HIGH TEMPERATURE HIGH PRESSURE THERMODYNAMIC MEASUREMENTS FOR COAL MODEL COMPOUNDS

**Final Technical Report
May 1, 2000**

**Vinayak N. Kabadi
Chemical Engineering Department
North Carolina A&T State University
Greensboro, North Carolina 27411**

Prepared for

**United States Department of Energy
Federal Energy Technology Center
Pittsburgh, Pennsylvania 15236**

Under Grant Number: DE-FG22-95PC95214--07

This report was prepared with the support of the U.S. Department of Energy, Grant Number DE-FG22-95PC95214. However, any opinions, findings, conclusions, or recommendations expressed herein are those of the author and do not necessarily reflect the views of DOE.

Two graduate students completed Masters thesis based on their research contributions to this project. Mr. Ahmad Al-Ghamdi measured the vapor-liquid equilibrium (VLE) data for benzene-ethylbenzene system, and did the preliminary work for the incremental enthalpy measurements for the benzene-ethylbenzene system using the Setaram C-80 calorimeter. Mr. Qingwen Zhao's numerous contributions are listed as: (1) completion of the tetralin-quinoline VLE data set, (2) measurement of the ethylbenzene-quinoline VLE data, (3) measurement of the incremental enthalpies of benzene-ethylbenzene system using Setaram C-80 calorimeter, (4) measurement of heat of mixing of benzene-ethylbenzene system at 25C, (5) design of an apparatus for simultaneous measurement of density and incremental enthalpy, (6) design of an apparatus for measurement of heat of mixing at high temperatures. Based on this work four manuscripts have been submitted for publication:

1. S. Mahmood, Q. Zhao, V. N. Kabadi, "High Temperature VLE Data Measurement for Tetralin-quinoline System", *J. Chem. Eng. Data*, in Review.
2. A. Al-Ghamdi, V. N. Kabadi, "High Temperature VLE Data Measurement for Benzene-Ethylbenzene System", *J. Chem. Eng. Data*, submitted.
3. Q. Zhao, V. N. Kabadi, "High Temperature VLE Data Measurement for Ethylbenzene-Quinoline System", *J. Chem. Eng. Data*, Submitted.
4. Q. Zhao, A. Al-Ghamdi, V. N. Kabadi, "Incremental Enthalpies of Benzene-Ethylbenzene Liquid Mixtures", *J. Chem. Thermodynamics*, Submitted.

Abstract

The flow VLE apparatus designed and built for a previous project was upgraded and recalibrated for data measurements for this project. The modifications include better and

more accurate sampling technique, addition of a digital recorder to monitor temperature and pressure inside the VLE cell, and a new technique for remote sensing of the liquid level in the cell. VLE data measurements for three binary systems, tetralin-quinoline, benzene – ethylbenzene and ethylbenzene –quinoline, have been completed. The temperature ranges of data measurements were 325C to 370C for the first system, 180 C to 300 C for the second system, and 225 C to 380 C for the third system. The smoothed data were found to be fairly well behaved when subjected to thermodynamic consistency tests.

SETARAM C-80 calorimeter was used for incremental enthalpy and heat capacity measurements for benzene – ethylbenzene binary liquid mixtures. Data were measured from 30 C to 285 C for liquid mixtures covering the entire composition range.

An apparatus has been designed for simultaneous measurement of excess volume and incremental enthalpy of liquid mixtures at temperatures from 30 C to 300 C. The apparatus has been tested and is ready for data measurements. A flow apparatus for measurement of heat of mixing of liquid mixtures at high temperatures has also been designed, and is currently being tested and calibrated.

Table of Contents

	Page
Abstract	3
Table of Contents	4

Project Objectives and Scope	5	
Technical Highlights and Milestones	6	
Vapor-Liquid Equilibrium Measurements at High Temperatures	7	
Introduction	7	
Experimental Apparatus	8	
Procedure	14	
Tetralin-Quinoline Data	14	
Benzene-Ethylbenzene Data	23	
Ethylbenzene-Quinoline Data	28	
References	40	
Incremental Enthalpy Measurements for Benzene-Ethylbenzene System	42	
Apparatus for Incremental Enthalpy Measurements		42
Apparatus for Heat of Mixing Measurements	46	
Setaram C-80 Calorimeter for Enthalpy Measurement	51	
References	79	

Project Objectives and Scope

The overall objective of this project is to develop a better thermodynamic model for predicting properties of high-boiling coal derived liquids, especially the phase equilibria of different fractions at elevated temperatures and pressures. The development of such a model requires data on vapor-liquid equilibria (VLE), enthalpy, and heat capacity which would be experimentally determined for binary systems of coal model compounds and compiled into a database. The data will be used to refine existing models such as UNIQUAC and UNIFAC.

Technical Highlights and Milestones

The detailed account of the progress on this project is divided into two parts. The first part (pages 7 thru 41) includes the experimental apparatus and the data for vapor-liquid equilibrium measurements for the three binary systems tetralin-quinoline, benzene-ethylbenzene, and ethylbenzene-quinoline. The second part (pages 42 thru 79) reports on the experimental apparatus and data for enthalpy measurements using Setaram C-80 calorimeter.

VAPOR-LIQUID EQUILIBRIUM MEASUREMENTS AT HIGH TEMPERATURES

Introduction

High temperature, high pressure thermodynamic data measurements available in the literature are quite limited. Such data are essential for development of thermodynamic models and correlations that are necessary for design of many chemical processes. A static method has been commonly used for the measurement of the vapor-liquid equilibria at high pressures and has allowed the collection of accurate data at low temperatures. In this type of VLE apparatus, the equilibrium cell is kept at constant temperature in a bath. It is filled by known amounts of compounds. Pressure and compositions of two phases at equilibrium are measured respectively by a pressure transducer and chemical analysis

equipment. Several VLE measurements using static cells are available in the literature. They differ by their sampling systems and their range of operation. The traditional static VLE measurements suffered from the drawback that the sampling process disturbed the equilibrium state especially for measurements at high pressures and/or high temperatures. To overcome this problem, a number of new sampling techniques have been recently devised.

The apparatus with micro expansion sampling system was proposed by Figuiere *et al.* (1980), and has been used by Laugier *et al.* (1980,1983) at pressures up to 40 Mpa and temperatures up to 623 K for studying mixtures containing hydrogen and hydrocarbons. Samples are directly injected in the carrier gas flow of a chemical analysis equipment (gas chromatograph) by very short time opening of micro valves. Legret *et al.* (1981,1982) used a similar sampling method in their VLE measurements at pressures as high as 100 Mpa. Samples were transferred from equilibrium cell into micro cells, each micro cell was taken off and attached to the port of a special chemical analysis equipment. Another modification of the micro valve sampling method called the capillary micro valve sampling system was designed by Guillevic *et al.* (1983,1985) especially for water-ammonia systems. Here, a micro bore capillary tubing separates the micro valve from the chromatographic injection port thereby allowing on-line sampling as well as precise control of equilibrium temperature and injection port temperature individually. A further modified version of this technique is given by Richon *et al.* (1991).

Meskel-Lesavre *et al.* (1981) and Rousseaux *et al.* (1983a,1983b) describe a static VLE apparatus that uses a variable volume VLE cell and requires no sampling. The compounds of the mixture are weighed and introduced separately into the equilibrium cell. The cell is brought to the equilibrium temperature inside a constant temperature fluid bath. The pressure versus volume curve is recorded and the break point displayed in the curve gives the equilibrium bubble point pressure and the saturated volume of the liquid mixture. A more recent and modified version of this apparatus for high pressure measurements has been presented by Richon *et al.* (1992). Because no sample analysis is carried out, this technique provides accurate data of P,T,X or P,T,Y type, but cannot provide composition data for both the coexisting phases at the same time. An excellent comprehensive review of static methods for VLE measurements has been done by Richon,1996.

In recent years, a number of high temperature VLE data sets have been measured using flow VLE method. In this type of apparatus, feed of desired composition is held in a feed tank and pumped continuously into the VLE cell. Temperature, pressure and liquid level in the VLE cell are monitored and controlled accurately. Vapor and liquid streams are continuously removed, sampled and returned to the feed tank. The main advantage of this method over the static method is that substantial amounts of vapor and liquid sample can be obtained for analysis without disturbing the equilibrium in the cell. Three flow VLE apparatuses of special note include those of Niesen *et al.* (1986), Hutchenson *et al.* (1990), and Inomata *et al.* (1986). The first two of these use a view cell to monitor the liquid level, whereas the last one uses a capacitance sensor to sense and control the liquid level. The flow apparatus designed and built in this work, uses a number of features of the above three apparatuses.

In what follows, we describe our flow VLE apparatus and the procedure for data measurement. Data are measured and reported for three binary systems, tetralin-quinoline, benzene-ethylbenzene, and ethylbenzene-quinoline. Some modifications in the apparatus were made from data set to data set, and are discussed. Results are also presented for successful application of thermodynamic consistency tests to the measured data.

Experimental Apparatus

The apparatus can be divided into four sections, i.e., feed section, equilibration section, sampling section, and lastly the control-panel section. The maximum design temperature and pressure for the system are 500C and 2000 psi, respectively. All parts and tubing, including the ones exposed to the high temperature zones, are made of stainless steel (type 316). The tubing used in the fabrication is mostly of 1/4 inch diameter. The fittings used are swagelok compression type, made of the same material SS-316. A schematic of the apparatus is shown in Figure 1 in which all the parts of the apparatus are clearly labeled. The pump is a Pulsafeeder positive displacement metering pump with a capacity of 2.4 gallons per minute and pressure rating from ambient to 3000 psi. The main and the pre-heater ovens are made by Applied Test Systems, Inc. The main oven has a temperature range of -25 C to +500 C, and the temperature is controlled to within 1 C by Honeywell's UDC 5000 digital controller. The heat exchangers on the vapor and liquid exit lines are fabricated in house by welding concentric tubing of larger diameter and circulating cold water through the jacket. The control panel for the apparatus consists of main and pre-heater oven controls, level and pressure chart recorder, controllers for the pressure and level control loops, one thermocouple switch and display, and pressure gages.

The critical part of the apparatus is the VLE cell a cross-section of which is shown in Figure 2. It is cylindrical and made of stainless steel 316 with an outside diameter of 6 inches and an overall height of 6 inches, the wall thickness is 1 inch. It is fitted with a threaded lid sealed by a vented inconel metal 'O' ring with silver coating made by Advanced Products Company. The inside dimensions of the cell are 4 inches diameter and 3 inches long with a total volume of 37.7 cubic inches or 590 cubic centimeters. Openings are provided for feed inlet, vapor and liquid outlet, thermocouple sensor, pressure sensor, and liquid level sensor. The liquid level sensor is Model LC 2300 conductivity probe made by Delta M Corporation. The probe is mounted on a 3 inch diameter flange which is bolted to the top of the VLE cell. It is also sealed using a metal 'O' ring made by Advanced Products Company.

The sensing element in the LC2000 Series level probes is a wire the electrical resistance of which is a function of temperature and thermal conductivity of the surrounding medium. Thermal conductivity of the liquid whose level is to be measured is generally significantly greater (as much as 100 times) than the vapor phase above it. Therefore an increment of resistance (ΔR) in the sensor wire is directly proportional to

the length not submerged in the liquid. With many level sensing techniques, a change in the process temperature will alter the operation of the device, requiring many calibrations over the desired range of temperatures. The LC2000 Series design avoids this problem by having two probes, a heated probe that is at a slightly higher temperature than an unheated reference probe that is maintained at the process temperature. The sensor signal is the difference in resistances of the two probes which is relatively temperature independent. After calibration, the 4-20 mA signal output of the level sensor corresponds to 0 to 100% liquid in the cell. The signal is then used to record and control the liquid level.

