Liquid–Vapor Equilibria: Experimental Determination of the P–X Diagram for a Binary System

Luis H. Blanco,* Carmen M. Romero, and Edgar F. Vargas

Departamento de Química, Universidad Nacional de Colombia, A.A. 52680, Bogota, D.C., Colombia S.A., lhblanco@ciencias.ciencias.unal.edu.co

Abstract: An experimental method for the determination of the pressure–composition diagram of a binary system consisting of liquid and vapor phases is described. The experiment is suggested for use in physical chemistry courses. The results are compared with those obtained using other methods for the system hexane/ethyl iodide.

Introduction

The topic of liquid–vapor equilibrium is included in most general chemistry and introductory physical chemistry courses. A common approach is to begin with Raoult´s law to introduce ideal solutions; then, the nonideal cases are discussed. Both are presented at constant temperature. An alternative method of presenting this material is to consider the three-dimensional phase diagram with the three axes being pressure, P; temperature, T; and composition, X. (See Figure 1.) The two-dimensional diagrams are then easy to show as planes: the P–X plane with T constant (Figure 2) and the T–X plane with P constant (Figure 3). Usually, the P–T plane with X constant is not shown. This situation has not changed much over the years [1–4]. Emphasis is placed on the P–X diagram because it is easy to explain and to understand. Plots of ideal solution behavior and positive and negative deviations from it are shown, Figure 4. Afterwards, the T–X diagram is studied in detail to show its application in distillation [2, 4]; see Figure 5.

From an experimental standpoint, a T–X diagram and a simple distillation are common. The P–X diagram is not normally attempted because of experimental difficulties that make it impractical. In recent years, an experiment that determines a P_T versus X curve has been published [5]. Also, two experiments that are rather difficult to perform have been proposed. They create P–X diagrams using some unconventional methods [6, 7]. In this paper we describe an experiment designed to establish the P–X diagram of a binary system.

Experimental

The apparatus used is shown in Figure 6. It was made to our specifications by a commercial glass-blowing shop. A is the boiler flask; it has a stopcock at the bottom for sampling the liquid phase. We use a 500-mL flask, but a smaller flask could be used. G is a glass well in which to place a thermometer with 0.1 °C divisions or a temperature sensor. B is a Claissen-type head for working under reduced pressure. E$_1$ and E$_2$ are high-vacuum stopcocks for sampling liquid and condensate. C is a double-efficiency condenser of approximately 60 cm in length. Figure 7 shows the sampling bulb.

The upper part of the apparatus is connected to a ballast tank where pressure is measured by means of a sensor. Pressure is read using Vernier (Vernier Software & Technology. 13979 SW Millikan Way,

Beaverton, Oregon 97005-2886) instruments and software and a portable or desktop computer. Figure 8 is a schematic representation of the vacuum system and the setup for pressure measurement.

The temperature of flask A should be near the experimental temperature. To accomplish this some heating might be needed. We use heating tape connected to a 500-W light-bulb dimmer. The composition is analyzed by refractometry.

A Typical Experimental Run

The system we selected is ethyl iodide/hexane, which can be compared to the results published in reference 6. A paper by Halban [8] in the early literature gives data for this system at 65 °C. Normal hexane was obtained from Merck and used without further purification. Ethyl iodide was synthesized in our laboratory and purified by distillation. The physical constants were checked against the literature values [9] and the agreement was considered satisfactory for our purpose.

Data of total pressure versus composition at the selected temperature, 25 °C, had been determinated previously. Otherwise, it can be obtained from the literature [6]. A curve of refractive index versus composition at 25 °C was determined. The vapor pressure of the pure components was measured as a check.

Before students begin their work, the instructor should inform the students about the special precautions needed to use equipment that works under reduced pressure.

The whole apparatus is evacuated using the vacuum pump. Pressure should remain constant. If it does not, search for leaks. Once the condition of constant pressure is attained, the apparatus is brought to atmospheric pressure and 200 mL of hexane is placed in boiler flask A. This can be added through the thermometer well. The system is evacuated and brought to the temperature selected for the experiment. The pressure is recorded when it reaches a constant value.

