High Temperature High Pressure Thermodynamic Measurements for Coal Model Compounds

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INCREMENTAL ENTHALPY MEASUREMENTS FOR BENZENE – ETHYLBENZENE SYSTEM

The enthalpy of a fluid measured with respect to some reference temperature and pressure (enthalpy increment or Cp) 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.

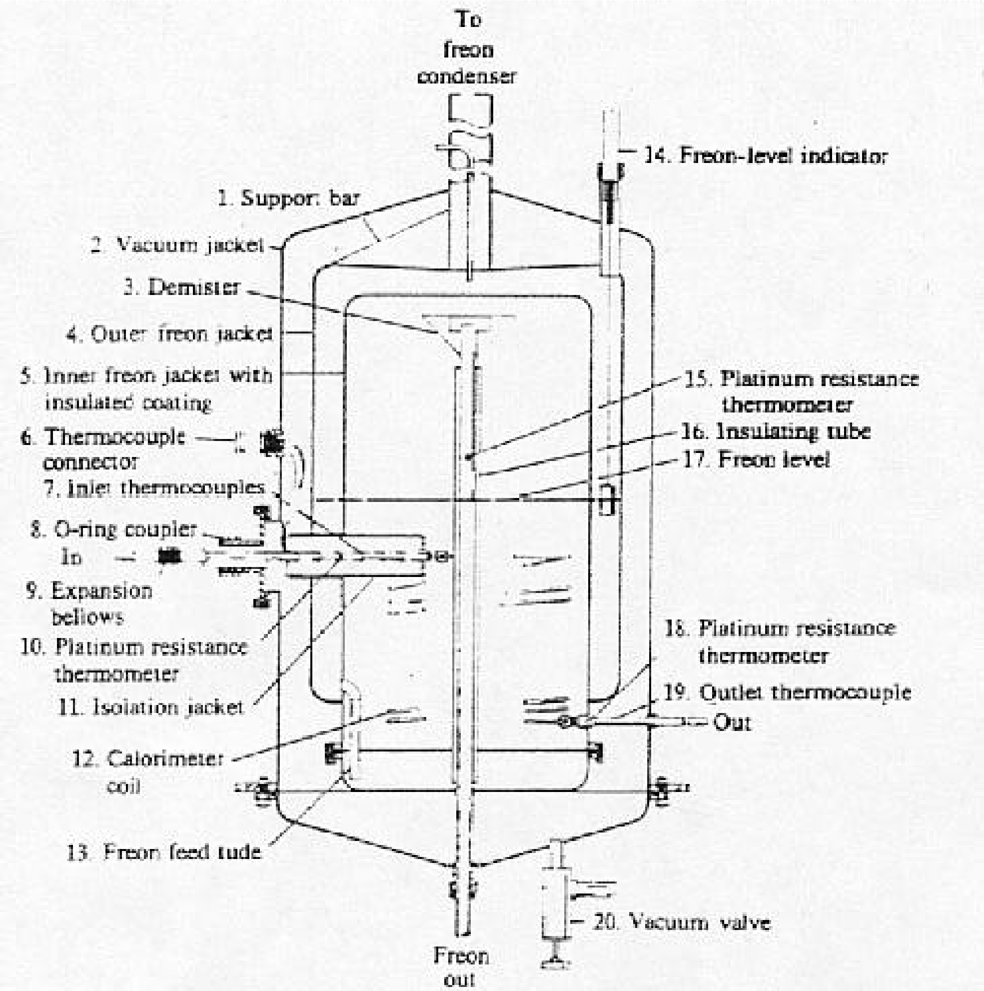


Figure 1: Flow calorimeter

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.

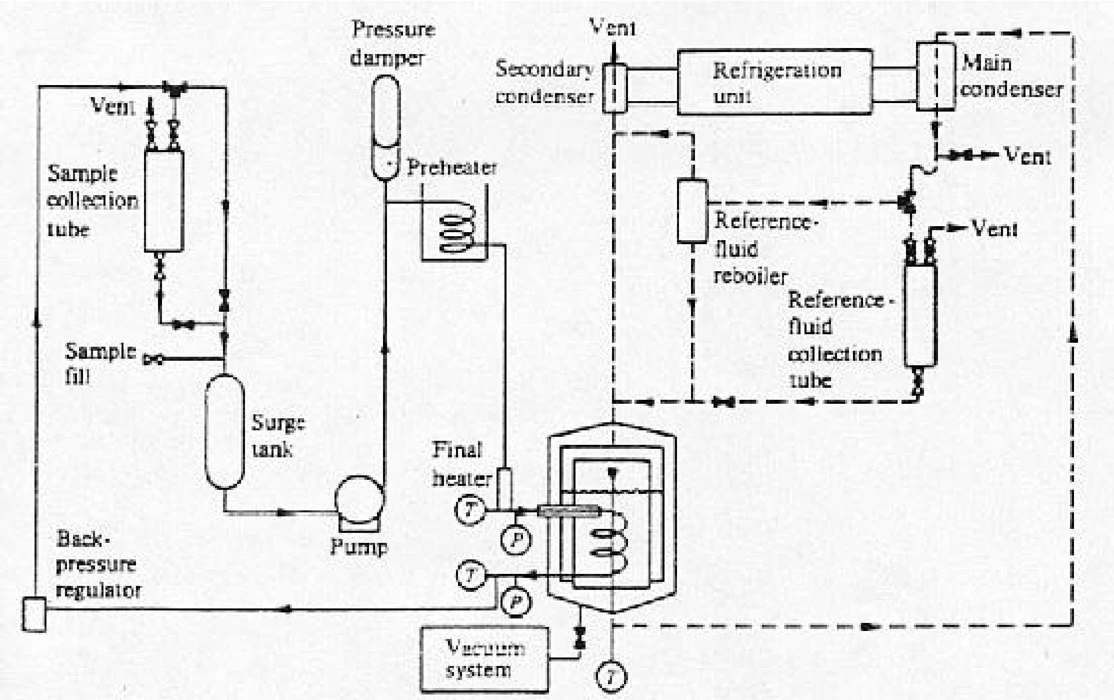
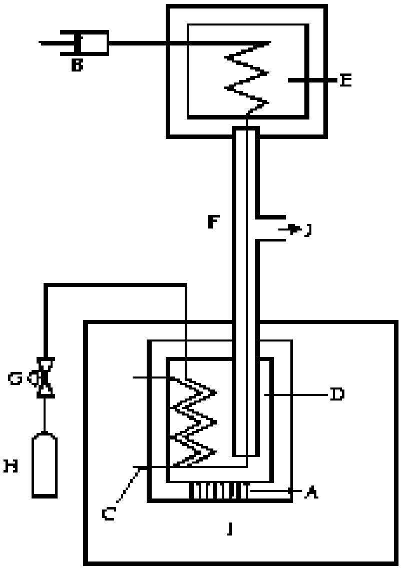


Figure 2: Process flow diagram

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.

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

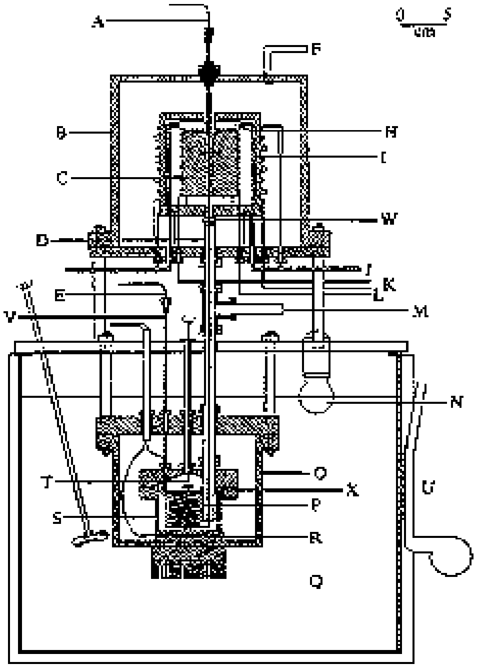


Legend:

A: Thermoelectric cooling device
B: Syringe pump;
C: Calorimeter heater
D: Calorimeter Vessel
E: Conditioning block
F: Connecting tube
G: Back-pressure regulator
H: Collection tank
I: Calorimeter thermostat
J: Vacuum connection

Figure 3: Schematic drawing of flow calorimeter

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



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
O: Outer aluminum can
P: Matching heater
Q: bath oil
R: Thermoelectic cooling devices
V: Fluid outlet to back pressure regulator
T: Stirrer
U: Thermostat cooler
W: Trim heater;
X: Fins for enhance heat exchange.

