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ENTITLED Measurement of Limiting Activity Coefficients Using a Differential

Dew Point Technique

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science in Chemical Engineering

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**MEASUREMENT OF LIMITING ACTIVITY COEFFICIENTS  
USING A DIFFERENTIAL DEW POINT TECHNIQUE**

**By**

**Erika Leigh Hendricksen**

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**Thesis**

**for the**

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## I. INTRODUCTION

The purpose of this study was to design an experimental apparatus to measure dew point temperatures. With successful results, this apparatus can be used to measure differential dew points between a pure solvent stream and a dilute mixture of a solute in a solvent. This information is to be used in determining limiting activity coefficients of various binary systems. There is a need for new methods of determining this property since weaknesses lie in the current methods. The largest problems occur with systems having high relative volatilities.

Very volatile solutes tend to remain in the vapor phase. Results then do not accurately represent the desired system. The strength of the dew point apparatus is that it does not have this uncertainty in the vapor stage. The systems are run in the vapor phase.

The results of this design, construction, and test runs will be discussed in the following report. The feasibility of this method will be discussed. Along with conclusions, recommendations regarding further investigation of this method are included.

## II. Differential dew point, measuring activity coefficients

### A. Introduction

Limiting activity coefficients are used for predicting and correlating phase equilibria. These values are often determined by measuring the behavior of a minute amount of one component in a large quantity of the other component. The equation below gives the value of the limiting activity coefficient, obtained from a differential bubble point technique. The vapor phase corrections and Poynting factor have been omitted.

$$\gamma_1^\infty = \frac{P_2^s - \left(\frac{dP_2^s}{dT}\right)\left(\frac{dT}{dx_1}\right)_p}{P_1^s}$$

The value that is experimentally measured is  $(dT/dx)_p$ , the change in temperature with the corresponding change in composition. Some methods utilize the bubble point to determine limiting activity coefficient values.

The weakness in the bubble point measurement lies in systems having high relative volatilities. The solute will preferentially remain in the vapor region. So measurement of the liquid's bubble point composition does not accurately represent the system.

### B. Theory

The purpose of a dew point apparatus is to avoid the composition uncertainties of a boiling liquid mixture. Since the solute prefers to remain in the vapor phase, the entire system is run in the vapor phase. The dew point measurement is of



of  $(dT/dy)_p$ . Using this method eliminates the uncertainty of the solution composition. However, the limiting activity coefficient must now be derived with the value of  $(dT/dy)_p$ .

The limiting activity coefficient equation is derived completely in the appendix, pages 21 to 24. Nomenclature is included in the appendix on page 29.

The limiting activity coefficient is expressed as:

$$\gamma_1^\infty = \frac{\phi_2^s \phi_1 (P_2^s)^2}{\phi_1^s \phi_2 P_1^s \exp \left[ \frac{v_1 (P_2^s - P_1^s)}{RT} \right] \left\{ P_2^s - \frac{\phi_2^s P_2^s}{\phi_2} \left( \frac{\partial \phi_2}{\partial y_1} \right) + \left( \frac{\partial T}{\partial y_1} \right)_p \left( \frac{\partial P_2^s}{\partial T} \right) \left( 1 - \frac{\phi_2^s P_2^s v_2}{\phi_2 RT} \right) \right\}}$$

where  $(dT/dy)_p$  is determined experimentally. This equation can be simplified by disregarding the fugacity coefficients and the Poynting correction factor:

$$\gamma_1^\infty = \frac{(P_2^s)^2}{P_1^s \left\{ P_2^s + \left( \frac{\partial T}{\partial y_1} \right)_p \left( \frac{\partial P_2^s}{\partial T} \right) v_1 \right\}}$$

An error analysis was completed to determine whether temperature or pressure inaccuracies have the bigger effect on the resulting limiting activity coefficient values. Errors were incorporated systematically into sample data, and the resulting  $dT/dy$  were calculated. Temperature inaccuracies affected experimental values less.

Table 1 through Table 4 display several systems with differing relative volatilities. Table 1 contains data for the system of methanol in cyclohexane which has a relative volatility of 14.39. Incorporating errors of  $\pm 0.002$  °C results in a  $dT/dy$  error of 0.64 percent, and this in turn affects the limiting activity coefficient value by 8.46 percent. Estimating an error of 0.002 °C is very conservative. This amount of accuracy should be obtained rather easily. A more realistic estimate of  $\pm 0.0002$  °C results in a 0.067 percent error in  $dT/dy$ , which results in an 0.83 percent error in the limiting activity coefficient value.

Table 2 contains data for the same system, methanol in cyclohexane; however, in this case a pressure inaccuracy of  $\pm 0.002$  torr is estimated. This accuracy would be very difficult to achieve. The resulting  $dT/dy$  values contain a 41.79 percent error, which drastically affects the limiting activity coefficients value by 125 percent.

Table 3 and Table 4 further investigate effects of temperature inaccuracies. Table 3 contains the system of cyclohexane in methanol, which has a very high relative volatility of 100.8. Temperature errors of  $\pm 0.002$  °C produce errors of 0.079 percent in  $dT/dy$  which result in an error in the limiting activity coefficient value of 0.68 percent. In Table 4, the results for the system of carbon tetrachloride in acetone, which has a relative volatility of 1.039, again shows that the limiting activity coefficient value is hardly affected by temperature inaccuracies.

The dew point technique is also good for systems with a positive  $dT/dy$  because it avoids differences of large numbers in the denominator. On the other hand, the bubble point is better for systems with a negative  $dT/dx$ .

### C. Comparison to past methods of determining limiting activity coefficients.

As mentioned earlier bubble points are often used in determining limiting activity coefficients. In order to do this, bubble points are measured at varying compositions. The solution temperature is measured at each point, after a minute amount of solute is added, the temperature re-equilibrates and is recorded. This continues throughout a run. A plot of  $dT$  versus mole fraction of solute will produce a straight line in most cases.

Other methods of obtaining limiting activity coefficients include differential ebulliometry, which utilizes the bubble point data (Thomas, 1982). As mentioned

previously, bubble point methods are weak for systems with relatively high volatilities. The boiling liquid composition is uncertain.

Another possible method is a microwave technique (Fogh,1989). This method of detecting dew and bubble points at high pressures has been recently explored. Potential exists in applying this to differential dew and bubble point measurements. Possibly, very accurate limiting activity coefficient values may be obtained.

