
59   READ(13,59) X(1),X(2),Y(1),Y(2)
      FORMAT(4D)
ENDIF

IF(X(1).LE.0.0000)THEN
      CLOSE(13)
      GOTO 195
ENDIF

X(3)=1.-X(1)-X(2)
Y(3)=1.-Y(1)-Y(2)

DO 1 I=1,3
      Z(I)=(X(I)+Y(I))/2.

IF(NEQ.EQ.1)THEN
      IF(MR.EQ.1.OR.MR.EQ.2)THEN
            CALL SRKKV(TC,PC,W,RP,EY,T,P,X,Y,3,NEQ,KP,K)
      ENDIF
```

```

IF(MR.EQ.3.OR.MR.EQ.4)THEN
  CALL VSRKKV(TC,PC,W,RP,EY,T,P,X,Y,3,NEQ,
  AV,BV,K)
ENDIF

```

```

IF(MR.EQ.5)THEN
  CALL LSRKKV(TC,PC,W,RP,EY,T,P,X,Y,3,NEQ,
  AL,CL,K)
ENDIF

```

```

ELSEIF(NEQ.EQ.2)THEN

```

```

  IF(MR.EQ.1.OR.MR.EQ.2)THEN
    CALL SRKKV(TC,PC,WN,RP,EY,T,P,X,Y,3,NEQ, KP, K)
  ENDIF

```

```

  IF(MR.EQ.3.OR.MR.EQ.4)THEN
    CALL VSRKKV(TC,PC,WN,RP,EY,T,P,X,Y,3,NEQ,
    AV,BV,K)
  ENDIF

```

```

  IF(MR.EQ.5)THEN
    CALL LSRKKV(TC,PC,WN,RP,EY,T,P,X,Y,3,NEQ,
    AL,CL,K)
  ENDIF

```

```

ENDIF

```

```

1      CONTINUE

```

```

70     L = 1
       M = 1
       V = 0.5
       FRACT = 0.1

```

```

80     G = 0.0
       DGDV = 0.0

```

```

DO 90 I = 1,3
  Q = (K(I) - 1.)/(V*(K(I) - 1.) + 1.)
  G = G + Q*Z(I)

```

```

C      WRITE (6,*) 'K(I),V,Q,Z(I)=',K(I),V,Q,Z(I)
       DGDV = DGDV + Q**2*Z(I)

```

```

C      WRITE (6,*) G,DGDV

```

```

90     CONTINUE

```

```

VNEW = V + G/DGDV

```

```

IF (ABS(VNEW - V) .GT. 0.0001) THEN
  V = (VNEW - V)*FRACT + V
  FRACT = (1. - FRACT)*0.3 + FRACT
  M = M + 1
  GO TO 80
ENDIF

VOLD = V
V = VNEW

C   WRITE (6,*)'Z, V, K=', Z, V, K

DO 100 I = 1, 3
  XN(I) = Z(I)/(V*(K(I) - 1.) + 1.)
  YN(I) = XN(I)*K(I)
100 CONTINUE

C   WRITE (6,*)'XN, YN=', XN, YN

IF (L .GT. 50) GO TO 180

CHECK = ABS(VOLD - VNEW)

DO 120 I = 1, 3
  CHECK = CHECK + ABS(X(I) - XN(I))
120 CONTINUE

EPS = 0.0001*(N + 1)

IF (CHECK .GT. EPS) THEN
  DO 130 I = 1, 3
    X(I) = XN(I)
    Y(I) = YN(I)
130 CONTINUE

  IF (NEQ .EQ. 1) THEN
    IF(MR.EQ.1.OR.MR.EQ.2)THEN
      CALL SRKKV(TC, PC, W, RP, EY, T, P, X, Y, 3, NEQ, KP, K)
    ENDIF