The apparatus is brought to atmospheric pressure. A small quantity of hexane is removed and enough ethyl iodide is added so that the mole fraction of iodide X_I in the resultant mixture is approximately 0.1. Using refractive index data, the composition of the mixture is determined.

Using P_T versus X data previously determined, the P_T value corresponding to the mole fraction X_I for the mixture at the temperature of the experiment is obtained. The pressure is reduced until the desired value is reached. The boiler flask is heated carefully to a temperature near the one selected. The equilibrium temperature is fixed by the composition and the total pressure according to the phase rule.
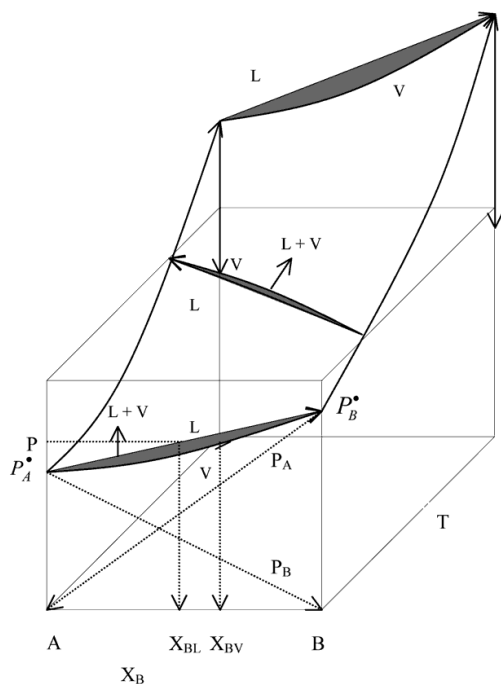
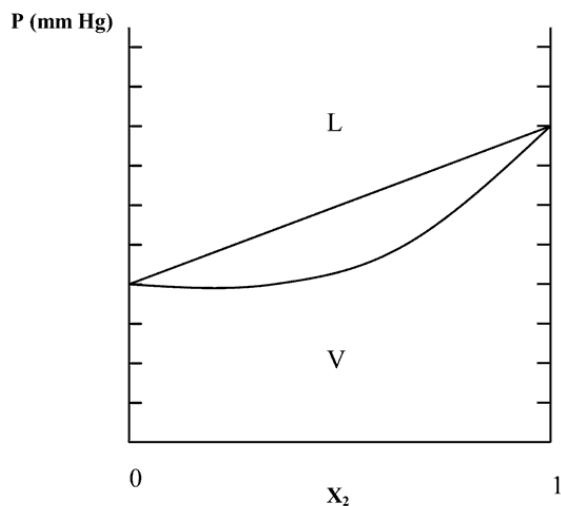**Figure 1.** Three dimensional phase diagram for a binary system containing only liquid and vapor phases.

Figure 2. Pressure–composition diagram.

Figure 3. Temperature–composition diagram.

Figure 4. (a) Negative deviations and (b) positive deviations from Raoult´s Law.

The pressure should remain constant at the selected value. Otherwise, adjust it by letting air in or applying vacuum. The temperature should reach a single constant value so that the readings of the two thermometers are equal. At this point, equilibrium has been reached.

When a sample of about 5 mL of condensate is collected using stopcock E_1, the sampling flask is isolated from the apparatus. By means of stopcock E_4, the flask is brought to atmospheric pressure and removed for analysis. A similar procedure is followed to get a sample of the liquid phase in boiler flask A. When the procedure begins the pressure of the sampling flask should be the same as that of the main apparatus. The refractive index of the two samples is read and their composition is determined using the calibration curve.