Figure 4: Detail of flow calorimeter

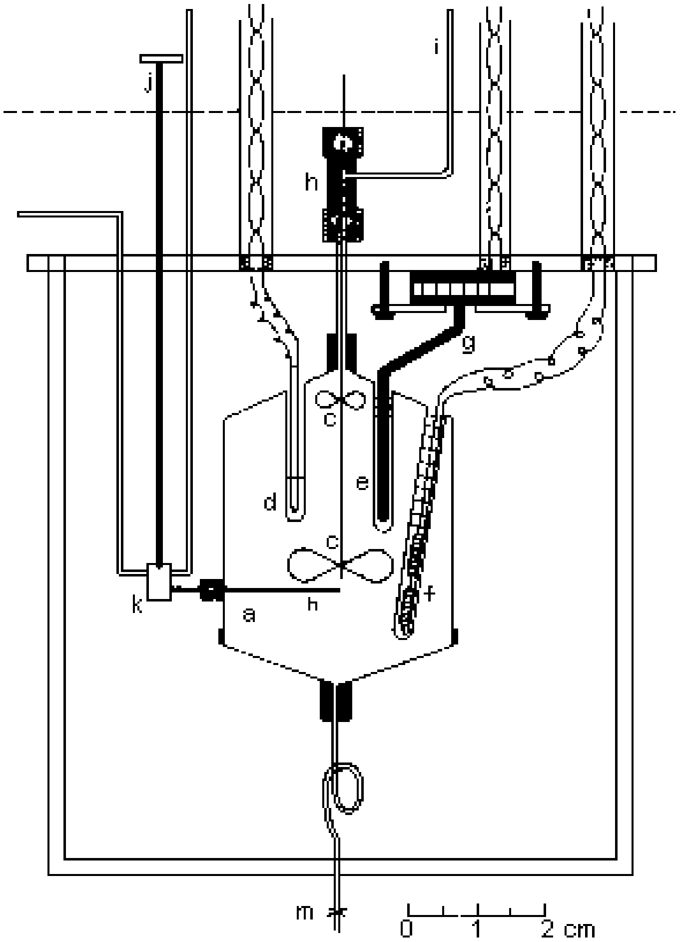
cooling device A. Before pumping fluid from the syringe pump B, the power removed by the cooling water was matched by the addition of electrical power from the heater C to maintain the temperature of the calorimetric vessel D constant to ±0.002 K at the chosen reference temperature, 298.15 K. Upon flowing 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.

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: (telflon+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 100Ω standard resistor in series with the heater.

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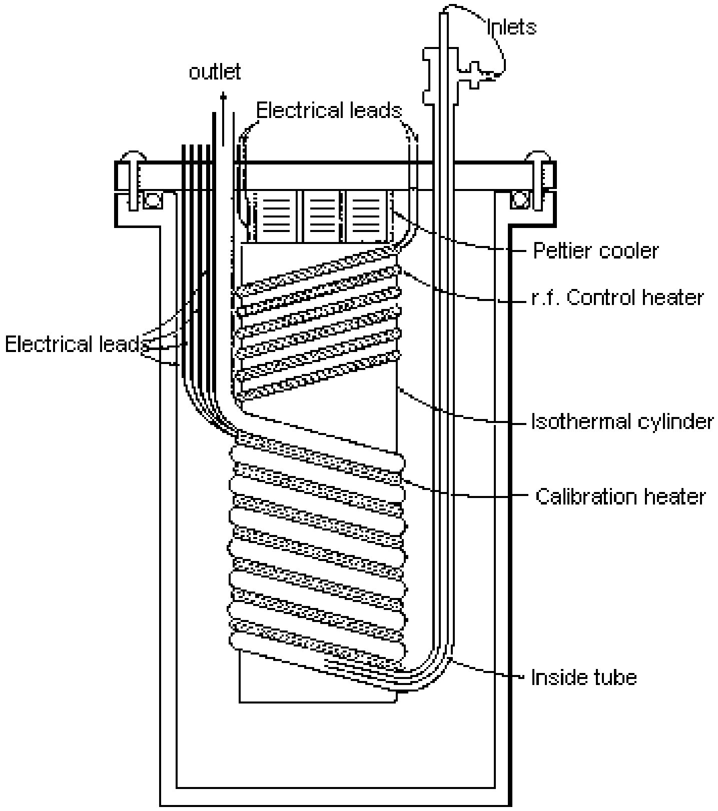


Figure 6: Schematic diagram of the isothermal calorimeter.

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.

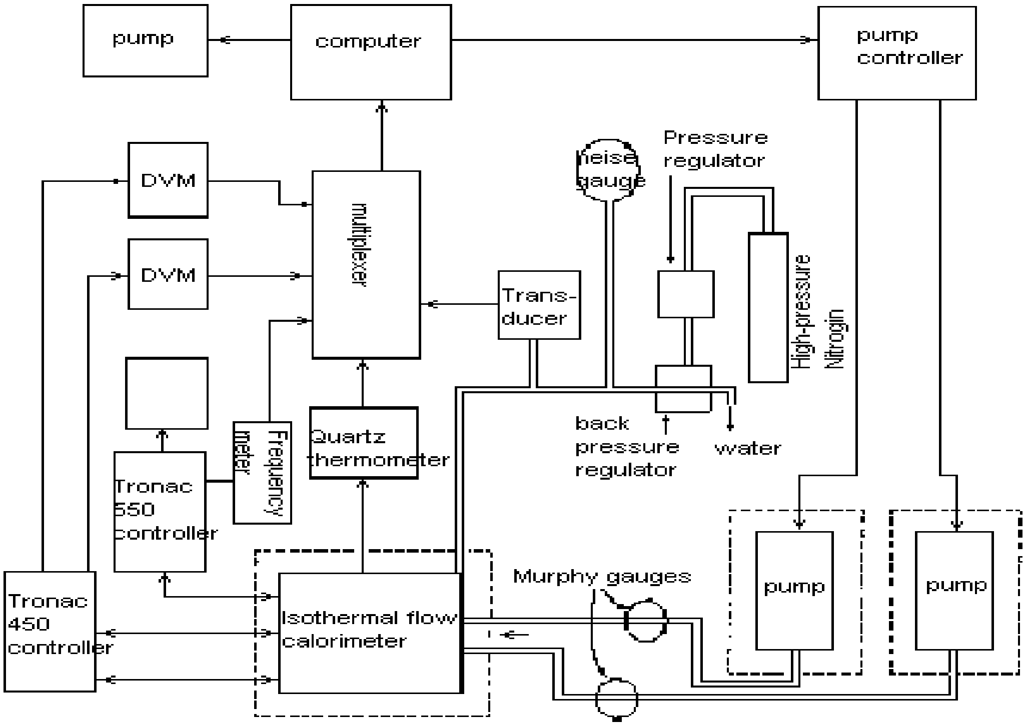


Figure 7: Schematic diagram of the data collection, control and flow system of the isothermal calorimeter.

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.

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.

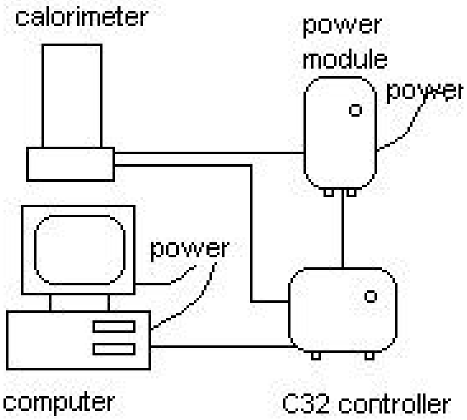


Figure 8: C80 calorimeter and the data acquisition and processing system

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.