After the VLE measurements for the tetralin-quinoline system, the apparatus was modified by bringing the sampling points closer to the VLE cell. Also, one-way check valves were introduced in the liquid and the vapor outlet lines one foot downstream from the sampling points. The latter was done because we suspected the backflow of the liquid into the vapor line at lower pressures and at low vapor flow rates. At these conditions, the measured vapor compositions showed larger uncertainties.

For the high temperature measurements for ethylbenzene-quinoline system, we had problems calibrating the LC2000 liquid level sensor. The signal seemed to be a stronger function of both temperature and pressure at temperatures in excess of 350C. A new manual liquid level indicator was designed and employed for this binary system. The indicator consists of a spherical float about 1.5 cm diameter and made of high quality borosilicate glass. It is connected by a thin and rigid tungsten wire to an optical marker which is visible through the window of the Jerguson level gage mounted on top of the oven. A scale is attached to the view window to indicate the liquid level in the desired range. The liquid level is controlled manually by adjusting the valve on the liquid outlet line. The float assembly is shown in Figure 3. The entire VLE apparatus with the new liquid level indicator is shown in Figure 4.

Figure 1: VLE flow diagram with the following labeled parts: (1) feed tank, (2) pump, (3) preheat oven, (4) main oven, (5) equilibrium cell, (6) liquid level probe, (7) pressure controller, (8) liquid level controller, (9) chart recorder, (10) pressure transducer, (11,12) heat exchangers, (13,14,17) sampling bottles, (15) preheater temperature controller, (16) main oven temperature controller, (18,19) system drain ports, (20) system vent port, (22) feed funnel, (23,24) control valves, (p) pressure gages

Figure 2: Equilibrium cell with conductivity liquid level probe

1. Main oven	12. Level gage window
2. VLE cell	13. Shinning material
3. Jerguson level gage (insulated)	14. Plug valve
4. Thermocouple	15. Pressure sensing tube to transducer
5. Glass ball float	16. Vapor phase outlet (1/4" tubing)
6. Solid rod to hold the float from wandering	17. Feed inlet tubing (1/4")
7. Liquid phase outlet tubing	18. 1/2" NPT male connector
8. Oven opening	19. 1/4" tubing coils
9. Tungsten wire	20. Flange
10. 1/4" tubing	21. Top lid
11. Ruler	22. Swagelok tubing fitting

Figure 3. The VLE cell with the new glass float level indicator

1. Feed tank; 2. Pump; 3. Preheat oven; 4. Main oven; 5. Equilibrium cell; 6. Level gage; 7. Vapor line controller; 8. Liquid line controller; 9. Pressure recorder; 10. Pressure transducer; 11. Vapor line heat exchanger; 12. liquid line heat exchanger; 13. Vapor sampling tank; 14. Liquid sampling tank; 15. Preheat controller; 16. Main oven controller; 17. Feed sampling tank; 18. 19. System drain port; 20. System vent port; 21. Equilibrium cell vent port; 22. Feed funnel; 23. Vapor line controller; 24. Liquid line controller.

Figure 4: VLE apparatus with the new level indicator
Procedure

Feed from the feed tank (1) is filtered through two strainers of 60 and 230 microns respectively and is pumped, by a positive displacement metering pump (2), to the pre-heater oven (3). The liquid stream is heated while it passes through a coil shaped tubing in the pre-heater oven. The temperature of the liquid is raised to within 5 C of the desired experimental temperature. The feed then enters the second coil placed inside the main heater oven (4) where the temperature of the liquid stream is raised to the desired temperature before it enters the vapor-liquid equilibrium cell (5). The vapor and liquid flow rates out of the VLE cell are controlled by two control valves (23,24), placed in the respective lines. The two controllers (7,8) manipulate these valves to maintain a constant pressure and required liquid level in the cell. The vapor and liquid from the cell are cooled by two jacketed heat exchangers (11,12), combined together and returned to the feed tank. Before the point where these streams are combined, each line is provided with a sampling port (13,14). The third sample point (17) is provided on the feed input line near the outlet of the pump. The samples of the feed, the vapor, and the liquid streams can be taken once the equilibrium conditions are established. The quantity of the samples removed, are easily controlled with the use of metering valves. Once the samples are collected, they are tested and analyzed by the liquid chromatographic methods. The pressure and liquid levels are controlled by two feedback control loops. The pressure of the VLE cell is measured by the Rosemount pressure transmitter, which sends a 4-20 mA signal to the controller which then manipulates the flow rate of the vapor out of the VLE cell through a Badger control valve placed in the vapor line. The liquid level inside the VLE cell is measured by the Delta-M LC2300 level sensor. The probe, after sensing the level, sends the signal to the controller which manipulates the control valve in the liquid outlet line to keep the level constant. For ethylbenzene-quinoline system, the only difference was that the liquid level was observed visually through the Jerguson view cell, and was controlled by manipulating valve 24 manually.

Tetralin-Quinoline Data

To test the newly designed and built flow VLE apparatus, we chose the tetralin-quinoline binary system. The goal was to measure one of the isotherms already available in the literature (Niesen and Yesavage, 1988b), and then go on to measure a couple of isotherms at higher temperatures. A quick review of literature for thermophysical properties of the two pure components showed that consistent sets of data for critical properties and vapor pressures are available for tetralin, but same is not true for quinoline, especially at high temperatures above 350 C. Discrepancies are observed in high temperature vapor pressures and critical pressure of quinoline. We, therefore decided to measure vapor pressure data of quinoline in the temperature range from 250C to 400C. This was done by the procedure described above, but only the liquid phase was circulated, and the vapor phase was held static. The vapor pressure data measured are shown in Table 1. Only high temperature vapor pressure data available in the literature are those of Glaser and Ruland, 1957 and Sebastian *et al.*, 1978. The former data set represents the most extensive data covering a temperature range from 237.7C to 462C. Our data agrees fairly

well with these two data sets with deviations of less than a percent. Discrepancies in quinoline vapor pressure representation comes from smoothed data extended to the critical temperature, and correlations that have been developed using these smoothed data. Two such data sets in the literature are found in API Monograph Series, 1979 and Engineering Sciences Data Unit, 1978. Two prominent correlations available are both based on the Cox equation, one by Chao *et al.*, 1983 and the other by Das *et al.*, 1993. Uniformly accepted value for critical temperature of quinoline is 782 K measured by Ambrose, 1963. A reliable measurement for critical pressure, however is not available. Two values are available: 46.6 bar given in API Monograph Series and tables of Reid *et al.*, 1987, and 48.6 bar extrapolated from their correlation by Das *et al.* In this work, using $T_c=782$ K and $P_c=46.6$ bar, and using the data sets of Steele *et al.*, 1988, Ruland and Glaser and the data of Table 1, we regressed the four parameters in the Wagner equation (see Reid *et al.*, 1987) given below

$$\ln(P_r^{\text{sat}}) = (A\tau + B\tau^{1.5} + C\tau^3 + D\tau^6) / T_r \quad (1)$$

Where $\tau = (1-T_r)$

Constants A,B,C,D were regressed as -6.98143, -0.0017808, -1.48936, and -4.73306. The regressed equation was found to agree very well with the data, with a maximum deviation of under 0.8%. The results of the three correlations and the experimental data are shown in Figure 5. The correlation predictions are shown as curves and the data are represented by symbols. The data from Engineering Sciences Data Unit and predictions of Chao *et al.* correlation are significantly lower than our data and those of Glaser and Ruland with deviations of as much as 18% at the highest measured temperature. On the other hand, the Cox equation of Das *et al.* agrees very well with our regressed Wagner equation at temperatures upto 470C. Deviations observed at higher temperatures are because of different values of critical pressures used in the two correlations. With the current status, the critical properties used here and the correlation based on Wagner equation provide as good a method for vapor pressure calculation for quinoline. A more reliable value for critical pressure is much desired.

For tetralin, on the other hand, consistent data sets for vapor pressure are available. Review and analysis of literature data are given by Niesen and Yesavage, 1988b, and smoothed data upto the critical temperature are listed in API Monograph Series, 1978. No extensive data set for vapor pressure of tetralin was measured.

Three isotherms were measured for the binary tetralin-quinoline system at 325C, 350C and 370C. The analysis of the sample obtained from the apparatus was carried out by the liquid chromatographic methods. Some details of the instrument and the method are listed below:

Instrument: Perkin-Elmer LC410 pump
 Detector: Perkin-Elmer UV Spectrophotometric detector kept at 254 nm.
 Column: Perkin-Elmer 3 cm x 3mm C-18 column
 Mobile Phase: 65% Acetonitrile, 35% Water

Flow Rate: 1.8 mL/min
Sample Concentration: One part sample to 2 parts solvent by volume
Sample Size: 6 microliters
Column Pressure: 1700 psi
Data Analysis: Millipore chromatographic software

With this method we were able to reproduce measurements on test samples to within 1% at all times.

The data are listed in Table 2 and PXY diagrams are shown in Figure 6. The Figure also shows PXY diagrams for the data of Niesen and Yesavage, 1988b. It is clear that our data agree very well with those of Niesen and Yesavage at 325C. 350C and 370C data provide previously not available isotherms for this system.

The VLE data were analyzed for thermodynamic consistency by first calculating activity coefficients, and then applying the Gibbs-Duhem equation in the form of area test (see, for, example, Prausnitz *et al.*, 1999). The activity coefficients were calculated using the following equation

$$\gamma_i = (y_i P \Phi_i) / (x_i P_i^{\text{sat}} \Phi_i^{\text{sat}} \text{Poynt}) \quad (2)$$

where,

γ_i is the activity coefficient of component i, P is total pressure,

P_i^{sat} is the vapor pressure of pure liquid i at T

Φ_i and Φ_i^{sat} are the fugacity coefficient of component i in the vapor phase and the fugacity coefficient of pure vapor of component i at equilibrium with liquid at T and P_i^{sat} respectively

Poynt is the Poynting correction factor for pure liquid i at T and between pressures P_i^{sat} and P

For calculations using equation 2, the following critical properties were used

Tetralin: $T_c = 719$ K, $P_c = 35.1$ bar, $\omega = 0.303$

Quinoline: $T_c = 782$ K, $P_c = 46.6$ bar, $\omega = 0.33$

Peng Robinson equation of state (Peng and Robinson, 1976) with $k_i=0$ was used for fugacity coefficients. The liquid molar volumes necessary for calculation of the Poynting correction factors were calculated using the HBT method (Hankinson and Thomson, 1979) for tetralin and using the modified Rackett equation of Spencer and Danner, 1972 for quinoline with $Z_{RA} = 0.2679$. Vapor pressures of the two components were calculated using Wagner equation (equation 1) with parameters for quinoline given above and the following parameters for tetralin: $A = -5.32759$, $B = -3.06718$, $C = 1.25547$, $D = -8.67456$ (Wang and Kabadi, 2000).

The calculated activity coefficients and the excess Gibbs free energies are shown in Table 2. The area test for thermodynamic consistency requires that the area under the curve $\ln(\gamma_2/\gamma_1)$ versus x_1 from $x_1=0$ to $x_1=1$ be zero. Figure 7 shows a plot of $\ln(\gamma_2/\gamma_1)$ versus

x_1 . Although it does not cover the entire range from $x_1=0$ to $x_1=1$, the curves cross the X-axis at around $x_1=0.5$, and if extrapolated would satisfy the area test within reasonable error limits. For more accurate application of thermodynamic consistency tests, more extensive data measurements would be necessary.

