Chromatographic Determination of Isothermal Vapor-Liquid Equilibrium

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Isothermal vapor-liquid equilibrium data are presented for several binary liquids: benzene–cyclohexane at 40 °C, ethyl alcohol–heptane at 30 °C, benzene–ethyl alcohol at 25 °C, and toluene–ethyl alcohol at 35 °C. Data are obtained by a static equilibrium; gas chromatography is used to analyze the two phases. The method is fast and efficient in that an experimental point may be obtained in 30 min with only 7 cm^3 of sample. Data obtained are compared with data reported in the literature and are thermodynamically consistent. The proposed method can be extended to extractive solvent hydrocarbon systems for systematic study of extraction agents for extractive distillation.

A static method is presented for measuring the relative volatility of hydrocarbons in mixtures with alcohols and hydrocarbons. This method permits the rapid measurement of thermodynamics data such as equilibrium constants and activity coefficients of the liquid.

Most of the experimental methods described in the literature (*3*) utilize stills in which the liquid and vapor recirculate. The greatest disadvantage of these methods is the need to use large samples, in general between 80 and 200 cm^3 of products to obtain a single equilibrium point. This type of equilibrium still is difficult to use in determination of vapor-liquid equilibria in systems of limited miscibility, since two layers are formed in the condensed vapor.

Static equilibrium stills avoid these difficulties and, in addition, offer two possibilities. One implies the measurement of the total pressure of the system; the precision obtained depends on how completely degassed the products are. An excellent system of pressure measurement must be used, which in many cases is very sophisticated (*2, 14*). Without a doubt, it is the most precise experiment for measuring vapor-liquid equilibrium data.

The other possibility consists of directly measuring the composition of the vapor phase with gas-liquid chromatography. The greatest disadvantages of this method concern the sampling of the vapor phase to the gas chromatograph. It must be reproducible and representative. In particular, the vapors must not condense. Wichterle and Hála (*15*) have developed a rapid semimicromethod based on sampling of very small volumes of the vapor phase which is then analyzed by gas chromatography. More recently (*9*), an experiment has been presented with a similar principle; unfortunately, it cannot provide data at temperatures different from that of the laboratory, and it requires a highly trained technician.

The method proposed here represents a synthesis of the previous techniques. Vapor from the equilibrium still is injected in the gas chromatograph by means of an introductory gas valve situated outside the still. The quantities of vapor injected are relatively smaller than that of the liquid contained in the still so that several repeated injections can be made without modifying significantly the liquid composition staying within the accuracy range of gas chromatographic analysis. Thus, we observed that injecting the same vapor sample three times did not change the liquid molar fraction by more than 1%.

To determine the composition, samples of the liquid are injected at the beginning and at the end of the vapor injection series.

Experimental

Apparatus. The general scheme of the experiment is shown in Figure 1. The apparatus consists of three parts: the equilibrium still, the chromatograph and its recorder, and the vacuum pump.

The pyrex still has a volume of 28 cm^3, the useful part for the liquid being 7–9 cm^3. The liquid mixture is stirred magnetically; one must be careful that droplets of the liquid do not fall onto the walls of the still. Stirring is stopped when the vapor is injected. The still is connected to a needle pass valve by means of a 3-cm length latex tubing that covers the external walls so that vapors leaving the still are never in contact with the internal wall of this tubing (Figure 2).

The needle valve is then connected to the gas introduction valve by means of teflon tubing of ¼-in. diameter. The still, latex connector, and part of the needle valve are submerged in a constant temperature bath, controlled to within ±0.05 °C. The teflon tubing, gas injection valve, and all connectors between the chromatograph and the sampling valve are always maintained at a temperature above that of the bath by