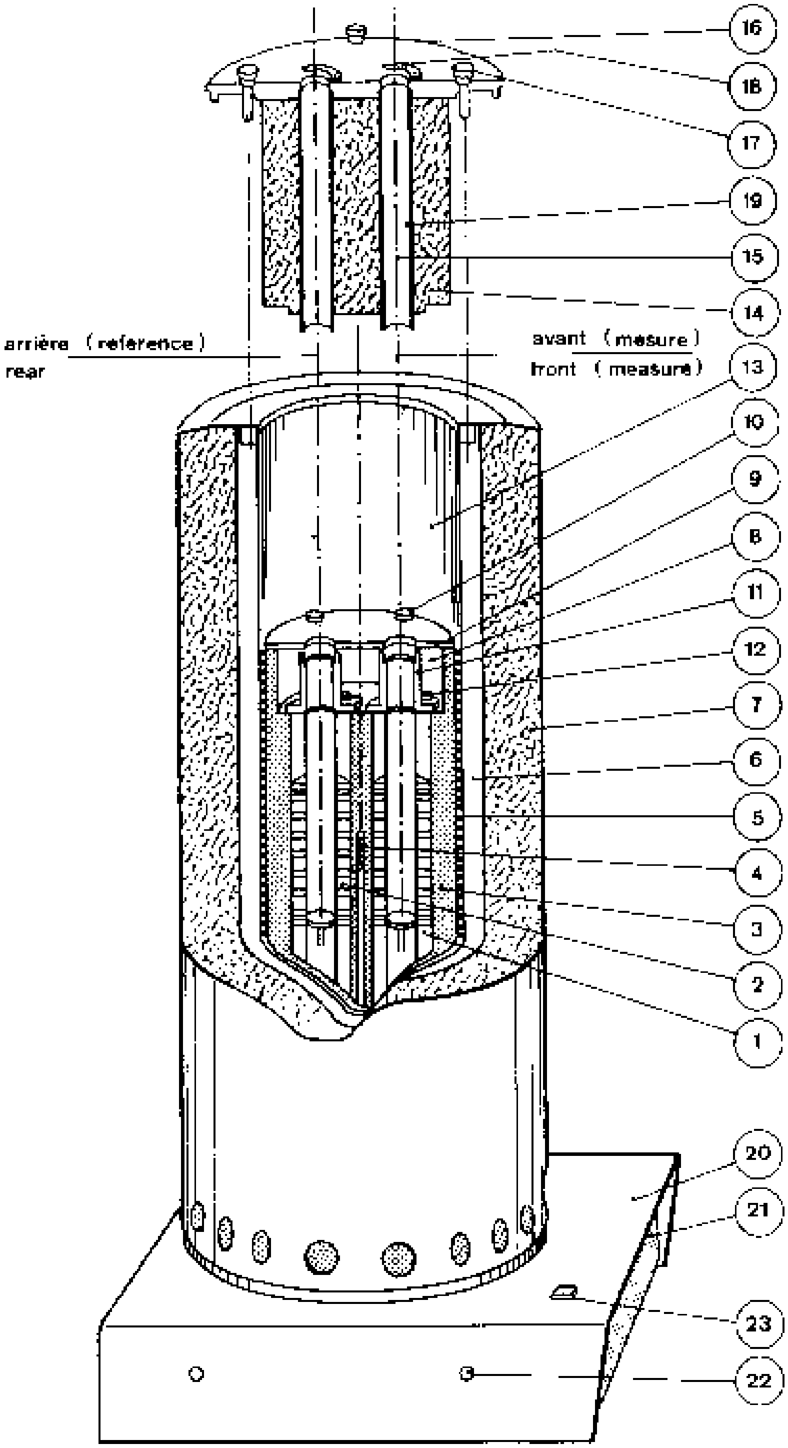


Figure 9: Internal structure of the C80 Calorimeter

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.

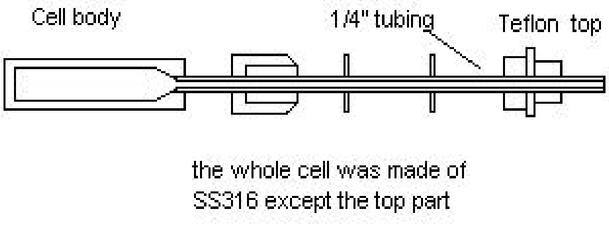


Figure 10: Cell used to measure enthalpy data

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.

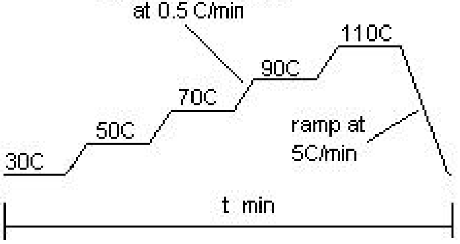


Figure 11: Typical temperature programming

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^{o}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^{o}C/min (ramp rate) to 50^{o}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^{o}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^{o}C to 50^{o}C. The heat requirements from 50^{o}C to 70^{o}C, 70 to 90^{o}C and 90 to 110^{o}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^{o}C. In the final phase of the program, the temperature may not be able to drop at a rate of 5^{o}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^{o}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.

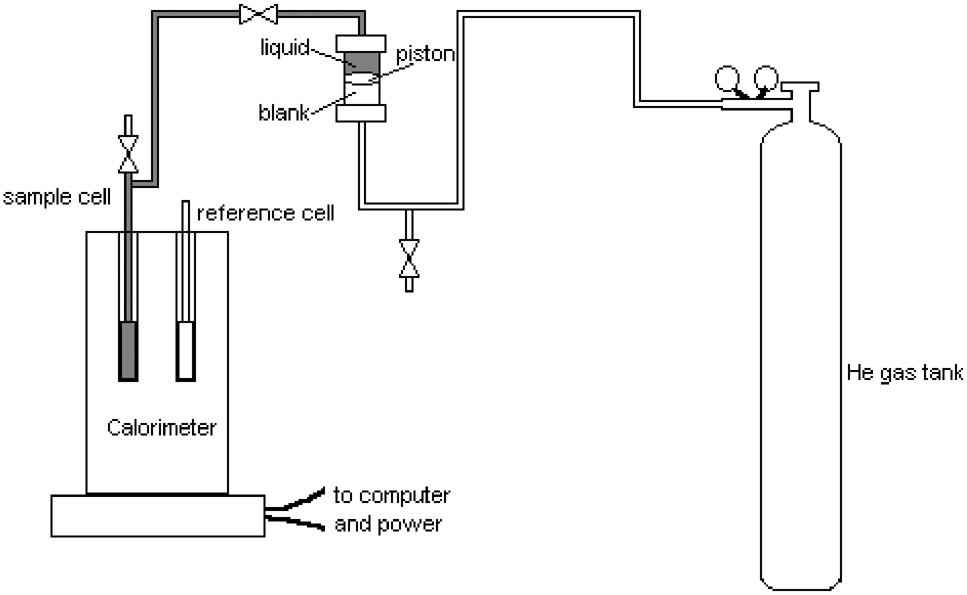


Figure 12: Previous setup for the enthalpy measurement

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.