TABLE 1: Measured vapor pressure of quinoline

<u>Temperature C</u>	<u>Vapor pressure, bar</u>
250.2	1.358
260.0	1.689
269.8	2.053
275.0	2.196
280.0	2.425
289.9	2.938

300.0	3.454
310.0	4.120
320.0	4.850
325.0	5.213
329.6	5.564
340.1	6.628
350.6	7.750
360.2	8.828
369.9	10.029
380.0	11.494
390.1	13.082
400.0	14.892

TABLE 2: VLE data for Tetralin-Quinoline binary system

<u>Temp, C</u>	<u>Press, bar</u>	<u>X₁</u>	<u>Y₁</u>	<u>γ₁</u>	<u>γ₂</u>	<u>G^E/RT</u>
325.0	5.213	0.0	0.0			
	5.500	0.062	0.103	1.1423	1.0028	0.0109
	5.860	0.143	0.216	1.1015	1.0130	0.0249
	6.220	0.242	0.337	1.0677	1.0195	0.0305
	6.740	0.376	0.484	1.0504	1.0358	0.0405
	7.220	0.527	0.627	1.0302	1.0431	0.0356
	7.870	0.732	0.798	1.0119	1.0689	0.0265
	8.667	1.000	1.000			
350.0	7.597	0.0	0.0			
	7.940	0.057	0.086	1.0968	1.0057	0.0106
	8.410	0.140	0.197	1.0712	1.0159	0.0232
	8.900	0.243	0.320	1.0483	1.0234	0.0290

	9.630	0.400	0.490	1.0363	1.0314	0.0328
	10.200	0.525	0.611	1.0281	1.0395	0.0330
	10.920	0.700	0.763	1.0123	1.0566	0.0251
	12.128	1.000	1.000			
370.0	10.042	0.0	0.0			
	10.400	0.057	0.080	1.0635	1.0031	0.0065
	10.980	0.135	0.180	1.0526	1.0171	0.0216
	11.600	0.245	0.310	1.0403	1.0229	0.0268
	12.620	0.435	0.513	1.0299	1.0278	0.0283
	13.150	0.530	0.605	1.0258	1.0328	0.0287
	13.920	0.685	0.743	1.0129	1.0443	0.0225
	15.492	1.000	1.000

Figure 5: Experimental data and correlations for vapor pressure of quinoline (P in kPa and T in K). Symbols represent experimental data and curves represent correlations as follows: Δ - Glaser and Ruland, 1957; ∇ - this work; $\square$ - Sebastian *et al.*, 1978; $\circ$ - Niesen and Yesavage, 1988a; $\circ$ - Steele *et al.*, 1988; ——— Wagner equation of this work; - - - Cox equation of Das *et al.*, 1993; — · — Cox equation of Chao *et al.*, 1983.

Figure 6: VLE data for tetralin-quinoline system; ●, ▲, ■, ▼ data of Niesen and Yesavage, 1988b at 250 C, 275 C, 300 C, and 325 C; ▽, ○, ◇, our data at 325 C, 350 C, 370 C.

Figure 7: Area test for thermodynamic consistency, ●, ■, ▲ indicate 325C, 350C and 370C isotherms.

Benzene-Ethylbenzene Data:

Data were measured along four isotherms, 180C, 210C, 250C and 280C. The analysis of the samples (benzene, ethylbenzene mixtures) obtained from the Vapor-Liquid apparatus were carried out by the gas chromatographic method. The method specifically

designed for the benzene-ethylbenzene binary system is given below:

Instrument: Perkin-Elmer AutoSystem gas chromatograph
Injector: Programmed split-splitless (PSS), with narrow glass liner
Column: Supelco Beta-Dex 110, Fused silica capillary column, 30m, 0.25mm ID
Detector: Flame Ionization detector (FID)
Carrier Gas: Helium (inlet pressure 15psi)
Injection size: 0.1 microliter
Dilution solvent: Methanol
Injector temperature: 200 C
Column temperature: 50 C
Detector temperature: 260 C
Data analysis: Waters Maxima chromatographic software

The standard used for calibration was a solution of equal volumes of benzene and ethylbenzene. The solution was diluted by methanol solvent so that 0.1 microliter of the solution would contain approximately 100 nanograms of each of benzene and ethylbenzene, a limit as recommended by Supelco, the distributor of the GC column. The chromatogram for the standard and the data analysis are given in the appendix. Assuming a linear relation between the response and concentration, the concentration of benzene in an unknown solution would then be given by

$$\text{Vol \% benzene in unknown} = \text{RB} / (\text{RB} + k * \text{REB})$$

where RB and REB are responses of benzene and ethylbenzene in the unknown sample in microvolts-sec, and k is the ratio of the response factor of ethylbenzene to that of benzene corresponding to the standard solution (see the appendix). After a few calibration runs, the following values of k were determined for two different concentration ranges: 1.135 for mixtures with vol % benzene greater than 50%, and 1.168 for mixtures with vol % benzene less than 50%.

Pure benzene and pure ethylbenzene have been very well studied and thermophysical data such as vapor pressures, liquid and vapor densities and heat capacities are available in the literature. A good review of all the data available for benzene is given by Goodwin, 1988. For ethylbenzene, the vapor pressure data of Chirico *et al.*, 1997, Osborn and Scott, 1980, and Ambrose, 1987, covers the temperature range 306 K to the critical temperature. Using these data, constants in the Wagner equation (equation 1) have been regressed by Wang and Kabadi, 2000, and are given below:

Benzene: A=-6.95798, B=1.27757, C=-2.56466, D=-3.40352

Ethylbenzene: A=-7.28289, B=0.87944, C=-2.14624, D=-5.63893

Wagner equation with above constants represents the vapor pressure data for the two liquids with accuracy of better than 0.5%. No vapor pressure measurements for the two pure liquids were therefore carried out in this work.

Temperature, pressure, mole fraction of benzene in liquid (X_1) and mole fraction of benzene in vapor (Y_1) are given in Table 3. The P-X-Y diagram is shown in Figure 8. The area test for thermodynamic consistency was again applied, and activity coefficients were calculated using equation 2. The following critical properties were used

Benzene: $T_c = 562.16$ K, $P_c = 48.98$ bar, $\omega = 0.212$

Ethylbenzene: $T_c = 617.2$ K, $P_c = 36.1$ bar, $\omega = 0.302$

Peng Robinson equation of state (Peng and Robinson, 1976) with $k_{ij}=0$ was used for fugacity coefficients. The liquid molar volumes necessary for calculation of the Poynting correction factors were calculated using the modified Rackett equation of Spencer and Danner, 1972 with $Z_{RA} = 0.2698$ for benzene and 0.2600 for ethylbenzene. Vapor pressures of the two components were calculated using Wagner equation (equation 1) with the parameters given above.

The calculated activity coefficients and the excess Gibbs free energies are shown in Table 3. Figure 9 shows a plot of $\ln(\gamma_2/\gamma_1)$ versus x_1 . Although it does not cover the entire range from $x_1=0$ to $x_1=1$, the curves cross the X-axis at around $x_1=0.5$, and if extrapolated would satisfy the area test within reasonable error limits. Again, for more accurate application of thermodynamic consistency tests, more extensive data measurements would be necessary.

Table 3

Experimental VLE Data for Benzene (1) - Ethylbenzene (2) System

T(C)	P (bar)	X1	Y1	γ_1	γ_2	G^E/RT
180	3.452	0.0778	0.2200	1.0846	1.00	0.0063
	3.950	0.1411	0.3500	1.078	1.0081	0.0175
	5.702	0.3701	0.6437	1.0545	1.0307	0.0387
	7.750	0.6421	0.8366	1.0322	1.0620	0.0419

	8.817	0.7859	0.9095	1.0218	1.0825	0.0339
	9.082	0.8228	0.9265	1.0188	1.0853	0.0298
	9.857	0.9390	0.9760	1.0054	1.0912	0.0104
210	6.220	0.0919	0.2203	1.0643	1.0007	0.0064
	7.100	0.1711	0.3603	1.0506	1.0024	0.0104
	9.409	0.3737	0.6070	1.0320	1.0146	0.0208
	12.257	0.6110	0.7925	1.0224	1.0397	0.0287
	14.269	0.7803	0.8918	1.0130	1.0574	0.0223
	15.013	0.8446	0.9254	1.0086	1.0625	0.0167
	16.350	0.9517	0.9777	1.0062	1.0722	0.0092
250	11.353	0.0631	0.1312	1.0518	1.0021	0.0052
	13.400	0.1801	0.3233	1.0380	1.0026	0.0088
	16.856	0.3638	0.5418	1.0279	1.0134	0.0185
	21.274	0.5934	0.7388	1.0141	1.0256	0.0186
	25.160	0.7735	0.8620	1.0113	1.0441	0.0185
	26.366	0.8338	0.9002	1.0075	1.0466	0.0138
	28.758	0.9499	0.9705	1.0013	1.0545	0.0039
280	17.352	0.0637	0.1127	1.0375	1.00	0.0023
	19.200	0.1411	0.2308	1.0331	1.0036	0.0077
	24.700	0.3680	0.4995	1.0184	1.0102	0.0131
	31.459	0.6113	0.7145	1.0135	1.0204	0.0160
	37.200	0.7893	0.8467	1.0109	1.0329	0.0154
	39.000	0.8433	0.8855	1.0092	1.0359	0.0133
	42.337	0.9546	0.9666	1.0018	1.0404	0.0036

Figure 8: VLE data for benzene-ethylbenzene system; ●, ▲, ■, and ▼ Represent data for 180C, 210C, 250C, and 280C isotherms

Figure 9: Area test for thermodynamic consistency of benzene-ethylbenzene data; $\bullet$, $\blacktriangle$, $\blacksquare$, and $\blacktriangledown$ represent 180C, 210C, 250C, and 280C isotherms.

Ethylbenzene-Quinoline Data:

To analyze the vapor and liquid samples from the VLE apparatus liquid Chromatography was employed. The equipment and the method used for the data analysis are summarized below.

Instrument: Perkin-Elmer LC410 pump
Injector: Rheodyne Model 7125 Sample Injection Valve
Detector: Perkin-Elmer UV spectrophotometric detector kept at 254 nm
Column: Perkin-Elmer 3cmX3cm C-18 column
Mobile phase : 70% methanol, 30% water
Flow rate: 1.8 ml/min
Sample concentration: 5 microliter sample dissolved in 1 ml methanol
Sample size : 3 microliter
Operation pressure : 1900-2200 psia
Data analysis : Software Perkin-Elmer Turbochrom 4, Rev 4.1

The standard solutions used for calibration were made by weighing. The balance used for this purpose has a resolution of 0.0001g. Nine standard solutions over the entire concentration range (ethylbenzene 0-100%) were prepared. From the chromatogram for a standard with known molar ratio of ethylbenzene to quinoline, the corresponding ratio of the areas were obtained. A linear relationship between the molar ratios and the area ratios was assumed.

$$\frac{Me}{Mq} = K \frac{Ae}{Aq} \quad \text{.....(3)}$$

In the above equation, Me is the mole amount of ethylbenzene, Mq is the mole amount of quinoline, Ae is the peak area of the ethylbenzene, Aq is the peak area of quinoline, K is the proportionality or calibration constant. A plot of area ratios versus molar ratios indeed followed a linear relationship. K was obtained as the slope of this line as 11.585. Using this calibration constant, mole fraction of ethylbenzene in an unknown solution is then calculated from the following equation.

$$X_e = \frac{Me}{Me + Mq} = \frac{KAe}{KAe + Aq} = \frac{K \frac{Ae}{Aq}}{1 + K \frac{Ae}{Aq}} \quad \text{..... (4)}$$

During the actual analysis, every sample was run at least twice, the final area ratio was the average of all the individual runs. The overall error of this method is estimated as about 2%.