    IF(MR.EQ.3.OR.MR.EQ.4)THEN
      CALL VSRKKV(TC, PC, W, RP, EY, T, P, X, Y, 3, NEQ,
        AV, BV, K)
    ENDIF

    IF(MR.EQ.5)THEN
      CALL LSRKKV(TC, PC, W, RP, EY, T, P, X, Y, 3, NEQ,
        AL, CL, K)
    ENDIF
  ENDIF

```

```

        ENDIF

ELSEIF(NEQ.EQ.2)THEN

    IF(MR.EQ.1.OR.MR.EQ.2)THEN
        CALL SRKKV(TC,PC,WN,RP,EY,T,P,X,Y,3,
            NEQ,KP,K)
    ENDIF

    IF(MR.EQ.3.OR.MR.EQ.4)THEN
        CALL VSRKKV(TC,PC,WN,RP,EY,T,P,X,Y,3,NEQ,
            AV,BV,K)
    ENDIF

    IF(MR.EQ.5)THEN
        CALL LSRKKV(TC,PC,WN,RP,EY,T,P,X,Y,3,NEQ,
            AL,CL,K)
    ENDIF
ENDIF

L = L + 1
FRACT = 0.3
GO TO 80
ENDIF

WRITE (6,140)

IF (V .LT. 0.0) THEN
    WRITE (6,*) 'NO VAPORIZATION'
    WRITE(10,*) 'NO VAPORIZATION'
    GO TO 170
ENDIF

IF (V .GT. 1.0) THEN
    WRITE (6,*) 'COMPLETE VAPORIZATION'
    WRITE (10,*) 'COMPLETE VAPORIZATION'
    GO TO 170
ENDIF

140    FORMAT(1X,/)

IF(ED.EQ.1)THEN
    WRITE (6,*) 'LIQUID MOLE FRACTIONS'
    WRITE (6,150) (X(I), I = 1,3)

    WRITE (6,*) 'VAPOR MOLE FRACTIONS'
    WRITE (6,150) (Y(I), I = 1,3)
    WRITE (6,160) V

```

```

ENDIF

150   FORMAT (1X,F6.4,/)
160   FORMAT (1X,' THE FRACTION VAPORIZED IS: ',F6.4)

      IF(ED.EQ.2)THEN
          WRITE (10,166) X(2),X(1)
          WRITE (10,166) Y(2),Y(1)
      ENDIF

166   FORMAT (1X,F6.4,1X,F6.4)
170   CONTINUE
      GO TO 190

180   WRITE (6,*) 'NO CONVERGENCE'
190   CONTINUE

      IF(ED.EQ.1)THEN
          WRITE (6,*)
          WRITE(6,*) 'TRY ANOTHER POINT FROM TERMINAL?'
          WRITE(6,*)'                1 - YES'
          WRITE(6,*)'                2 - NO  '
          READ(5,*) NED

          IF(NED.EQ.1) GOTO 700
          IF(NED.EQ.2) GOTO 1000
      ENDIF

      IF(X(1).GT.0.0)GOTO 197  ! NEXT POINT IN DATA FILE

195   WRITE (6,*)
      WRITE(6,*) 'TRY DIFFERENT MIXING RULE? (Y/N)'
      READ(5,200) AMR

      IF(AMR.EQ.'Y') GOTO 60

      IF(AMR.NE.'N') THEN
          WRITE(6,*) '*****'
          GOTO 195
      ENDIF

      WRITE(6,*) 'READ FROM ANOTHER DATA FILE? (Y/N)'
      READ(5,200) ANSWER

```

```

200    FORMAT(A1)
      IF(ANSWER.EQ.'Y') GOTO 600

      IF (ANSWER .NE. 'N') THEN
        WRITE (6,*) '*****'
        WRITE (6,*) '*****'
        WRITE (6,*) '*****'
        WRITE (6,*) '*****'
        GO TO 195
      ENDIF

1000   END

      SUBROUTINE SRKKV(TC,PC,W,RP,EY,T,P,X,Y,N,NEQ,KP,K)
      DIMENSION TC(3),PC(3),W(3),X(3),Y(3),A(3),B(3),
                PHIV(3),RP(3)

      REAL KP(3,3),K(3),M

      R = 82.05*14.696*0.0068947

      IF(NEQ.EQ.1)THEN          ! SRK
        DO 10 I = 1, N
          M = 0.48 + 1.574*W(I) - 0.176*W(I)**2
          ALPHA = 1.0 + M*(1.0 - SQRT(T/TC(I)))

