

LIQUID-VAPOR EQUILIBRIUM IN BINARY SYSTEMS

Apparatus

Boiling apparatus with heating mantle and variac (S), 1/100° thermometer (S), refractometer (L), glass beads or boiling chips (S), weighing bottles (D), small stoppered vials (D), 250 ml n-hexane (S) and 250 ml absolute ethanol (S).

Other binary systems which may be investigated are (1) cyclohexane (S)-ethanol (S); (2) ethyl acetate (S)-ethanol (S); (3) Methanol (S)-ethyl acetate (S); (4) isopropanol (S)-n-hexane (S); (5) isopropanol (S)-cyclohexane (S); (6) isopropanol (S)-ethylacetate (S); (7) Acetone (S)-cyclohexane (S); (8) Acetone (S)- hexane (S); and (9) cyclohexane (S)-2-propanol (S), (10) 1 Propanol-water. CONSULT YOUR LAB INSTRUCTOR TO FIND OUT WHICH SYSTEM YOU ARE TO INVESTIGATE.

CAUTION: The ORGANIC LIQUIDS are TOXIC and FLAMMABLE! Use all necessary precautions to avoid accidents!

CAUTION: DISPOSE OF THESE ORGANIC LIQUIDS by placing in the Waste Containers provided. DO NOT POUR DOWN THE DRAIN!



Figure 1. Picture of the Cottrell boiling point apparatus.

The Cottrell boiling point apparatus has been chosen to perform this experiment (see Figure 1). Assemble the apparatus with care; consult instructor if you are at all doubtful how to put the pieces together. A 3-way stopcock (shown in Figure 2) is provided as a means of withdrawing samples of distillate and residue at the appropriate time. Best procedure is to withdraw distillate first, then the residue.



Figure 2. Three way stopcock for Cottrell boiling point apparatus.

Procedure

Clean the apparatus by rinsing with a few milliliters of pure n-hexane. Make sure vials are clean and DRY and have labels for marking. Add glass beads to flask (carefully).

There are three particularly important requirements in this experiment.

- Make sure that the condensed distillate and the liquid residue samples are collected under equilibrium conditions
- Read the equilibrium temperature accurately
- Analyze the compositions accurately

Place the thermometer in a position near the top and center of the three legs of the first insert as seen in Figure 3. The hole in the second insert should be placed pointed towards the condenser

Place 50 ml n-hexane in a flask. Adjust the variac (not more than 100 -110 volts) so that liquid boils "reversibly" (very moderate boiling with only very tiny bubbles formed) and so that distillate comes over at a rate which will fill the sample tube once every two or three minutes.

