

VAPOR - LIQUID EQUILIBRIUM DATA
FOR TETRAHYDROFURAN AND RELATED ORGANICS

by

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A MASTER'S THESIS

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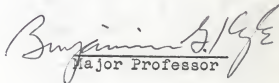
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PURPOSE

The purpose of this work was to evaluate previously undetermined vapor-liquid equilibrium data for binary systems containing the chemical compound, tetrahydrofuran. This work was designed to determine temperature-composition relationships for the binary systems of tetrahydrofuran with benzene, cyclohexane and hexane.

NOMENCLATURE

D	100I/Σ (Herington's test)
I	$\left[\frac{1}{2.303} \right] \int_0^1 \ln(\gamma_1/\gamma_2) dx_1$ or $\int_0^1 \log(\gamma_1/\gamma_2) dx_1$
J	150 Θ/T_{\min}
ln	logarithm to the base e
log	logarithm to the base ten
P _i	partial pressure of the i th component
P ^o	vapor pressure of the pure component in mm. of mercury
S	$0.4343/(x_1 d \log P_1^o/dT + x_2 d \log P_2^o/dT)$
THF	tetrahydrofuran
T ^o C	temperature in degrees centigrade
T _{min}	lowest measured boiling temperature (^o K) in the system (Herington's test)
x	mole fraction in liquid phase
y	mole fraction in vapor phase
α	relative volatility defined as $y_1 x_2 / y_2 x_1$

- γ activity coefficient with the standard state taken as the pure substance
- π total pressure in mm. of mercury
- Σ absolute sum of the magnitude of the positive and negative areas in the $\ln(\gamma_1/\gamma_2)$ versus x plot
- θ temperature difference between the highest and lowest temperature of the system

Subscripts:

THF tetrahydrofuran

Ben benzene

CH cyclohexane

Hex hexane

INTRODUCTION

Tetrahydrofuran is a cyclic ether of the structure



This relatively new compound has found industrial uses mainly as a solvent. It is miscible with water and most organic compounds even to the extent that it can be mixed with less active solvents to improve their solvent power. The compound is especially effective with vinyl chloride polymers where its high and rapid solvent power accompanied with a low boiling point and a high rate of diffusion make the solvent extremely desirable. This affinity for vinyl chlorides creates industrial uses in film coatings, adhesives and printing inks. Tetrahydrofuran's unique solvent ability is currently being expanded into uses as a reaction solvent in such reactions as acid or basic anhydride reductions and Grignard reactions - reduction of higher organics into alcohols in the presence of magnesium. Uses are also being found for the compound as an extractive solvent where its low boiling point and water miscibility make for inexpensive mixing and separation.

As industrial and commercial uses for tetrahydrofuran develop, an increasing need becomes apparent for more knowledge of the compound's physical and chemical properties. Uses as a reaction or extraction solvent are especially demanding on

a knowledge of vapor-liquid equilibrium data. Design of proper extraction or distillation columns and chemical reactors necessitate equilibrium data on the systems involved. Hence the purpose of this thesis is to present such data. Benzene, cyclohexane and n-hexane are chosen as the second constituent in a binary mixture with tetrahydrofuran because these represent three basic classes of organics - an aromatic, a cyclic compound, and a straight-chained paraffin. The intention of this choice is that the user of this information can relate this data to analogous organics with which he might be working.

The data reported here are the temperature, vapor composition, liquid composition, relative volatility, and activity coefficient relationships. All three binary systems were determined at a constant pressure of one atmosphere leaving only temperature and vapor-liquid compositions as variables.

THEORETICAL BACKGROUND

Above every liquid exists a vapor consisting of the components of the liquid; the amount of a component in the vapor phase is related to the concentration of this component in the liquid phase. Also, the component in the vapor phase exerts a pressure on its environment that is a partial of the total pressure and is dependent on the concentration in the liquid phase. The sum of the partial pressures is naturally the total pressure. Frequently the partial pressure of an individual component can be expressed as its mole fraction in the vapor phase times the total pressure; such expression is referred to as an ideal vapor phase and represents the usual definition of partial pressure. For a limited number of systems the partial pressure can be expressed as the mole fraction in the liquid phase times the component's vapor pressure at the system's temperature and pressure. Thus for systems having ideal liquid and vapor phases the partial pressure is given by

$$P_1 = y_1 \pi = x_1 P_1^{\circ} \quad (1)$$

Because there are only a few systems that behave as ideal solutions a correction factor called an activity coefficient is introduced to account for the solutions' deviation from liquid phase ideality.

$$P_1 = y_1 \pi = \gamma_1 x_1 P_1^{\circ} \quad (2)$$

This activity coefficient must be determined by experimentation.

In a constant pressure system the activity coefficient is a function of temperature and composition. For a given pressure the temperature directly determines a component's vapor pressure. This vapor pressure and the equilibrium values of x and y for the given temperature are then used in equation 2 to calculate the value of the activity coefficient. Such vapor-liquid equilibrium data can be presented graphically in several ways.

There exist several tests for the data's validity and accurateness. One such test, which demonstrates errors in composition, is a plot of y minus x versus x for a particular component as outlined by Hala, Pick, Fried and Vilim (3). A smooth curve indicates a consistency of the composition data. A plot of the relative volatility versus x is more sensitive to discrepancies in composition due to the definition of relative volatility.

However, the more exacting tests for data are those involving thermodynamic consistency. These are tests derived from fugacity relationships for phase equilibrium. A simple method for checking isothermal data, which can be extended to data of small temperature ranges, is a test proposed by Redlich and Kister (5) derived from the standard free energy relationships. The condition for the Redlich-Kister test is

$$\int_0^1 \ln(\gamma_1/\gamma_2) dx_1 = 0 \quad (3)$$

A graph of $\ln(\gamma_1/\gamma_2)$ versus x_1 should give zero area underneath the curve. This test supplies a very strong criterion for thermodynamic consistency, because if the deviation from zero area is reasonable in this test, all other tests are usually in agreement.

E. F. Herington generalized the Redlich-Kister test to include isobaric data (4). In this test $[1/2.303] \int_0^1 \ln(\gamma_1/\gamma_2) dx_1$ is denoted by the symbol I. A percentage deviation is then defined as $D=100I/\bar{\epsilon}$ which is compared to the value $J=150 \theta/T_{\min}$. (Refer to the nomenclature for the meaning of the symbols.) If $D < J$ the measured data can be assumed correct; even if $D - J < 10$ Herington states that the data can still be considered correct.