          A(I) = 0.42747*(TC(I)*ALPHA*R)**2/PC(I)
          B(I) = 0.08664*TC(I)*R/PC(I)
10      CONTINUE

      ELSEIF(NEQ.EQ.2)THEN      ! YESAVAGE MOD TO SRK

        DO 11 I=1,N
          M=0.480+1.574*W(I)-0.176*W(I)**2

          ALPHAN=1.0+M*(1-SQRT(T/TC(I)))
          ALPHAP=1+RP(I)*EXP(-RP(I)**EY)-
#           RP(I)*EXP(-((RP(I)*TC(I))/T)**EY)

          ATC=(0.42747*R**2*TC(I)**2)/PC(I)

          A(I)=ALPHAN**2*ALPHAP*ATC
          B(I)=0.08664*R*TC(I)/PC(I)

```

```

11      CONTINUE
      ENDIF

      AMIX = 0.0
      BMIX = 0.0

      DO 30 I = 1,N
        BMIX = BMIX + Y(I)*B(I)

        DO 20 J = 1,N
          AMIX = AMIX + Y(I)*Y(J)*SQRT(A(I)*A(J))*
            (1.0 - KP(I,J))
20      CONTINUE

30     CONTINUE

      CAPA = P*AMIX/(R*T)**2
      CAPB = P*BMIX/(R*T)

      D = -1.0
      E = CAPA - CAPB - CAPB**2
      F = -CAPA*CAPB

      ID = -1

      CALL VCUB(D,E,F, ID,Z)

C      WRITE (6,*) 'ZV= ',Z

      DO 50 I = 1,N
        Q = 0.0

        DO 40 J = 1,N
          Q = Q + 2.0*Y(J)*SQRT(A(I)*A(J))*
            (1.0 - KP(I,J))
40     CONTINUE

        Q1 = B(I)*(Z - 1.0)/BMIX - ALOG(Z - CAPB)
        Q2 = CAPA*(Q/AMIX - B(I)/BMIX)*ALOG(1. + CAPB/Z)
          /CAPB
        PHIV(I) = EXP(Q1 - Q2)
C      WRITE (6,*) 'PHIV', I, '= ', PHIV(I)

50    CONTINUE

      AMIX = 0.0
      BMIX = 0.0

```

```

DO 70 I = 1,N
  BMIX = BMIX + X(I)*B(I)

  DO 60 J = 1,N
    AMIX = AMIX + X(I)*X(J)*SQRT(A(I)*A(J))*
      (1.0 - KP(I,J))
60    CONTINUE

70    CONTINUE

CAPA = P*AMIX/(R*T)**2
CAPB = P*BMIX/(R*T)

D = -1.0
E = CAPA - CAPB - CAPB**2
F = -CAPA*CAPB

ID = 1

CALL VCUB(D,E,F, ID,Z)

C    WRITE (6,*) 'ZL = ',Z

DO 90 I = 1,N
  Q = 0.0

  DO 80 J = 1,N
    Q = Q + 2.0*X(J)*SQRT(A(I)*A(J))*
      (1.0 - KP(I,J))
80    CONTINUE

  Q1 = B(I)*(Z - 1.0)/BMIX - ALOG(Z - CAPB)
  Q2 = CAPA*(Q/AMIX - B(I)/BMIX)*ALOG(1.+CAPB/Z)
    /CAPB
  K(I) = EXP(Q1 - Q2)/PHIV(I)

90    CONTINUE

RETURN
END

SUBROUTINE VSRKKV(TC,PC,W,RP,EY,T,P,X,Y,N,NEQ,
  AV,BV,K)

DIMENSION TC(3),PC(3),W(3),X(3),Y(3),A(3),B(3),

```

```

          PHIV(3),RP(3),AV(3,3),BV(3,3),PHIL(3)
REAL KP(3,3),K(3),M
R=82.05*14.696*0.0068947
IF(NEQ.EQ.1)THEN          ! SRK
  DO 11 I=1,N
    M=0.48+1.574*W(I)-0.176*W(I)**2
    ALPHA=1.0+M*(1.0-SQRT(T/TC(I)))