Other methods often used are headspace chromatography and gas chromatography. Both these techniques utilize different retention times and the separation of peaks to calculate values for limiting activity coefficients. Headspace chromatography is a static technique, while gas chromatography is a dynamic technique.

Another method of obtaining limiting activity values does not entail an actual measurement. Solubility data from supercritical liquids is used in predicting values.

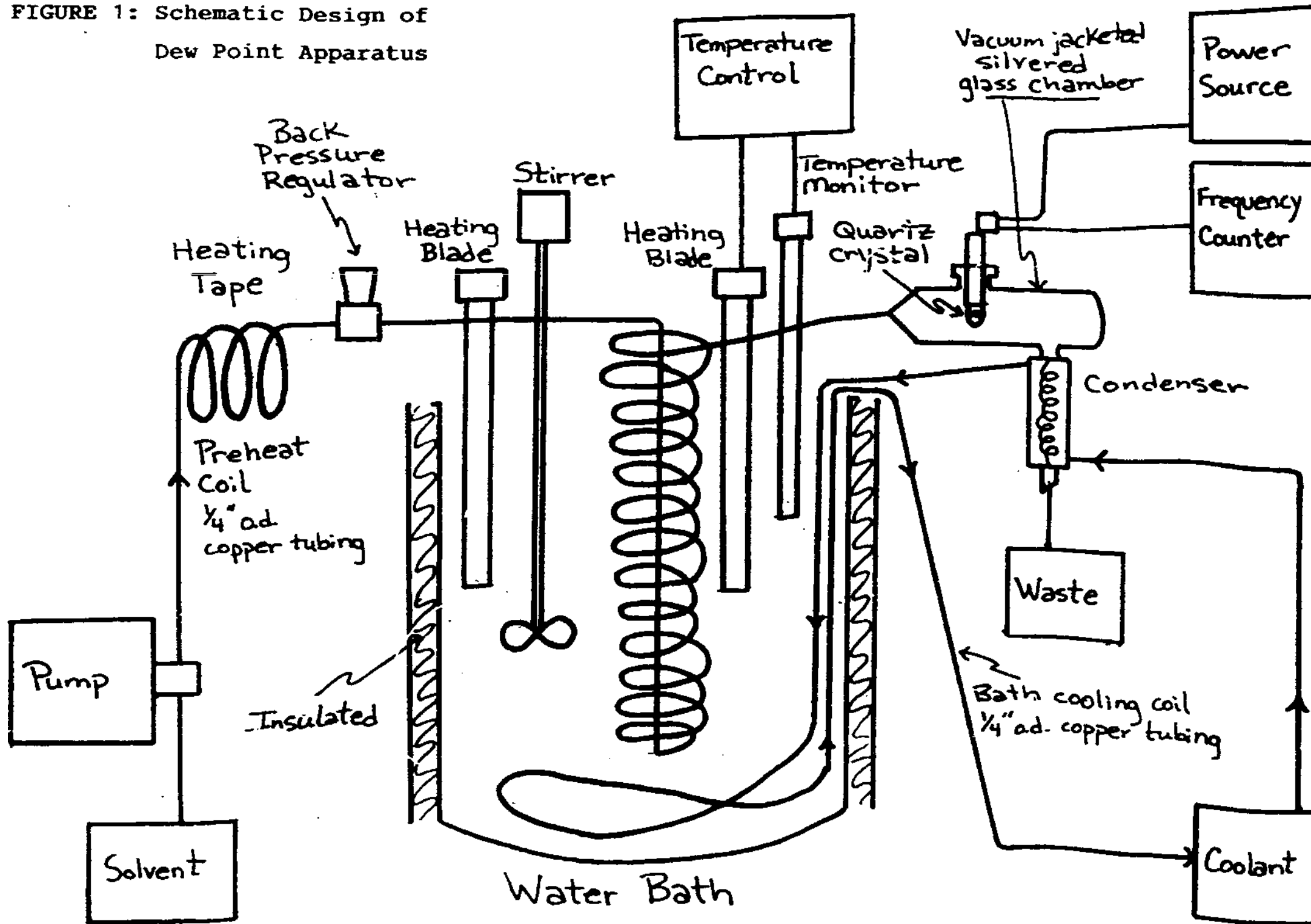
#### D. Equipment:

The apparatus design is schematically represented in Figure 1.

1. Quartz Crystal: The quartz crystal is the site for detecting condensation. The crystal oscillates at a certain frequency. The smallest layer of condensation changes the mechanical properties of the crystal, resonance becomes changed and the output frequency from the crystal is reduced. A frequency counter is used to monitor the change in frequency. A noticeable change would indicate condensation has occurred. The dew point temperature is then recorded.

The quartz crystal oscillates stage oscillates because the output signal is in phase with the transistor input signal. The oscillation frequency is affected by the capacity across the crystal, the crystal temperature, and the mechanical properties of the

FIGURE 1: Schematic Design of Dew Point Apparatus



crystal. The ratio of the output voltage to the input voltage is multiplied times the transistor gain, and that voltage is sent back to the crystal. In the beginning the overall gain is high. As the crystal becomes saturated, the gain decreases. The transistor gain should be kept high so that the crystal doesn't damp out.

The oscillator circuit is schematically represented in Figure 2.

2. Liquid Pump: Milton Roy: This displacement pump was used for flowing liquids into and through the apparatus. It had a capacity of 1 gallon per hour.