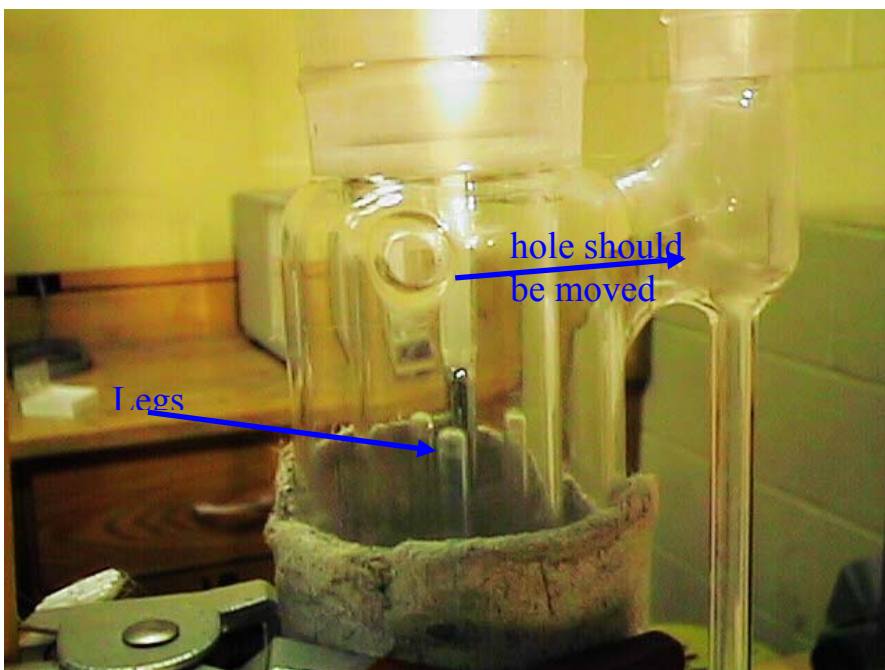


Figure 3. Close picture of thermometer of Cottrell boiling point apparatus

Draw off the first fraction (containing impurities) which comes over and discard (use waste container). When a constant boiling mixture is obtained, record the boiling point and withdraw samples from distillate and residue into marked vials. Add 1 ml ethanol to the distillate in the flask, obtain equilibrium-boiling, record the boiling point, and again withdraw samples of distillate and residue for analysis. Boiling points and refractive indices of the distillate and residue are then determined after successive additions of 0.2, 0.5, 1, 2, 5 and 5 ml of ethanol. The refractive indices are used to obtain the mole fractions of ethanol in these solutions.

Clean the apparatus by rinsing with a few milliliters of ethanol, and repeat the process starting with 50 ml of ethanol in the flask. Now, however, boiling points are to be determined after successive additions of 0.5, 1, 2, 5, 15 and 20 ml of n-hexane to the flask.

In order to construct a plot of refractive index versus mole percent ethanol, the refractive indices are determined for the pure hexane and ethanol and for a series of solutions containing accurately known weights of hexane and ethanol. Mixtures about 5 ml in volume containing approximately 1 volume of ethanol to 1, 3, and 6 volumes of hexane are convenient. To obtain a decent standardization curve of refractive index versus mole fraction, a series of 6 to 8 solutions containing accurately known weights of n-hexane and ethanol must be prepared and their refractive indices measured. Only a few milliliters of each of these solutions are required, so do not waste chemicals when preparing them. The required data for the vapor pressures of the organic liquids are available as follows:

<u>Compound</u>	<u>Vapor Pressure Equation</u>
Acetone	$\log P(\text{mm}) = 7.29958 - [1312.253/(t + 240.705)]$
Cyclohexane	$\log P(\text{mm}) = 6.85532 - [1209.299/(t + 223.527)]$
n-hexane	$\log P(\text{mm}) = 6.89122 - [1178.802/(t + 225.200)]$
Ethanol	$\log P(\text{mm}) = 8.11576 - [1595.76/(t + 226.5)]$
Ethyl acetate	$\log P(\text{mm}) = 7.10319 - [1245.702/(t + 217.961)]$
Isopropanol	$\log P(\text{mm}) = 7.73610 - [1357.427/(t + 197.336)]$
Methanol	$\log P(\text{mm}) = 8.07919 - [1581.341/(t + 239.650)]$ ¹

Where t is in centigrade

NOTE: During the first working period one student should prepare the standardization curve, while the other measures the boiling points for n-hexane and for the solutions of ethanol in n-hexane. In the second period the boiling points for ethanol and for the solutions of n-hexane in ethanol are to be determined. You should easily be able to get 13 points. It is desirable to have even more, especially in the vicinity of the azeotropic point, so take the boiling points of as many mixtures as possible during the two periods. Also, it is important to measure the refractive indices of the distillate and residue as soon as these samples have been extracted. **DO NOT STORE IN THE DESK AND MEASURE THE REFRACTIVE INDICES THE FOLLOWING WEEK. (WHY?)** Use the same refractometer for all Refractive Index measurements! (WHY?) Measure the barometric pressure at the beginning and end of each working period.

Boiling-point and vapor-composition data for a binary solution system at constant pressure may be correlated in a graph of temperature versus composition. Data for such a plot are obtained in this experiment, in which the liquid and vapor compositions are determined refractometrically. The calculation of the activity coefficients for the components in the liquid phase and their representation by the van Laar equations are considered.

The Variac is adjusted so that the liquid boils vigorously at a constant rate, and the vapor condenses in the reflux condenser. The boiling is continued until the pocket below the reflux condenser has been thoroughly rinsed out with condensed liquid and the thermometer reading has become constant. The current is then turned off, and samples of about 1 ml are taken from the distillate in the pocket and then from the residue in the flask through the three way stopcock on the sidearm. Care should be taken to remove any liquid which remains at the end of the stopcock by removing a small amount of liquid and recycling it before obtaining a sample of either the distillate or residue. The refractive indices of the samples are determined with a refractometer. Samples for this determination may be preserved for a short time in small stoppered vials

¹ Computer Aided Data Book of Vapor Pressure, Dr. Eng Shuzo Ohe, Data Book Publishing Company, Tokyo, Japan (1976).

or test tubes, but errors caused by partial evaporation of the samples must be considered. It is important to close the jaws of the refractometer quickly to avoid evaporation from the liquid film on the prism.