A third test derived by Redlich et al (5) applicable to isobaric data relates the boiling temperature to the system's composition by the relationship:

$$dT/dy_1 = S(x_1 - y_1)/y_1 y_2 \quad (4)$$

where $S = 0.4343/(x_1 d\log P_1^0/dT + x_2 d\log P_2^0/dT)$. (5)

The dT/dy_1 is the tangent of the boiling point vapor composition curve at y_1 ; $d\log P_1^0/dT$ and $d\log P_2^0/dT$ are the tangents to the respective logarithm of vapor pressure versus temperature curves at the equilibrium temperature, T .

Thermodynamic consistency tests in themselves are not an absolute guarantee of the data's validity and accurateness for there exists the possibility of identical systems being thermodynamically consistent by the above tests and yet containing dissimilar data, and also the possibility of data fitting none of the tests and yet being reproducible data. Only repeated experimentation with similar results can insure truly accurate data. However, the data's fit to these described tests gives a strong indication of its worth in future uses.

EXPERIMENTAL PROCEDURE

The apparatus employed in gathering the equilibrium data, shown in figure 1, was the Ellis equilibrium still developed by S. R. M. Ellis (2). Not shown in the figure is the insulation and heating coil around the still's upper portion to prevent heat losses in the vapor space. The two thermocouple wells contained previously calibrated copper-constantan thermocouples. The heat to the still jacket was supplied by a resistance wire imbedded in the insulation. The heat served only to prevent vapor condensation in the top portion of the still. Heat was provided to the bottom heater at such a rate as to manifest a drop rate of 40 to 60 drops/minute from the water condenser.

The system was held at a constant pressure of 760 ± 1 mm. throughout a run by a constant pressure system. The procedure in establishing the constant pressure was to raise the pressure within the system to 760mm. and then seal off the system, which included a manometer for checking the pressure. Once the pressure was fixed, which took some time due to volume expansion of the heating liquid, little variation was experienced.

A typical run would start by heating the bottom element a few minutes prior to charging the still; this ensured even boiling throughout the heating surface. The two components were then added in approximately the desired concentrations.

The system was brought up to the desired pressure, and the condenser cooling water started. Usually after a short time a pressure adjustment had to be made. About once an hour the two thermocouple temperatures were checked until an equilibrium condition was established. Equilibrium existed when the temperature measured from the bottom thermocouple well remained constant for a period of time, usually an hour. This condition took several hours to achieve. This temperature is that of the vapor-liquid mixture impinging on the well from the spiral tubing arising from the heating area. The temperature measured at the still's top simply showed the degree of superheat due to the heating jacket. The vapor in the still's top was kept two to four degrees above the boiling temperature to prevent condensation in this portion of the still, for condensing vapor here would result in rectification. When this top temperature fell below the bottom temperature, the bottom temperature would decrease. Likewise if the top temperature rose above this working range, the bottom temperature would be too high. In order to maintain this temperature interval, adjustments to the jacket heat input were made during the run.

The vapor is condensed in the right-hand portion of the still where it is recirculated back to the heating area. Vapor samples were drawn off the vapor condensate in a five milliliter bottle; liquid samples were taken off the still's side. The samples were immediately analyzed with an Abbe'

refractometer capable of determining the refractive index to a precision of $\pm .0001$. Calibration curves were previously constructed for the three binary systems by weighing known samples on the analytical balance to a precision of $\pm .0001$ gram and determining the refractive index at 25°C of each known sample. The data and curves for this calibration are shown in Appendix I. All samples were then measured at a refractometer temperature of 25°C .

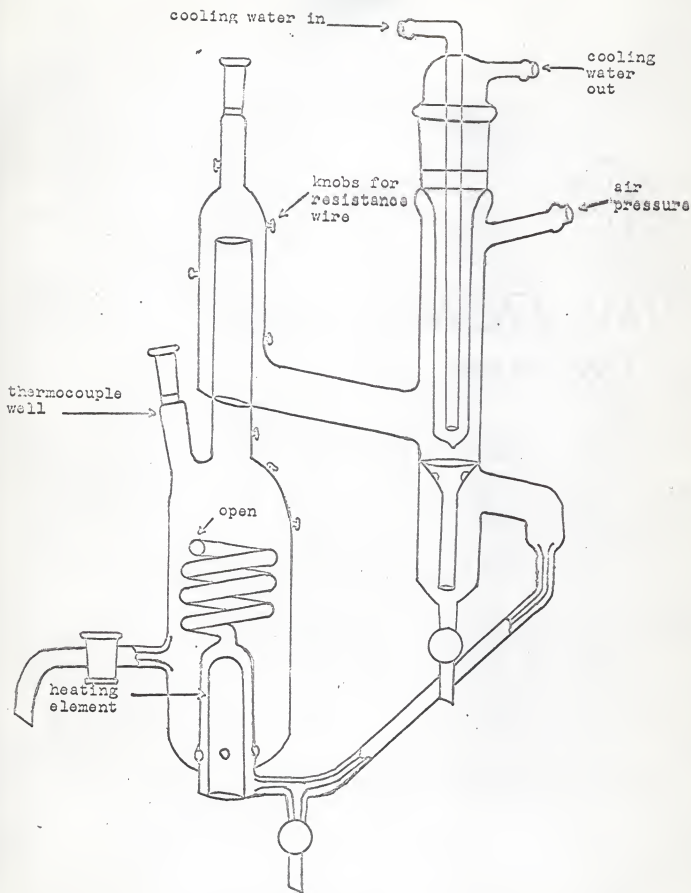


Fig. 1. Diagram of apparatus.

EXPERIMENTAL RESULTS

Benzene - Tetrahydrofuran:

The data presented below represents fifteen points covering the whole range of mole fractions. The system proved somewhat unique in that it shows a negative deviation in activity coefficients. Figures 2 through 7 give the data in graphical form and demonstrate the consistency tests described previously. Notice on the graph of $\ln \gamma$ versus mole fraction THF that the extremities of the curves should approach the zero axis asymptotically because when the composition is that of the pure component the activity coefficient should be one. By setting the activity coefficient equal to one in equation 2 and solving for the vapor pressure for composition values near the end of the range, a corrected temperature can be determined. The difference in temperature required to bring the activity coefficients at the lower compositions up to the asymptotic value is about one degree. This discrepancy suggests a constant temperature error of about one degree above normalcy especially since a similar discrepancy exists in the other two systems.