Seven isotherms were generated for this system; they are 225°C, 250°C, 280°C, 310°C, 340°C, 365°C, 380°C. The chemicals were all bought from Aldrich Chemical Company. Quinoline has a purity of over 98%, and the purity of the ethylbenzene is above

99.8%. Because quinoline is very easy to get contaminated at high temperature, great caution was taken during the whole measurement, and once the quinoline was found contaminated, all the chemicals in the system were drained out, fresh chemicals were introduced into the system to continue the runs.

The raw data were massaged by keeping T and X fixed and varying P and Y in a very narrow range around the experimentally measured values, so that a smooth representation of data is obtained over the entire isotherm. This is necessary if the data are expected to satisfy the thermodynamic consistency tests. Variations of Y and P within the range of possible experimental errors ($\pm 3\%$ for Y and $\pm 1\%$ for P) can cause a large effect on the results of the integrated or the point-by-point thermodynamic consistency tests. Data massaging of this type is quite time-consuming, and was performed for all the data, but especially for the 310 C and 340 C isotherms, for which data were measured over the entire range of concentrations. For the vapor pressure of pure ethylbenzene, and pure quinoline, data available in the literature were used as discussed in the previous sections.

Table 4 shows all the data measured, and Figures 10 and 11, represent the various isotherms in y-x and P-x-y diagrams respectively. Our apparatus cannot be operated at sub-atmospheric or close to atmospheric pressures. For this reason, for the 225°C isotherm, only four points in the ethylbenzene rich end were measured. 365°C and 380°C isotherms are also incomplete; this is because the critical temperature of ethylbenzene is 343°C and that of quinoline is 427°C. Above 343C, it is not possible to measure the isotherms over the entire concentration range.

Table 4. VLE data at for ethylbenzene-quinoline system

Temperature K	Pressure Pa	X _{ethylbenzene} (mol%)	Y _{ethylbenzene} (mol%)
498.25	394721.6	43.591	98.002
498.15	489000.0	60.056	98.805
498.25	575514.4	77.448	99.302
498.15	660510.1	93.955	99.611
498.15	682250.0	100.0	100.0

523.15	134875.0	0.0	0.0
523.15	192005.0	4.42	82.868
523.15	436003.2	29.996	95.303
523.15	591723.8	45.002	96.837
523.25	722013.0	59.403	97.100
523.25	852805.5	77.349	97.400
523.25	983091.9	94.235	98.500
523.15	1025400.0	100.0	100.0

553.15	243200.0	0.0	0.0
553.55	311302.6	2.18	26.362
553.55	484080.0	14.694	78.996
553.55	673600.0	28.750	85.800
553.05	925620.0	47.699	89.453
553.25	1120000.0	61.500	91.700
553.25	1314799.0	77.500	94.752
553.25	1560409.0	93.603	98.050
553.15	1695000.0	100.0	100.0

583.15	412750.0	0.0	0.0
583.25	489005.6	19.19	15.236
583.15	839763.0	17.073	54.483
583.15	1085360.0	30.285	67.634
583.55	1307506.0	42.839	75.299
583.25	1648495.0	61.532	82.759
583.35	1964306.0	78.233	89.070
583.15	2301589.0	95.354	97.044
583.15	2394782.0	100.0	100.0

Table 4: (Continued)

Temperature K	Pressure Pa	X _{ethylbenzene}	Y _{ethylbenzene}
613.15	655900.0	0.0	0.0
613.25	788122.4	3.402	17.856

613.15	1166550.0	17.564	48.282
613.25	1403450.0	27.744	59.584
613.15	1793009.0	44.000	71.375
613.25	2280410.0	62.257	80.226
613.15	2709882.0	77.582	86.800
613.15	3207578.0	93.732	95.075
613.15	3470751.0	100.0	100.0

638.15	944000.0	0.0	0.0
638.15	1016947.0	0.384	1.510
638.25	1131282.0	2.806	13.123
638.55	1506090.0	14.892	42.164
638.15	1894330.0	27.199	55.151
638.15	2479886.0	42.976	67.962
638.15	2796077.0	55.485	74.219

653.15	1148000	0.0	0.0
653.15	1224283	0.501	1.327
653.15	1415206	4.189	10.046
653.15	1772640	15.112	37.388
653.15	2269410	28.757	53.700
653.15	2888604	42.778	65.956

Figure 10. Ethylbenzene-Quinoline x-y diagram for all Isotherms

Figure 11: Ethylbenzene-Quinoline P-xy diagram for all the isotherms

Both the area and the point-to-point thermodynamic consistency tests (see Prausnitz *et al.*, 1999) were applied to the data. In the point to point test, one must have enough data points on one isotherm to regress a polynomial out of the $\ln g_1$ versus x_1 curve. Next, an overall criterion for acceptance or rejection of data set needs to be set based on the cumulative errors for all the data points summed together, as it is expected that singular data points are likely to exhibit varying deviations. The area test by its very nature involves cumulative errors for the data points within an isotherm. Also for better application of the area test, one would need the infinite dilution data on both ends which is quite difficult to obtain. In our case, we have only seven data points on each isotherm, also we do not have the infinite dilution data, so both the point to point and the area tests could not be performed very accurately. Nevertheless, as is usually done, we plot the $\ln g_1$ versus x_1 and the $\ln g_2$ versus x_1 curves in the point to point test and plot the $\ln \frac{g_1}{g_2}$ versus x_1 curve for the area test, then we just simply judge if the two tests are satisfied by visual observation. Table 5 gives the thermodynamic consistency test results for 310°C and 340°C isotherms. Figures 12 and 13 show the curves for the point to point tests. Figure 14 shows the area test.

From Figure 12 through Figure 14, we can notice that for both 310°C and 340°C isotherms, both the point to point and area thermodynamic consistency tests can be satisfied, Figure 15 illustrates the G^E data generated from the VLE data.

Table 5. Thermodynamic consistency test result for 310°C Isotherm

310C

$X_{\text{ethylbenzene}}$	g_1	g_2	$\ln \frac{g_1}{g_2}$	$\ln g_1$	$\ln g_2$	G^E (J/mol)
0.01919	2.3174	0.9997	0.84075	0.84045	-0.0003	76.776
0.1707	1.5207	1.0001	0.41907	0.41917	0.00001	347.31
0.3028	1.3199	1.0236	0.25423	0.27756	0.02333	486.32
0.4289	1.2023	1.0767	0.11034	0.18424	0.07390	588.13
0.6153	1.0859	1.2716	-0.1579	0.08241	0.24028	694.11
0.7823	1.0273	1.5495	-0.4110	0.02693	0.43793	564.58
0.9535	1.0019	2.0938	-0.7371	0.00190	0.73898	175.38

340C

$X_{\text{ethylbenzene}}$	g_1	g_2	$\ln \frac{g_1}{g_2}$	$\ln g_1$	$\ln g_2$	G^E (J/mol)
0.034	1.9587	0.9956	0.67669	0.67228	-0.0044	94.822
0.1757	1.4234	0.9992	0.35385	0.35305	-0.0008	312.85
0.2774	1.2842	1.015	0.23525	0.25014	0.01489	408.63
0.4400	1.1581	1.0787	0.07102	0.14678	0.07576	545.49
0.6226	1.0726	1.2357	-0.1416	0.07009	0.21164	629.71
0.7758	1.0221	1.4473	-0.3478	0.02186	0.3697	508.98
0.9373	0.9938	1.8829	-0.6390	-0.0062	0.63281	172.55

Figure 12: Thermodynamic point to point consistency test for 310°C isotherm

Figure 13: Thermodynamic point to point consistency test for the 340°C isotherm

Figure 14. Thermodynamic area consistency test for 310°C and 340°C isotherms

Figure 15: Excess Gibbs Free Energy of ethylbenzene-quinoline system at 310°C and 340°C

Literature Cited

- Ambrose, D. *Trans. Faraday Soc.* **1963**, 59, 1988
- Ambrose, D. *J. Chem. Thermodynamics* **1987**, 19, 1007
- API Monograph Series*; Tetralin; Refining Department; API Publication 705, **1978**.
- API Monograph Series*; Quinoline; Refining Department; API Publication 711, **1979**.
- Chao, J.; Lin, C.T.; Chung, T.H. *J. Phys. Chem. Ref. Data* **1983**, 12(4), 1033.
- Chirico, R.D.; Knipmeyer, S.E.; Nguyen, A.; Steele, W.V. *J. Chem. Eng. Data* **1997**, 42, 772.
- Das, A.; Frenkel, M.; Gadalla, N.A.M.; Kudchadker, S.; Marsh, K.N.; Rodgers, A.S.; Wilhoit, R.C. *J. Phys. Chem. Ref. Data* **1993**, 22(3), 659.
- Figuiere, P.; Hom, J.F.; Laugier, S.; Renon, H.; Richon, D.; zwarc, H. *AIChE J* **1980**, 26, 872.
- Flanigan, D.A.; Joyce, T.P.; Yesavage, V.F. *J. Chem. Thermodynamics* **1988**, 20, 169.
- Glaser, F.; Ruland, H. *Chem. Ing. Tech.* **1957**, 29, 772.
- Goodwin, R.D. *J. Phys. Chem. Ref. Data* **1988**, 17, 1541.
- Guilevic, J.L.; Richon, D.; Renon, H. *Ind. Eng. Chem. Fundam.* **1983**, 22, 495.
- Guilevic, J.L.; Richon, D.; Renon, H. *J. Chem. Eng. Data* **1985**, 30, 332.
- Hankinson, R.W.; Thomson, G.H. *AIChE J* **1979**, 25, 653.
- Hutchenson, K.W.; Roebbers, J.R.; Thies, M.C. *Fluid Phase Equilibria* **1990**, 60, 309-317.
- Inomata, H.; Tichiya, K.; Aria, K.; Saito, S. *J. Chem. Eng. Jap.* **1986**, 19(5), 386.
- Joyce, T.P.; Yesavage, V.F. *J. Chem. Thermodynamics*, **1991**, 23, 1001.
- Krevor, D.H.; Lam, F.W.; Prausnitz, J.M. *J. Chem. Eng. Data* **1986**, 31, 353.
- Lauret, A.; Richon, D.; Renon, H. *Inv. J. of Energy Research* **1994**, 18, 267.
- Laugier, S.; Richon, D.; Renon, H. *J. Chem. Eng. Data* **1980**, 25, 274.
- Laugier, S.; Richon, D.; Renon, H. *Fuel* **1983**, 62, 842.
- Legret, D.; Richon, D.; Renon, H. *AIChE J* **1981**, 27, 203.