The Abbe refractometer makes use of the principle of the grazing angle. The field in the telescope will show a light region and a dark region, the sharp line of demarcation between which corresponds to the grazing angle.

White light from a frosted electric light bulb is used for convenience, and if it were not for the compensating Amici prism of different kinds of glass in the telescope, the line of demarcation between the dark and light fields would be colored and indistinct because the refraction of light is different for different wavelengths. The light of different wavelengths is dispersed by the refractometer prism, by the first compensating prism, and by the sample of liquid. Since the extent of the dispersion differs for each liquid, the second compensating prism is adjusted manually so that its dispersion is exactly equal and opposite to the dispersion produced by the refractometer and the liquid. A knurled ring in the middle of the telescope barrel is turned until the compensation is complete and the color orange disappear, leaving a sharp line of demarcation between the two parts of the field as seen in Figure 4.

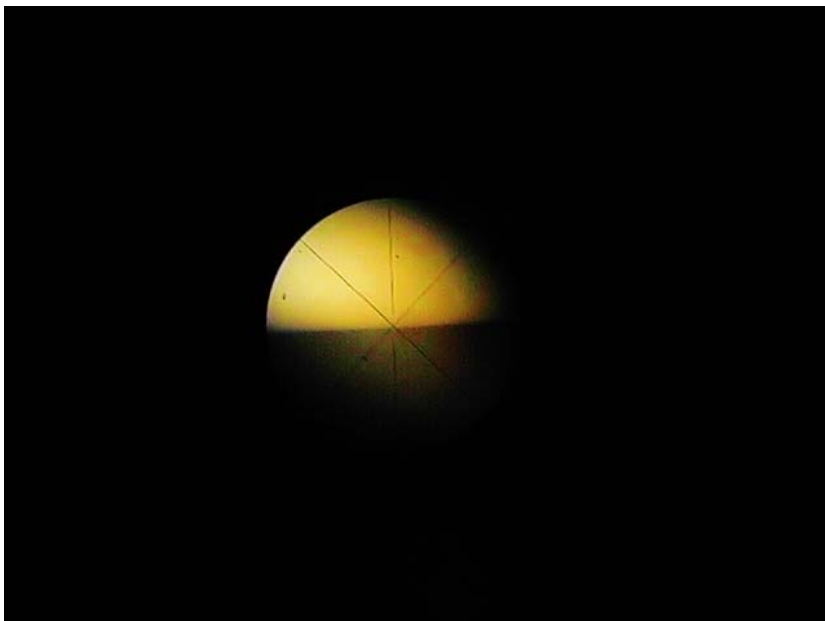


Figure 4. Sharp line of demarcation between the two parts of the field for ABBE refractometer.

Although white light is used, the refractive index measured is for the Na, D line, 5893 \AA , because the Amici compensating prisms are constructed with special glasses so that light of this wavelength is not deviated but all other light is deviated.

The Abbe refractometer has two prisms, the first of which has a ground glass face. It is used to confine the thin sample of liquid and to illuminate it with scattered light. The upper prism is the refracting prism. The prisms are jacketed so that the temperature may be controlled to 0.2° with water from a thermostat. The refractometer prism is rotated by a protruding arm so as to set the edge of the shadow directly on the intersection of the cross hairs.

The prisms are opened like jaws after turning the lock nut, and they are wiped with lens tissue paper, care being taken not to scratch the prism surfaces. A few drops of liquid are placed on the face of the lower prism, and the prism jaws are then closed and locked. The compensating ring is turned to eliminate color fringes. The telescope is set in a convenient position, and the mirror is adjusted to reflect the light from a frosted electric lamp into the refractometer. The prism is rotated by means of the arm until the border between the dark and light fields passes exactly through the intersection of the cross hairs. The telescope eyepiece is adjusted until the cross hairs are in good focus, and the eyepiece on the movable arm is adjusted to give a sharp focus on the scale. The scale is graduated directly in terms of refractive index calculated for the glass used in the prism. The reproducibility of the individual readings on the scale is ± 0.0002 in refractive index. Accurate temperature control is important because the refractive indices of many organic liquids change 0.0004 per degree. After a liquid is used, it is absorbed with lens paper or rinsed off with a volatile liquid in which it is soluble.