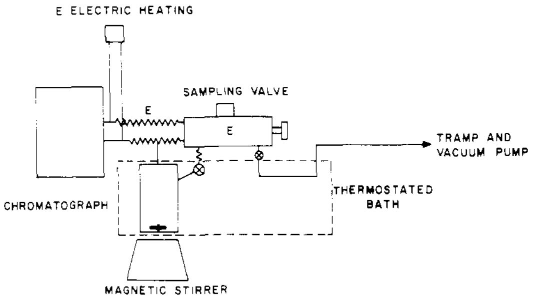

Figure 1. Schematical diagram of apparatus

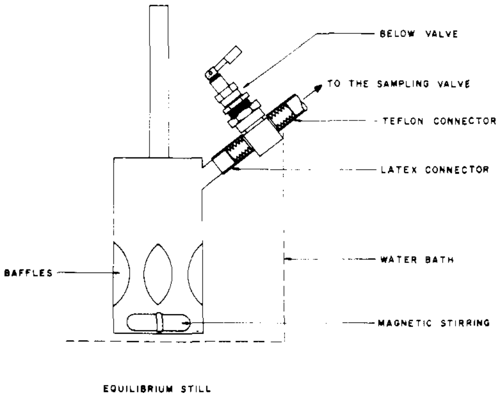

Figure 2. Equilibrium still

means of controlled resistance heating; therefore, we never observed any condensation that would affect the chromatographic elution and cause systematic errors in the values of the relative volatilities.

The linear gas injection valve, designed and made of stainless steel in our laboratory, is a six-port push-pull type using 5 Viton o rings which insure a positive seal.

The reproducibility of the data obtained was checked by injecting various gases as well as vapors of the pure liquids studied in this work. The average deviation was between 1 and 2%. When the valve was heated to 60 °C, no significant adsorption of hydrocarbons was noted on the o rings, insuring the perfect seal of the various ports. It was also verified with a mercury manometer that there was no leak in the vacuum when the line through the injection valve to the pass valve was evacuated.

The chromatograph used was an Intersmat Model IGC 120 with thermal conductivity detector. The carrier gas was helium with a flow of 25 cm^3/mn. The operating conditions and chromatographic columns were different for each binary studied: system benzene(1)-cyclohexane(2): oven temperature 110 °C, detector temperature 150 °C, current 150 mA, column of 20 wt % dinonylphthalate on chromosorb W-DMCS, 4-ft coil, $\frac{1}{8}$ in. i.d.; system ethyl alcohol(1)-*n*-heptane(2): oven temperature 220 °C, detector temperature 230 °C, current 150 mA, column of Porapak Q, 80-100 mesh, 8-ft coil, $\frac{1}{8}$ in. i.d.; system benzene(1)-ethyl alcohol(2): oven temperature 215 °C, detector temperature 230 °C, current 150 mA, column of Porapak Q, 80-100 mesh, 4-ft coil, $\frac{1}{8}$ in. i.d.; and system toluene(1)-ethyl alcohol(2): identical conditions as previous system.

Reagents. All three hydrocarbons were Merck spectroscopic grade and were used without further purification. The ethyl alcohol was reagent grade, supplied by Técnica Química S.A., and was treated with 4 Å molecular sieve; a chromatographic assay gave a 99.96% purity. Refractive indexes were measured in our laboratory and are listed in Table I.

Procedure. *Obtaining vapor-liquid equilibrium.* Each run began with determination of the liquid composition using gas-liquid chromatography, having previously taken the chromatographic calibration coefficients. Some 7-8 cm^3 of the binary mixture were transferred in the still, and the sampling valve was connected. The still was introduced in the thermal bath, and the liquid was agitated 5-10 min, a period considered necessary for obtaining vapor-liquid equilibrium. During this interval, the vacuum pump evacuated the tubes leading to the sampling valve and the teflon connector through the gas injection valve, while the pass valve remained closed so that the equilibrium still was kept isolated from the outside circuit. Next, the agitation was stopped, and the equilibrium still was left to settle for 30 s. The circuit at the exit of the sampling valve opening was closed at the same time as the circuit between the sampling valve and the equilibrium still; then the vapor sample was injected in the chromatograph. The same process was repeated three times. Then the liquid composition was changed to obtain another equilibrium point. Throughout the course of the experiment, it was necessary to control the temperature in the connecting tubes, valves, and other components outside the thermal bath. This temperature must be greater than the bath temperature; for this purpose, a heating system was used. In addition, the splashing of droplets onto the wall must be eliminated by utilizing a soft magnetic stirring.

Obtaining chromatographic data. In the first approximation the area of the elution peaks was considered proportional to the partial pressure of the compound in the vapor phase. For the first three systems studied, the area of elution peak was calculated by taking the product of the height by the width at half height. In this work the following deviations obtained agree with those of the literature (*6*). For peaks of areas 301-1200 mm^2 (average values of our peaks), the error in the area was taken to be 2.6%. For the last system investigated, because of the asymmetrical peaks, the weighting method was chosen. From this we obtained an average area error of 2.5%. Electronic integration of the peak areas would greatly improve the experimental data.