- Legret, D.; Richon, D.; Renon, H. *J. Chem. Eng. Data* **1982**, 27, 165.
- Meskel-Lesavre; Richon, D.; Renon, H. *Ind. Eng. Chem. Fundam.* **1981**, 20, 284.
- Niesen, V.; Palavra, A.; Kidnay, A.J.; Yesavage, V.F. *Fluid Phase Equilibria* **1986**, 31, 283-298.
- Niesen, V.G.; Yesavage, V.F. *J. Chem. Eng. Data* **1988a**, 33, 138.
- Niesen, V.G.; Yesavage, V.F. *J. Chem. Eng. Data* **1988b**, 33, 253.
- Osborn, A.G.; Scott, D.W. *J. Chem. Thermodynamics* **1980**, 12, 429.
- Peng, D.Y.; Robinson, D.B. *Ind. Eng. Chem. Fundam.* **1976**, 15, 59.
- Prausnitz, J.M.; Lichtenthaler, R.N.; de Azevedo, E.G. *Molecular Thermodynamics of Fluid-Phase Equilibria*; Third Edition; Prentice-Hall, **1999**.
- Reid, R.C.; Prausnitz, J. M.; Poling, B.E. *The Properties of Gases and Liquids*; Fourth Edition; McGraw-Hill, **1987**.
- Richon, D. *Fluid Phase Equilibria* 116, 421-428, **1996**.
- Richon, D.; Laugier, S.; Renon, H. *J. Chem. Eng. Data* **1991**, 36, 104.
- Richon, D.; Laugier, S.; Renon, H. *J. Chem. Eng. Data* **1992**, 37, 264-268.
- Rousseaux, P.; Richon, D.; Renon, H. *Fluid Phase Equilibria* **1983a**, 11, 153.
- Rousseaux, P.; Richon, D.; Renon, H. *Fluid Phase Equilibria* **1983b**, 11, 169.
- Sebastian, H.M.; Simnick, J.J.; Lin, H.M.; Chao, K.C. *J. Chem. Eng. Data* **1978**, 23, 305.
- Spencer, C.F.; Danner, R.P. *J. Chem. Eng. Data* **1973**, 18, 230.
- Steele, W.V.; Archer, D.G.; Chirico, R.D.; Collier, W.B.; Hossenlopp, I.A.; Nguyen, A.; Smith, N.K.; Gammon, B.E. *J. Chem. Thermodynamics* **1988**, 20, 1233.
- Thies, M.C.; Daniel, W.E.; Todd, M.A. *J. Chem. Eng. Data* **1988**, 33, 134.
- Toscani, S.; Figuiere, P.; Szwarc, H. *J. Chem. Thermodynamics* **1989**, 21, 1263-1277.
- Wang, J.; Kabadi, V.N. *Fluid Phase Equilibria* Submitted.

INCREMENTAL ENTHALPY MEASUREMENTS FOR BENZENE – ETHYLBENZENE SYSTEM

The enthalpy of a fluid measured with respect to some reference temperature and pressure (enthalpy increment or C_p) is required for many engineering designs. Different techniques for determining enthalpy increments include direct measurement, integration of heat capacity as a function of temperature at constant pressure, and calculation from accurate density measurements as a function of temperature and pressure with ideal-gas enthalpies. Techniques have been developed for measurement of heat capacities using differential scanning calorimeters, but routine measurements with a precision better than 3% are rare⁽⁹⁾. For thermodynamic model development, excess enthalpies or enthalpies of mixing of binary and ternary systems are generally required. Although these data can be calculated from measured values of incremental enthalpies of mixtures and corresponding pure components, the method of calculation involves subtraction of large numbers, and it is impossible to obtain accurate results from relatively accurate incremental enthalpy data. Directly measured heats of mixing provide better data for model development. In what follows, we give a brief literature survey of experimental methods available for measurement of incremental enthalpies as well as heats of mixing.

APPARATUS FOR INCREMENTAL ENTHALPY MEASUREMENTS:

Mohr et al⁽⁸⁾ used a boil off calorimeter to measure the enthalpy increment of coal derived liquids. The mechanism of the boil off calorimeter is that the sample liquid is heated up to the desired temperature and pressurized to the desired pressure, then enters the calorimeter. The calorimeter contains the reference liquid whose boiling point is very low (such as Freon). Heat exchange occurs as the sample liquid enters the calorimeter. The temperature of the sample is brought down to the boiling point of the reference liquid, and at the same time, some amount of reference liquid evaporates and exits the calorimeter. The heat exchanged between the sample and the reference liquid is calculated from the amount of the reference liquid vaporized. Thus the enthalpy increment of the sample can be obtained. What is critical is that the calorimeter must have very good insulation with the ambient world. Figure 1 illustrates the structure of the calorimeter. Figure 2 shows the flow diagram of the set up. The sample is withdrawn from the surge tank, which is at normal temperatures and pressurized to the desired operating pressure in the diaphragm pump. The pressure surges generated by the pump are removed by the pressure damper. The sample is then brought to approximately the operating temperature in the preheater, and finally adjusted to the desired temperature with a small in-line heater. At this point, the temperature and the pressure of the sample are measured. The sample then passes through the calorimeter, cooling to the outlet temperature of approximately 291 K by heat transfer to the boiling reference fluid. At the exit, the temperature and the pressure are again measured. The sample pressure is then reduced to ambient with a back pressure regulator. The sample then goes back to the collection tube.

Figure 1: Flow calorimeter

The reference fluid is Freon-11, its boiling point is about 291K, thus all the heat transferred from the sample converts the reference fluid to vapor, which leaves the calorimeter and travels through a heated line to the main condenser where it is converted to subcooled liquid. This liquid then goes to a collection tube (if a measurement is being made) or to the reboiler. The purpose of the reboiler is to ensure that only saturated liquid is returned to the calorimeter. Vapors from the reboiler and the calorimeter itself are condensed in the secondary condenser and returned to the calorimeter as saturated liquid.

Figure 2: Process flow diagram

Boil off calorimeters are generally large, and the amount of fluid required for an individual measurement can be excessive. Further, the reference temperature cannot be readily varied to allow measurements on materials which are either solids or near their critical points at the usual reference temperature which is the boiling point temperature of the fluid⁽³⁾.

Castro-Gomez et al⁽²⁾ presented a flow enthalpy-increment calorimeter, as Figures 3 and 4 illustrate, designed to measure the enthalpy increment of fluid for up to 20 Mpa of pressure and a temperature between 170 K-700 K. In Figure 3, the energy was removed from the calorimeter at a constant rate by a current-regulated thermoelectric cooling device A. Before pumping fluid from the syringe pump B, the power removed by the cooling water was matched by the addition of electrical power from the heater C to maintain the temperature of the calorimetric vessel D constant to ± 0.002 K at the chosen reference temperature, 298.15 K. Upon flowing the fluid at a known rate and known inlet temperature, controlled by the conditioning block E, the power supplied to the heater C was changed to keep the calorimeter at a constant temperature. The enthalpy increment was determined from the values of the flow rate and the change in power. The connecting tube F, evacuated through J, was designed to reduce temperature gradients as far as possible in the region where the fluid enters the calorimeter cell. The pressure was maintained by a back pressure regulator G, and the mass flow rate was determined from the change in mass of the collection tank H. Further details of the apparatus are shown in Figure 4. A large variety of methods and procedures to measure the enthalpy increments of different kind of chemicals are available in the literature. Johnson et al⁽⁵⁾ describe a Freon-11 boil-off calorimeter which was designed to measure the enthalpy increment of fluid up to 700 K and 200 bar. Karlsruhe⁽⁶⁾ reports

another design of flow calorimeter for the measurement of isobaric enthalpy increment (150 bar and 600 K), which can produce very good results.

Legend:

A: Thermoelectric cooling device
C: Calorimeter heater
E: Conditioning block
G: Back-pressure regulator
I: Calorimeter thermostat

B: Syringe pump;
D: Calorimeter Vessel
F: Connecting tube
H: Collection tank
J: Vacuum connection

Figure 3: Schematic drawing of flow calorimeter

A: Inlet-temperature probe	B: Outer aluminum can	C: Copper conditioning block	D: Connecting tube
E: Outlet-temperature probe	F: Vacuum connection	H: Cooling module	I: Aluminum shield with heater and cooling coil
J: Connection to cooling unit	K: Fluid entrance	L: Heater connections	M: Connection to vacuum
N: Thermostat heater bath oil	O: Outer aluminum can	P: Matching heater	Q: R: Thermoelectric cooling devices
S: Stirrer	T: U: Thermostat cooler	W: Trim heater;	X: Fins for enhance heat exchange.

Figure 4: Detail of flow calorimeter

APPARATUS FOR HEAT OF MIXING MEASUREMENTS:

Excess enthalpy or heat of mixing measurements have long been of great interest in the thermodynamic treatment of liquid mixtures. Different kinds of apparatus were developed to tackle the measurement. Stokes⁽¹²⁾ presented a method called the mixture-displacement technique to measure the low temperature heats of mixing. Figure 5 illustrates the diagram of the apparatus. The mixing cell ,a, was first filled with liquid 1 through tube, b, all the way to the top of the cell, extra liquid being allowed to exit through i, thus the possible vapor phase is driven out of the cell. Then certain amount of mercury is filled in the cell through m. Close tube i and open

a: Brass mixing vessel, about 30cc;	b: Inlet tube, about 0.4 mm bore
c: Stirrers(6 s^{-1})	d: Thermistor in well
e: Silver cooling rod in well	f: Heater in well
g: Peltier cooling element	h: (teflon+ MoS_2) packed gland
i: Solution-exit tube	j: Valve control
k: Three way valve for flushing	m: Drain cock

Figure 5: Solution-displacement calorimeter vessel

valve m, pump the second liquid into the cell through valve k and tube b, mercury will be displaced by liquid 2. By this way, both liquid 1 and liquid 2 can be quantified by simply measuring the displacement of the mercury. During the experiment, liquid 1 in the mixing cell is brought to the equilibrium temperature first, liquid 2 passes through a 1.5 m coil to reach the desired temperature, then is injected in the cell in small pulse, with sufficient time separation to allow mixing. Constant temperature is maintained in the endothermic case, by running the immersed heater continuously and adjusting the interval between injection pulse so as to balance the electrical energy input. The small energy input due to stirring is balanced out by the Peltier cooler. This set-up produces good results, but is limited to measurements around room temperature.

In the last few years, there has been much interest in measuring heats of mixing at temperatures and pressures considerably above ambient. Ott et al⁽¹⁰⁾ presented a set-up,

which is called isothermal calorimeter, designed for conditions upto 475 K and 15 Mpa. Figure 6 shows the construction of their calorimeter. Inside of the calorimeter, a pulse heater, calibration heater, and mixing tube were wound and vacuum silver-braised to a 1.6X8.9 cm nickel-plated copper cylinder. The mixing tube was made of Hasteloy. The heaters were made with stainless-steel clad thermocouple wire insulated with MgO. Mixing occurred as the two liquids made contact and flowed through the coil of tubing wound around the cylinder. In operation, the cylinder was kept at the temperature of bath by adjusting the frequency of the pulsed heater to balance the cooling from the Peltier cooler. When energy was added or removed due to the mixing process, the frequency of the pulsed heater change to maintain the balance. Hence, the change in frequency was a measure of the enthalpy change. Electrical calibration was carried out by adding power to the calibration heater from a d.c. source. The electrical power was measured from the potential drop across the calibration heater and across a 100 Ω standard resistor in series with the heater.

Figure 7 displays the schematic diagram of the calorimeter assembly. Pure liquid 1 and liquid 2 were pumped separately to enter the calorimeter block, Murphy gauges were used to monitor the pressure and to prevent over-pressurizing the system. The pressure of the whole system was maintained by the back pressure regulator, which was in turn controlled by the nitrogen gas, pressure was measured by the transducer. Tronac 550 Controller was used to control the calorimeter, the Tronac 450 Controller was used as the power source for the calibration heater, the frequency to the pulsed heater was measured with the frequency meter and fed to the computer through the multiplexer. Temperature of the calorimeter was monitored by the quartz thermometer. The BCD outputs from the transducer, quartz thermometer, frequency meter, and the digital voltmeters were all fed to the computer to be processed. Additionally, Mathonat et al⁽⁷⁾ designed a mechanism to measure heat of mixing using Setaram C80 calorimeter, which is the same calorimeter as we have used in this study and will be described in detail in the next section.

Figure 6: Schematic diagram of the isothermal calorimeter.

Figure 7: Schematic diagram of the data collection, control and flow system of the isothermal calorimeter.