3. Power supply for crystal: The crystal's oscillator circuit was connected to a 15 Volt power supply.

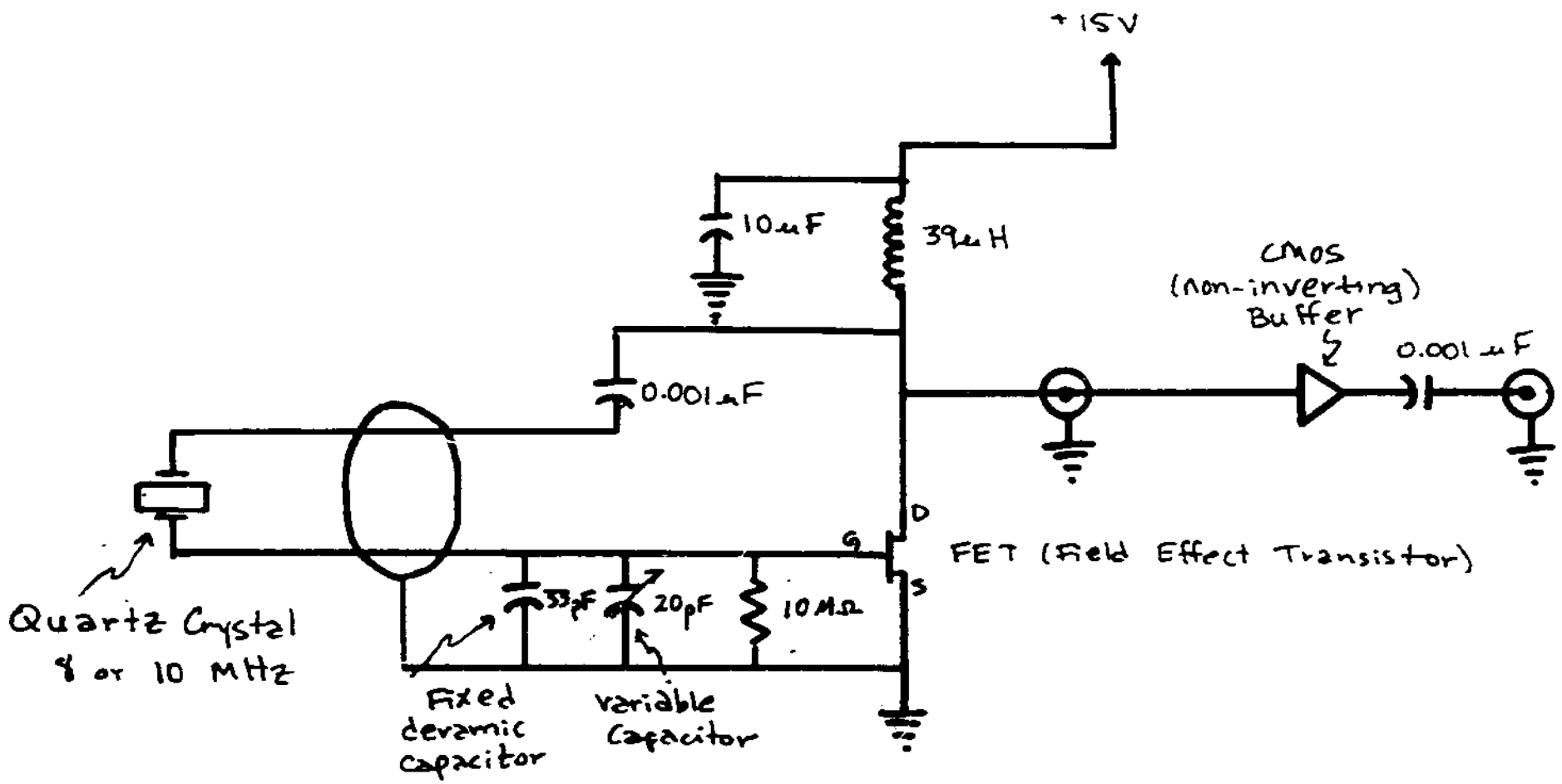
4. Frequency counter: The frequency counter gave a digital readout of the frequency of oscillation. The readings of the quartz crystal were approximately 8 and 10 MHz.

5. Hart thermometer: The Hart thermometer is a very accurate temperature measuring probe. Readings can be taken to 0.00001 °C. The probes are 16 inches long, and 1/8 inch in diameter. The device was easily connected to a chart recorder for monitoring temperatures. Also, the Hart thermometer has the capability to measure a temperature difference. This is necessary in order to obtain a differential dew point temperature.

6. Thermostat: This device was used to control the bath temperature. A sensing probe monitored the temperature. Meanwhile, a heating blade turned off and on, as heat was needed.

7. Heating elements: Two additional heating blades are used to maintain the bath temperature at 65 °C. These blades were of 250 Watts, and the power to each was controlled by a variable voltage device.

FIGURE 2: Diagram of Oscillator Circuit



8. Heating Tape: Heating tape was used in two locations of the apparatus. First, during the preheat the tape heated the acetone liquid. Second, during super-heated runs the tape was wrapped around the glass chamber. Both heating tape temperatures were controlled by a variable voltage device.

9. Bath stirrer: A simple three blade stirrer was used in the water bath. The speed of mixing was controlled by a variable voltage device.

10. Probe and design: (see Figure 3) The probe consisted of a 6 inch long, 1/2 inch diameter stainless steel rod. Down through the center, a 1/8 inch hole was drilled within 1/16 of an inch from the opposite face. In this hole the Hart temperature probe was inserted. Down the side of the stainless steel rod were two grooves. They were used for the wire to connect the quartz crystal to the oscillator circuit. The stainless steel rod was placed in a teflon rod 4 inches long and 1 inch in diameter. The inserted face of the probe was flush, and the disk shaped quartz crystal was positioned perpendicular to the face.

11. Glass chamber: The vacuum jacketed and silvered glass chamber is where the probe and crystal are located. The glass piece is 17 inches long. A ball and socket joint is used to connect the chamber to the acetone flow. On the top side, 6 inches back, there is a teflon/O-ring 1-1/2 hole in which to insert the probe. The teflon screw/O-ring piece forms a tight seal to avoid leaks. At the bottom side of the chamber, near the back, the acetone exits and passes through a condenser. Figure 4 contains a schematic of the chamber design.

12. Back Pressure Regulator: A back pressure regulator was put in the system after the preheat coil and before the water bath. The regulator controls the pressure within the apparatus. This is useful with high boiling point systems. They can be run at pressures under one atmosphere so the boiling temperature is reduced. A