Notice also a certain amount of arbitrariness in the extremities of the $\ln(\gamma_{\text{THF}}/\gamma_{\text{Ben}})$ versus mole fraction plot. This is due to the curves' extremities approaching very high values at the pure components making an area estimation somewhat difficult. All three systems exhibit this trait.

Even so the area sums to .0041 which can be considered quite good.

Herington's test on this system shows $D = 2.39$, less than $J = 6.24$, making the system consistent by this test.

Table 1. Data for the system Benzene - Tetrahydrofuran at 760mm.

$T^{\circ}\text{C}$	y_{THF}	x_{THF}	γ_{THF}	γ_{Ben}	$\alpha(\text{THF to Ben})$
80.10	0	0	-	1.000	-
78.99	.136	.100	.880	1.037	1.418
78.19	.268	.202	.900	.972	1.457
77.59	.338	.259	.906	.965	1.460
76.95	.414	.318	.918	.946	1.513
75.49	.543	.428	.927	.924	1.590
74.60	.608	.495	.937	.933	1.587
74.38	.622	.515	.934	.928	1.550
72.36	.753	.652	.939	.903	1.626
72.36	.763	.662	.926	.893	1.643
71.12	.829	.742	.935	.882	1.685
69.88	.912	.852	.928	.833	1.800
68.75	.931	.883	.945	.857	1.790
68.64	.932	.885	.944	.855	1.782
67.83	.960	.931	.949	.807	1.736
67.15	.978	.954	.952	.726	2.140
66.00	1.000	1.000	.944	-	-

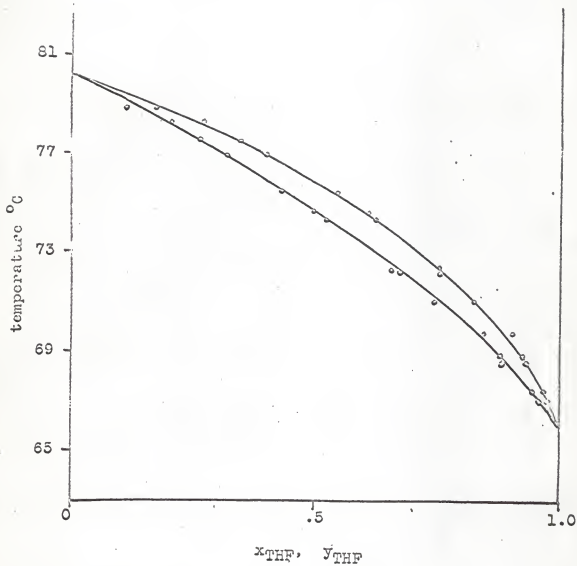


Fig. 2. Temperature versus mole fraction THF at 760mm. pressure, Benzene - THF.



Fig. 3. Mole fraction THF in liquid versus mole fraction in vapor at 760mm. pressure, Benzene - THF.

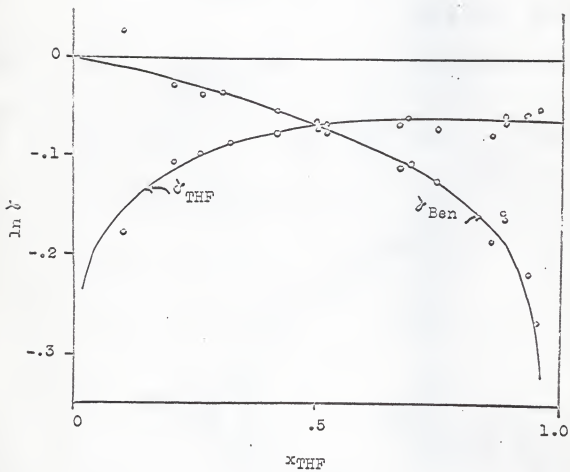


Fig. 4. $\ln \gamma$ versus mole fraction THF in liquid at 760mm. pressure, Benzene - THF.

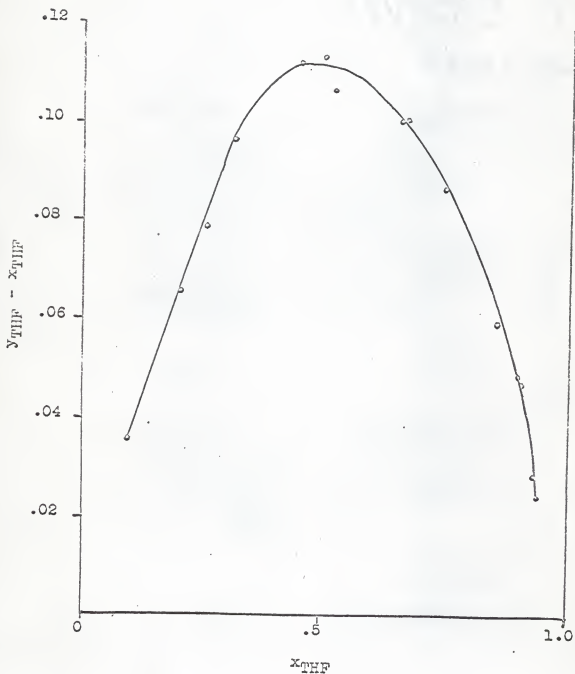


Fig. 5. $y_{THF} - x_{THF}$ versus mole fraction THF in liquid at 760mm. pressure, Benzene - THF.

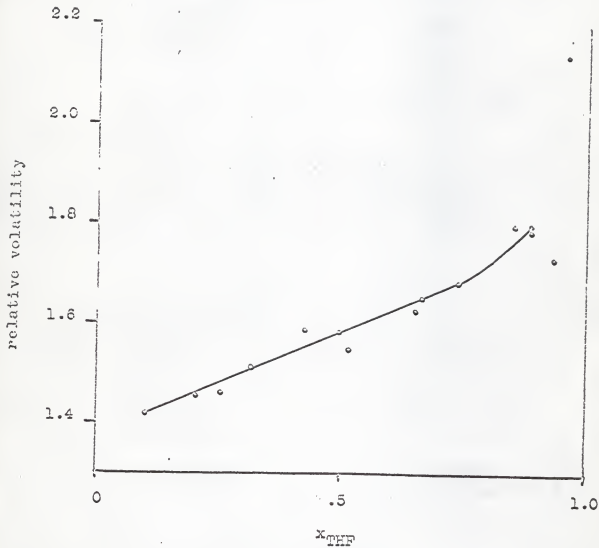


Fig. 6. Relative volatility versus mole fraction THF in liquid at 760mm. pressure, Benzene - THF.