SETARAM C-80 CALORIMETER FOR ENTHALPY MEASUREMENT:

The calorimeter used in this work is the Setaram C80 calorimeter set up. The whole set up is shown in Figure 8.

Figure 8: C80 calorimeter and the data acquisition and processing system

The apparatus consists of 4 parts: the calorimeter where the signal comes from; the power module which provides steady power supply; the C32 controller which serves as an interface transforming the voltage signal into digital signal; the computer which records and processes the signal.

The C80 calorimeter is the core part of the whole system. Its internal structure is shown in Figure 9. The Setaram C80 differential heat-flux apparatus is based on the Calvet principle. Two identical wells (diameter 17mm, depth 128mm) for inserting the removable confinement cylinders with cells are located in a heated calorimetric block fixed inside a cylinder surrounded by insulating material. The heat evolved or absorbed during the process is transferred between the cell and the calorimetric block through the thermopiles surrounding the lower two third of both wells over a length of 80 mm. Thermopiles consist of 162 copper/constantan thermocouples connecting the outer surface of the well wall with the block. Due to fast transport of the heat through the thermocouples the difference in temperature between the cells and the block is negligible.

Figure 9: Internal structure of the C80 Calorimeter

The two thermopiles are connected differentially and the resulting signal is proportional to the difference in the heat exchange between the cells and the block. In C80 system the signal will enter the controller at first, the special program in the computer will process the signal, the computer displays results in the form of a temperature line and a heat flux line which represents the heat flux difference between the two wells. The cells used in the enthalpy measurement in this work is shown in Figure 10, the cells for sample side and the reference side were made all the same.

Figure 10: Cell used to measure enthalpy data

The C80 calorimeter is a very precision instrument for the enthalpy measurement. It has a resolution of 0.001°C for temperature and a resolution of 0.001mw for heat flux. Once it is setup like what figure 8 shows, it is ready for the measurement.

Figure 11: Typical temperature programming

At first, the two cells (sample cell and the reference cell) were introduced into the wells of the calorimeter. The cells might be of different kinds and they might hold different substance for different purposes of measurement. The next procedure is to manipulate the

software and set a proper program to run the designed experiment. Figure 11 illustrates a typical heating program.

In this program, the temperature of inside of the calorimeter starts at 30°C. Because of the symmetrical design of the calorimeter, both wells will keep the same temperature all the time. Then the temperature was designated by the program to rise at a rate of 0.5°C/min (ramp rate) to 50°C. Next part of the program (horizontal line) is called isothermal hold where the temperature is held constant at 50°C for a period of 1.5 to 2 hours. This period is necessary to allow the system to come back to equilibrium state of almost '0' heat flux recovering from the temperature and heat flux overshoots at the end of the ramp stage. The ramp can be designed from 0°C/min to whatever value the calorimeter can handle. But to reduce the overshoot value, it is better to maintain this value small. By integrating the resulting heat flux signal we can get the amount of heat used to heat the substance in the sample cell from 30°C to 50°C. The heat requirements from 50°C to 70°C, 70 to 90°C and 90 to 110°C are also obtained in the same way. If the heat rate is small enough, the actual temperature of the calorimeter will follow the program perfectly all the way to 150°C. In the final phase of the program, the temperature may not be able to drop at a rate of 5°C/min, this will not affect the results because we are not interested in this period. The temperature drop line only tells the calorimeter that the final temperature is 30°C. Al-Ghamdi⁽¹⁾ has discussed the details about how to set a temperature program and no further discussion is necessary here. Data processing necessary to obtain the final results will be discussed later.

Preliminary work and problems encountered:

For a long time, we were misled by the distributor of Setaram that the C80 calorimeter was designed to have double heating zones. We understood that the thermostat in the instrument extended to twice the length of the cells above the bottom of the wells. If the calorimeter were actually made this way, one would never need to bother with the heat loss anymore. With the above idea on his mind, Al-Ghamdi⁽¹⁾ built his set-up for the enthalpy measurement of benzene-ethylbenzene system as shown by Figure 12.

Figure 12: Previous setup for the enthalpy measurement

The pressure he chose was 750 psia, the piston in the diagram was used to separate the liquid and the gas phase, it had a viton o-ring and could move up and down in the cylinder. The program he used was just like the one in Figure 11 except that the temperature ranged from 30 C to 285°C. While the results were fine in the low temperature region he started to get noisy signals after 180 °C at which point he also noticed a considerable baseline shift of the heat flux signal. The problem got worse as the temperature increased. Figure 13 shows this situation. According to the design of this experiment, the baseline of the desired heat flux signal should always be around '0' when the temperature is constant. Figure 13 is, therefore, useless for obtaining incremental enthalpy data.

Figure 13: Heat flux signal of the calorimeter of the former work

In the process of seeking the possible reason, misled by the wrong information of the distributor, he eliminated the heat loss and the natural convection in the cell at first. Then he considered many other factors which might produce the noise and eliminated them one by one. At last he concluded that the noise was produced by the gas bubble in the liquid, then all the effort he made was to drive out the possible gas pocket in the liquid samples. He made a many modifications including changing the structure of the cell, add a piston to separate the gas and the liquid phase, designing new filling process to eliminate the bubbles. But after all these efforts, no evident improvement was observed.

Solution to problems and apparatus for incremental enthalpy measurements:

We contacted the Setaram technical service department in France and found out that there are no double heat zones at all. The problem became simple suddenly. Without another zone to prevent the heat loss from the sample cell, the heat loss might be significant by natural convection or conduction. After careful calculations, the heat conduction effect on the heat flux signal was judged negligible. We decided to turn the calorimeter upside down to eliminate the natural convection effect. Figure 14 shows how the natural heat convection affects the signal. Case A illustrates how the calorimeter worked before. At high temperature, the liquid sample inside the calorimeter is hot, whereas the liquid outside the calorimeter is cold, and the liquid is continuous. In the whole process, the liquid in the hot region which has a smaller density will rise, while in the cold zone, the liquid which has a larger density will drop. The whole effect will look like what Case A shows, with the liquid at the top dropping and the liquid at the bottom rising, the whole body of liquid sample in the sample cell keeps on moving. This causes a heat loss from the sample cell, thereby explaining the noise and the shift of the signal as seen in Figure 13. If the cell is turned upside down (as in case B of Figure 14), the lighter part of the liquid will be on the top and the heavier part will be at the bottom, thereby eliminating any natural convection effects. According to this mechanism we design the new setup for the enthalpy measurement. Figure 15 illustrates the new setup used for the incremental enthalpy measurements. The mercury in the buffer tank is used to separate the liquid sample and the gas phase, and the reference cell was left blank. The filling process is very important, as errors can still result if any air bubbles are trapped in the sample cell.

Figure 14: Effect of natural convection

The filling process is shown in Figure 16. The sample cell is filled at first with a long needle syringe. The cell is held upright as the needle is introduced all the way to the bottom of the cell, the piston is then pushed in very slowly all the time knocking the cell body until the liquid overflows. The syringe is pulled out slowly pushing the piston in at the same time to maintain the overflow until the whole syringe is pulled all the way out. The cell is then connected to the funnel assembly as shown in Figure 16.

The filling process is finished by the mechanism shown by the left part of the figure. The buffer tank was filled with sample liquid at first, then fill mercury through funnel 2 and v6 till the mercury reaches the level as shown in the figure, the overflow liquid at port 2 and port 3 is collected during this process.

Figure 15: Apparatus for the enthalpy measurement in this work

. Figure 16: Filling process

The final phase of the filling process involves filling of the upper horizontal tubing between valves v1 and v6. First, put liquid into funnel 1 keep v3 open all the time, open v2 and v1, let the liquid overflow at port 1, knock the tubing at the same time, close v1 and v2, open v4 and v5 to let the liquid overflow at port 2, close v4 and v5, repeat the process several times, then disconnect the funnels. The cell is connected to v2 with a $\frac{1}{4}$ "- $\frac{1}{8}$ " swagelok reducing union, this union allows the cell to turn 180° without leaking. After turning the cell upside down as the right side of Figure 16 shows, the filling process is completed. The pressure we used in this measurement is 750psia; the temperature program was just the same as the former work.

Figure 17: Heat flux signal of the calorimeter from this work

Pretty good signal was obtained by this setup. Figure 17 illustrates the signal while pure benzene was heated from 230°C to 250°C. Remarkable improvement in the signal is observed when Figures 13 and 17 are compared. We used this apparatus to measure the enthalpy and the Cp data of benzene-ethylbenzene system. The results will be given in a later section.

Apparatus for excess enthalpy measurement at 25°C:

As it is well known, the 0 enthalpy point for a system is arbitrary, one can designate a 0 enthalpy point for a system, then the enthalpies of the whole system are all referred to this point. If we have the heat of mixing data at a certain temperature for a system, also we have the enthalpy data relative to the same reference temperature, we should be able to calculate the heat of mixing data from the enthalpy data.

One of our goals has been to calculate the heat of mixing data from the incremental enthalpy data measured using the apparatus of Figure 15. We, therefore, devised a very simple method to measure the heat of mixing of benzene-ethylbenzene system at ambient temperature. Our procedure takes advantage of the symmetrical design of the calorimeter. First of all, we set the temperature of the calorimeter at 25°C, fill the sample cell with known amount of benzene and fill the corresponding amount of ethylbenzene into the reference cell (the ethylbenzene is used to balance the heat capacity of the sample cell and the reference cell, the heat capacities of both side should be about the same). The cells are introduced into the calorimeter. The syringes used in this work are gas tight syringes, they can hold the liquid in their body without leaking when they were set upright as Figure 18 shows. Their needles can reach the bottom of the cells. The syringes are weighed empty, and weighed again after being filled with equal volumes of ethylbenzene. They are introduced into the cells, and once the temperature and the heat flux signals are stable, ethylbenzene from the two syringes is released slowly and simultaneously into the two cells. We allow 5 hours for the mixing process to finish, although in general the heat signal is seen to level off in only thirty minutes. The syringes are pulled out from the cells and weighed again. The exact mass of ethylbenzene injected into the two cells are obtained from the differences in the weights. In the experiment, we injected ethylbenzene very slowly to avoid any temperature fluctuations, because if the temperature did vary too much during the process, the noise in the heat signal increased considerably, making it difficult to accurately integrate the signal and obtain reliable data. Figure 19 shows the typical signal obtained by this procedure, it can be noticed that the temperature fluctuations are limited to about 0.01°C. By integrating the signal of Figure 19, we can get the heat of mixing of the benzene in the sample cell and the ethylbenzene in the syringe at 25°C.

Figure 18: Apparatus for the heat of mixing measurement at 25°C

Figure 19: Heat flux signal for the heat of mixing measurement at 25°C

Data processing and analysis of calorimetric data:

At this point, it is very appropriate to discuss a very important part of all the calorimetric measurements –data processing. Special software named <Thermal Analysis Software> by Setaram was installed in the computer to handle the signals. As discussed earlier, the signal as Figure 17 reveals is actually a heat flux difference between the reference cell and the sample cell. If the sample cell and the reference cell were made absolutely identical, then this signal just shows the net effect of heating pure benzene from 230°C to 250°C. But in general, the two cells would not be identical. This means the signal displayed in Figure 17 not only represents the heat effect of heating pure benzene from 230°C to 250°C, but also the difference in the heats required to heat the two cells.