FIGURE 3: Design of Quartz Crystal Probe

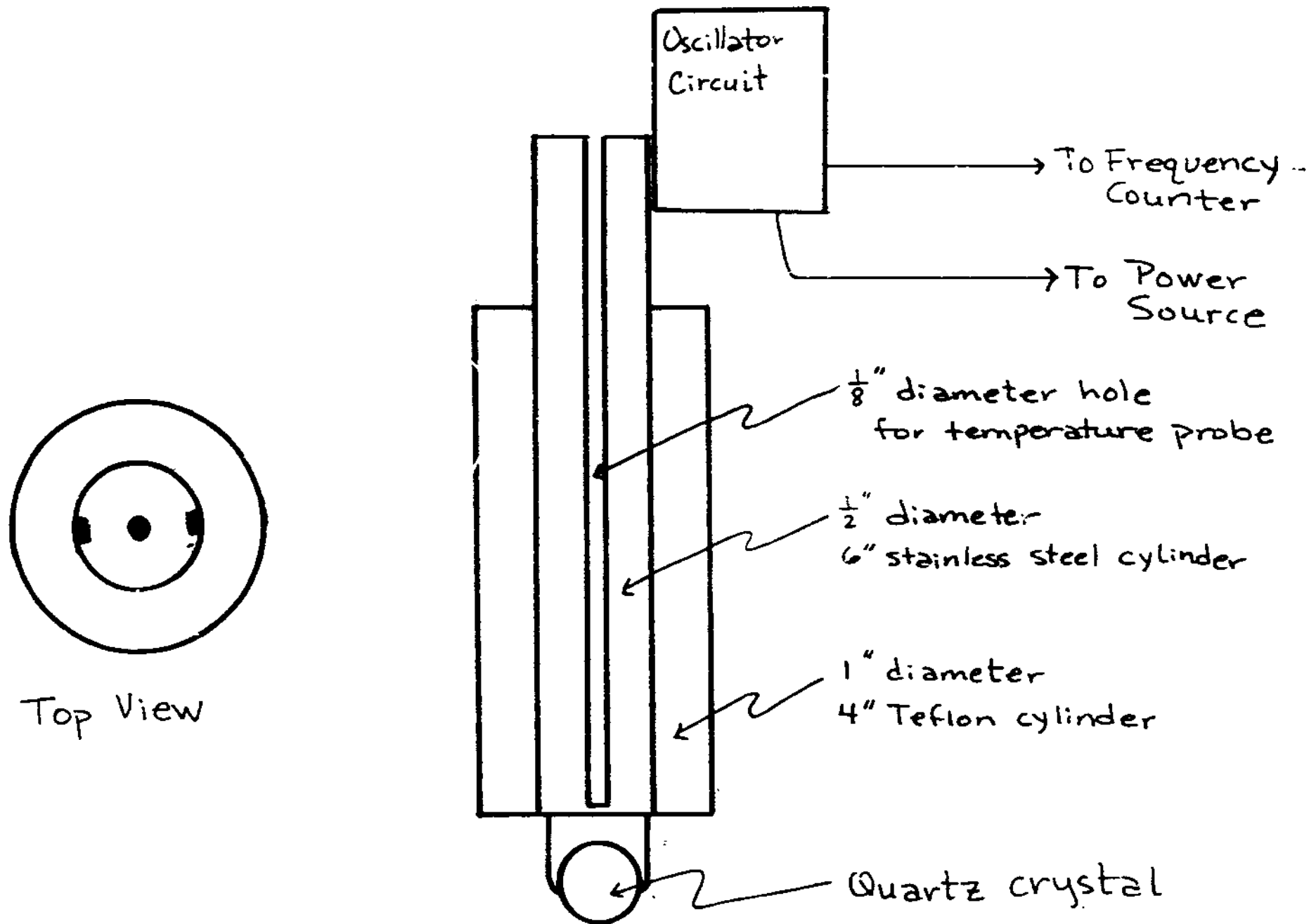
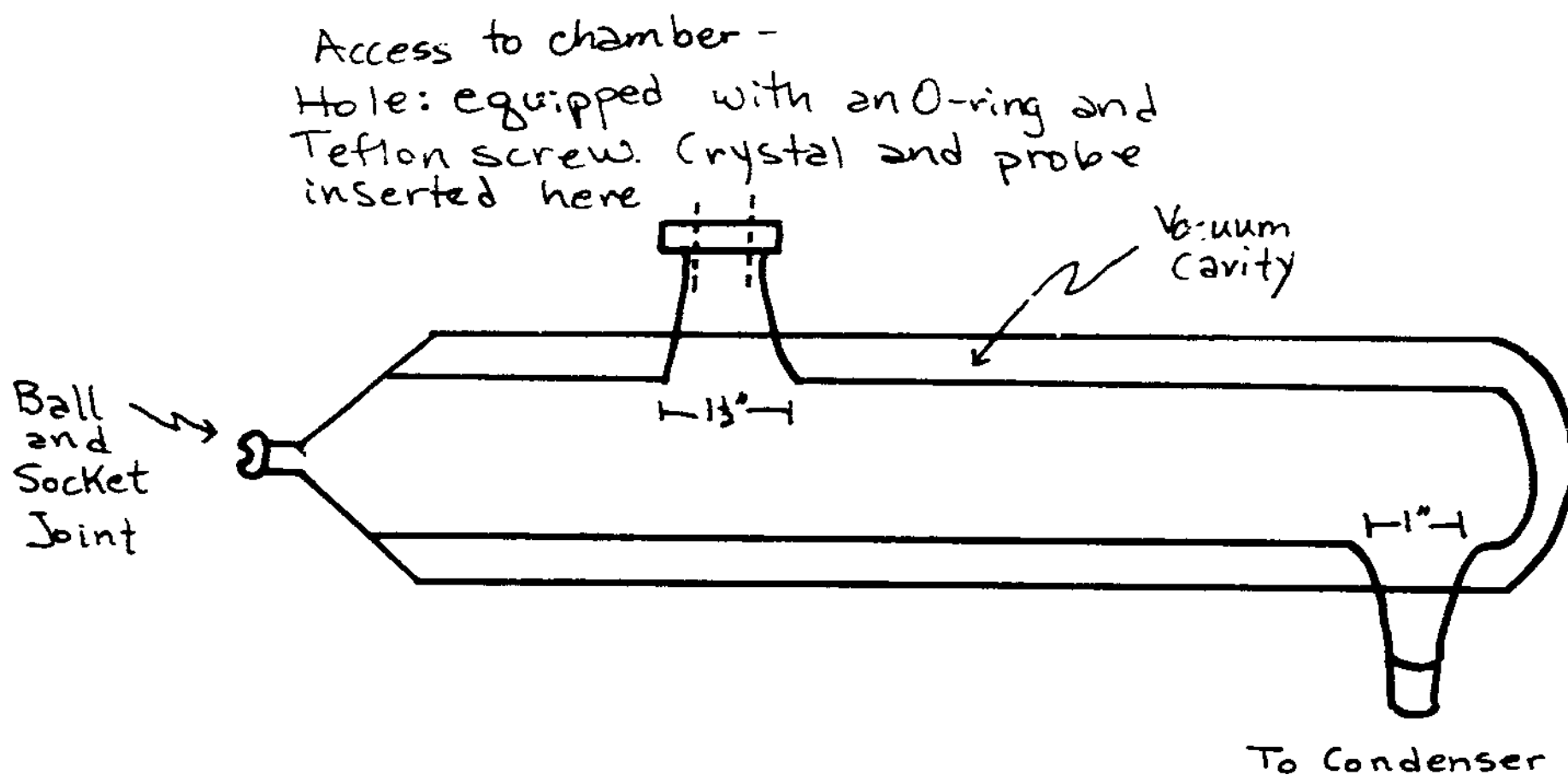




FIGURE 4: Design of Glass Chamber



Glass Chamber: Vacuum Jacketed & Silvered  
inner diameter: 2 inches  
outer diameter: 3 inches  
Overall length: 17 inches

Tescom back pressure regulator was used, having a maximum regulated pressure of 6000 psi. An important consideration was that acetone distorted the common rubber, so acetone resistant O-rings had to be used. This consideration will be necessary for all chemicals, resistant materials must be used.