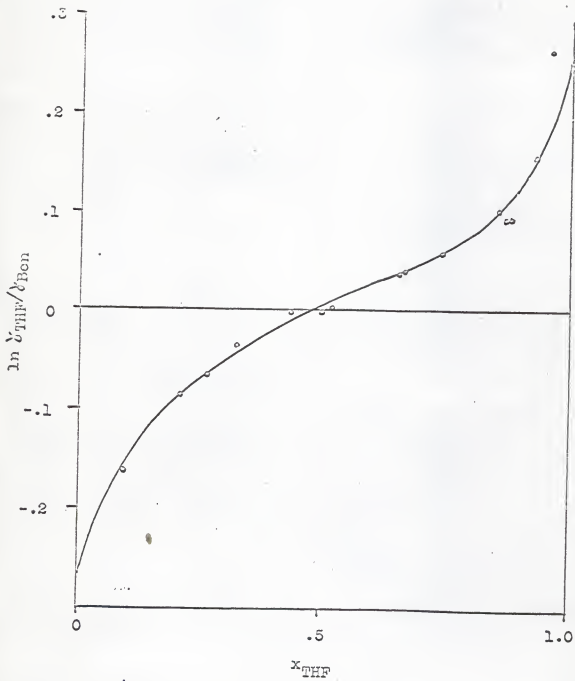


Fig. 7. $\ln \delta_{\text{THF}}/\delta_{\text{Ben}}$ versus mole fraction THF in liquid at 760mm. pressure, Benzene - THF.

Cyclohexane - Tetrahydrofuran:

Of the three systems investigated, this system shows the greatest deviation from thermodynamic consistency. The basic reason for this inconsistency is the inexplicably high boiling temperatures for the THF-rich region. The boiling temperature of the pure THF as measured in the equilibrium still rose from 66.0°C to 67.5°C for this system. This system's data for high mole fraction THF were the last to be obtained; consequently, the other systems were not affected. The refractive index shows pure THF, and the THF boils correctly in another still. The fault then seems to be within the Ellis still, but exactly what it is remains unknown.

This discrepancy in boiling temperature is reflected in the plot of $\ln \gamma$ versus mole fraction where the curves' deviation from the zero axis are disproportionate. The points should not go below the zero axis, and once again a degree's difference in temperature is suggested by calculating the vapor pressure from equation 1 and then finding the corresponding temperature for low equilibrium compositions. The curve of $\ln(\gamma_{\text{THF}}/\gamma_{\text{CH}})$ is also disproportionate even with a slightly arbitrary judgment of the area underneath the curve. An area's sum of .0752 could barely be considered significantly different from zero. However, there is some measure of consistency indicated by the plots of $y_{\text{THF}} - x_{\text{THF}}$ versus x_{THF} and relative volatility versus x_{THF} . These plots show a fitness of the

mole fraction data. Herington's test shows thermodynamic consistency by $D = 11.1$ and $J = 6.81$ making $D - J$ less than ten.

The curve of temperature versus x_{THF} and y_{THF} shows the boiling temperature of pure THF to be 67.5°C . The test proposed by Redlich (5) correlating the slope of the temperature - y_{THF} line with calculatable data indicates that the curve approaches pure THF by the dotted line shown on figure 8.

Table 2. Data for the system cyclohexane - tetrahydrofuran at 760 mm.:

$T^{\circ}\text{C}$	y_{THF}	x_{THF}	γ_{THF}	γ_{CH}	$\alpha(\text{THF to CH})$
80.74	0	0	-	.962	
78.79	.060	.010	4.060	1.028	6.32
76.94	.202	.055	2.644	.950	4.34
75.54	.285	.122	1.723	.962	2.87
74.19	.365	.200	1.412	.991	2.30
73.84	.418	.232	1.390	.946	2.38
72.99	.510	.338	1.197	.952	2.04
72.34	.560	.382	1.181	.931	2.058
71.41	.642	.515	1.039	.997	1.690
70.51	.729	.631	.990	1.031	1.573
69.54	.792	.748	.928	1.136	1.284
68.80	.850	.815	.937	1.189	1.287
68.57	.865	.849	.924	1.331	1.140
68.05	.901	.890	.927	1.391	1.250
67.50	1.000	1.000	.927	-	-

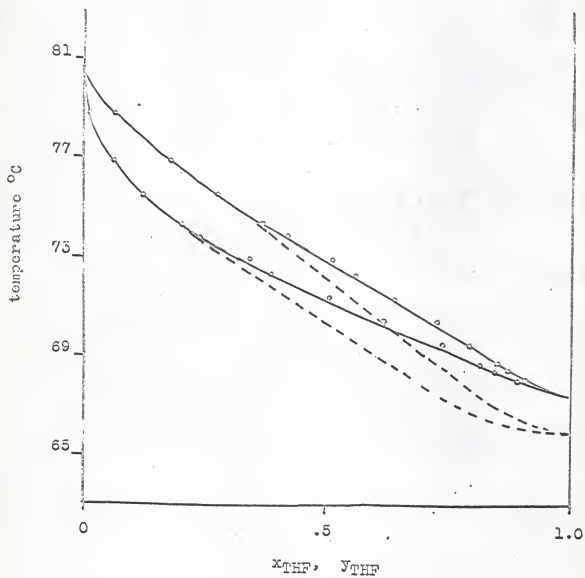


Fig. 8. Temperature versus mole fraction THF in liquid at 760mm. pressure, Cyclohexane - THF.