Ethyl iodide is added again to obtain data for a second mixture whose composition should be near $X_I = 0.2$, and the procedure
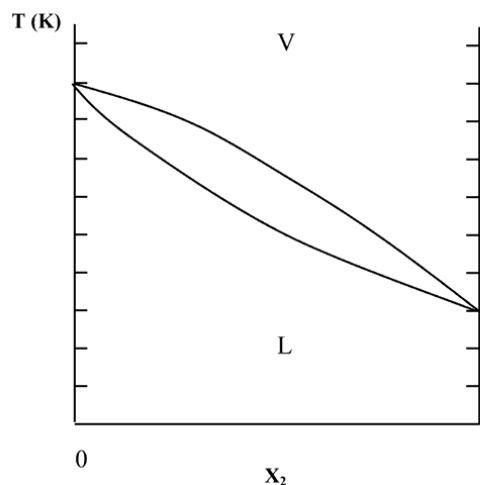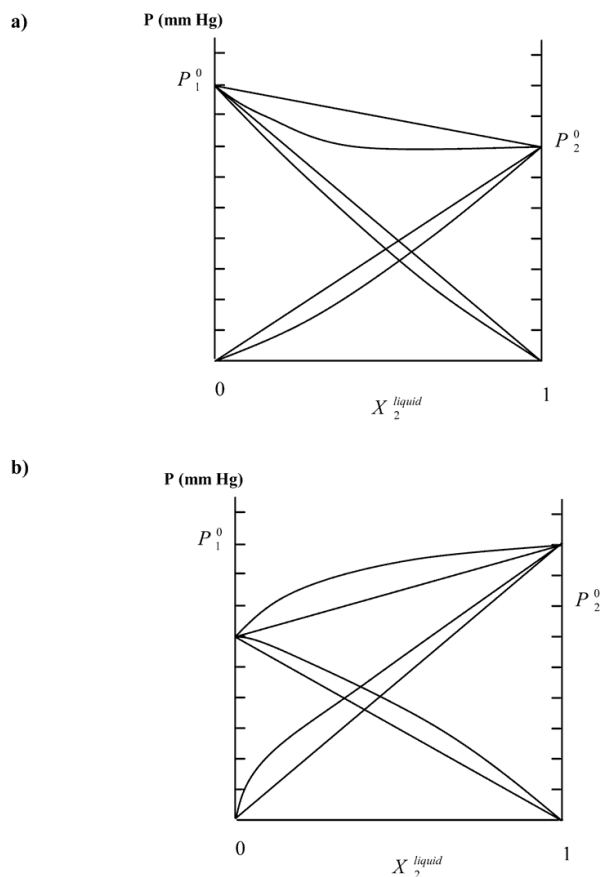
described is repeated. The number of data points that can be taken depends on the available time for the laboratory session.

At least ten data points should be obtained, two for the pure components and eight for mixtures covering the whole range of composition. This is not easily accomplished in one regular laboratory session. Two consecutive sessions of one group or two groups working simultaneously, or in different sessions, are usually enough.
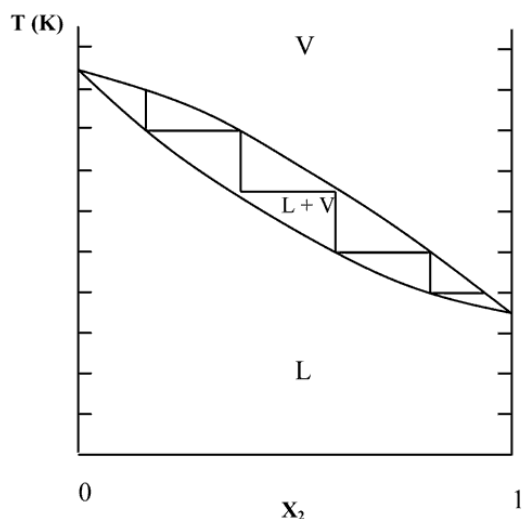
Figure 5. Simple isobaric distillation.

Figure 7. The sampling bulb. D. Round-bottom flask, 25-mL capacity; E_1, E_2. high-vacuum stopcock; H. ground-glass joint.
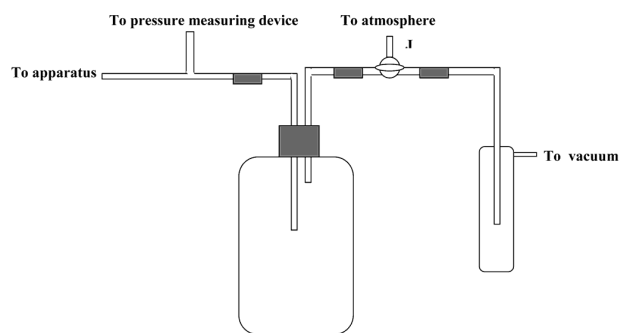
Figure 8. Vacuum connection. H. Ballast tank of 20-L (approx.) capacity; I. cold trap; J. three-way stopcock.