13. Acetone supply and collection: The acetone continuously flowed through the apparatus. The pump was supplied with liquid from a 500 ml volumetric flask. Waste was collected after the condenser in a flask.

14. Copper and teflon tubing: The apparatus must be resistant to the solvents and solutes that are to be run. The acetone set up required teflon tubing and copper tubing. The teflon tubing was used to join the acetone reservoir to the pump and then from the pump to the apparatus. The tubing in the apparatus was copper tubing, 1/4" and 3/8".

15. Coolant: An ethylene glycol bath was used in two parts of the apparatus: in the bath to help control the temperature and in the condenser after the chamber to recondense the acetone vapor.

#### E. Procedure

Acetone at one atmosphere boils at a temperature of 56.2 °C. Acetone is used because it is relatively safe, and the boiling point can be achieved using a simple water bath. Water, the safest choice, would require an oil or air bath.

(1) The first step during the test runs involved turning on the stirrer, the heating blades, and the thermostat. The bath was warmed up before the acetone flow was started. Meanwhile, the acetone reservoir was filled. When the water bath reached a temperature of 65°C, the apparatus was ready to go.

(2) The acetone flow was started by turning on the pump. The coolant

flow was started at this point. Using a cotton swab and acetone, the quartz crystal surface was cleaned. The crystal oscillation frequency was monitored in atmospheric conditions for a while. After the crystal achieved a steady reading, the frequency was recorded.

(3) As the acetone flow continued, the temperature in the chamber was monitored. When the temperature was relatively constant and above the dew point, the chamber was ready for the crystal/temperature probe to be inserted.

(4) The probe was placed in the chamber, and a stop watch was started. The initial crystal oscillation frequency was recorded.

(5) It took a least a half hour for the crystal/temperature probe to heat up to acetone's boiling point. More time was need as it was super-heated. The temperature of the probe slowly came to an equilibrium. As the temperature changes, so does the oscillation frequency. Waiting is necessary until the two readings become somewhat steady. At this point, the reading should be near atmospheric reading ( $\pm 0.00200$  MHz). The temperature of the probe has reached a steady state.

(6) Dew point detection could now begin. The heating tape on the chamber was slowly cooled. The frequency was recorded, along with the corresponding temperature. The variac setting of the heating tape was also recorded.

(7) If a dew point is detected, then reheat up past this determined dew point, and then re-approach dew-point.

## F. Results

Ending Point of Research Project: Work was done up to the point of finding a functional quartz crystal and finding if condensation could be determined through the

observation of a substantial frequency change upon condensation. Consistency of readings from run to run indicated possible errors that might occur later upon completion of a full apparatus. Below are the aspects of the apparatus that were investigated.

### 1. Varied Flow Rates:

Flow rates between 15 - 25 percent of the pump capacity, one gallon per hour, resulted in the chamber temperature remaining constant. The observed temperature range for these runs were monitored with a chart recorder. The results are discussed in part 3. below.

### 2. Super-heated Vapor:

Introduction of the cool probe unit caused condensation. Heating tape was wrapped around the chamber, resulting in super-heated vapor. The extra heat in the super-heated vapor warmed the probe, and there still remained enough heat to avoid condensation. The probe can also be pre-heated to aid in the process.

### 3. Monitoring Glass Chamber Temperature with a Chart Recorder

The temperature was monitored in the glass chamber. In the chamber, the quartz crystal and temperature probe are mounted. A plug was constructed which fits in place of the quartz crystal probe. There is a hole down the center of this teflon cylinder the size of the Hart thermometer probe. The plug was placed in the chamber and several runs of acetone were completed while the temperature was monitored. The temperature was recorded both digitally and with a chart recorder. The vacuum jacketed chamber maintained the temperature quite well at flow rates between 15 and 25% of capacity.

At flow rates of less than 15 % pump capacity (1 gal/hour) the temperature did not remain constant. Sometimes the boiling temperature of acetone was not reached. The heat loss was greater than the heat input. At flow rates of 15 to 25 % of pump capacity, temperature would initially fluctuate, but all runs eventually hit a thermal equilibrium at about the same temperature. This temperature ranged from 55.568 to 55.590 °C. At flow rates of higher than 25 % there were spurts of liquid that would be blown through the apparatus. This resulted from too much liquid and not enough heat transferred. This fluid would cause a back up in the condenser and the pressure would fluctuate slightly, also affecting the temperature in the chamber.

#### 4. Quartz Crystals: sensitivity, size, oscillating frequency and their corresponding results

The critical part of the apparatus was finding a quartz crystal that was both sensitive enough to detect condensation, but at the same time not so much that it would quit oscillating when the concentrated acetone vapor surrounded the crystal. The three variables in the crystals were their size, oscillating frequency, and their sensitivity. The crystal behavior could not be correlated to any one of these factors.

Most obviously, one would think the larger the size, the more sensitive the crystal. There exists a larger surface area in which to detect condensation. However, mechanically it would take more energy to keep the crystal oscillating, so sensitivity would be lost there. So size can not be directly related to any behavior. There was no correlation seen in the results.

The oscillating frequency differed between the crystals; however, this did affect the overall sensitivity of a crystal. The percentage of the signal lost and sent back from the crystal would be approximately the same, making sensitivity independent of

the frequency.

Sensitivity of two identical crystal should be the same; however, this was not found to be true either. Some crystals would damp themselves out, while others wouldn't. This behavior also seemed to be unpredictable with any given crystal. Finding the working crystal was a matter of trial and error.

### III. Recommendations for future utilization of a differential dew point apparatus

The dew point apparatus has several weak points which should be further investigated.