Results

Reduction of chromatographic data. For a binary liquid mixture, the relation between the areas and response factors is given by the following equation:

$$\frac{k_1^\circ}{k_2^\circ} = \frac{A_1^\circ}{A_2^\circ}\frac{x_2}{x_1} \tag{1}$$

Thus, the peak area is proportional to the liquid molar fraction. Synthetic samples were made by weight for the four systems studied, and the values of the constants k_1°/k_2° were calculated for each system (Table II).

From the above relation, the liquid molar fraction x_1 can be computed from the equation

$$x_1 = \frac{1}{1 + \dfrac{A_2^\circ}{A_1^\circ}\dfrac{k_1^\circ}{k_2^\circ}} \tag{2}$$

in which A_2°/A_1° is the ratio of the peak areas corresponding to solutes 2 and 1 in the mixture.

In the vapor if the constant k_1/k_2 is independent of the concentration, then

$$\frac{k_1}{k_2} = \frac{A_1}{A_2}\frac{\pi_2}{\pi_1} \tag{3}$$

This relation is obtained when the peak area of the solute is respectively proportional to its partial vapor pressure when it is in the mixture at equilibrium temperature T and to its vapor pressure at the same temperature when it is pure.

The factor π_2/π_1 is calculated using the equation of Antoine. To calculate the coefficient k_1/k_2, the vapors of the pure solutes are injected in the chromatograph at the same temperature as the equilibrium temperature of the binary. The k_1/k_2 values are listed in Table II. The constants k_1°/k_2° and k_1/k_2 are thus found with a respective absolute precision of ±0.01 and 0.02.

In the same way for vapor:

$$\frac{k_1}{k_2} = \frac{A_1}{A_2}\frac{y_2}{y_1} \tag{4}$$

Table I. Refractive Indexes at 20 °C for Sodium D Light

Substance	Measured	Lit value (*5*)
n-Heptane	1.3875	1.38764
Benzene	1.5011	1.5011
Toluene	1.4961	1.4961
Ethyl alcohol	1.3611	1.3611

Table II. Response Factors for Liquid and Vapor Samples for Thermal Conductivity Detector

System	Liquid $\frac{k_1^\circ}{k_2^\circ}$	Vapor $\frac{k_1}{k_2}$
Benzene(1)-cyclohexane(2)	0.89	0.86
Ethyl alcohol(1)-*n*-heptane(2)	0.49	0.56
Benzene(1)-ethyl alcohol(2)	1.46	1.26
Toluene(1)-ethyl alcohol(2)	1.61	1.00

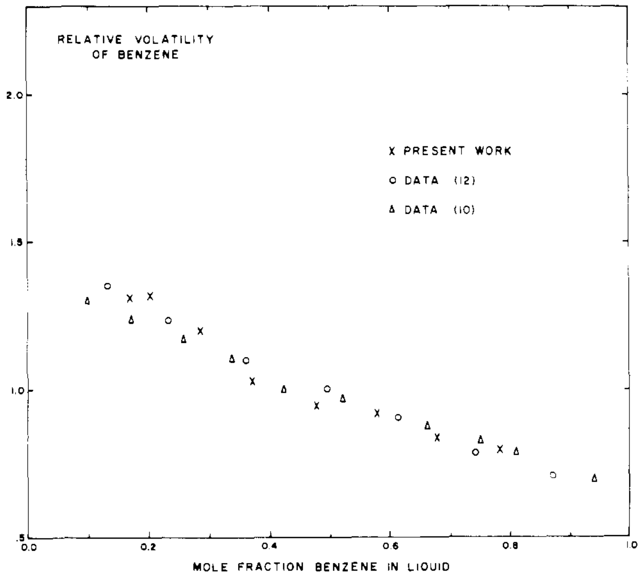

Figure 3. Relative volatility-composition diagram for benzene-cyclohexane at 40 °C