Results and Discussions

Table 1 shows the results obtained in the laboratory for P_T as a function of X_2. These data must be given to the students at the beginning of the experiment. The values for the vapor pressure in mm of Hg for the pure components are 136.2 and 151.3 [8]; the values obtained are 138 and 148 and those of reference 6 are 134.0 and 151.1. The small differences could be due to the purity of the substances or to the method itself; however, they do not affect the overall purpose of the experiment.

Table 2 gives the results obtained by one group of our students. Figure 9 shows the curves for partial pressures versus composition and includes the total pressure curve.

The phase diagram obtained using our results is shown in Figure 10. Figure 11 was obtained from the literature values [6] given in Table 3. It can be seen that the results show good agreement with literature data. There is some scatter of points in both cases, but it does not affect the shape of the equilibrium diagram.

The main purpose of the experiment is the determination of the phase diagram. Depending on the level of the course, the collected data can be interpreted in different ways. The activity coefficients can be calculated by the usual method because there are enough data to do so. The equation needed is
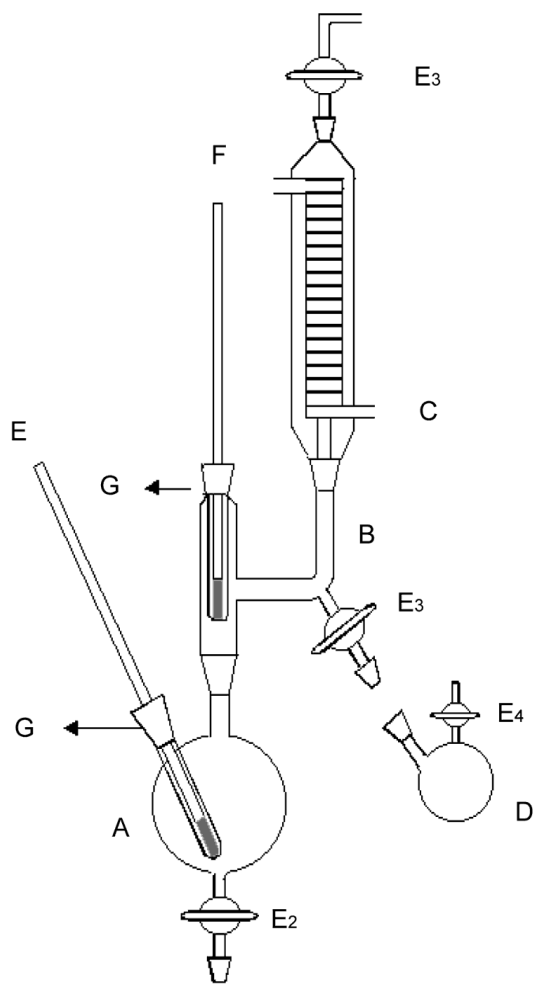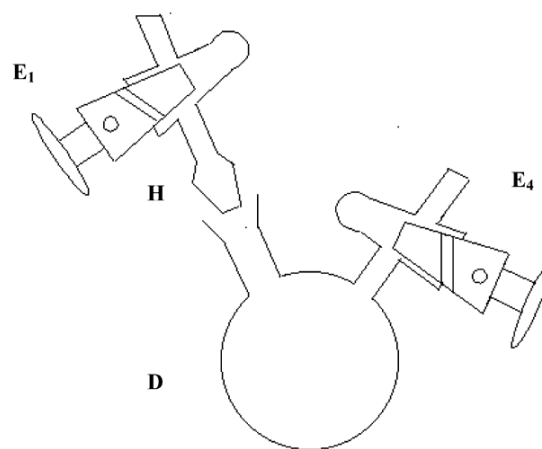

Figure 6. Apparatus for liquid–vapor equilibria. A. Boiler flask, 500-mL capacity; B. Claissen-type distilling head; C. double-efficiency condenser; D. sampling bulb; E_1, E_2, E_3, E_4. high-vacuum stopcocks; F. thermometer or temperature sensor, 0.1 °C sensibility; G. glass well.