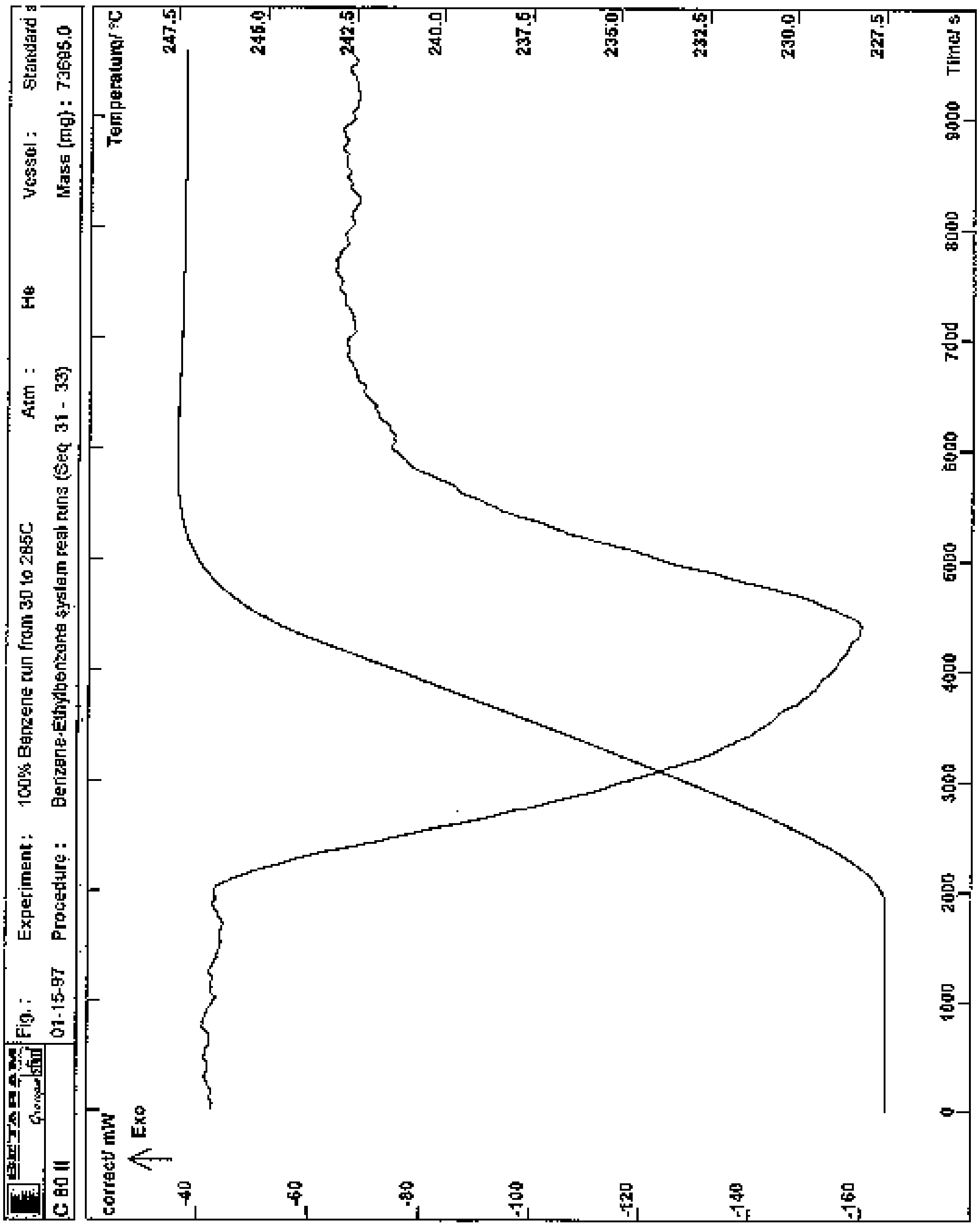


Figure 13: Heat flux signal of the calorimeter of the former work

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

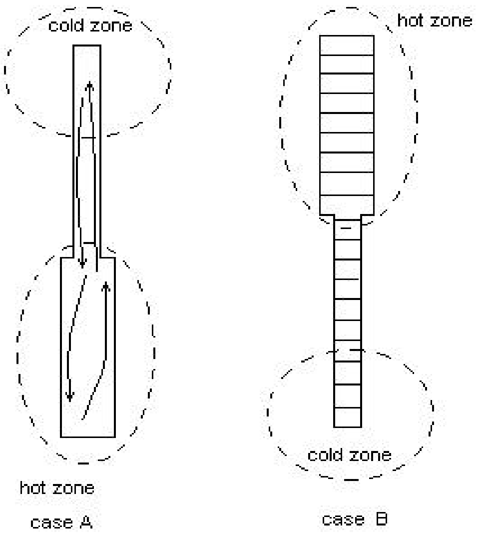


Figure 14: Effect of natural convection

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.

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.

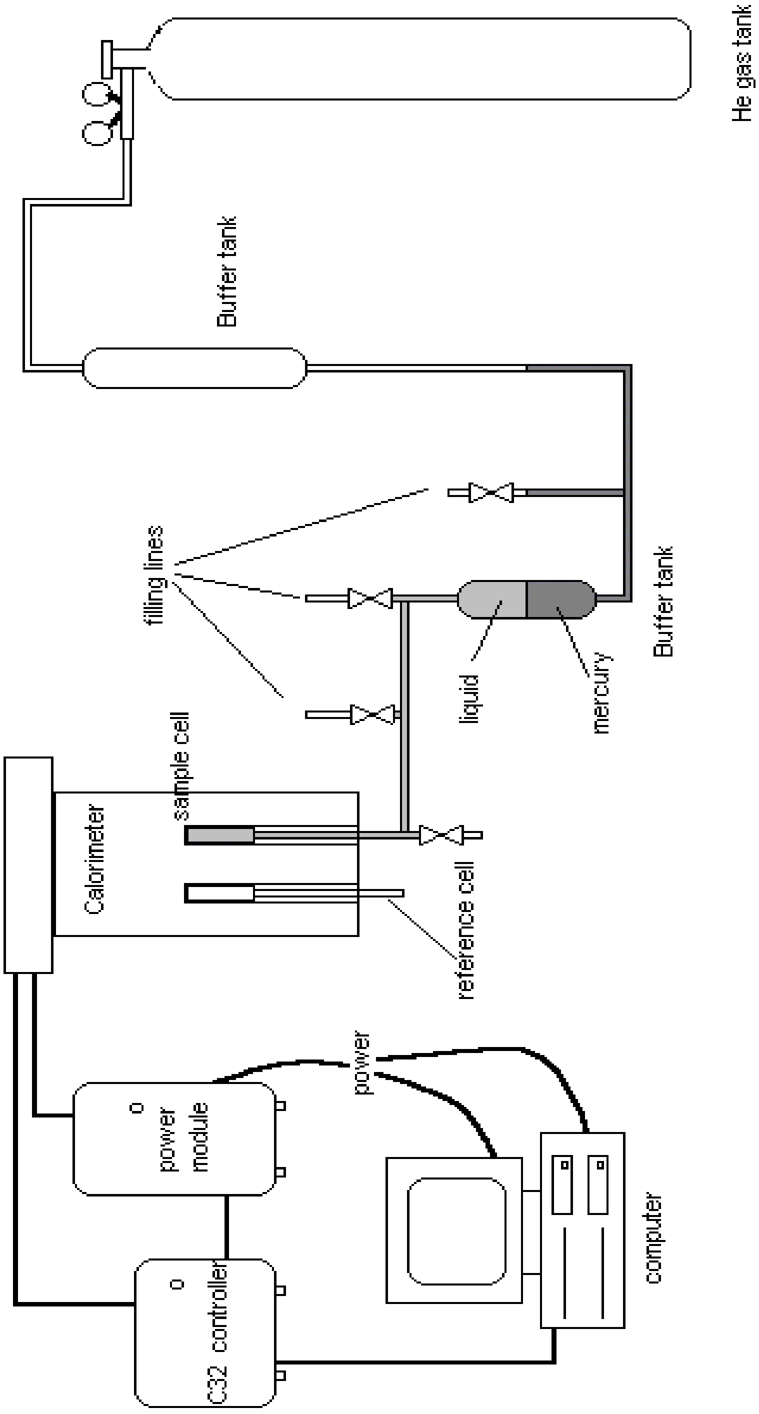
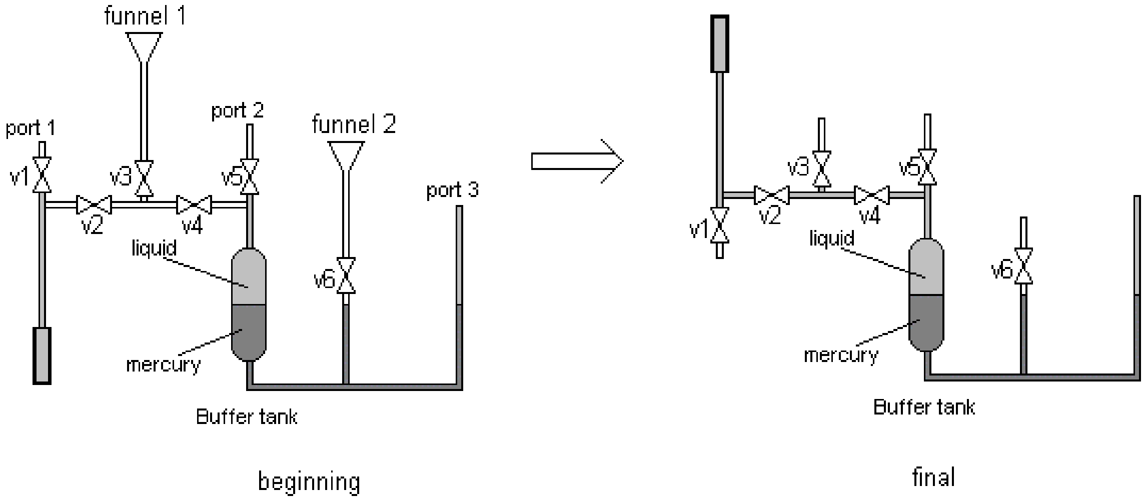


Figure 15: Apparatus for the enthalpy measurement in this work

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 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 ¼”-1/8” swagelok reducing union, this union allows the cell to turn 180^{o} 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.