- o The sensitivity of the crystal to determine the magnitude of change in the oscillating frequency upon condensation.
- o The temperature difference between the two chambers and their probe units should be known.
- o The temperature difference between probe and chamber (observed and actual) should be determined. It may be better to insert the probe directly into the chamber.
- o A chart recorder could be used to monitor both the frequency of oscillation and chamber temperature. Maybe there is a correlation between the two. Dew points could be detected easier this way.
- o Pressure control is needed for other systems, especially those with high boiling points.
- o A design is needed for solvent/solute containment, so that mixture does not evaporate, and stays well mixed.

Experimental procedure for completely working apparatus would entail running two apparatus in parallel. The first would contain pure solvent as the reference, and the second would run solvent and have incremental amounts of solute added. Actually five solution would be prepared, each with an increasing amount of solute.

The microwave technique discussed previously may be worth investigating. Applied to limiting activity coefficients, this method would allow determination of both differential dew and bubble points.

#### IV. CONCLUSIONS

A crystal can be used to detect condensation; however, many questions exist to its applicability to differential dew point detection. These uncertainties must be investigated before the full potential of a dew point apparatus can be used to measure limiting activity coefficients. Temperature control will be one of the biggest limiting factors. Other things that will limit the effectiveness:

(1) Solute effect on the dew point, relating to sensitivity. Condensation must be controlled so that it will occur in the two chambers at similar times. Conditions in the chamber must be the same.

(2) If the relatively volatile solutes still remain in gas phase, then the dew point of the pure solvent will be measured.

If a working differential dew point apparatus could be devised, this method would be a great means of obtaining limiting activity coefficients for systems with relative high volatilities, and also those for which  $dT/dy$  is positive.



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**APPENDIX**

$$P = y_1 P + y_2 P \quad (1)$$

$$y_1 P = x_1 \gamma_1 P_1^S \quad (2)$$

solving (2) for  $y_1$  and substituting into (1)

$$P = x_1 \gamma_1 P_1^S + x_2 \gamma_2 P_2^S \quad (3)$$

$$\left(\frac{\partial P}{\partial y_1}\right)_T = P_1^S \left[ \frac{\partial x_1}{\partial y_1} \gamma_1 + \frac{\partial \gamma_1}{\partial y_1} x_1 \right] + P_2^S \left[ \frac{\partial x_2}{\partial y_1} \gamma_2 + \frac{\partial \gamma_2}{\partial y_1} x_2 \right] \quad (4)$$

using identities:

$$\frac{\partial \gamma_1}{\partial y_1} = \frac{\partial \gamma_1}{\partial x_1} \cdot \frac{\partial x_1}{\partial y_1}$$

$$\text{and} \quad \frac{\partial \gamma_2}{\partial y_1} = \frac{\partial \gamma_2}{\partial x_1} \cdot \frac{\partial x_1}{\partial y_1}$$

results in:

$$\left(\frac{\partial P}{\partial y_1}\right)_T = P_1^S \left[ \frac{\partial x_1}{\partial y_1} \gamma_1 + \frac{\partial \gamma_1}{\partial x_1} \frac{\partial x_1}{\partial y_1} x_1 \right] + P_2^S \left[ \frac{\partial x_2}{\partial y_1} \gamma_2 + \frac{\partial \gamma_2}{\partial x_1} \frac{\partial x_1}{\partial y_1} x_2 \right] \quad (5)$$

since  $x_2$  decreases by the same amount  $x_1$  increases

$$\frac{\partial x_2}{\partial x_1} = -1 \quad \partial x_2 = -\partial x_1 \quad (6)$$

using (6) in (5) and factoring  $\frac{\partial x_1}{\partial y_1}$

$$\left(\frac{\partial P}{\partial y_1}\right)_T = \frac{\partial x_1}{\partial y_1} \left\{ P_1^S \left[ \gamma_1 + \frac{\partial \gamma_1}{\partial x_1} x_1 \right] + P_2^S \left[ -\gamma_2 + \frac{\partial \gamma_2}{\partial x_1} x_2 \right] \right\} \quad (7)$$

with infinite dilution

$$x_1 \rightarrow 0 \quad P = P_2^S \quad x_2 \rightarrow 1 \quad \frac{\partial \gamma_2}{\partial x_1} \rightarrow 0 \quad \gamma_1 \rightarrow \gamma_1^\infty$$

(7) simplifies to:

$$\left(\frac{\partial P}{\partial y_1}\right)_T = \left(\frac{\partial x_1}{\partial y_1}\right) [P_1^S \gamma_1^\infty - P_2^S] \quad (8)$$

Modified Raoult's law:  $x_1 = \frac{y_1 P}{\gamma_1 P_1^s}$      $\frac{x_1}{y_1} = \frac{P}{\gamma_1 P_1^s}$     22

$$\text{now: } \left( \frac{\partial x_1}{\partial y_1} \right)_T = \frac{P}{\gamma_1 P_1^s} + \frac{y_1}{\gamma_1 P_1^s} \left( \frac{\partial P}{\partial y_1} \right) + \frac{y_1 P}{P_1^s} \left( -\frac{1}{\gamma_2} \right) \frac{\partial \gamma_1}{\partial x_1} \quad (9)$$

at infinite dilution  
 $P = P_2^s$

$$\left( \frac{\partial x_1}{\partial y_1} \right)_T^\infty = \frac{P_2^s}{\gamma_1^\infty P_1^s}$$

from (8):

$$\left( \frac{\partial P}{\partial y} \right)_T^\infty = P_2^s - \frac{(P_2^s)^2}{\gamma_1^\infty P_1^s} \quad (10)$$

using identity:

$$\left( \frac{\partial P}{\partial y_1} \right)_T = - \left( \frac{\partial T}{\partial y_1} \right)_P \left( \frac{\partial P}{\partial T} \right)_{y_1}$$

$$\left( \frac{\partial P}{\partial y_1} \right)_T^\infty = - \left( \frac{\partial T}{\partial y_1} \right)_P^\infty \left( \frac{\partial P_2^s}{\partial T} \right)_{y_1} = P_2^s - \frac{(P_2^s)^2}{\gamma_1^\infty P_1^s} \quad \leftarrow \text{from (10)}$$

rearrange and solve for  $\gamma_1^\infty$

$$\gamma_1^\infty = \frac{(P_2^s)^2}{P_1^s \left\{ P_2^s + \left( \frac{\partial T}{\partial y_1} \right)_P^\infty \left( \frac{\partial P_2^s}{\partial T} \right)_{y_1} \right\}} \quad (11)$$