The barometer should be read occasionally. In case the atmospheric pressure changes considerably, it is necessary to estimate a correction for the boiling point, taking an average correction for the two liquids as an approximation. Such a correction may usually be avoided by performing all the distillation experiments within a few hours.

THEORY.[1,2] The relation between the composition of a liquid solution (phase l) of two volatile liquids and that of the vapor (phase v) in equilibrium with it at a given temperature and pressure may be established by use of the thermodynamic requirement that the chemical potentials μ_j for component i have a common value for the two equilibrium phases.

$$\mu_{i,l} = \mu_{i,v}$$

The fugacity f_i for component i, irrespective of the phase in which it is present, is defined by the relation

$$\mu_i = \mu_i^\circ + RT \ln f_i \quad (1)$$

where μ_i° corresponds to the chemical potential that component i would have as an ideal gas at 1 atm pressure at the temperature T. This definition makes the

fugacity of a component of an ideal-gas mixture identical with its formal partial pressure $P_i = X_{i,v}P$, where $X_{i,v}$ is the mole fraction of constituent i present and P the total pressure of the gas phase. For a real-gas mixture, $f_{i,v} = \phi_i P_i = \phi_i X_{i,v}P$, where the fugacity coefficient ϕ_i is a function of temperature, pressure, and composition which can be calculated from the equation of state of the gas phase. For a condensed phase, the fugacity of a constituent can be found by determining its value for the equilibrium vapor phase. Condensed phases are of interest, however, under conditions in which no such calculation is possible, as, for example, a solid of unmeasurably low vapor pressure or a solution of a nonvolatile solute such as sodium chloride in aqueous solution. It is thus convenient to introduce the thermodynamic activity a_i for a constituent of a given phase by the relation

$$\mu_i = \mu_i^{\circ} + RT \ln a_i = \mu_i^{\circ} + RT \ln \left(\frac{f_i}{f_i^{\circ}} \right) \quad (2)$$

where f_i° is the fugacity for a selected standard state for which the chemical potential is μ_i° . The activity a_i is a ratio of two fugacities and may readily be determined even when the individual fugacities involved cannot be. The standard state employed may be selected arbitrarily on a basis of practical convenience but will normally be so chosen as to provide the simplest possible relation between the activity and the concentration of the constituent in the phase concerned. It thus becomes common to select a different standard state for a component for each phase in which it is present, so that the activity, unlike the fugacity, usually does not have a common value for different equilibrium phases.

For nonelectrolytic solutions the standard state for each component is normally taken to be the pure liquid at the temperature and pressure of the solution, and the activity is correlated with the concentration on the mole-fraction scale by means of the activity coefficient γ_i .

$$a_i = \frac{f_{i,l}}{f_{i,l}^{\circ}} = \gamma_i X_{i,l} \quad (3)$$

For what is called an ideal solution, γ_i as defined above is identically equal to unity for any component at any concentration. For real solutions the activity coefficients must be determined by experiment.

The fugacity $f_{i,l}$ for this standard state is calculated as follows. The vapor pressure $P_i^*(T)$ of pure liquid i at the given temperature is multiplied by the fugacity coefficient $\phi_i^*(P_i^*, T)$ of the vapor as calculated from the equation of state of the vapor to obtain the fugacity of the saturated vapor at the temperature, T . This then gives the fugacity of pure liquid i for temperature T and pressure P . The fugacity $f_{i,l}^{\circ} = f_{i,l}(P, T)$ may then be calculated by taking into account the difference between P_i^* and P . using the thermodynamic relation

$$\ln f_{i,l}^0 = \ln f_{i,l}(P, T) = \ln \mathcal{G}_i^* P_i^* + \int_{P_i^*}^P \frac{\bar{V}_i^*}{RT} dP \quad (4)$$

where V_i is the molar volume of pure liquid i . The integral in Eq. (4) will be negligible if $P_i^* - P$, is not large.