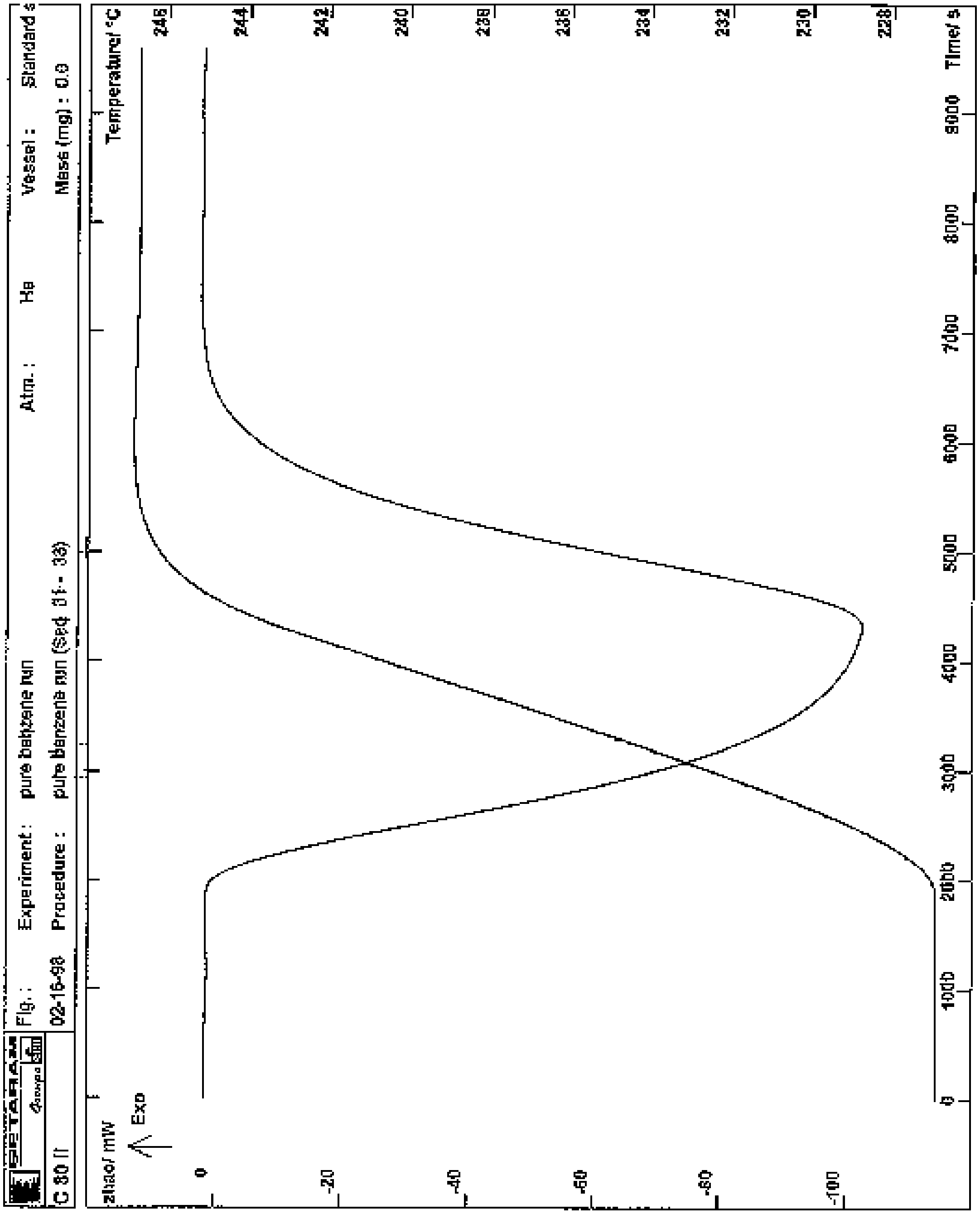


Figure 17: Heat flux signal of the calorimeter from this work

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 refereed 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, deviced 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

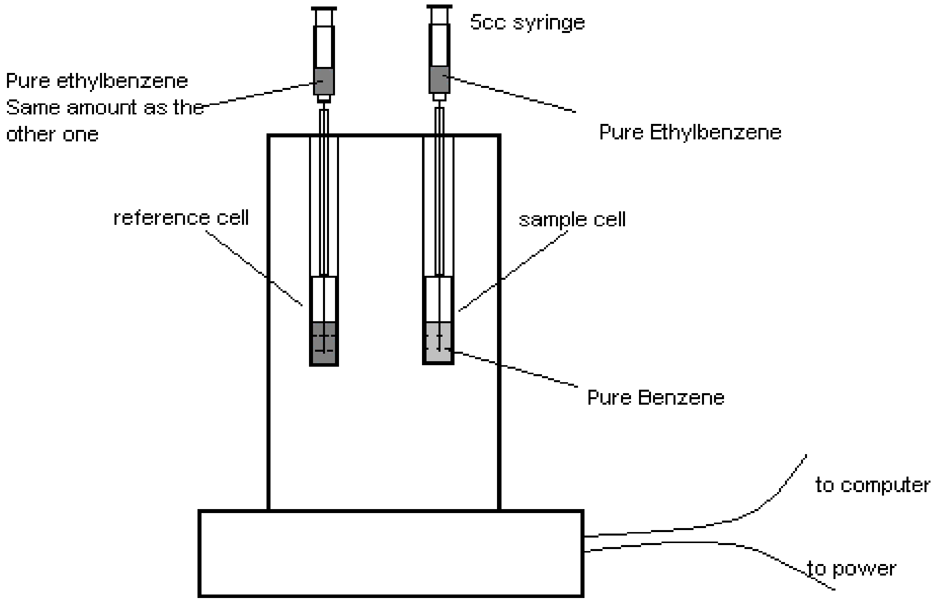


Figure 18: Apparatus for the heat of mixing measurement at 25°C

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.

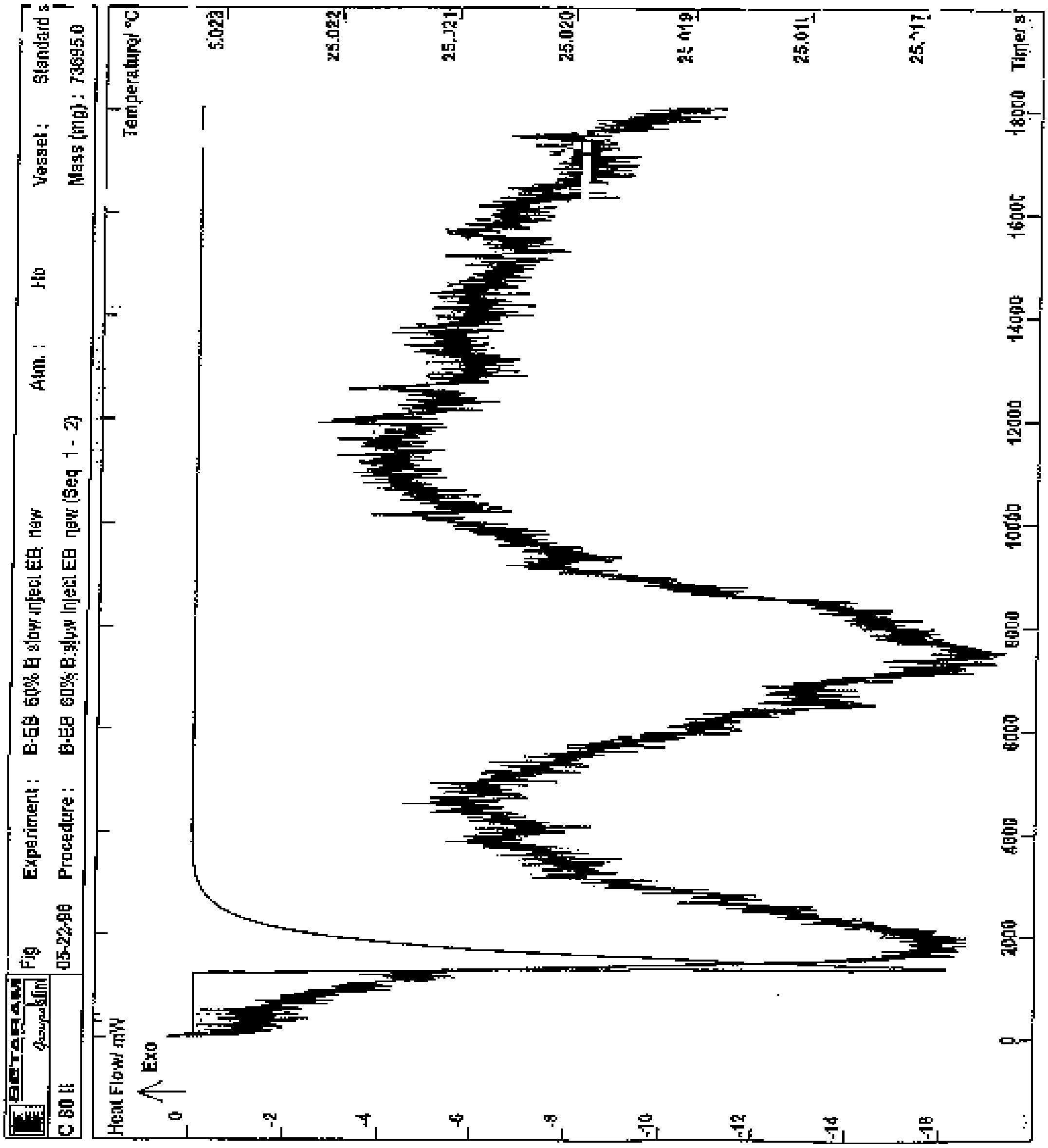


Figure 19: Heat flux signal for the heat of mixing measurement at 25°C

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.