    A(I)=0.42747*(TC(I)*ALPHA*R)**2/PC(I)
    B(I)=0.08664*TC(I)*R/PC(I)
11    CONTINUE

ELSEIF(NEQ.EQ.2)THEN      ! YESAVAGE MOD TO SRK
  DO 12 I=1,N
    M=0.480+1.574*W(I)-0.176*W(I)**2

    ALPHAN=1.0+M*(1.0-SQRT(T/TC(I)))
    ALPHAP=1.0+RP(I)*EXP(-RP(I)**EY)-
#      RP(I)*EXP(-((RP(I)*TC(I))/T)**EY)

    ATC=(0.42747*R**2*TC(I)**2)/PC(I)

    A(I)=ALPHAN**2*ALPHAP*ATC
    B(I)=0.08664*R*TC(I)/PC(I)
12    CONTINUE
  ENDIF

C FOR VAPOR PHASE

AMIX=0.0
BMIX=0.0

DO 15 I=1,N
  BMIX=BMIX+Y(I)*B(I)

  DO 17 J=1,N
    AMIX=AMIX+Y(I)*Y(J)*SQRT(A(I)*A(J))
17  CONTINUE

15  CONTINUE

CONV=P/(R*T)              ! CONVERSION FOR QUAD SOLVER
CV1=0.0                   ! CONSTANTS FOR QUAD SOLVER

```

```

CV2=0.0

DO 18 I=1,N

    DO 20 J=1,N
        CV1=CV1+(Y(I)*Y(J)*SQRT(A(I)*A(J))*(1.-AV(I,J)))
        CV2=CV2+(Y(I)*Y(J)*SQRT(A(I)*A(J))*BV(I,J))
20    CONTINUE

18    CONTINUE

QVA=-1.0
QVB=CONV*(-BMIX**2*CONV-BMIX+CV1*CONV/P)
QVC=CONV**3/P*(-BMIX*CV1+CV2)
QVD=-BMIX*CV2*CONV**4/P

ZB=BMIX*P/(R*T)

CALL QUAD(QVA,QVB,QVC,QVD,ROOT,1,ZB)

Z=ROOT
V=Z*R*T/P
C    WRITE(6,*) 'V,Z V =',V,Z
C    WRITE(6,*) 'KROOT=',KROOT

C    TERMS FOR FUGACITY EQN

DO 30 KK=1,N

    SUMV1=0.0
    SUMV2=0.0

    DO 33 I=1,N
        SUMV1=SUMV1+(Y(I)*SQRT(A(KK)*A(I))*
            (1.-AV(KK,I)))
        SUMV2=SUMV2+(Y(I)*SQRT(A(KK)*A(I))*BV(KK,I))
33    CONTINUE

    TERMV1=B(KK)/(V-BMIX)+ALOG(V/(V-BMIX))+CV1*B(KK)/
        (R*T)*(1./BMIX**2*ALOG((BMIX+V)/V)-
            1./(BMIX*(BMIX+V)))
    TERMV2=-2./(BMIX*R*T)*ALOG((BMIX+V)/V)*SUMV1+
        CV2*B(KK)/(R*T)*((BMIX+2.*V)/(BMIX**2*V*
            (BMIX+V))-2./BMIX**3*ALOG((BMIX+V)/V))
    TERMV3=-1./(R*T)*(2.*SUMV2+CV2)*(1./(BMIX*V)-
        1./BMIX**2*ALOG((BMIX+V)/V))

    PHIV(KK)=EXP(TERMV1+TERMV2+TERMV3-ALOG(Z))

```

30 CONTINUE

C NOW DO SAME THING FOR THE LIQUID

AMIX=0.0

BMIX=0.0

DO 40 I=1,N

BMIX=BMIX+X(I)*B(I)

DO 42 J=1,N

AMIX=AMIX+X(I)*X(J)*SQRT(A(I)*A(J))

42 CONTINUE

40 CONTINUE

CL1=0.0

CL2=0.0

DO 43 I=1,N

DO 44 J=1,N

CL1=CL1+(X(I)*X(J)*SQRT(A(I)*A(J))*(1.-AV(I,J)))

CL2=CL2+(X(I)*X(J)*SQRT(A(I)*A(J))*BV(I,J))

44 CONTINUE

43 CONTINUE

QLA=-1.0

QLB=CONV*(-BMIX**2*CONV-BMIX+CL1*CONV/P)

QLC=CONV**3/P*(-BMIX*CL1+CL2)

QLD=-BMIX*CL2*CONV**4/P

ZB=BMIX*P/(R*T)

C WRITE(6,*) 'Z B =',ZB

CALL QUAD(QLA,QLB,QLC,QLD,ROOT,0,ZB)

Z=ROOT

V=Z*R*T/P

C WRITE(6,*) 'V,ZL = ',V,Z

C WRITE(6,*) 'KROOT =',KROOT

C TERMS FOR FUGACITY EQN

DO 50 KK=1,N

SUML1=0.0