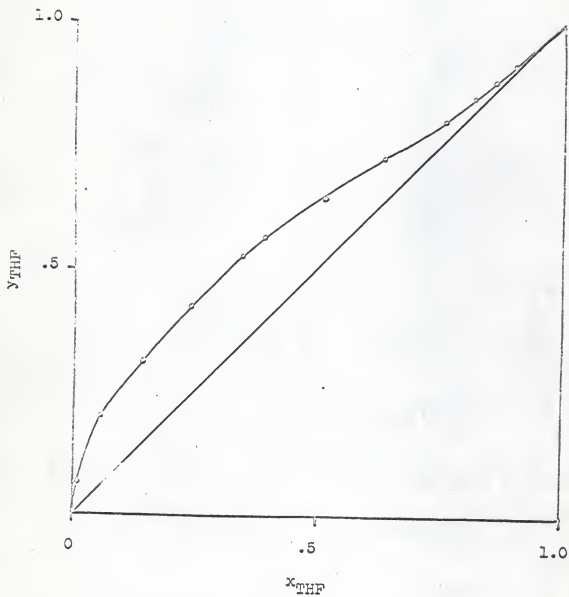


Fig. 9. Mole fraction THF in vapor versus mole fraction in liquid at 760mm. pressure, Cyclohexane - THF.

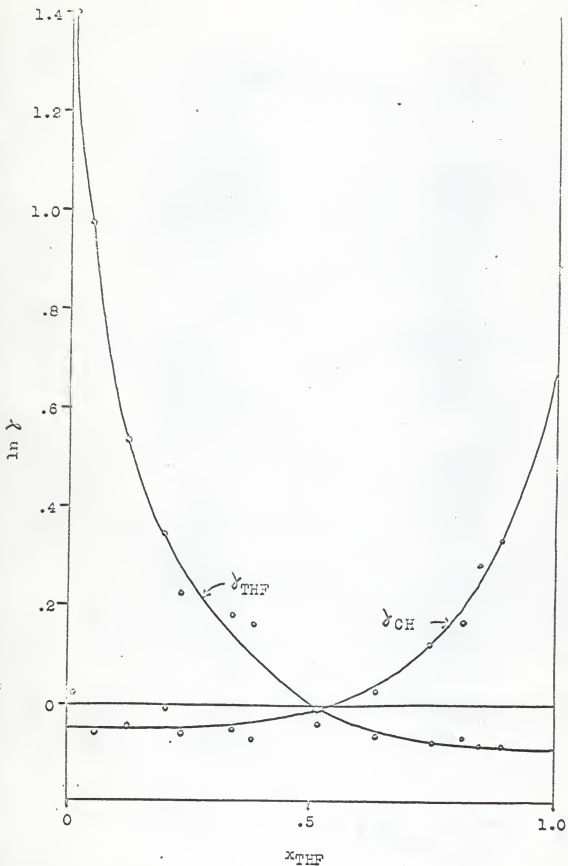


Fig. 10. $\ln \gamma$ versus mole fraction THF in liquid at 760mm. pressure, Cyclohexane - THF.

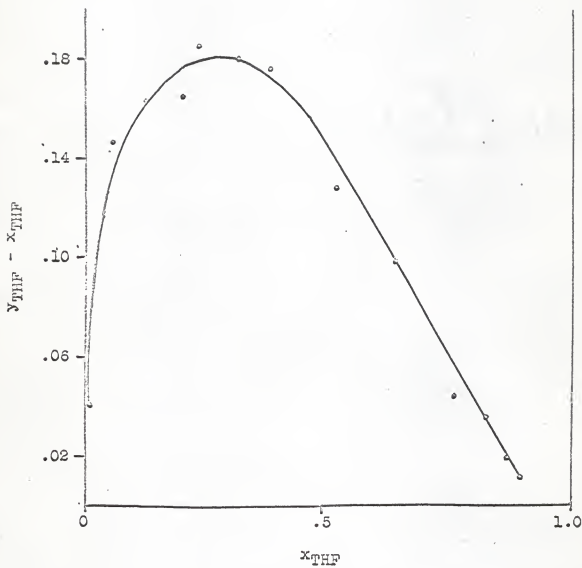


Fig. 11. $y_{THF} - x_{THF}$ versus mole fraction in liquid at 760mm. pressure, Cyclohexane - THF.

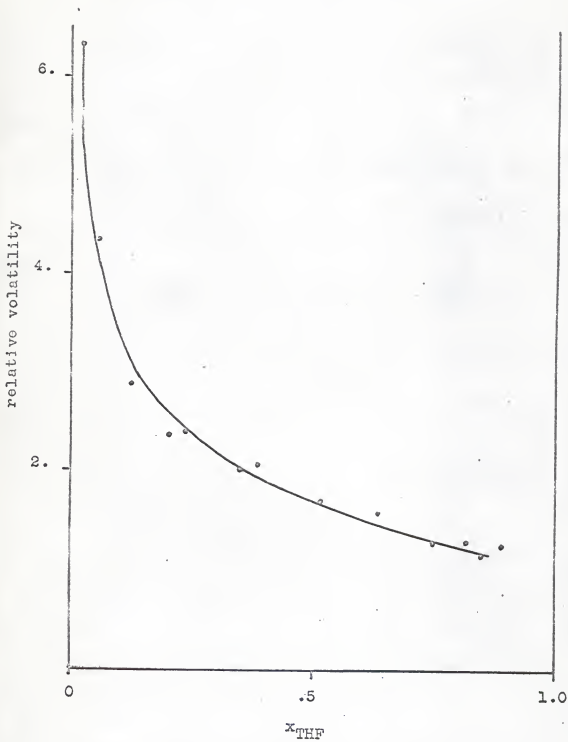


Fig. 12. Relative volatility versus mole fraction THF in liquid at 760mm. pressure, Cyclohexane - THF.

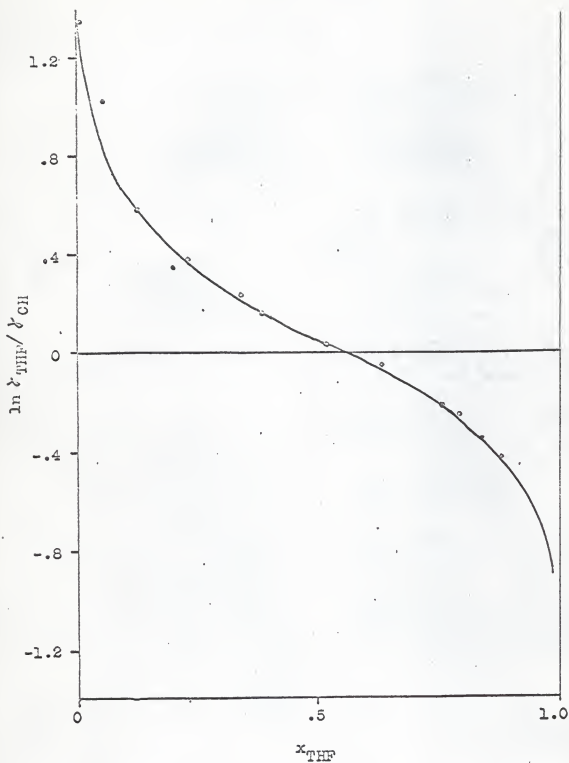


Fig. 13. $\ln \gamma_{\text{THF}} / \gamma_{\text{CH}}$ versus mole fraction THF in liquid at 760mm. pressure, Cyclohexane - THF.