For liquid-vapor equilibrium, since the fugacity of each constituent must have a common value for both phases,

$$f_{i,l} = \gamma_i f_{i,l}^0 X_{i,l} = f_{i,v} = \mathcal{G}_i X_{i,v} P \quad (5)$$

Assuming the effect of pressure on the fugacity of the pure liquid to be negligible,

$$f_{i,l}^0 = \mathcal{G}_i^* P_i^* \text{ and} \\ X_{i,l} = \frac{1}{\gamma_i} \frac{\mathcal{G}_i}{\mathcal{G}_i^*} \frac{P}{P_i^*} X_{i,v} \quad (6)$$

If the gas phases involved are considered to behave ideally,

$$X_{i,l} = \frac{1}{\gamma_i} \frac{P}{P_i^*} X_{i,v} \quad (7)$$

For ideal liquid solutions, this desired relation between the liquid and vapor compositions further simplifies to

$$X_{i,l} = \frac{P}{P_i^*} X_{i,v} \quad (8)$$

For real solutions the activity coefficients are functions of concentration, temperature, and pressure. For a binary nonelectrolytic solution system the concentration dependence may often be represented to a good degree of approximation by the van Laar equations, which have been written as follows by Carlson and Colburn:[3]

$$\log \gamma_1 = \frac{A_1}{\left[1 + \frac{A_1 X_1}{A_2 X_2}\right]^2} \quad ; \quad \log \gamma_2 = \frac{A_2}{\left[1 + \frac{A_2 X_2}{A_1 X_1}\right]^2} \quad (9)$$

The van Laar coefficients A_1, A_2 are functions of temperature and pressure. Even substantial changes in pressure have only a small effect. The dependence on

temperature is more important, but over a range of 10 or 20° the resultant change in a typical activity coefficient will usually be only a few percent. Real solution systems vary widely in their degree of departure from the ideal solution rule, for which the boiling points of the solutions are always intermediate between those of the pure liquids. In many cases, however, the deviation from ideality becomes so great that a minimum or maximum results in the plot of boiling point versus liquid or vapor composition. At such a maximum or minimum, the equilibrium vapor and liquid compositions are identical. Such solutions are called azeotropes. A comprehensive description of methods for the experimental study of vapor-liquid equilibria and for the correlation of the results has been given by Hala et al.[1] An extensive table of azeotropes has been prepared by Horsley et al.,[4] and data for many binary solution systems have been summarized by Timmermans.[5]

CALCULATIONS. The refractive indices of the weighed samples and the pure liquids are plotted against the compositions of the solutions expressed in mole fractions of ethanol. The composition of each sample of distillate and residue may then be determined by interpolation on this graph. In a second graph three sets of curves are plotted:

The Boiling-point Diagram (I) for the System as Determined Experimentally. Two curves are plotted, one in which boiling temperature is plotted against the mole fraction of ethanol in the residue; in the other, the same boiling temperatures are plotted against the mole fraction of ethanol in the distillate. The composition as mole-fraction ethanol is plotted along the horizontal axis. Different symbols should be used for the two sets of points. The significance of this graph should be discussed with respect to the feasibility of separating benzene and ethanol by fractional distillation.

The Boiling-point Diagram (II) for the System as Predicted by the Ideal-solution Rule. Points for the two curves involved may be calculated as follows for a given pressure P. A temperature T is selected between the boiling points of the two pure liquids as calculated from accurate relations such as those given below. The terms $P_1^*(T)$, $P_2^*(T)$ represent the calculated vapor pressures of the pure liquids at this temperature.

$$\begin{aligned}
 P &= P_1 + P_2 = X_{1,l}P_1^*(T) + X_{2,l}P_2^*(T) \\
 &= P_1^*(T) + X_{2,l}[P_2^*(T) - P_1^*(T)]
 \end{aligned}
 \tag{10}$$

From Eq. (10) there is then calculated the mole fraction $X_{2,l}$ of component 2 in the solution having vapor pressure P at temperature T. Then the mole fraction $X_{2,v}$ for the equilibrium vapor phase is given by

$$X_{2,v} = \frac{P_2}{P} = \frac{X_{2,l}P_2^*(T)}{P} \quad (11)$$

The Boiling-point Diagram (III) for the System as Predicted by the van Laar Equations for Values of A_1, A_2 consistent with the Experimentally Determined Azeotrope Temperature and Composition. In this calculation it will be necessary to assume that the activity coefficients are functions of composition only; that is, $A_1, A_2 = \text{constants}$, an approximation justified by the small temperature range involved.