Table 1. Total Pressure Versus Composition for the System C_2H_5I/C_6H_{14} at 25 °C

| X_I	P_T (mm Hg) experimental	P_T (mm Hg) Literature
1.000	138	136.2 (8)
0.872	146	
0.785	157	
0.684	168	
0.611	174	
0.405	176	
0.279	174	
0.200	168	
0.103	161	
0.000	148	151.3 (8)

Table 2. Total Pressure and Iodide Mole Fraction in the Vapor and Liquid Phases Determined in the Experiment for the System C_5H_5I/C_6H_{14} at 25 °C and Calculated Partial Pressures of C_2H_5I (P_I) and Hexane (P_H)

P_T (mm)	Y_I	X_I	P_I (mm)	P_H (mm)
138	1.000	1.000	138	0
146	0.770	0.902	112.42	33.58
157	0.683	0.806	107.23	49.77
168	0.584	0.702	98.11	69.89
174	0.502	0.623	87.35	86.65
176	0.425	0.408	74.80	101.20
174	0.322	0.283	56.03	117.97
169	0.246	0.191	41.57	127.43
161	0.108	0.102	17.39	143.61
148	0.000	0.000	0	148.00
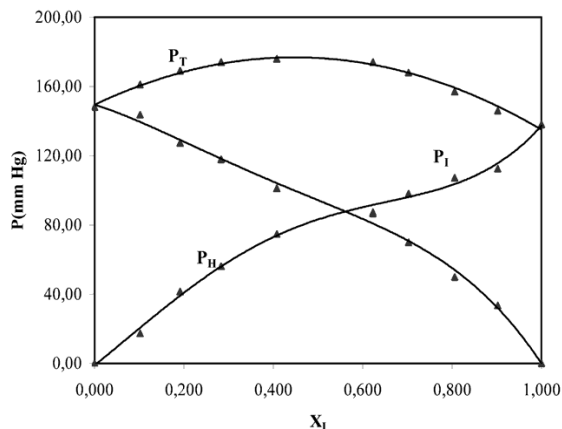
Figure 9. Partial and total pressures versus composition for the system C2H5I/C_6H_{16} at 25 °C.

$$\gamma_i = P_i / P_i^0 X_i \qquad (1)$$

In eq 1, P_i is the partial pressure of the *i*th component calculated from Dalton´s Law; this is $P_i = Y_i P_T$, where Y_i is the mole fraction of *i* in the vapor phase and P_T is the total pressure. P_i^0 is the vapor pressure of pure component *i* at temperature T and X_i is the mole fraction of *i* in the liquid phase.
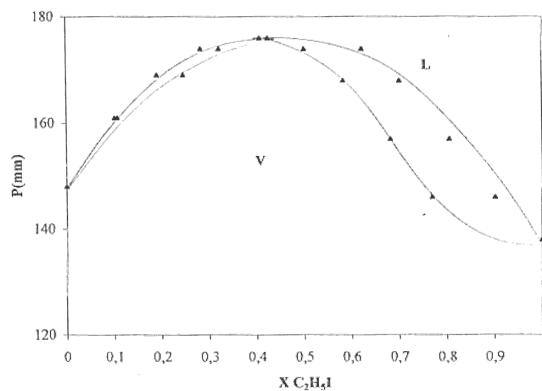
Figure 10. Plot of the experimental data for C_2H_5I/C_6H_{16} at 25 °C.
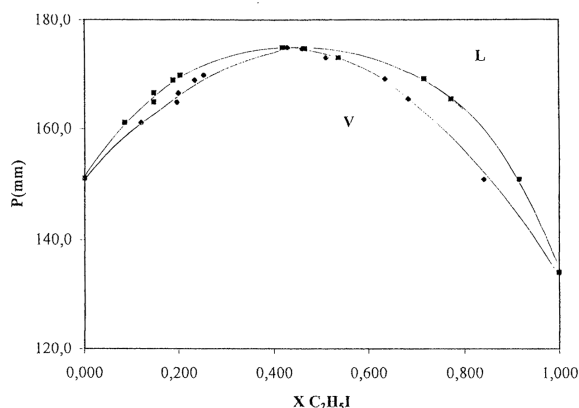
Figure 11. The P–X diagram determined by P.F. Knewstubb [6].
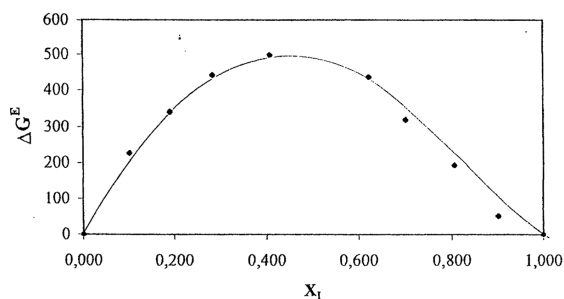
Figure 12. Excess free energy for the mixture ethyl iodide/hexane at 25 °C.