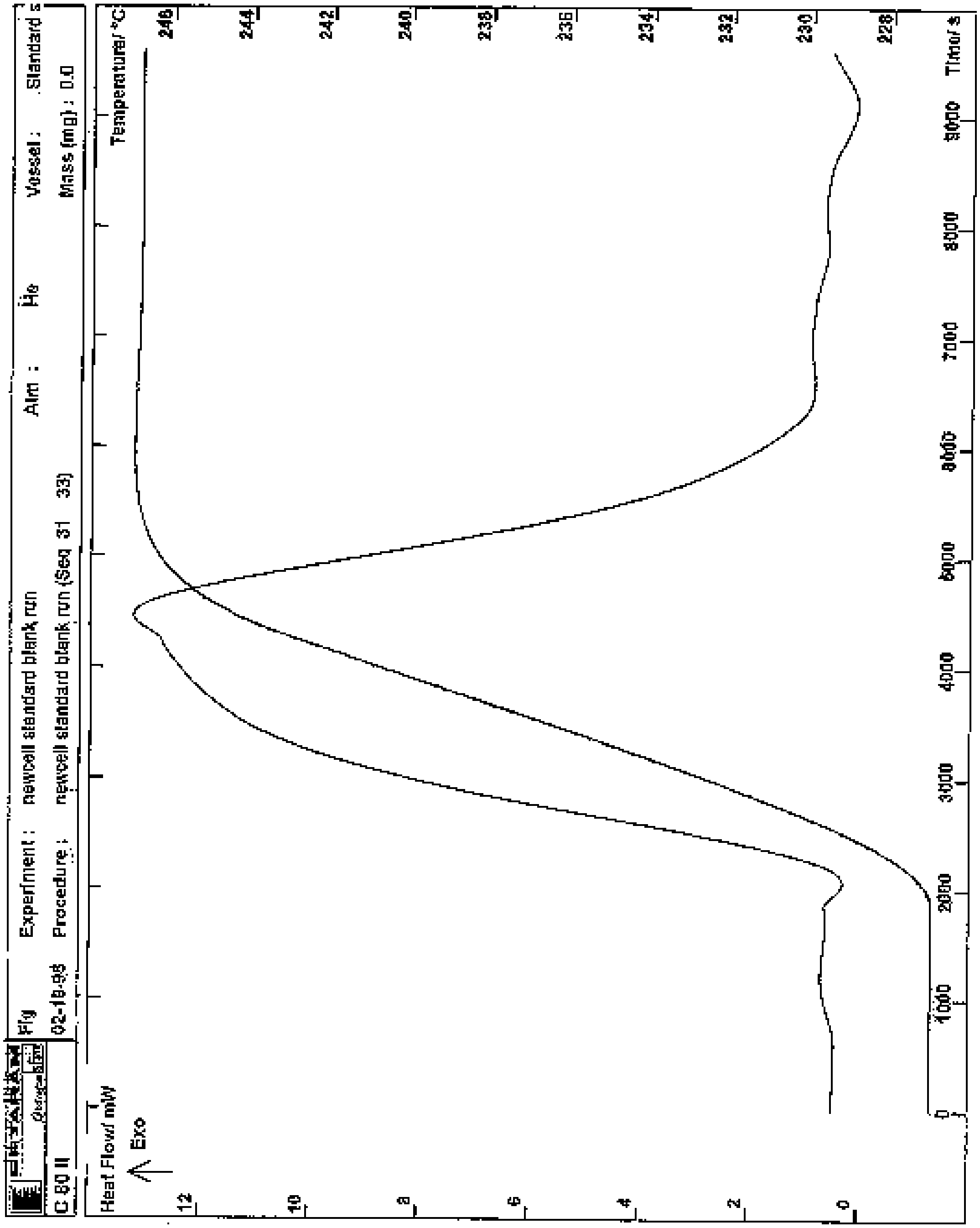


Figure 20: Heat flux signal for the blank run

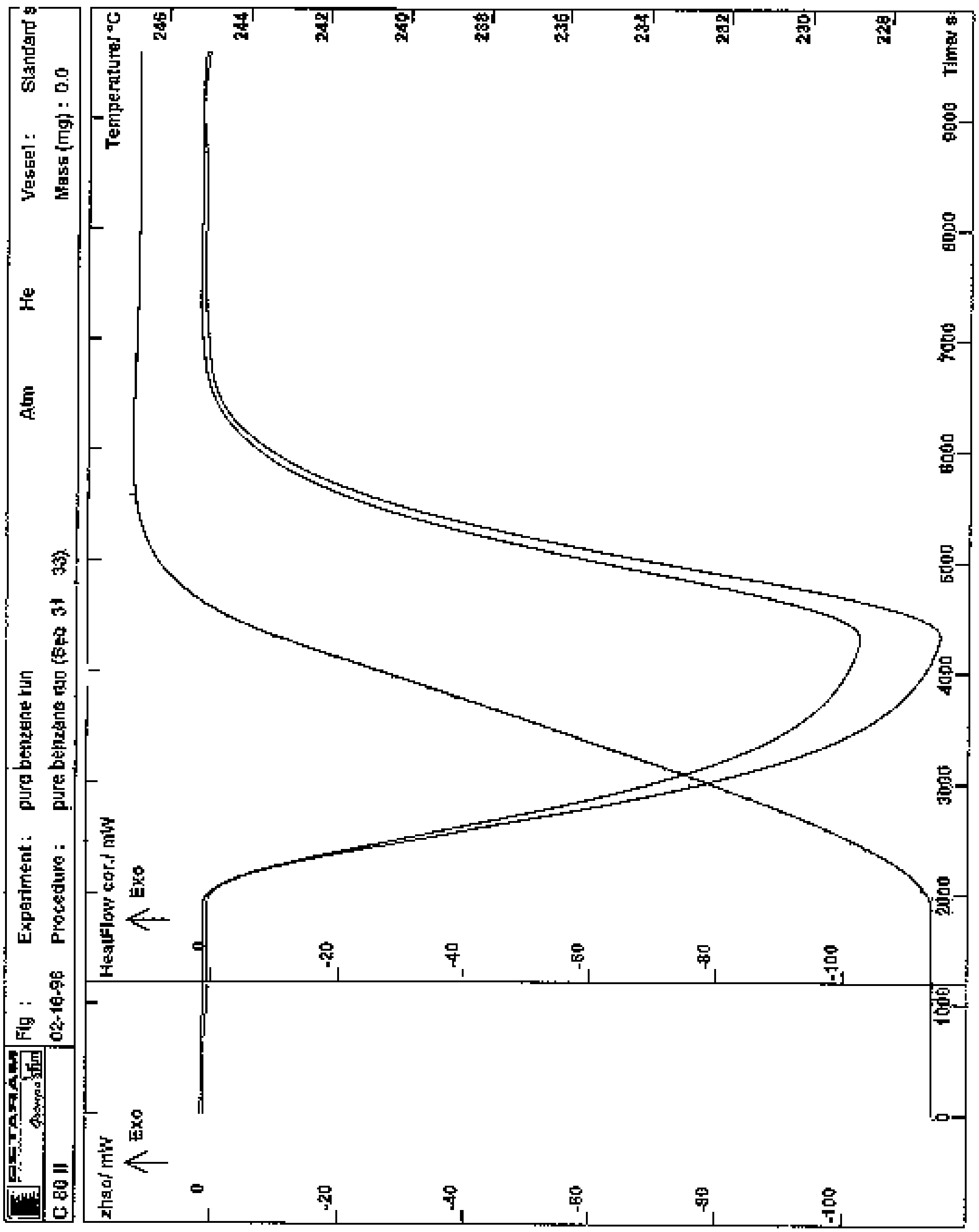


Figure 21: The baseline subtraction operation

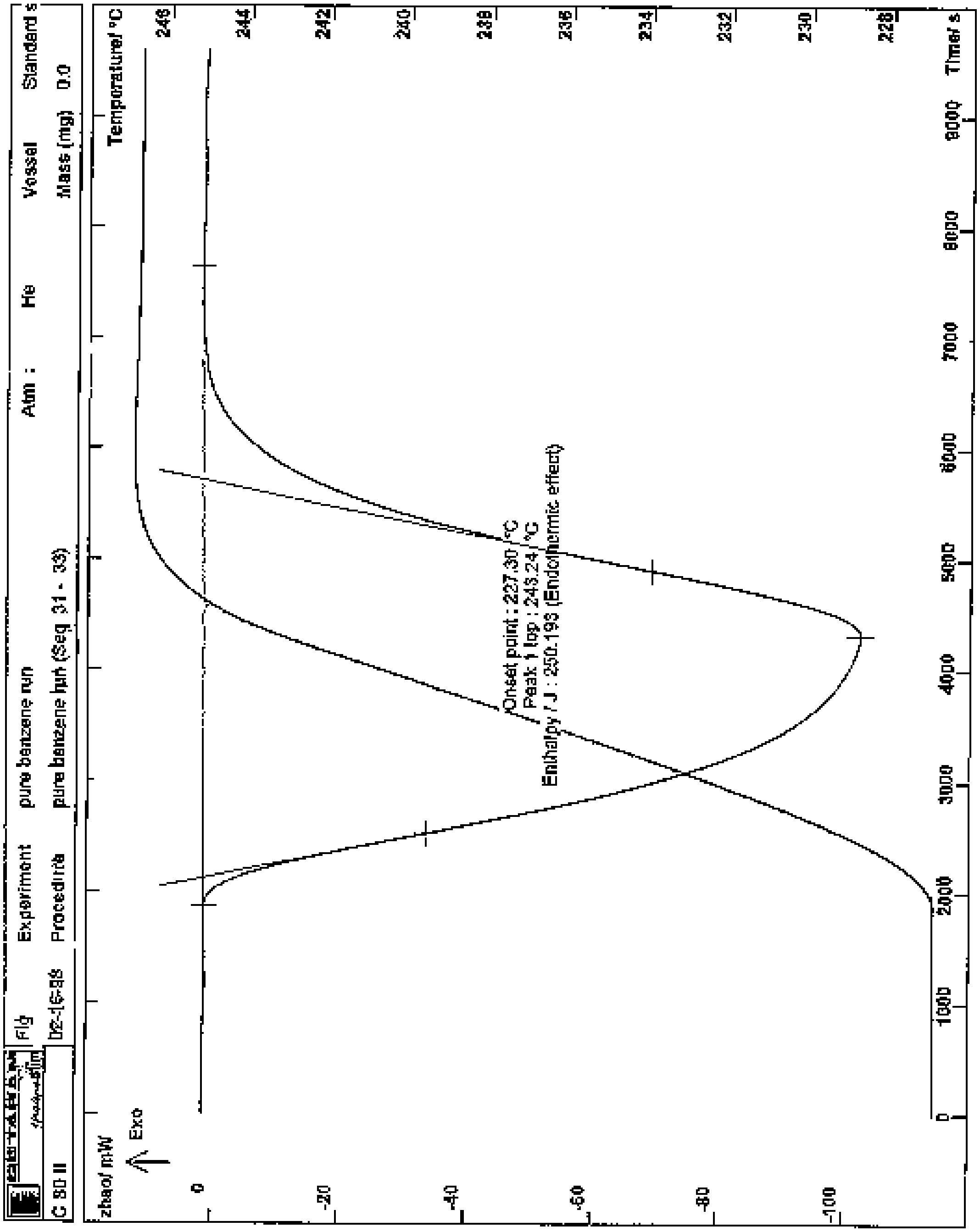


Figure 22: Heat flux signal integration operation

Incremental Enthalpy data for Benzene-Ethylbenzene system:

Data were measured for pure benzene, pure ethylbenzene and 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 corresponding temperatures. If we know the molar density D (mol/ml) of the liquid at a temperature, say at 361.40 K, we can get the mole amount of the liquid in the specific volume by 7.92 times D, the enthalpy of this point can be found by 728.4048 divided by (7.92D). In the calculation, we select evenly 500 points within the temperature range for each composition, get the enthalpy value by the method just mentioned above.

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).

As for the density of the mixtures, we just assumed that the excess volume of benzene-ethylbenzene system is very small and can be ignored. This makes sense because the maximum excess volume of this system at 25°C is only 0.1167 ml/mol(13). So the density of the mixture at a certain temperature is calculated from the composition of the mixture and the densities of pure benzene and ethylbenzene at this temperature.