```

SUMML2=0.0

DO 53 I=1,N
  SUMML1=SUMML1+(X(I)*SQRT(A(KK)*A(I))*(1.-
    AV(KK,I)))
  SUMML2=SUMML2+(X(I)*SQRT(A(KK)*A(I))*BV(KK,I))
53 CONTINUE

TERML1=B(KK)/(V-BMIX)+ALOG(V/(V-BMIX))+CL1*B(KK)/
  (R*T)*(1./BMIX**2*ALOG((BMIX+V)/V)-
  1./(BMIX*(BMIX+V)))
TERML2=-2./(BMIX*R*T)*ALOG((BMIX+V)/V)*SUMML1+
  CL2*B(KK)/(R*T)*((BMIX+2.*V)/(BMIX**2*V*
  (BMIX+V))-2./BMIX**3*ALOG((BMIX+V)/V))
TERML3=-1./(R*T)*(2.*SUMML2+CL2)*(1./(BMIX*V)-
  1./BMIX**2*ALOG((BMIX+V)/V))

PHIL(KK)=EXP(TERML1+TERML2+TERML3-ALOG(Z))

K(KK)=PHIL(KK)/PHIV(KK)

50 CONTINUE

RETURN
END

SUBROUTINE LSRKKV(TC,PCL,W,RP,EY,T,PL,X,Y,N,NEQ,
  AL,CL,K)

DIMENSION TC(3),PC(3),W(3),X(3),Y(3),A(3),B(3),
  ATC(3),PHIV(3),PHIL(3),RP(3),AL(3,3),
  CL(3,3),PCL(3)

REAL KP(3,3),K(3),M

C CONVERTING PRESSURE TO KPA

DO I=1,N
  PC(I)=PCL(I)*1000.
ENDDO

P=PL*1000.

R=8314.41

IF(NEQ.EQ.1)THEN          ! SRK

```

```

DO 10 I=1,N
  M=0.48+1.574*W(I)-0.176*W(I)**2
  ALPHA=1.0+M*(1.0-SQRT(T/TC(I)))
  ATC(I)=(0.42747*R**2*TC(I)**2)/PC(I)

  A(I)=ATC(I)*ALPHA**2
  B(I)=0.08664*TC(I)*R/PC(I)
10  CONTINUE

ELSEIF(NEQ.EQ.2)THEN      !  YSRK

  DO 12 I=1,N
    M=0.48+1.574*W(I)-0.176*W(I)**2

    ALPHAN=1.0+M*(1.0-SQRT(T/TC(I)))
    ALPHAP=1.0+RP(I)*EXP(-RP(I)**EY)-
#      RP(I)*EXP(-((RP(I)*TC(I))/T)**EY)
    ATC(I)=(0.42747*R**2*TC(I)**2)/PC(I)

    A(I)=ALPHAN**2*ALPHAP*ATC(I)
    B(I)=0.08664*R*TC(I)/PC(I)
12  CONTINUE

  ENDIF

C  FOR VAPOR PHASE

  CL1=0.0
  CL2=0.0
  BMIX=0.0

  DO 15 I=1,N

    BMIX=BMIX+Y(I)*B(I)

    DO 17 J=1,N
      CL1=CL1+Y(I)*Y(J)*SQRT(A(I)*A(J))*(1.-AL(I,J))
      CL2=CL2+Y(I)*Y(J)*(Y(I)*CL(I,J)*ATC(I)**2+
#      Y(J)*CL(J,I)*ATC(J)**2)
17  CONTINUE

15  CONTINUE
  CL2=CL2/(8314.41*T)

  CONV=P/(R*T)