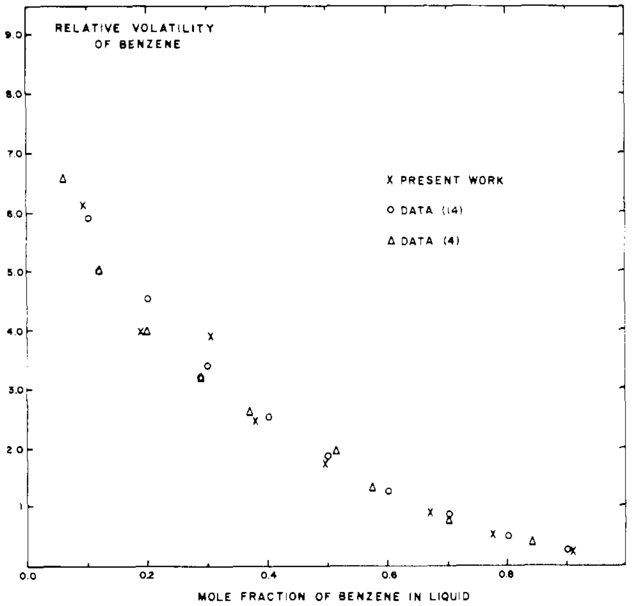

Figure 5. Relative volatility-composition diagram for benzene-ethyl alcohol system at 25 °C

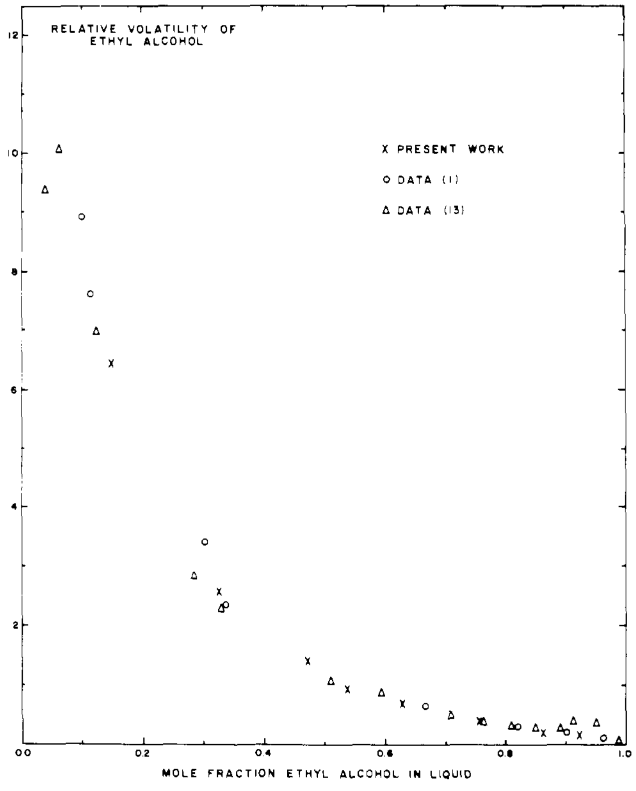

Figure 4. Relative volatility-composition diagram for ethyl alcohol-*n*-heptane system at 30 °C

Chromatographic determination of relative volatility $\alpha_{1,2}$. By definition the relative volatility of compound 1 with respect to compound 2 is given by the relation:

$$\alpha_{1,2} = \frac{K_1}{K_2} = \frac{y_1/x_1}{y_2/x_2} = \frac{y_1x_2}{y_2x_1} \tag{5}$$

where K is the equilibrium constant. We can replace the values y_1/y_2 and x_2/x_1 by their values obtained from Equations 1 and 4 giving:

$$\alpha_{1,2} = \frac{A_1}{A_2}\frac{A_2^{\circ}}{A_1^{\circ}}\frac{k_2}{k_1}\frac{k_1^{\circ}}{k_2^{\circ}} \tag{6}$$

where A_1, A_2, A_1°, and A_2° are, respectively, the peak areas of solutes 1 and 2 in the vapor and liquid phases at equilibrium.

Data and Test of Consistency

The functioning of the still has been verified with four binary systems at different temperatures. The volatilities $\alpha_{1,2}$ of the various components were determined; the relative volatilities $\alpha_{1,2}$ vs. the liquid molar fraction are presented in Figures 3–6.

To compare the results obtained with the isothermal and isobaric data reported in the literature, we converted isobaric data to isothermal data using the following relation obtained by the equation of the equilibrium:

$$\alpha_{1,2} = \frac{\gamma_1}{\gamma_2}\frac{\pi_1}{\pi_2} \tag{7}$$

in which γ_1 and γ_2 are the activity coefficients of solutes 1 and 2 in the liquid.