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.

For each composition in the above table, we used the following sixth order polynomial to regress the enthalpy data

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

The parameters A,B,C,D,E,F,G are given in Table 3. Also the enthalpies of the benzene-ethylbenzene system behave as shown in Figure 23.

Table 2: Enthalpies of the Benzene-Ethylbenzene system

Xb H J/mol T 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
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

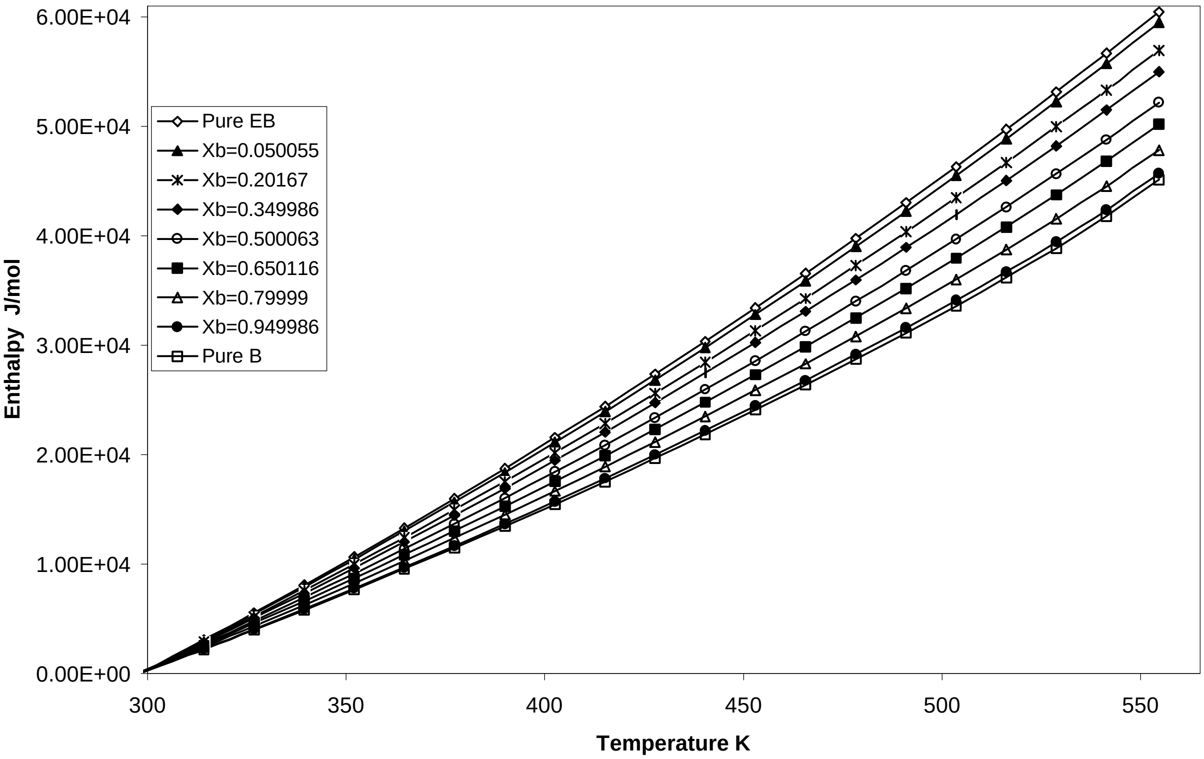


Figure 6.1. Enthalpies of the Benzene-Ethylbenzene System

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.

$$H^E=-4469.000188Xb^6+13670.6146Xb^5-15578.6257Xb^4+7834.31479Xb^3-1891.02145Xb^2+433.24655Xb+0.293127 \qquad \ldots\ldots. (1)$$

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	

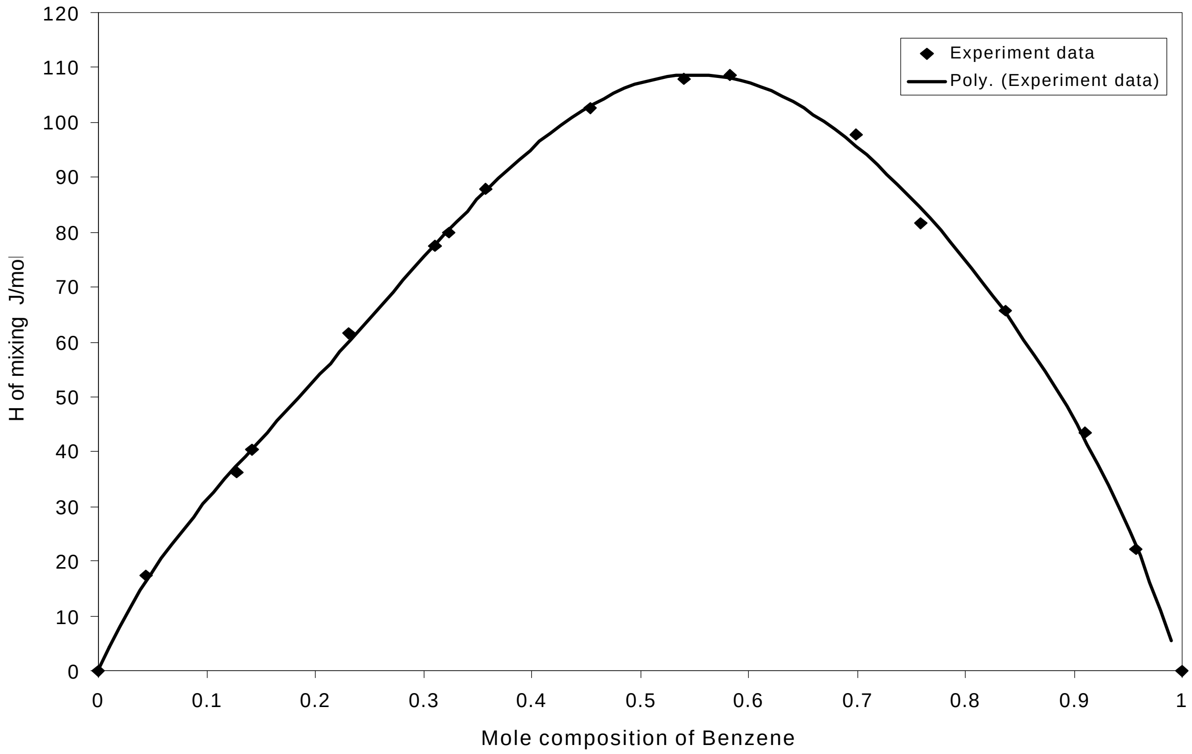


Figure 24: Heat of mixing data at 298.15 K for Benzene-Ethylbenzene system

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

In Table 6, Cp is expressed as: $Cp=A+BT+CT^2+DT^3+ET^4+FT^5+GT^6$. It is quite interesting to look at the Cp 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