If the plot of the activity coefficients, γ, versus X is constructed, the students can show that the Gibbs–Duhem relationship is satisfied.

Having obtained the activity coefficients the excess free energy, ΔG^E, can be obtained from

$$\Delta G^E = X_1 RT \ln \gamma_1 + X_2 RT \ln \gamma_2 \qquad (2)$$

The calculated values from our data are given in Table 4 and Figure 12. Table 5 and Figure 13 show the corresponding values from literature data [6].

The data can be fitted to the Redlich–Kister equations [10] to establish the behavior of the system. Furthermore, data

Table 3. Total Pressure and Iodide Mole Fraction in the Vapor and Liquid Phases for the System C_5H_5I/C_6H_{14} at 25 °C, Data from Reference 6

P_T (mm)	Y_I	X_I
151.1	0.000	0.000
161.1	0.120	0.085
164.8	0.196	0.147
166.5	0.199	0.147
168.8	0.233	0.188
169.7	0.252	0.203
174.8	0.429	0.419
174.6	0.460	0.466
172.9	0.510	0.537
169.0	0.634	0.716
165.4	0.683	0.772
150.9	0.840	0.915
134.0	1.000	1.000

Table 4. Activity Coefficients and Mole Fraction for Ethyl Iodide and Hexane and Excess Free Energy for the Mixture at 25 °C

X_I	γ_I	X_H	γ_H	ΔG^E (J mol^{-1})
1.000		0.000		0
0.902	0.9031	0.098	2.315	51.63
0.806	0.9641	0.194	1.733	191.32
0.702	0.9874	0.298	1.585	317.83
0.623	1.0160	0.377	1.554	435.55
0.408	1.3285	0.592	1.155	498.44
0.283	1.4346	0.717	1.1117	441.17
0.191	1.5773	0.809	1.0643	340.52
0.102	1.2353	0.898	1.0806	225.82
0.000		1.0000		0

Table 5. Excess Free Energy for the System C_5H_5I/C_6H_{14} at 25 °C from Literature Data [6]

X_I	ΔG^E (J mol^{-1})
0.000	0
0.85	168
0.147	239
0.147	262
0.188	316
0.203	332
0.419	405
0.466	497
0.537	490
0.716	453
0.772	406
0.915	209
1.000	0

could be taken at other temperatures by different groups of students to complete the analysis by the method of Redlich–Kister.

The proposed experiment shows in a clear way the *P–X* behavior of the binary system in the region where only liquid and vapor phases are present. The time it takes to complete this experiment is rather long, but this is compensated for by the relevance of the results and the understanding of the subject that is afforded to the students.

Supporting Material. Student and instructor notes are available at (http://dx.doi.org/10.1007/s00897000481b and http://dx.doi.org/10.1007/s00897000481c).

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