The term ln γ_1/γ_2 was taken to be independent of temperature, a reasonable supposition for systems whose components have near boiling points, as in the systems we studied. We calculated the deviation from ideality in the vapor phase by means of a fugacity coefficient based on the virial equation of state. The pure and mixed second virial coefficients for polar and nonpolar gases were obtained from the correlation of O'Connell and Prausnitz (*11*).

This type of data was incorporated to permit a more exhaustive comparison between the literature data and our experimental results.

If we consider the integrated form of the Gibbs-Duhem equation for a binary system at constant pressure and temperature, we have:

$$\int_{x_1=0}^{x_1=1} \ln\frac{\gamma_1}{\gamma_2}\,dx_1 = 0 \tag{8}$$

This equation provides an area test of phase equilibrium data: a plot of ln γ_1/γ_2 vs. x_1 gives a curve that delimits an area which is the integral of the left-hand side of Equation 8 and is equal to zero. Figures 7–10 show the calculated curves fitted on the isothermal data of the literature and our experimental points. The Gibbs-Duhem consistency test area ratio defined following the relation

$$\left|\frac{\text{Area above } x\text{-axis} - \text{area below } x\text{-axis}}{\text{Area above } x\text{-axis} + \text{area below } x\text{-axis}}\right|$$

gives 0.004 for the benzene-ethyl alcohol system and 0.02 for the other systems. One system that exhibits slight deviations from ideality, the benzene-cyclohexane system, presents two experimental points that are slightly erroneous. Vapor-liquid equilibrium data for the four systems are given in Tables III–VI.

If we consider the Redlich-Kister expansion, we obtain the expression for the term ln γ_1/γ_2

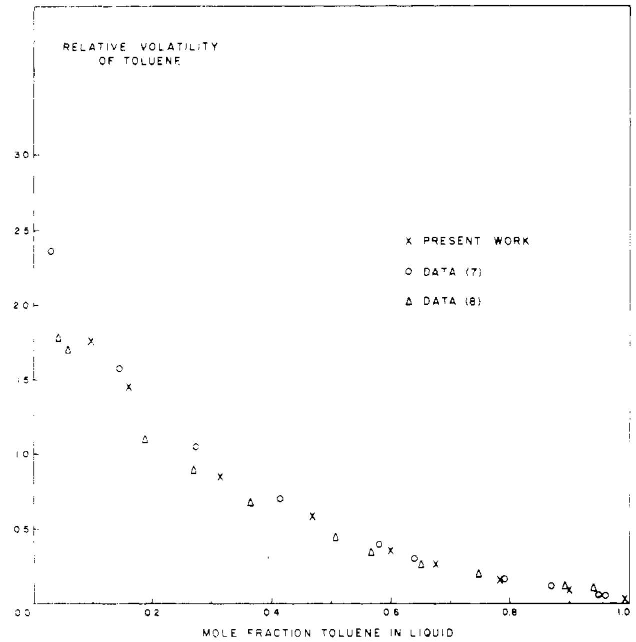

Figure 6. Relative volatility-composition diagram for toluene-ethyl alcohol system at 35 °C