n-Hexane - Tetrahydrofuran:

This system shows a minimum boiling azeotrope at 64.2°C and 0.621 THF mole fraction. This compares to a temperature of 63°C for the azeotrope reported in the literature (1). The temperature-composition graph has a minimum at $T = 64.2^{\circ}\text{C}$, and the $y_{\text{THF}} - x_{\text{THF}}$ versus x_{THF} also goes through a minimum. The y_{THF} versus x_{THF} curve crosses the diagonal at 0.621 since one side of the azeotrope has the vapor composition higher than the liquid composition for a given temperature, and the other side has just the opposite.

The thermodynamic consistency tests for this system show a good agreement for the data. The curves of $\ln \gamma$ versus x_{THF} are proportionate and similar even though they show a deviation below the zero axis equivalent to a degree's difference in temperature as determined by the method described in the previous systems. The plot of $\ln(\gamma_{\text{THF}}/\gamma_{\text{Hex}})$ gives a total area of 0.0233 which could be considered significant. Herington's test has $D = 4.24$, $J = 2.02$ and therefore $D - J$ is less than ten indicating consistency. The curves of $y_{\text{THF}} - x_{\text{THF}}$ versus x_{THF} are smooth enough to indicate a correctness in the compositions.

Table 3. Data for the system hexane - tetrahydrofuran at 760 mm.

$T^{\circ}\text{C}$	y_{THF}	x_{THF}	γ_{THF}	γ_{Hex}	$\alpha(\text{THF to Hex})$
68.74	0	0	-	.960	-
68.71	.088	.052	1.558	.964	1.758
67.85	.213	.151	1.301	.956	1.521
67.17	.267	.200	1.256	.962	1.485
66.99	.284	.220	1.229	.970	1.406
66.90	.293	.229	1.227	.973	1.398
65.97	.385	.336	1.118	1.011	1.237
65.17	.476	.412	1.160	1.000	1.298
64.80	.530	.491	1.089	1.046	1.168
64.35	.584	.578	1.040	1.132	1.026
64.26	.621	.621	1.039	1.152	1.000
64.32	.675	.692	1.004	1.211	.924
64.36	.688	.710	.999	1.238	.901
64.55	.717	.758	.969	1.335	.808
64.90	.788	.830	.959	1.410	.761
65.08	.804	.851	.948	1.478	.716
65.54	.901	.933	.965	1.632	.653
66.00	1.000	1.000	.948	-	-

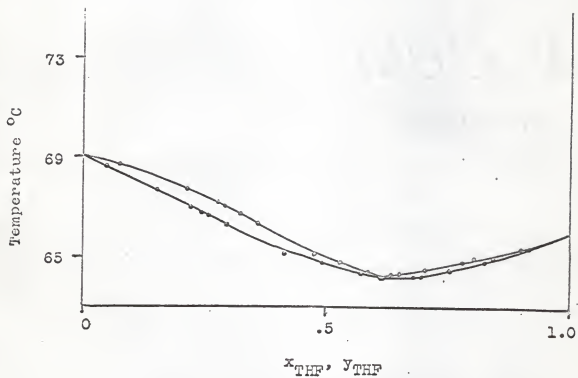


Fig. 14. Temperature versus mole fraction THF at 760mm. pressure, n-Hexane - THF.

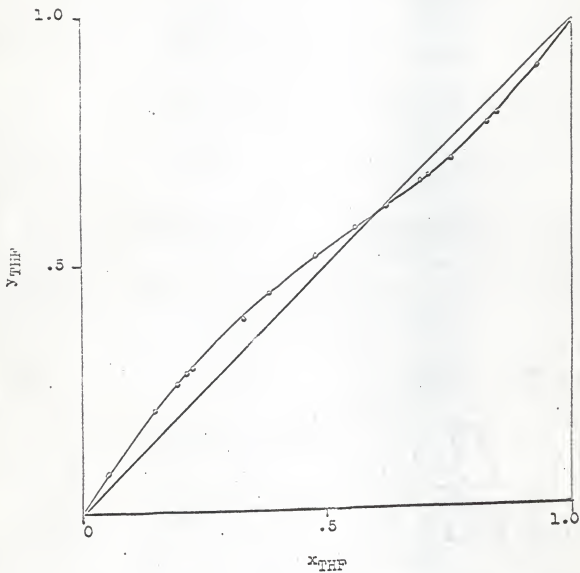


Fig. 15. Mole fraction THF in liquid versus mole fraction in vapor at 760mm., n-hexane - THF.

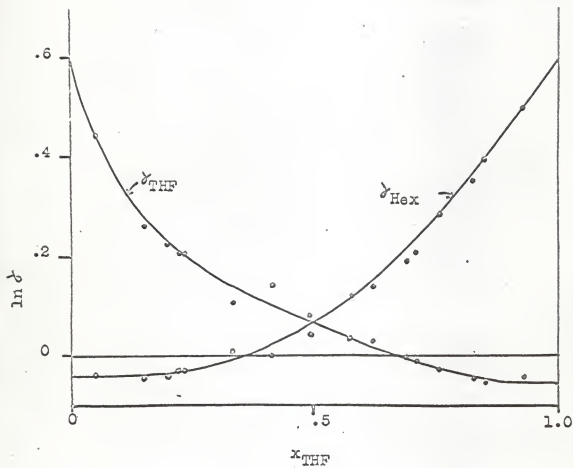


Fig. 16. $\ln \gamma$ versus mole fraction THF in liquid at 760mm. pressure, n-Hexane - THF.