$$P = \frac{\gamma_1 \phi_1^s P_1^s x_1}{\phi_1} \exp\left[\frac{v_1(P-P_1^s)}{RT}\right] + \frac{\gamma_2 \phi_2^s P_2^s x_2}{\phi_2} \exp\left[\frac{v_2(P-P_2^s)}{RT}\right] \quad (12)$$

taking partial of (12):  $\left(\frac{\partial P}{\partial y_1}\right)_T$   
and factoring  $\exp\left[\frac{v_1(P-P_1^s)}{RT}\right]$

$$\begin{aligned} \left(\frac{\partial P}{\partial y_1}\right)_T &= \phi_1^s P_1^s \exp\left[\frac{v_1(P-P_1^s)}{RT}\right] \left\{ \frac{\gamma_1}{\phi_1} \frac{\partial x_1}{\partial y_1} + \frac{x_1}{\phi_1} \frac{\partial \gamma_1}{\partial y_1} - \frac{\gamma_1 x_1}{\phi_1^2} \frac{\partial \phi_1}{\partial y_1} + \frac{\gamma_1 x_1 v_1}{\phi_1 RT} \frac{\partial P}{\partial y_1} \right\} \\ &+ \phi_2^s P_2^s \exp\left[\frac{v_2(P-P_2^s)}{RT}\right] \left\{ \frac{\gamma_2}{\phi_2} \frac{\partial x_2}{\partial y_1} + \frac{x_2}{\phi_2} \frac{\partial \gamma_2}{\partial y_1} - \frac{\gamma_2 x_2}{\phi_2^2} \frac{\partial \phi_2}{\partial y_1} + \frac{\gamma_2 x_2 v_2}{\phi_2 RT} \frac{\partial P}{\partial y_1} \right\} \quad (13) \end{aligned}$$

as  $x_1 \rightarrow 0$   $P \rightarrow P_2^s$   $\gamma_2 \rightarrow 1$   $\frac{\partial \gamma_2}{\partial x_2} \rightarrow 0$  then  $\gamma_1 \rightarrow \gamma_1^\infty$

using identity:  $\frac{\partial \gamma_2}{\partial y_1} = \frac{\partial \gamma_2}{\partial x_1} \frac{\partial x_1}{\partial y_1}$

Simplify (13):

$$\left(\frac{\partial P}{\partial y_1}\right)_T^\infty = \phi_1^s P_1^s \exp\left[\frac{v_1(P_2^s - P_1^s)}{RT}\right] \frac{\gamma_1^\infty}{\phi_1} \frac{\partial x_1}{\partial y_1} + \phi_2^s P_2^s \left\{ \frac{1}{\phi_2} \frac{\partial x_2}{\partial y_1} + \frac{-\gamma_2}{\phi_2^2} \frac{\partial \phi_2}{\partial y_1} + \frac{\gamma_2 v_2}{\phi_2 RT} \frac{\partial P}{\partial y_1} \right\}$$

simplifying further:

$$\left(\frac{\partial P}{\partial y_1}\right)_T^\infty = \phi_1^s P_1^s \exp\left[\frac{v_1(P_2^s - P_1^s)}{RT}\right] \frac{\gamma_1^\infty}{\phi_1} \frac{\partial x_1}{\partial y_1} + \frac{-\phi_2^s P_2^s}{\phi_2^2} \frac{\partial \phi_2}{\partial y_1} + \frac{\phi_2^s P_2^s v_2}{\phi_2 RT} \frac{\partial P}{\partial y_1}$$

$$\left(\frac{\partial P}{\partial y_1}\right)_T^\infty \left(1 - \frac{\phi_2^s P_2^s v_2}{\phi_2 RT}\right) + \frac{\phi_2^s P_2^s}{\phi_2^2} \frac{\partial \phi_2}{\partial y_1} = \frac{\partial x_1}{\partial y_1} \left[ \phi_1^s P_1^s \exp\left[\frac{v_1(P_2^s - P_1^s)}{RT}\right] \frac{\gamma_1^\infty}{\phi_1} - \frac{\phi_2^s P_2^s}{\phi_2} \right] \quad (14)$$

Solving for  $\frac{\partial x_1}{\partial y_1}$

$$\gamma_1 = \frac{\gamma_1 \phi_1 P}{\gamma_1 \phi_1^s P_1^s \exp\left[\frac{v_1(P-P_1^s)}{RT}\right]}$$

$$\frac{\partial x_1}{\partial y_1} = \left[ \frac{\phi_1 P}{\gamma_1} + \frac{\gamma_1 P}{\gamma_1} \frac{\partial \phi_1}{\partial y_1} - \frac{\gamma_1 \phi_1 P}{\gamma_1^2} \left(\frac{\partial \gamma_1}{\partial y_1}\right) - \frac{\gamma_1 \phi_1 P v_1}{\gamma_1 RT} \frac{\partial P}{\partial y_1} + \frac{\gamma_1 \phi_1}{\gamma_1} \left(\frac{\partial P}{\partial y_1}\right) \right] \frac{1}{\phi_1^s P_1^s \exp\left[\frac{v_1(P-P_1^s)}{RT}\right]}$$

So as  $x_1 \rightarrow 0$   $y_1 \rightarrow 0$   $P \rightarrow P_2^s$

$$\frac{\partial y_1}{\partial y_1} = \frac{\phi_1 P_2^s}{\gamma_1^\infty \phi_1^s P_1^s \exp\left[\frac{v_1(P_2^s - P_1^s)}{RT}\right]}$$

$$\left(\frac{\partial P}{\partial y_1}\right)_T^\infty \left(1 - \frac{\phi_2^s P_2^s}{\phi_2} \frac{v_2}{RT}\right) + \frac{\phi_2^s P_2^s}{\phi_2} \frac{\partial \phi_2}{\partial y_1} = \frac{\phi_1 P_2^s}{\gamma_1^\infty \phi_1^s P_1^s \exp\left[\frac{v_1(P_2^s - P_1^s)}{RT}\right]} \left\{ \phi_1^s P_1^s \exp\left[\frac{v_1(P_2^s - P_1^s)}{RT}\right] \gamma_1^\infty - \phi_2^s P_2^s \right\}$$

simplifying

$$= P_2^s - \frac{\phi_2^s P_2^s \phi_1 P_2^s}{\gamma_1^\infty \phi_1^s \phi_2 P_1^s \exp\left[\frac{v_1(P_2^s - P_1^s)}{RT}\right]}$$

identity

$$\left(\frac{\partial P}{\partial y_1}\right)_T^\infty = -\left(\frac{\partial T}{\partial y_1}\right)_P^\infty \left(\frac{\partial P_2^s}{\partial T}\right)$$