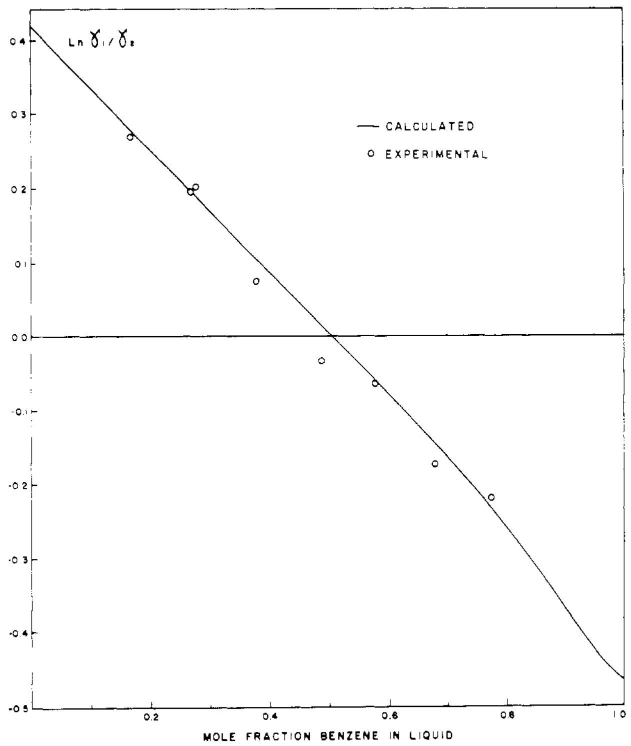

Figure 7. Redlich-Kister plot for benzene–cyclohexane at 40 °C

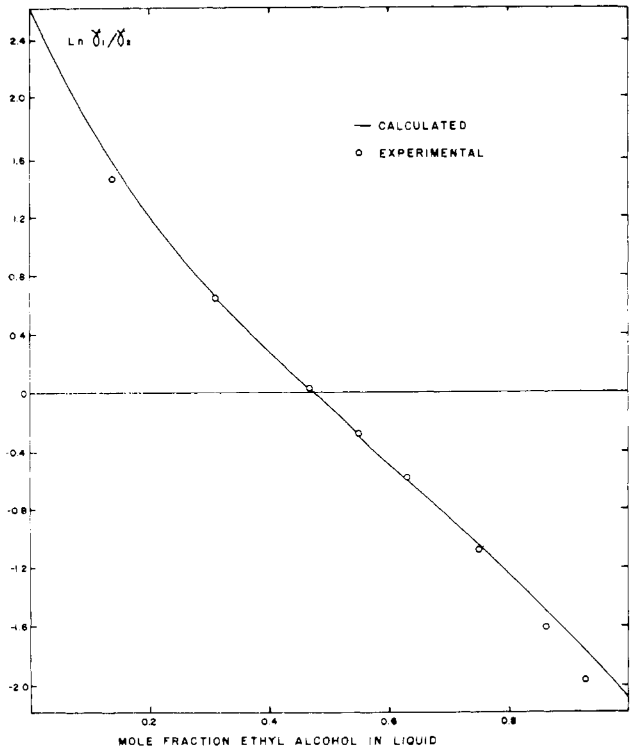

Figure 8. Redlich-Kister plot for ethyl alcohol-*n*-heptane system at 30 °C

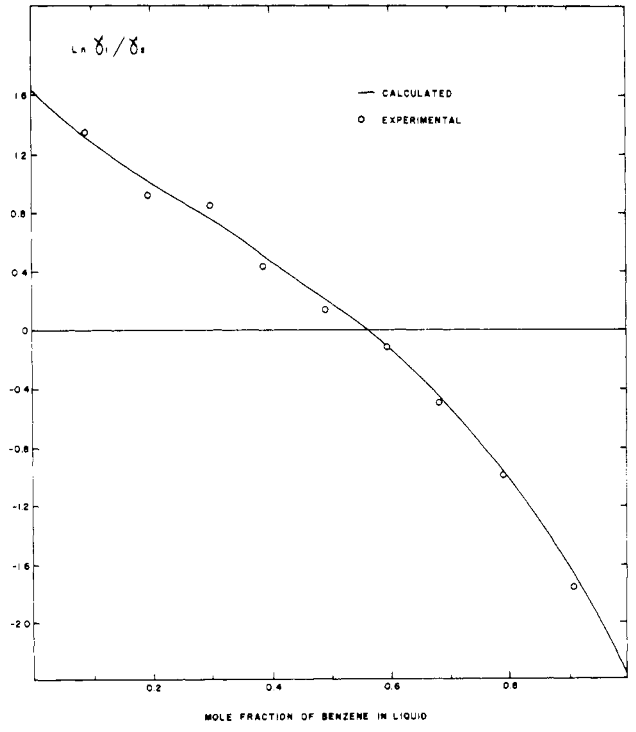

Figure 9. Redlich-Kister plot for benzene–ethyl alcohol system at 25 °C

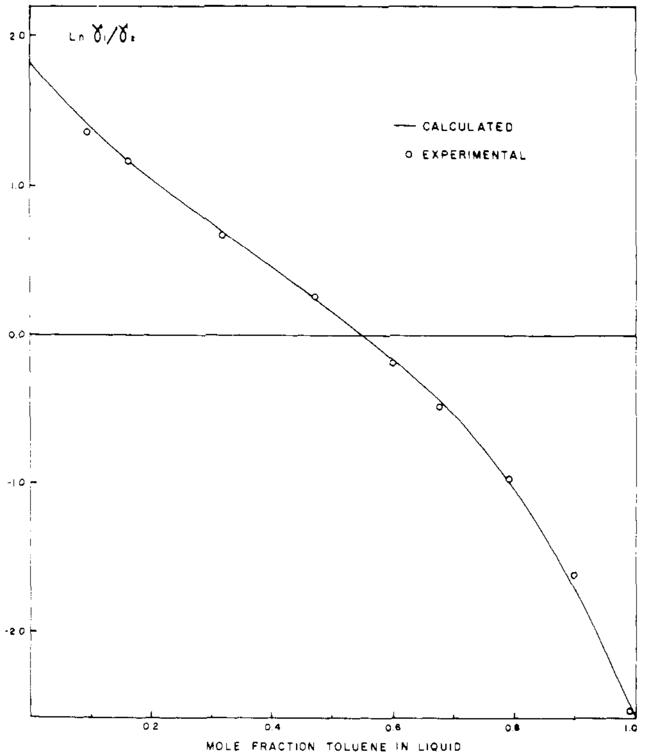

Figure 10. Redlich-Kister plot for toluene-ethyl alcohol system at 35 °C

$$RT \ln \frac{\gamma_1}{\gamma_2} = A(x_2 - x_1) + B(6\, x_1x_2 - 1) + C(x_1 - x_2)(8\, x_1x_2 - 1) + D(x_1 - x_2)^2(10\, x_1x_2 - 1) + \ldots \quad (9)$$

The constants A, B, C, and D are calculated from this expansion, and results are given in Table VII.

Discussion

From the four systems studied, that of the benzene-cyclohexane mixture shows somewhat larger deviations. For this system the absolute average deviation, respective to the relative volatility, is 3.0%. We defined the absolute average deviation as

$$\sigma = \frac{1}{N}\sum_{i}^{N} |\alpha_{i\,\mathrm{exp}} - \alpha_{i\,\mathrm{LIT}}| \quad (10)$$

$\alpha_{i\,\mathrm{exp}}$ and $\alpha_{i\,\mathrm{LIT}}$ are, respectively, our experimental value of α_{ij} and the correspondent value of α_{ij} given in the literature at the same liquid composition. In the other three cases, the deviation is less than 2%, which permits the composition in the vapor phase to be determined with a relative deviation less than 1.0%. The deviation grows in the region of low concentration, that is, molar fraction below 0.10 and above 0.90.