To get rid of this side effect, a blank run is made with both the sample and the reference cells kept empty during the heating process. The temperature program for the blank run is the same as the program that the actual experiment is going to use. Figure 20 shows the blank run we made by heating the two empty cells from 230°C to 250°C. Because the heat flux signal of the calorimeter always represents the difference between the heat requirement for the reference cell and the corresponding heat for the sample cell, if the two cells are identical, the heat flux signal should be always around 0. You can tell from the figure that these two cells are far from being identical. The software allows an operation named “subtract baseline”. Figure 21 show this operation. The bottom curve is the overall signal gotten by heating the sample cell with benzene inside and the blank reference cell (the same curve as figure 17 shows). After the “ subtract baseline” (signal in Figure 17 minus the signal in Figure 20), we got the top curve which is the net effect of heating the pure benzene. This curve is the desired curve.

By integrating the new signal, the total amount of heat to heat the liquid sample from 230°C to 250°C can be obtained. Figure 22 displays this operation. Pick up a point on the heat flux curve where the temperature is 230°C as the beginning point, then pick another point on the 250°C side as end point, select the straight line between these two points as baseline, the computer can integrate the area between the curve and the baseline and show the result.

Figure 20: Heat flux signal for the blank run

Figure 21: The baseline subtraction operation

Figure 22: Heat flux signal integration operation
Incremental Enthalpy data for Benzene-Ethylbenzene system:

Data were measured for pure benzene, pure ethylbenzene and mixtures of benzene and ethylbenzene of seven different compositions. The results are shown in Table 1.

Table 1: Raw data of the enthalpy measurement

Pure ethylbenzene		Xb=0.050055		Xb=0.20167		Xb=0.349986		Xb=0.500063	
T k	Q J	T k	Q J	T k	Q J	T k	Q J	T k	Q J
301.98	0.0	301.98	0.0	301.99	0.0	301.98	0.0	301.99	0.0
321.81	245.3974	321.81	243.0958	321.81	241.7475	321.82	243.1412	321.82	240.9078
341.61	247.7383	341.61	245.6387	341.62	243.8124	341.63	245.3911	341.65	242.5849
361.40	250.8266	361.41	248.8504	361.42	247.1646	361.43	248.6907	361.43	245.6715
381.20	252.1044	381.23	252.1926	381.23	251.4174	381.24	252.3017	381.24	248.6037
401.00	256.6374	401.03	255.1081	401.03	252.5382	401.03	254.0778	401.04	250.2513
420.80	258.9492	420.82	257.2570	420.85	255.1743	420.84	257.7214	420.86	252.8491
440.62	262.1056	440.65	260.0798	440.65	258.9243	440.66	259.3574	440.69	255.4599
460.44	262.6635	460.46	262.2820	460.47	260.8735	460.47	259.9492	460.51	256.4355
480.25	263.8636	480.27	262.5544	480.29	259.6864	480.29	259.4252	480.33	256.3292
500.08	262.9586	500.10	262.7717	500.11	260.9994	500.13	259.5852	500.16	254.3992
519.93	260.9145	519.93	260.1982	519.96	257.1215	519.96	256.8399	519.99	253.4883
539.79	261.4564	539.80	260.7296	539.81	256.8873	539.81	256.4301	539.84	252.8526
554.69	194.3236	554.70	192.9568	554.73	191.7487	554.71	190.3144	554.75	187.9164
Xb=0.650116		Xb=0.79999		Xb=0.949986		Pure benzene			
T k	Q J	T k	Q J	T k	Q J	T k	Q J		
301.99	0.0	301.98	0.0	301.97	0.0	301.98	0.0		
321.82	240.8348	321.82	241.7695	321.81	240.6084	321.81	241.9885		
341.62	242.0621	341.60	241.9520	341.61	240.9520	341.61	242.8282		
361.43	245.5785	361.40	244.8034	361.41	243.5960	361.40	243.5901		
381.21	247.9870	381.21	247.0763	381.21	246.0660	381.19	245.7067		
401.01	250.7745	400.99	248.1693	400.97	247.3457	401.01	248.4517		
420.81	251.7917	420.80	250.3463	420.76	248.7304	420.80	249.8598		
440.62	254.9682	440.61	252.5547	440.56	251.5243	440.64	252.1858		
460.41	255.6141	460.45	253.2919	460.37	250.5219	460.46	252.0853		
480.23	255.5213	480.26	253.4581	480.16	251.2803	480.27	251.5893		
500.04	255.2582	500.09	252.2679	499.99	251.2182	500.05	251.0693		
519.88	253.8461	519.92	251.5997	519.81	249.8832	519.88	250.2001		
539.73	253.7383	539.76	251.6721	539.69	254.0011	539.72	253.3194		
554.64	189.2173	554.67	189.8095	554.59	196.1525	554.64	199.5538		

In Table 1, Q indicates the amount of heat used to heat the liquid in the sample cell body from the temperature one row above it in the table to the temperature in the same horizontal line with it in the table. The volume of the cell body is 7.92 ml. To actually calculate the enthalpy and the heat capacity of the whole system, we need to know how much liquid is inside of the 7.92 ml volume at certain temperature. We use the benzene data in the table to illustrate the calculations. Suppose we just consider the liquid inside the 7.92 ml volume. At first, assume the enthalpy of this amount of benzene to be 0 at 302 K. As temperature increases, add Q to each corresponding enthalpy values (the enthalpy value at 321.81 K is 241.9885 J, at 341.61 K is 484.8167 J, at 361.40 K is 728.4048 J and so on). Then use a sixth order polynomial to regress the enthalpy values versus the

Densities of benzene and ethylbenzene necessary in the above calculations were obtained as follows. A nice compilation of pure benzene density data is given by Goodwin⁽⁴⁾. We regressed the data points from 300 K to 560K by a sixth order polynomial, then interpolated the density value at any desired temperature in the range. Alternatively, very accurate densities can also be calculated using the HBT equation⁽¹¹⁾ which includes a saturated volume model supplemented by the regressed parameters of the Tait equation to extend the density predictions to higher pressures. For ethylbenzene, no extensive experimental density data were found. Consequently, the latter approach was utilized. The vapor pressures necessary in the HBT density calculations were obtained using the Wagner equation⁽¹¹⁾.

Remember that we set the enthalpy to be 0 at 302 K at the beginning, so all the values we got from the above operation are relative to this point. One of our goals has been to calculate the excess enthalpy data from the incremental enthalpy values and the heat of mixing data we measured at 25°C. It is obvious that to take advantage of the heat of mixing data, we have to set the enthalpies of all compositions to be 0 at 298.15 K. In the actual calculation, we regressed the enthalpy data whose 0 value is at 302 K with sixth order polynomials, then extrapolated them to 298.15 K. Together with the heat of mixing data at 25°C, we were able to calculate the excess enthalpy data for this system. Table 2 gives the enthalpies of all compositions whose 0 point are at 298.15 K and 750 psia.

$$H = A + BT + CT^2 + DT^3 + ET^4 + FT^5 + GT^6$$

Table 2: Enthalpies of the Benzene-Ethylbenzene system

$\frac{X_b}{T \text{ K}}$	pure EB	0.050055	0.20167	0.349986	0.500063	0.650116	0.79999	0.949986	Pure Benzene
298.15	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
314.12	3072.5	2988.5	2841.6	2743.6	2588.9	2466.6	2351.4	2216.4	2194.7
					70				

326.75	5552.1	5411.4	5151.3	4965.7	4691.9	4470.0	4261.7	4020.1	3978.5
339.38	8079.7	7887.3	7512.6	7236.5	6841.0	6517.8	6212.0	5862.8	5797.9
352.01	10657.7	10416.5	9925.0	9559.5	9037.5	8612.1	8203.2	7745.8	7653.6
364.64	13289.4	13000.3	12388.3	11937.2	11282.1	10754.3	10236.7	9670.0	9546.6
377.27	15978.7	15641.4	14906.8	14370.7	13576.7	12945.3	12313.6	11637.7	11480.8
389.90	18728.0	18341.2	17480.4	16861.0	15922.4	15186.5	14435.7	13649.2	13458.4
402.53	21540.5	21102.8	20115.3	19408.6	18321.9	17479.3	16606.0	15707.7	15483.4
415.16	24417.8	23928.0	22812.4	22013.7	20776.8	19825.3	18826.7	17814.1	17558.5
427.79	27360.1	26817.6	25571.9	24676.7	23288.0	22225.8	21099.1	19970.8	19685.3
440.42	30368.1	29772.9	28397.7	27397.6	25857.9	24683.1	23427.2	22180.3	21867.5
453.05	33440.6	32792.8	31287.6	30176.6	28485.6	27198.1	25811.0	24442.0	24103.9
465.68	36575.5	35878.4	34240.5	33013.6	31172.7	29772.8	28254.2	26761.3	26395.8
478.31	39771.7	39028.3	37255.2	35909.5	33919.0	32408.6	30756.9	29137.4	28740.8
490.94	43027.7	42241.6	40330.3	38865.9	36726.4	35108.6	33322.8	31577.2	31148.4
503.57	46345.4	45518.8	43465.6	41885.4	39596.4	37877.2	35958.3	34089.9	33626.1
516.20	49726.2	48862.1	46663.3	44974.5	42536.8	40723.7	38674.6	36694.8	36195.4
528.83	53177.6	52273.8	49932.2	48144.2	45561.1	43665.3	41495.5	39427.3	38892.4
541.46	56712.4	55766.7	53295.7	51415.0	48701.2	46735.6	44467.2	42355.5	41806.3
554.60	60498.9	59499.3	56931.1	54964.1	52144.3	50130.9	47804.5	45735.0	45213.1

Table 3: Parameters of the sixth order polynomials for the enthalpy of B-EB system

Xb (mol)	A	B	C	D	E	F	G
0.0	101708.7	-2264.276	15.95251	-5.5329E-2	1.06981E-4	-1.0835E-7	4.5014E-11
0.050055	108366.6	-2227.650	14.97755	-4.9898E-2	9.32278E-5	-9.1620E-8	3.7075E-11
0.20167	280889.7	-4810.381	31.07460	-0.1030961	1.91248E-4	-1.8714E-7	7.5543E-11
0.349986	76289.39	-1778.291	12.69042	-4.4579E-2	8.79615E-5	-9.1337E-8	3.9064E-11
0.500063	263116.7	-4525.450	29.46207	-9.8761E-2	1.85418E-4	-1.8401E-7	7.5510E-11
0.650116	240504.5	-4168.646	27.27745	-9.1926E-2	1.73726E-4	-1.7376E-7	7.1961E-11
0.79999	391323.8	-6445.697	41.55655	-0.1393358	2.61464E-4	-2.5971E-7	1.0682E-10
0.949986	524395.6	-8519.972	55.08956	-0.1863184	3.52639E-4	-3.5348E-7	1.4674E-10
1.0	714536.0	-11466.75	73.91648	-0.2497349	4.71389E-4	-4.7075E-7	1.9117E-10

Figure 23. Enthalpies of the Benzene-Ethylbenzene System

The heat of mixing data at 298.15 K were measured as described earlier and are given in Table 4. The data can be represented by the following polynomial.

$$H^E = -4469.000188X_b^6 + 13670.6146X_b^5 - 15578.6257X_b^4 + 7834.31479X_b^3 - 1891.02145X_b^2 + 433.24655X_b + 0.293127 \quad \text{..... (1)}$$

Figure 24 shows how the polynomial matches the experimental data.

Table 4: Heat of mixing at 298.15 K for the Benzene-Ethylbenzene system

Xb (mol)	0.044498	0.12798	0.14194	0.23056	0.32387	0.31096	0.35811	0.45371	0.54082
H ^e	17.3333	36.2260	40.3133	61.4607	79.9379	77.5004	87.9956	102.614	108.0386
Xb (mol)	0.58251	0.69908	0.75942	0.83705	0.91056	0.956874	0	1.0	
H ^e	108.680	97.8794	81.4990	65.575	43.3560	22.1503	0	0

Figure 24: Heat of mixing data at 298.15 K for Benzene-Ethylbenzene system

Table 5 gives the C_p values derived by $C_p = \Delta H / \Delta T$, Figure 25 shows the C_p distributions as the temperature rises. The C_p data can be regressed by a sixth order polynomial, the parameters are given in Table 6.