The activity coefficient γ_i is given by relation (7) (for the ideal-gas approximation)

$$\gamma_i = \frac{X_{i,v}}{X_{i,l}} \frac{P}{P_i^*(T)}$$

For the azeotropic solution, the mole fraction of each component has the same value for the liquid and vapor phases; hence the activity Coefficients $\gamma_{1,az}$ and $\gamma_{2,az}$ for the azeotropic solution are given by

$$\gamma_{1,az} = \frac{P}{P_1^*(T)} \quad \gamma_{2,az} = \frac{P}{P_2^*(T)} \quad (12)$$

From the pair of activity coefficients so calculated and the composition of the azeotrope, the van Laar coefficients may be calculated. It is convenient first to calculate the ratio A_2/A_1

$$\frac{A_2}{A_1} = \frac{X_{1,l}^2 \log \gamma_1}{X_{2,l}^2 \log \gamma_2} \quad (13)$$

Then

$$A_2 = \left(1 + \frac{A_2}{A_1} \frac{X_{2,l}}{X_{1,l}} \right)^2 \log \gamma_2 \quad A_1 = \frac{A_2}{A_2/A_1} \quad (14)$$

Now select some concentration $X_{2,l}$, $X_{1,l} = 1 - X_{2,l}$ and calculate from the van Laar equations γ_2 and γ_1 .

$$P = P_1 + P_2 = \gamma_1 X_{1,l} P_1^*(T) + \gamma_2 X_{2,l} P_2^*(T) \quad (15)$$

The solver option in Microsoft's Excel provides a simple method of solving this kind of problem. On the course CD there is an excel layout called Liqvap. A

printout of the spread sheet is given in Figure 5. In the first row the Antoine constants for Ethanol and n-hexane are given. These constants are used to calculate the theoretical vapor pressure of ethanol, $X_{1,i} P^*_1(T)$, from composition & temperature data given in and columns H (the ethanol composition) and I. Column F is used to calculate P total (760 is assumed here) using the solver function based on varying the temperature data in column I.

A	B	C	D	E	F	G	H	I
8.11576	1595.76	226.6		6.89122	1178.802	225.2		Calculated
X1P1	X2P2		Gamma1	Gamm2			X1	Temperature
	0	760	9.288334	1	760			0 68.7358
36.02806	523.318		6.263728	1.021043	760		0.1	60.45268
65.76827	434.5413		4.36478	1.088357	760		0.2	58.41956
96.83444	374.9841		3.148511	1.213693	760		0.3	58.00893
129.0603	321.3178		2.355489	1.419156	760		0.4	58
160.7184	267.0129		1.831267	1.744042	760		0.5	57.91693
190.3814	211.5572		1.4826	2.258209	760		0.6	57.63201
219.2421	157.1361		1.252717	3.088734	760		0.7	57.3464
256.0749	106.472		1.107244	4.475002	760		0.8	57.82471
338.0283	59.97942		1.026252	6.887324	760		0.9	61.38877
	760	1.13E-13		1	11.29447	760		1 78.22834
								0 68.7358
							0.296934	60.45268
							0.377716	58.41956
							0.401164	58.00893
							0.4	58
							0.387261	57.91693
							0.371394	57.63201
							0.361379	57.3464
							0.373076	57.82471
							0.45645	61.38877
P1	P2	Gamma1	Gamma2	A2/A1	A1	A2		1 78.22834
322.6507	535.5297	2.355489	1.419156	1.087741	0.9679378	1.052866	0.4	58

Figure 5. A spread sheet layout for vapor liquid equilibrium calculations

In cells F25 and G25 the constants A_1 and A_2 are calculated based on an ethanol composition and temperature of the azeotrope given in cells H25 & I25 using equation (12) – (14). In columns D, the gamma values are calculated and stored for each temperature based on equation (9).