This behavior can be explained by the diminished detector response of the chromatograph, producing small peaks or infinitesimal droplets of liquid in the vapor phase.

In conclusion, from the data presented, the method is valid and has certain advantages. Among these, it is worth mentioning the relative simplicity of the still and the fact that a highly skilled technician is not required. In addition, the procedure is extremely rapid in obtaining a data point of vapor-liquid equilibrium of a binary mixture. The precision of the data can be improved using an electronic integrator.

Table III. Vapor-Liquid Equilibrium Data for System Benzene–Cyclohexane at 40 °C

Mole fraction of benzene		Exptl rel volatility of benzene
In liquid	In vapor	
0.171	0.213	1.31
0.200	0.251	1.34
0.270	0.309	1.21
0.280	0.322	1.22
0.378	0.394	1.07
0.487	0.477	0.96
0.585	0.569	0.94
0.685	0.646	0.84
0.779	0.738	0.80

Table IV. Vapor-Liquid Equilibrium Data for System Ethyl Alcohol–*n*-Heptane at 30 °C

Mole fraction of ethyl alcohol		Exptl rel volatility of ethyl alcohol
In liquid	In vapor	
0.146	0.520	6.34
0.314	0.540	2.57
0.469	0.553	1.40
0.549	0.546	0.99
0.632	0.551	0.74
0.755	0.581	0.45
0.860	0.624	0.27
0.924	0.673	0.17

Table V. Vapor-Liquid Equilibrium Data for System Benzene–Ethyl Alcohol at 25 °C

Mole fraction of benzene		Exptl rel volatility of benzene
In liquid	In vapor	
0.094	0.395	6.30
0.192	0.487	4.00
0.306	0.630	3.87
0.382	0.599	2.42
0.495	0.639	1.81
0.586	0.658	1.36
0.674	0.655	0.92
0.789	0.673	0.55
0.911	0.727	0.26

Table VI. Vapor-Liquid Equilibrium Data for System Toluene–Ethyl Alcohol at 35 °C