In Table 6, C_p is expressed as: $C_p = A + BT + CT^2 + DT^3 + ET^4 + FT^5 + GT^6$. It is quite interesting to look at the C_p behavior especially at the Benzene rich end, the only explanation to this might be that when the temperature is close to the critical temperature the heat capacity data increases faster than in the other region.

Table 5: Heat Capacities of the Benzene-Ethylbenzene system

$\frac{C_p}{T} \frac{X_b}{K}$	pure EB	0.050055	0.20167	0.349986	0.500063	0.650116	0.79999	0.949986	Pure Benzene
298.15	189.918	184.248	174.884	170.297	160.325	153.239	146.151	138.112	136.628
314.12	194.515	189.740	180.702	174.020	164.554	156.733	149.474	141.055	139.549
326.75	198.209	193.933	184.915	177.749	168.244	160.246	152.693	144.156	142.445
339.38	202.079	198.122	188.975	181.840	172.025	163.966	156.076	147.493	145.478
352.01	206.197	202.390	193.020	186.111	175.847	167.784	159.422	150.891	148.492
364.64	210.589	206.800	197.169	190.461	179.680	171.524	162.697	154.080	151.467
377.27	215.252	211.396	201.526	194.894	183.644	175.382	166.138	157.480	154.658
389.90	220.148	216.175	206.115	199.343	187.722	179.326	169.703	160.881	158.096
402.53	225.218	221.124	210.957	203.885	191.982	183.422	173.564	164.604	161.918
415.16	230.389	226.215	215.989	208.487	196.459	187.727	177.684	168.582	166.094
427.79	235.581	231.384	221.119	213.085	201.059	192.172	182.023	172.731	170.336
440.42	240.723	236.581	226.275	217.750	205.785	196.836	186.562	177.094	174.840
453.05	245.759	241.747	231.344	222.361	210.467	201.504	191.160	181.512	179.297
465.68	250.661	246.863	236.287	227.022	215.168	206.305	195.871	186.016	183.750
478.31	255.449	251.903	241.047	231.672	219.777	211.144	200.695	190.633	188.031
490.94	260.208	256.909	245.723	236.492	224.559	216.270	205.672	195.812	192.773
503.57	265.091	262.001	250.549	241.648	229.684	221.969	211.477	202.102	198.781
516.20	270.356	267.332	255.875	247.539	235.812	228.766	218.742	210.562	207.547
528.83	276.375	273.210	262.344	254.703	243.617	237.539	228.734	223.188	220.875
541.46	283.650	280.030	270.828	264.051	254.508	249.922	243.422	242.938	242.597
554.60	293.273	288.748	283.176	277.195	270.867	268.328	266.500	274.406	278.516

Table 6: Parameters for the C_p polynomials of Benzene-Ethylbenzene system

Xb (mol)	A	B	C	D	E	F	G
0.0	-637.2016	6.477461	-2.3836E-3	-1.2704E-4	5.05487E-7	-7.726E-11	4.2819E-13
0.050055	522.1124	-11.88433	0.113173	-5.0003E-4	1.15810E-6	-1.3596E-9	6.3975E-13
0.20167	3394.327	-61.01822	0.4547906	-1.7423E-3	3.65480E-6	-3.9932E-9	1.7804E-12
0.349986	10447.62	-155.1274	0.9684454	-3.2108E-3	5.97307E-6	-5.9094E-9	2.4285E-12
0.500063	12841.78	-198.5090	1.281625	-4.3775E-3	8.35160E-6	-8.4364E-9	3.5253E-12
0.650116	17073.48	-259.4769	1.644123	-5.5185E-3	1.03585E-5	-1.0309E-8	4.2503E-12
0.79999	20719.67	-319.2582	2.046604	-6.9450E-3	1.31662E-5	-1.3220E-8	5.4944E-12
0.949986	27411.81	-422.2064	2.702944	-9.1680E-3	1.73858E-5	-1.7478E-8	7.2781E-12
1.0	28776.85	-449.6438	2.918632	-1.0032E-2	1.92620E-5	-1.9587E-8	8.2414E-12

Figure 25: Composition and temperature dependence of the heat capacities of the Benzene-Ethylbenzene system (750 Psia)

Comparison with the literature data:

To justify our newly acquired data, we compare our enthalpy and heat capacity data with the literature data, as indicated by Table 7.

Table 7: Comparison of the H_{benzene} and the $H_{\text{ethylbenzene}}$ data of this work with the literature data

Temperature K	$H_{\text{ethylbenzene}}$ this work	$H_{\text{ethylbenzene}}$ Johnson's ⁽⁵⁾	Difference %
361.53	12911.1	12911.1	0.0
381.51	17169.06	17141.5	0.1608
401.32	21543.42	21480.2	0.2943
421.18	26088.58	25976.2	0.4326
441.04	30793.69	30621.2	0.5633
460.90	35656.75	35418.1	0.6738
480.74	40667.19	40365.4	0.7476
500.58	45826.69	45471.8	0.7804
520.42	51144.06	50741.7	0.7930
Temperature K	H_{benzene} this work	H_{benzene} Goodwin's ⁽⁴⁾	Difference %
298.15	2913.75	2913.7	0.0
300	3149.83	3155.5	0.1797
310	4528.11	4528.7	0.0130
320	5933.80	5924.0	0.1654
330	7361.09	7342.9	0.2478
340	8808.41	8787.2	0.2413
350	10274.22	10258.1	0.1571
360	11762.88	11756.6	0.0534
370	13275.03	13282.6	0.0645
380	14814.88	14839.5	0.1659
390	16383.81	16424.7	0.2489
400	17983.5	18039.1	0.3082
410	19616.63	19682.9	0.3367
420	21284.13	21355.9	0.3361
430	22983.88	23058.0	0.3215
440	24717.38	24789.3	0.2901
450	26482.88	26550.2	0.2536
460	28280.00	28341.4	0.2166
470	30107.75	30164.3	0.1875
480	31969.25	32021.4	0.1629
490	33870.25	33916.1	0.1352
500	35814.5	35854.0	0.1102
510	37814.5	37843.2	0.0758
520	39886.75	39896.9	0.0254
530	42096.50	42034.9	0.0680
540	44364.75	44296.8	0.1534
550	46838.25	46770.9	0.1440

In the Table 7, the 0 value of the enthalpy data of this work was chosen just following the literature. In Johnson' paper, his enthalpy value of ethylbenzene at 361.53 K is 12911.1 J/mol, so we set the enthalpy of ethylbenzene of this work at 361.53 K to be 12911.1 J/mol to make these two sets of data comparable. We choose the enthalpy data at 52 bar in Goodwin's paper⁽⁴⁾ as reference for the benzene enthalpy data comparison. His benzene enthalpy data at 298.15 K is 2913.75 J/mol, so we set the benzene enthalpy data at 298.15K of this work to 2913.75 J/mol. From the table we can see that the enthalpy data of this work agree with the literature data very well.

Table 8: Comparison of the $C_{p_{\text{benzene}}}$ of this work with the literature's

Temperature K	$C_{p_{\text{benzene}}}$ this work	$C_{p_{\text{benzene}}}$ Goodwin's ⁽⁴⁾	Difference %
300	136.87	136.28	0.4305
310	138.64	138.51	0.0975
320	140.86	140.87	0.00754
330	143.23	143.34	0.0744
340	145.63	145.91	0.1926
350	148.00	148.56	0.3783
360	150.38	151.28	0.5956
370	152.82	154.07	0.8086
380	155.38	156.90	0.9682
390	158.16	159.77	1.0076
400	161.11	162.68	0.9654
410	164.26	165.63	0.8261
420	167.68	168.60	0.5435
430	171.15	171.60	0.2609
440	174.68	174.66	0.00903
450	178.27	177.77	0.2832
460	181.73	180.98	0.4125
470	185.20	184.33	0.4694
480	188.68	187.91	0.4096
490	192.52	191.83	0.3574
500	196.98	196.30	0.3486
510	202.78	201.66	0.5560
520	210.94	208.54	1.1497
530	222.64	218.20	2.0351
540	239.59	233.67	2.5351
550	263.92	264.76	0.3166

Table 8 display the difference of the C_p value between this work and Goodwin's, these two sets of data basically agree with each other except close to the critical temperature where somewhat larger errors are observed.

Excess enthalpy calculation:

In the last section, we presented the incremental enthalpies of the benzene-ethylbenzene system relative to 298.15K, also we have the heat of mixing data of benzene-ethylbenzene at 298.15 K. Using these data, we calculated the excess enthalpy data for the benzene-ethylbenzene system along isotherms from 298.15 to 554.60 K. The results are shown in Figure 26. The calculation involves subtraction of large numbers to give a relatively small number as the result. The accuracy of these values is therefore not very high, resulting in very unusual looking isotherms.

Figure 26: Calculated excess enthalpy data of benzene-ethylbenzene system

It is obvious from the above figure that the excess enthalpies we calculated are of no use. Thus, although the incremental enthalpies and heat capacities we have measured are quite accurate, the accuracy is not high enough for calculation of heat of mixing data. Also, for further accuracy volume of mixing data for benzene-ethylbenzene system would be required. A number of other incremental data sets available in the literature suffer from this same limitation. For this reason, most reliable heat of mixing data sets come from direct measurements by methods discussed before including our own measurement at 25 C. Setaram C-80 calorimeter could be configured for such measurements with the benzene-ethylbenzene system.

REFERENCES:

- (1) AL-Ghamdi, A.M., M.S. Thesis, Chemical Engineering Department, North Carolina A&T State University, 1996.

- (2) Castro-Gomez, R.C.; Hall, K.R. and J.C. Holste, J. Chem. Thermodynamics, 22, 269-278, 1990.
- (3) Eubank, P. T.; Holste, J. C.; Cediol, L.E.; Moor, D. H. and K. R. Hall, Ind Eng. Chem. Fundam., 23, 105, 1984.
- (4) Goodwin, R.D., Journal of Physical Chemistry reference Data, 17, 1541-1636, 1988.
- (5) Johnson, M.G.; Haruki, S.; Williamson, A.G. and Philip T. Eubank, Journal of Chemical and Engineering Data, 35, 101-107, 1990.
- (6) Karlsruhe, F., J. Chem. Thermodynamics, 29, 949-971. 1997.
- (7) Mathonat, C.; Hynek, V.; Majer, V. and J-P.E. Grolier, J. of solution Chemistry, 23(11), 1161, 1994.
- (8) Mohr, G.; Mohr, M.; Kidnay, A.J. and V.F. Yesavage, J. Chem. Thermodynamics, 15, 425, 1983.
- (9) Mraw, S.C.; Heldman, J.L.; Hwang, S. C. and C. Tsonopoulos, Ind. Eng. Chem. Fundam., 23, 577, 1984.
- (10) Ott, J.B.; Stouffer, C.E.; Cornett, G.V.; Woodfield, B. F.; Wirthlin, R.C. and J.J. Christensen, J. Chem. Thermodynamics, 18, 1-12, 1986.
- (11) Reid, R.C.; Prausnitz, J. M.; and B. E. Poling, The Properties of Gases and Liquids, Fourth Edition.
- (12) Stokes, R.H., J. Chem. Thermodynamics, 20, 1349-1352, 1988.
- (13) Tanaka, R.; Kiyohara, O.; D'Arcy, P.J.; and Benson, G.C., CAN. J. CHEM., 53, 2262-2267, 1975.