Then the equation

$$X_{2,v} = \frac{P_2}{P} = \frac{\gamma_2 X_{2,l} P_2^*(T)}{P} \quad (16)$$

is used to calculate the mole fraction of the vapor in cells H14 - H24 and the temperature data copied to column K to complete the graph seen in Figure 6.

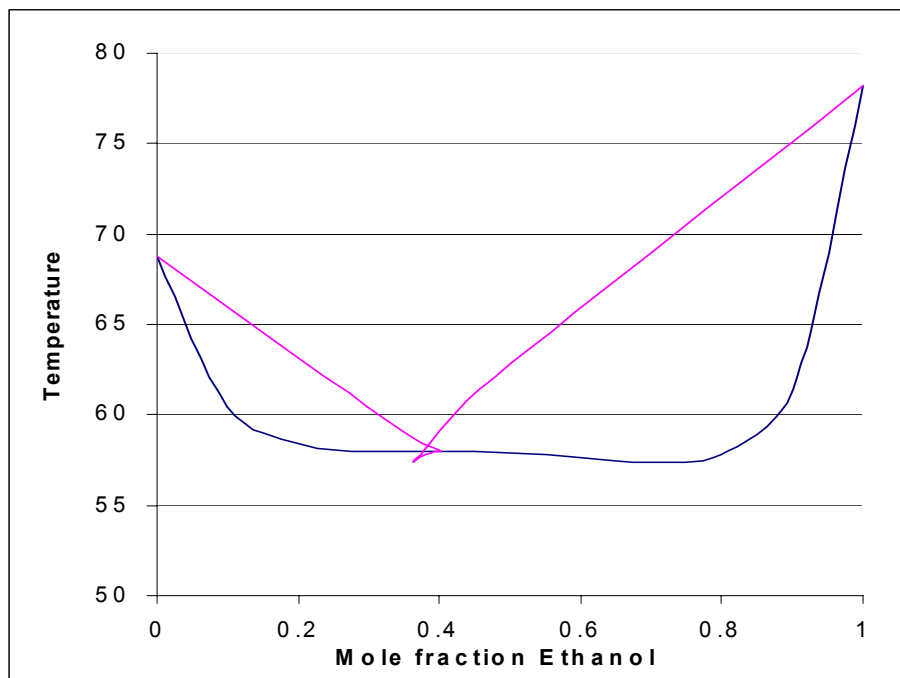


Figure 6. Boiling temperature as a function of composition for ethanol – n hexane mixtures.

The experimental data should be added to this graph and compared to a similar graph for an Ideal mixture. A minimum in the sum of the least square deviation between the observed temperature and the experimental temperature should be included in your report.

Practical applications. Vapor-composition curves are necessary for the efficient separation of liquids by distillation. Fractional distillation under controlled conditions is essential in the purification of liquids and in many industries, such as the petroleum industry and solvent industries.[7-9]

Suggestions for further work. Solutions of chloroform and acetone, giving a maximum in the boiling-point curve, may be studied in exactly the same manner as described for ethanol and benzene.

The maximum in the boiling-point curve of hydrochloric acid and water occurs at 108.5° and a composition of 20.2 percent hydrochloric acid at a pressure of 760 mm. The distillate at the maximum boiling point is so reproducible in composition at a given pressure and so easily obtained that it may be used to prepare solutions of HCl for volumetric analysis. A solution of hydrochloric acid is made up roughly to approximate the constant-boiling composition, and after boiling off the first third, the remaining distillate is retained. The barometer is read accurately, and the corresponding composition is obtained from the literature.

Solutions of chloroform and methanol, giving a minimum in the boiling-point curve, may be studied by using a Westphal density balance for determining the

compositions instead of a refractometer. A density-mole-fraction curve is plotted, and the compositions of the samples are determined by interpolation. Since larger samples are needed for the density measurements, more material and a larger flask are required.

The gas-saturation method for vapor-pressure measurements may be used in studying binary liquids. Using this technique, Smith and Engel[12] have determined vapor-pressure composition curves for a number of ideal and nonideal types.

Vapor-liquid equilibria at different total pressures provide an interesting study. The acetonitrile-water system has an azeotrope which varies considerably in composition as the pressure is reduced[13]. Othmer and Morley[14] describe an apparatus for the study of vapor-liquid compositions at pressures up to 500 psi. The earlier papers of Othmer may be consulted for a number of binary vapor-liquid equilibria.

References

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