Mole fraction of toluene		Exptl rel volatility of toluene
In liquid	In vapor	
0.099	0.162	1.76
0.156	0.211	1.45
0.316	0.287	0.87
0.470	0.347	0.60
0.605	0.362	0.37
0.675	0.359	0.27
0.785	0.383	0.17
0.900	0.447	0.09
0.985	0.697	0.03^5

Table VII. Four-Parameter Redlich-Kister Constants

	Benzene–cyclohexane	Ethyl alcohol–heptane	Benzene–ethyl alcohol	Toluene–ethyl alcohol
A	0.42772	2.11690	1.80116	1.85208
B	0.01872	−0.25713	0.37097	0.37232
C	0.01363	0.22863	0.23861	0.34629
D	−0.00064	0.00278	0.00193	0.00159

The method described here could be extended to the study of mixtures of hydrocarbons and solvents used in extractive distillation. Since one must work at a temperature at which the samples have a high volatility, the method would be suitable over a wide range of temperature, the only limitation being the necessity of maintaining the temperature of the external tubings higher than the bath temperature.

Nomenclature

A_i° = area of the chromatographic peak for a liquid sample
A_i = area of the chromatographic peak for a vapor sample
A, B, C, D = Redlich-Kister parameter
K_i = vapor-liquid equilibrium constant
k_i° = chromatographic response factor for the liquid
k_i = chromatographic response factor for the vapor
x_i = mole fraction in liquid phase
y_i = mole fraction in vapor phase

Greek Letters

$\alpha_{i,j}$ = relative volatility
γ_i = liquid activity coefficient
π_i = vapor pressure of pure component
σ = absolute deviation

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Thermal Diffusion: Separation in He–N_2 System with Temperature Gradient in Two Directions

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Separation in a nitrogen–helium system due to combined transverse and vertical temperature gradients was investigated experimentally using a conventional two-bulb system. The transverse gradients were obtained by using various metal inserts inside the tube connecting the two bulbs. Separation was greatly increased over that for simple vertical temperature gradient only. The separation was also strongly pressure dependent, with a maximum separation occurring at an optimum value of pressure. The effect of the width of the annular space was also studied, and an optimum value observed. An elementary analytical model was developed and gave a fair correlation with the observed experimental data and trends.

The separating effect due to thermal diffusion can be greatly enhanced through the use of a transverse temperature gradient, in which case the separation becomes the combined result of thermal diffusion and convection. Clusius and Dickel first reported this effect for a liquid separation column (*1*) and subsequently for gas mixtures (*2, 3*). These results promoted considerable research in the ensuing years (*9–12*). Furry et al. presented a rigorous theory for the separation column (*4, 5*), which was subsequently modified to a simpler form (*8*). These analytical and experimental results have been summarized by Grew and Ibbs (*6*), and in each case the temperature gradient was essentially one directional, i.e., in the transverse direction only. The present research is concerned with a system involving temperature gradients in both the vertical and transverse directions.

Experimental Equipment and Procedures

The schematic diagram of the experimental equipment is shown in Figure 1. The basic test package consists of two copper cells approximately 95 cc in volume, connected by a 1-in. diameter stainless-steel tube 6 in. long. The lower cell was surrounded with ¼-W carbon resistors and enclosed in a heat transfer can. Cooling was effected by immersing the can in a cryostat containing liquid nitrogen, and test tempera-

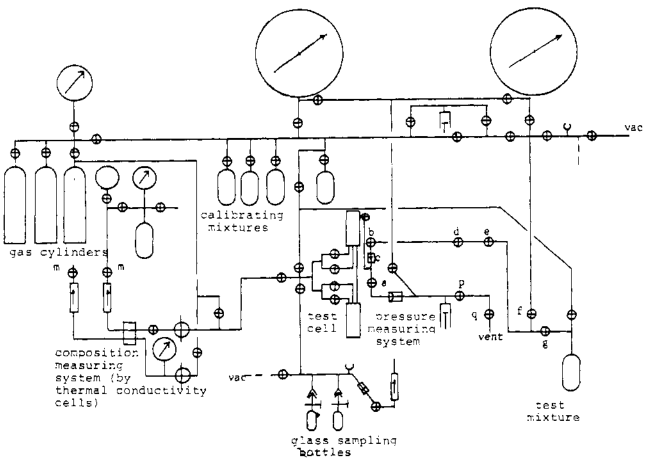

Figure 1. Schematic diagram

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