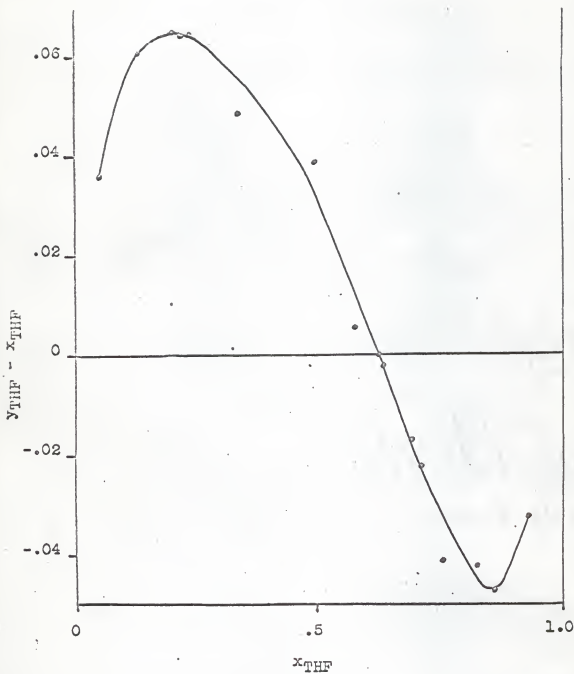


Fig. 17. $y_{THF} - x_{THF}$ versus mole fraction THF in liquid at 760mm. pressure, n-Hexane - THF.

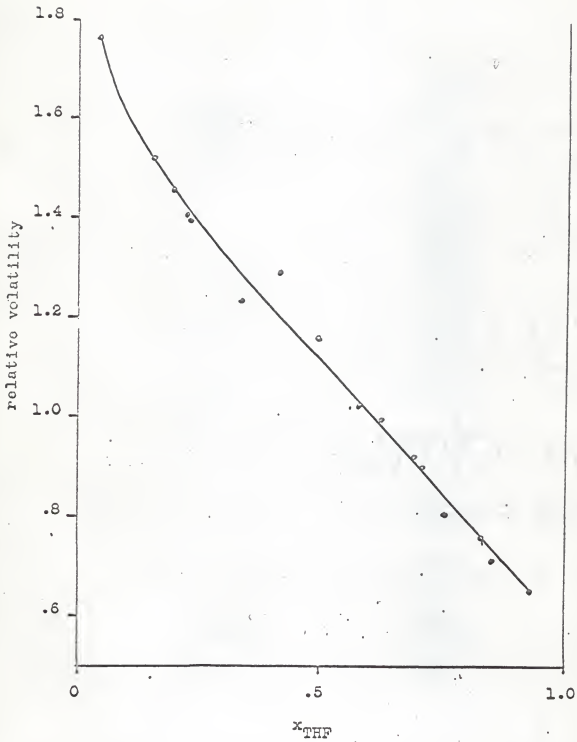


Fig. 18. Relative volatility versus mole fraction THF in liquid at 760mm. pressure, n-Hexane - THF.

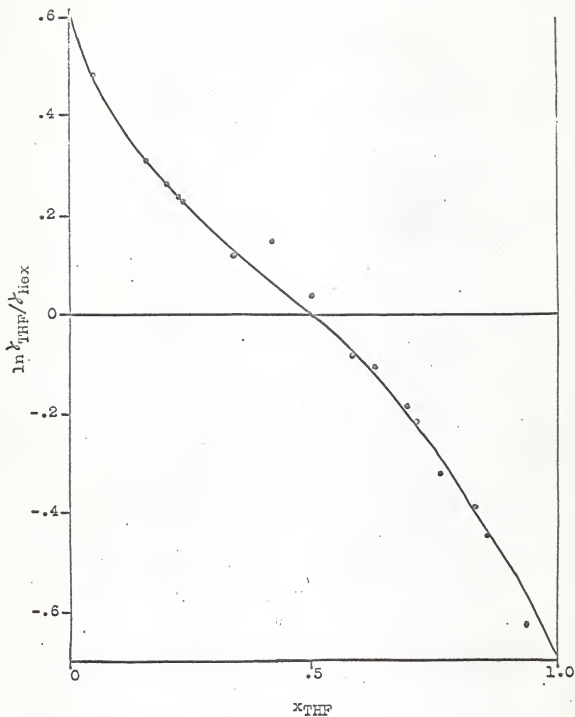


Fig. 19. $\ln \frac{\gamma_{\text{THF}}}{\gamma_{\text{Hex}}}$ versus mole fraction THF in liquid at 760mm. pressure, n-Hexane - THF.

ACKNOWLEDGMENT

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A P P E N D I X

PHYSICAL PROPERTIES OF CHEMICALS

The tetrahydrofuran used in this work was Fisher Scientific Company's reagent grade. The benzene, cyclohexane and hexane were Phillips Petroleum Company's "pure" grade reported to be 99 mole % pure. The ensuing table gives the density, boiling point, and refractive index of the pure component as determined by the refractometer used in the experiment.

Table 4. Physical Properties of the Chemicals.

Property	Tetrahydrofuran	Benzene	Cyclohexane	n-Hexane
Density at 25°C	.883 g/ml ²	.879 ¹	.779 ¹	.660 ¹
Refractive Index at 25°C	1.4046	1.4979	1.4220	1.3728
Refractive Index from the literature at 25°C	1.4073 ²	1.4979 ¹	1.4225 ¹	1.3722 ¹
Boiling Point at one atm.	66.0 °C ²	80.1°C ¹	80.74°C ¹	68.74°C ¹

Since the boiling points compared favorably to those found in the literature the vapor pressure data were not determined experimentally. However, prior to running any systems the

¹ reported by API tables.

² reported by Dupont technical bulletins on tetrahydrofuran.

vapor pressures of benzene and tetrahydrofuran were checked in the still. The pure component was boiled until equilibrium was established. The temperature was then measured and found to be congruent with the literature boiling temperature for that vapor pressure. The vapor pressure data for tetrahydrofuran were obtained from the Dupont technical bulletins.

Listed below is a table of refractive index versus composition for the three binary systems. This data is plotted in the next three figures, which were used for determining compositions.

Table 5. Refractive Index and Composition for the three systems.