  QVA=-1.0      !  CONSTANTS FOR QUAD SOLVER

```

```

QVB=CONV*(-BMIX**2*CONV-BMIX+CL1*CONV/P)
QVC=CONV**3/P*(-BMIX*CL1+CL2)
QVD=-BMIX*CL2*CONV**4/P

```

```
ZB=BMIX*P/(R*T)
```

```
CALL QUAD(QVA,QVB,QVC,QVD,ROOT,1,ZB)
```

```
Z=ROOT
```

```
V=Z*R*T/P
```

```
C WRITE(6,*)'V,ZV = ',V,Z
```

```
C WRITE(6,*)'KROOT = ',KROOT
```

```
C TERMS FOR FUGACITY EQUATION
```

```
DO 20 KK=1,N
```

```
SUMV1=0.0
```

```
SUMV2=0.0
```

```
SUMV3=0.0
```

```
DO 25 I=1,N
```

```
SUMV1=SUMV1+Y(I)*SQRT(A(KK)*A(I))*(1.0-AL(KK,I))
```

```
SUMV2=SUMV2+Y(I)*CL(KK,I)*ATC(KK)**2
```

```
SUMV3=SUMV3+Y(I)**2*CL(I,KK)*ATC(I)**2
```

```
25
```

```
CONTINUE
```

```
TERMV1=B(KK)/(V-BMIX)+ALOG(V/(V-BMIX))+CL1*B(KK)/
(R*T)*(1./BMIX**2*ALOG((V+BMIX)/V)-
1./(BMIX*(BMIX+V)))
```

```
TERMV2=-2./(R*T*BMIX)*SUMV1*ALOG((V+BMIX)/V)+
CL2*B(KK)/(R*T)*((BMIX+2.*V)/(BMIX**2*V*
(BMIX+V))-2./BMIX**3*ALOG((BMIX+V)/V))
```

```
TERMV3=-1./(8314.41*T)**2*(4.0*Y(KK)*SUMV2+
2.0*SUMV3)*(1./(BMIX*V)-1./BMIX**2*
ALOG((BMIX+V)/V))-ALOG(Z)
```

```
PHIV(KK)=EXP(TERMV1+TERMV2+TERMV3)
```

```
20 CONTINUE
```

```
C NOW DO SAME THING FOR THE LIQUID
```

```
CL1=0.0
```

```
CL2=0.0
```

```
BMIX=0.0
```

```

DO 30 I=1,N
    BMIX=BMIX+X(I)*B(I)
    DO 32 J=1,N
        CL1=CL1+X(I)*X(J)*SQRT(A(I)*A(J))*(1.-AL(I,J))
        CL2=CL2+X(I)*X(J)*(X(I)*CL(I,J)*ATC(I)**2+
#           X(J)*CL(J,I)*ATC(J)**2)
32    CONTINUE
30    CONTINUE

CL2=CL2/(8314.41*T)
C    WRITE(6,*)'CL1,CL2, BMIX = ',CL1,CL2, BMIX

CONV=P/(R*T)

QLA=-1.0          ! CONSTANTS FOR QUAD SOLVER
QLB=CONV*(-BMIX**2*CONV-BMIX+CL1*CONV/P)
QLC=CONV**3/P*(-BMIX*CL1+CL2)
QLD=-BMIX*CL2*CONV**4/P

ZB=BMIX*P/(R*T)

CALL QUAD(QLA,QLB,QLC,QLD,ROOT,O,ZB)

Z=ROOT
V=Z*R*T/P
C    WRITE(6,*)'V,ZL = ',V,Z
C    WRITE(6,*)'KROOT = ',KROOT

C    TERMS FOR FUGACITY EQUATION

DO 40 KK=1,N
    SUML1=0.0
    SUML2=0.0
    SUML3=0.0

    DO 45 I=1,N
        SUML1=SUML1+X(I)*SQRT(A(KK)*A(I))*(1.0-AL(KK,I))
        SUML2=SUML2+X(I)*CL(KK,I)*ATC(KK)**2
        SUML3=SUML3+X(I)**2*CL(I,KK)*ATC(I)**2
C    WRITE(6,*)'CL(I,KK),CL(KK,I)=' ,CL(I,KK),CL(KK,I)
45    CONTINUE