Cp J/mol K / Xb / T 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 Cp 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

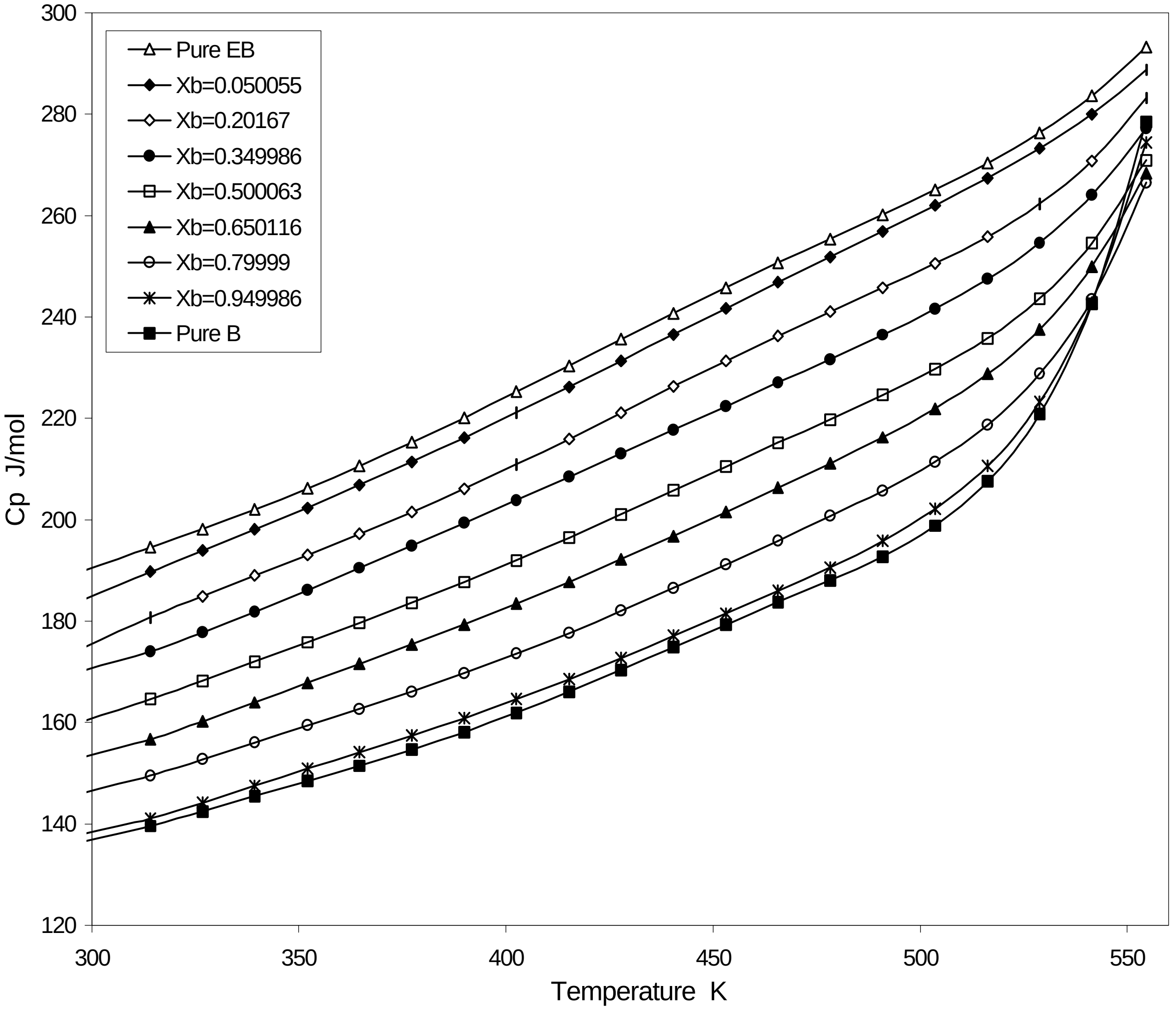


Figure 25: Composition and temperature dependence of the heat capacities of the Benzene-Ethylbenzene system (750 Psia)

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 $H_{ethylbenzene}$ data of this work with the literature data

Temperature K	$H_{ethylbenzene}$ this work	$H_{ethylbenzene}$ 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 $Cp_{benzene}$ of this work with the literature's

Temperature K	$Cp_{benzene}$ this work	$Cp_{benzene}$ 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 Cp 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.

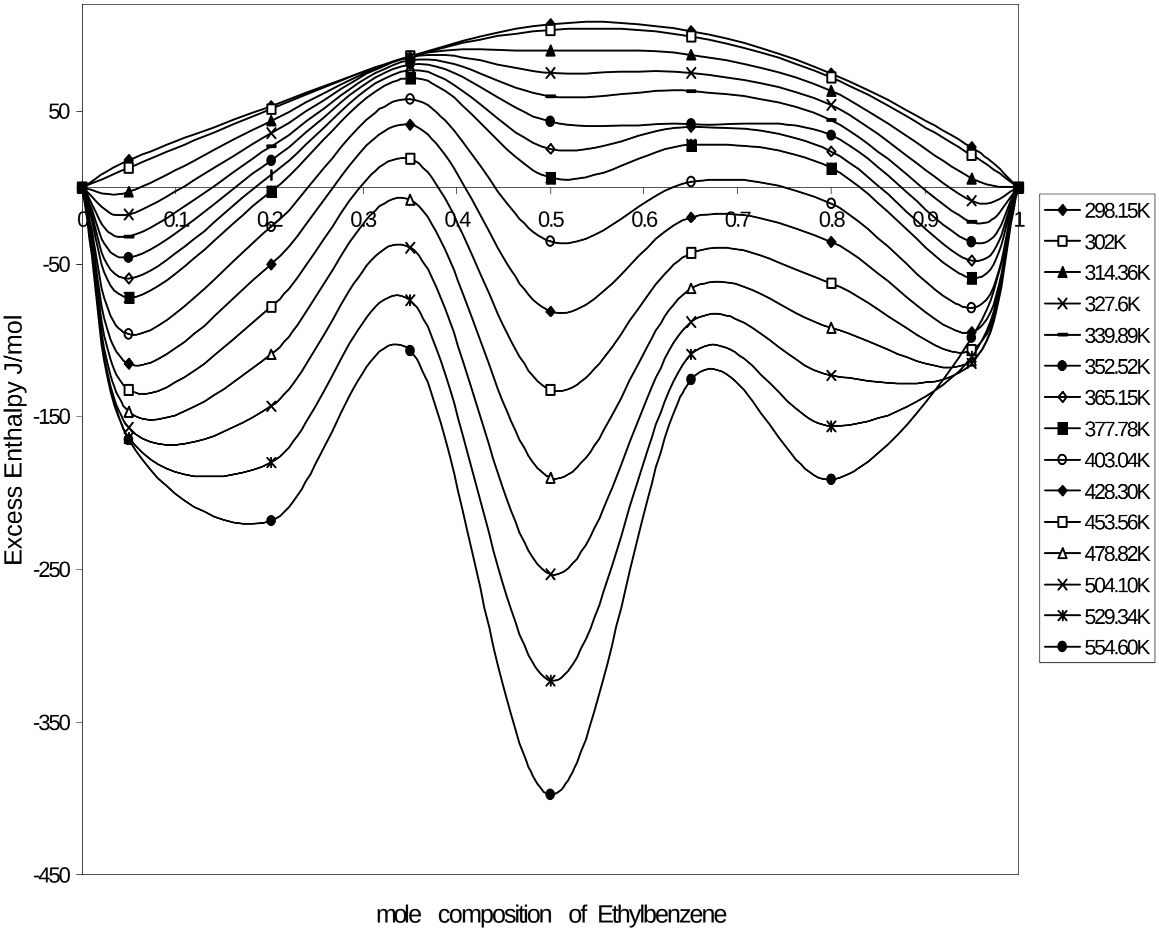


Figure 26: Calculated excess enthalpy data of benzene-ethylbenzene system

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.

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