THF - Benzene		THF - Cyclohexane		THF - Hexane	
Refractive Index	Composition x_{THF}	Refractive Index	Composition x_{THF}	Refractive Index	Composition x_{THF}
1.4979	0	1.4220	0	1.3728	0
1.4892	.105	1.4212	.036	1.3775	.267
1.4818	.206	1.4177	.250	1.3802	.389
1.4724	.304	1.4132	.498	1.3862	.594
1.4642	.383	1.4088	.751	1.3908	.704
1.4540	.508	1.4056	.950	1.3942	.790
1.4448	.606	1.4046	1.000	1.3970	.846
1.4350	.700			1.3990	.898
1.4255	.800			1.4022	.946
1.4152	.900			1.4049	1.000
1.4046	1.000				

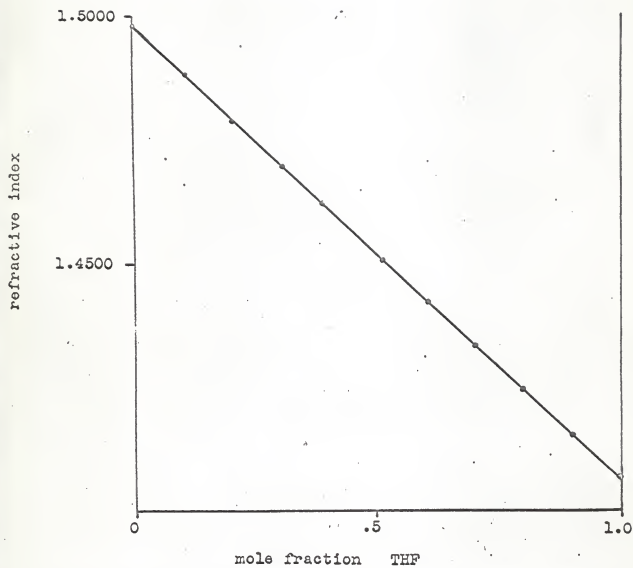


Fig. 20. Refractive index versus composition, Benzene - THF.

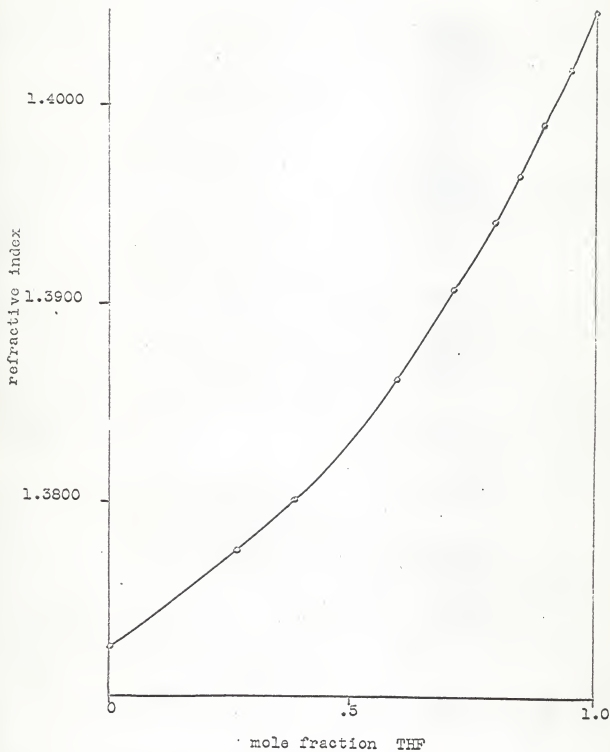


Fig. 21. Refractive index versus composition, n-Hexane - THF.

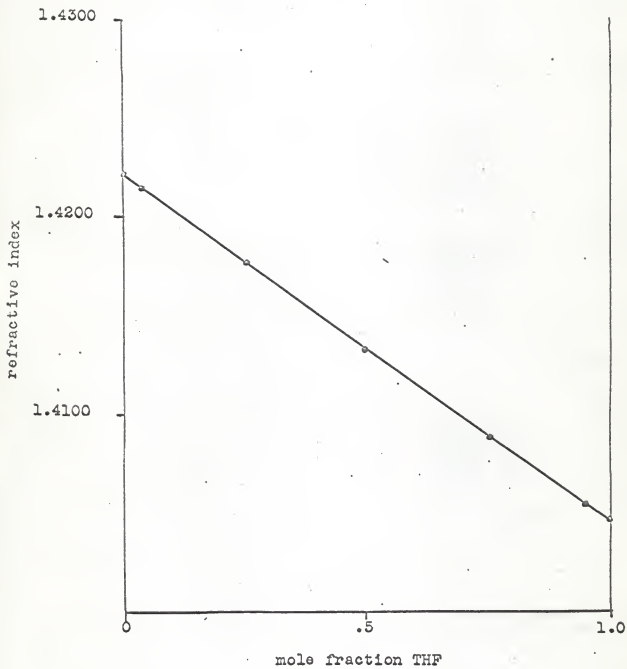


Fig. 22. Refractive index versus composition, Cyclohexane - THF.

VAPOR - LIQUID EQUILIBRIUM DATA
FOR TETRAHYDROFURAN AND RELATED ORGANICS

by

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AN ABSTRACT OF A THESIS

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Vapor-liquid equilibrium data were obtained for the binary systems benzene-tetrahydrofuran, cyclohexane-tetrahydrofuran, and hexane-tetrahydrofuran. An Ellis equilibrium still was used to obtain the equilibrium temperature and the corresponding equilibrium vapor and liquid compositions for the whole range of mole fractions. The data are presented graphically on plots of (1) vapor and liquid composition versus temperature, (2) liquid composition versus vapor composition, (3) natural logarithm of the activity coefficient versus the liquid mole fraction.

Various consistency tests were used to determine the data's accurateness. A plot of vapor composition minus liquid composition versus liquid mole fraction, and a plot of relative volatility versus liquid mole fraction tested the composition data for uniformity. The Redlich-Kister test, a plot of the natural logarithm of the ratio of activity coefficients versus liquid mole fraction, and a test analogous to the Redlich-Kister test devised by E. F. Herington were used to test for thermodynamic consistency.

Generally, the results of these various tests showed the composition data to be in good agreement in all tests, whereas the temperature-composition data as shown in the thermodynamic consistency tests showed a uniform error of about one degree in the temperature. This error was felt to be inherent in the still because varying the still's operating conditions

did not change the error, and the component's physical properties were congruent with available literature data.

The cyclohexane-tetrahydrofuran system proved to be a normal system, but the benzene-tetrahydrofuran system showed a negative deviation from Raoult's Law. The hexane-tetrahydrofuran system had a minimum boiling azeotrope at .621 mole fraction and 64.2°C .