TERML1=B(KK)/(V-BMIX)+ALOG(V/(V-BMIX))+CL1*B(KK)

```

$$\frac{1}{(R*T)} * \left(\frac{1}{BMIX^{**2}} * A \log\left(\frac{V+BMIX}{V}\right) - \frac{1}{BMIX * (BMIX+V)} \right)$$

$$TERML2 = -2. / (R*T*BMIX) * SUML1 * A \log\left(\frac{V+BMIX}{V}\right) + CL2 * B(KK) / (R*T) * \left(\frac{BMIX+2.*V}{BMIX^{**2}*V*(BMIX+V)} - 2. / BMIX^{**3} * A \log\left(\frac{BMIX+V}{V}\right) \right)$$

$$TERML3 = -1. / (8314.41 * T)^{**2} * (4.0 * X(KK) * SUML2 + 2.0 * SUML3) * \left(\frac{1}{BMIX*V} - \frac{1}{BMIX^{**2}} * A \log\left(\frac{BMIX+V}{V}\right) - A \log(Z) \right)$$

$$PHIL(KK) = \exp(TERML1 + TERML2 + TERML3)$$

$$K(KK) = PHIL(KK) / PHIV(KK)$$

40 CONTINUE

RETURN
END

SUBROUTINE VCUB(D,E,F, ID,Z)

C THIS SUBROUTINE CALCULATES THE REAL ROOTS OF A CUBIC
C EQUATION OF THE FORM $Z^{**3} + D*Z^{**2} + E*Z + F = 0$.

ABC = 1.0/3.0
G = (3.0*E - D*D)/3.0
H = -(9.0*D*E - 27.0*F - 2.0*D**3)/27.0
IF (G**3/27.0 + H*H/4.0 .LE. 0.0) GO TO 10

C ONLY ONE REAL ROOT EXISTS.

S = -H/2.0 + SQRT(G**3/27.0 + H*H/4.0)
TT = -H/2.0 - SQRT(G**3/27.0 + H*H/4.0)
IF (S) 5,6,6
5 S = -((-S)**ABC)
GO TO 7
6 S = S**ABC
7 IF (TT) 8,9,9
8 TT = -((-TT)**ABC)
GO TO 15
9 TT = (TT)**ABC

C Z IS THE VALUE OF THE SINGLE REAL ROOT.

15 Z = S + TT - D/3.0
GO TO 40

C THERE ARE THREE REAL ROOTS.

```

10   THETA = (ACOS(-0.5*H/SQRT(-G**3/27.0)))/3.0
      Z1 = 2.0*SQRT(-G/3.0)*COS(THETA)
      Z2 = 2.0*SQRT(-G/3.0)*COS(THETA + 2.0943951)
      Z3 = 2.0*SQRT(-G/3.0)*COS(THETA + 4.1887902)

```

C TAKE THE LARGEST ROOT FOR THE VAP COMPRESSIBILITY FACTOR

```

      IF (ID) 20,30,30
20   Z = AMAX1(Z1,Z2,Z3) - D/3.0
      GO TO 40

```

C TAKE THE SMALLEST ROOT FOR THE LIQ COMPRESSIBILITY FACTOR

```

30   Z = AMIN1(Z1,Z2,Z3) - D/3.0

```

```

40   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)/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))-
      P/DFLOAT(3)
      X2=DFLOAT(2)*RAD**(1./3.)*
      DCOS((THETA+DFLOAT(2)*PIE)/DFLOAT(3))-P/DFLOAT(3)

```

```

X3=DFLOAT(2)*RAD**(1./3.)*
  DCOS((THETA+DFLOAT(4)*PIE)/DFLOAT(3))-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

```

```

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)

C WRITE(6,*) 'QA,QB,QC,QD,KROOT = ',A,B,C,D,KROOT

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

```



```

                DD=A1+B1
                EE=A1-B1
                GO TO 99
            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
    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
C    WRITE(6,*) 'ROOTS = ',X(I)
    IF( ( X(I).LT.ZB ).AND.(KROOT.EQ.0) ) X(I)=99999999
100 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