$$\frac{\phi_2^s P_2^s \phi_1 P_2^s}{\gamma_1^\infty \phi_1^s \phi_2 P_1^s \exp\left[\frac{v_1(P_2^s - P_1^s)}{RT}\right]} = P_2^s - \frac{\phi_2^s P_2^s}{\phi_2} \frac{\partial \phi_2}{\partial y_1} + \left(\frac{\partial T}{\partial y_1}\right)_P^\infty \left(\frac{\partial P_2^s}{\partial T}\right) \left(1 - \frac{\phi_2^s P_2^s v_2}{\phi_2 RT}\right)$$

solving for  $\gamma_1^\infty$

$$\gamma_1^\infty = \frac{\phi_2^s \phi_1 (P_2^s)^2}{\phi_1^s \phi_2 P_1^s \exp\left[\frac{v_1(P_2^s - P_1^s)}{RT}\right]} \left\{ P_2^s - \frac{\phi_2^s P_2^s}{\phi_2} \left(\frac{\partial \phi_2}{\partial y_1}\right) + \left(\frac{\partial T}{\partial y_1}\right)_P^\infty \left(\frac{\partial P_2^s}{\partial T}\right) \left(1 - \frac{\phi_2^s P_2^s v_2}{\phi_2 RT}\right) \right\}$$

TABLE 1

INACCURACIES IN TEMPERATURE AND THEIR EFFECT ON THE SYSTEM  
OF METHANOL IN CYCLOHEXANE

$T = 34.11 \text{ }^\circ\text{C}$        $P = 200.2 \text{ torr}$

Relative Volatility = 100.8

$P_1^* = 0.19326 \text{ bars}$

$P_2^* = 0.26686 \text{ bars}$

$dP_2^*/dT = 0.0128$

$y_1$	actual T ( $^\circ\text{C}$ )	error = +/- 0.002		error = +/- 0.0002	
		T ( $^\circ\text{C}$ )	T ( $^\circ\text{C}$ )	T ( $^\circ\text{C}$ )	T ( $^\circ\text{C}$ )
0.0000	307.260				
0.0109	306.052	306.054	307.050	307.0522	307.0518
0.0225	306.815	306.817	306.813	306.8152	306.8148
0.0315	306.649	306.817	306.647	306.6492	306.6488
0.0405	306.479	306.477	306.481	306.4788	306.4792
0.0495	306.304	306.302	306.306	306.3038	306.3042
<hr/>					
$dT/dy_1$	-19.262	-19.386	-19.138	-19.274	-19.249
$\gamma_1^\infty$	18.150	19.685	16.831	18.285	17.999

1 percent error in  $dT/dy$ : -19.455       $\gamma_1^\infty = 20.660$

2 percent error in  $dT/dy$ : -19.647       $\gamma_1^\infty = 23.961$

3 percent error in  $dT/dy$ : -19.840       $\gamma_1^\infty = 28.547$

The  $y$  and  $T$  values were calculated from differential boiling point data taken by L. Scott and D.M. Trampe.

TABLE 2

INACCURACIES IN PRESSURE AND THEIR EFFECT ON THE SYSTEM  
OF METHANOL IN CYCLOHEXANE

T = 34.11 °C      P = 200.2 torr

Relative Volatility = 100.8

$P_1^* = 0.19326$  bars

$P_2^* = 0.26686$  bars

error = +/- 0.002 torr

$y_1$	actual P (torr)	P (torr)	P (torr)
0.0000	200.2000	200.2020	200.1980
0.0109	200.2027	200.2047	200.2007
0.0312	200.2055	200.2075	200.2035
0.0405	200.2100	200.2080	200.2120
0.0495	200.2122	200.2102	200.2142
-----			
$dP/dy_1$	0.24656	0.14366	0.34959
$\gamma_1^\infty$	18.15	2.991	-4.454



TABLE 3

INACCURACIES IN TEMPERATURE AND THEIR EFFECT ON THE SYSTEM  
OF CYCLOHEXANE IN METHANOL

$T = 25.57 \text{ }^\circ\text{C}$

Relative Volatility = 14.39

$P_1' = 0.17470 \text{ bars}$

$P_2' = 0.13346 \text{ bars}$

$dP_2'/dT = 0.005975$

error = +/- 0.002  $^\circ\text{C}$

$y_1$	actual T ( $^\circ\text{C}$ )	T ( $^\circ\text{C}$ )	T ( $^\circ\text{C}$ )
0.00000	298.7200	298.7220	298.7180
0.07825	297.0055	297.0075	297.0035
0.16108	294.7368	294.7348	294.7338
0.23039	292.9051	292.9031	292.9071
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$dT/dy_1$	-25.46	-25.48	-25.44
$\gamma_1^\infty$	5.463	5.426	5.500

TABLE 4

INACCURACIES IN PRESSURE AND THEIR EFFECT ON THE SYSTEM OF  
CARBON TETRACHLORIDE IN ACETONE

$$T = 33.88 \text{ }^{\circ}\text{C}$$

$$\text{Relative Volatility} = 1.039$$

$$P_1^* = 0.2227 \text{ bars}$$

$$P_2^* = 0.4430 \text{ bars}$$

$$dP_2^*/dT = 0.0178$$

errors = +/- 0.002  $^{\circ}\text{C}$

$y_1$	actual T ( $^{\circ}\text{C}$ )	T ( $^{\circ}\text{C}$ )	T ( $^{\circ}\text{C}$ )
0.0042	307.0254	307.0274	307.0234
0.0106	307.0188	307.0208	307.0168
0.0169	307.0135	307.0155	307.0115
0.0220	307.0099	307.0079	307.0119
0.0265	307.0069	307.0049	307.0089
<hr/>			
$dT/dy_1$	-0.8249	-1.033	-0.6167
$\gamma_1^{\infty}$	2.057	2.075	2.040

## NOMENCLATURE

$P$	Pressure
$P_i^s$	Vapor pressure of pure component $i$
$R$	Universal gas constant
$T$	Temperature
$v_i$	Liquid molar volume of component $i$
$x_i$	Mole fraction of component $i$ in liquid
$y_i$	Mole fraction of component $i$ in vapor
$\gamma$	Activity coefficient
$\gamma^\infty$	Activity coefficient at infinite dilution
$\phi_i$	Fugacity coefficient of pure component $i$
$\phi_i^s$	Fugacity coefficient of pure component $i$ at its vapor pressure