CHEM 360 L

EXPERIMENT 3

Liquid-Vapor Equilibrium

Introduction

This experiment shows how one constructs the boiling-point diagram (temperature vs. composition) for a binary solution system at constant pressure. The observed composition curves are compared with ideal-solution curves. The compositions of the liquid and vapor phases are determined refractometrically. For nonelectrolyte solutions, the activity (defined as the ratio of the fugacity of the component to its standard state fugacity) may be expressed as the product of the activity coefficient and mole fraction of that component:

$$a_i = \frac{f_{i,liquid}}{f^*_{i,liquid}} = \gamma_i x_{i,liquid}$$

where *f* is the fugacity, γ the activity coefficient, *a* the activity, and *x* the mole fraction. In an ideal solution, the activity coefficient is defined at unity for all compositions. In most cases, the fugacity is considered to be interchangeable with pressure.

Procedure

The instructor will show you how to set up the Cottrell apparatus and in the proper use of the Abbe refractometer. The liquids used will be acetone and chloroform. In order to construct a plot of refractive index versus mole fraction, refractive indices are determined for the pure liquids and for a series of mixtures of the liquids (1 mL acetone + 4 mL chloroform; 2 mL acetone + 3 mL chloroform; 3 mL acetone + 2 mL chloroform; 4 mL acetone + 1 mL chloroform). This plot will be used in the determination of the composition of the liquid and vapor samples. A sample (50 mL) of acetone is added to the flask, and the boiling point determined. Boiling points and refractive indices of residue and distillate are determined after the addition of 0.4, 1.0, 2.0, 10.0, 10.0, and 10.0 mL of chloroform. The flask is then drained, dried and refilled with chloroform (50 mL). The boiling point is determined for pure chloroform, then boiling points and refractive indices are determined for residue and distillate after successive additions of 4, 8, 10 14, and 20 mL of acetone. The barometer should be read occasionally throughout the experiment.

Calculations

A least-squares linear regression is used to determine the equation relating refractive index and composition. The composition of the residues and distillates may be determined from this equation. A second graph is plotted, in which the boiling temperature is shown as a function of distillate's acetone mole fraction. A second set of points on the same graph should show the boiling temperature as a function of the residue's acetone mole fraction. A third graph will show the Boiling Point Diagram for the ideal solution case. A temperature between the boiling points of the two pure liquids is chosen. The vapor pressure (in Torrs) of each liquid at this temperature is determined from the equation:

$$P^*(T) = B * 10^{-0.2185\frac{\mathrm{A}}{\mathrm{T}}}$$

where $P^*(T)$ is the pure liquid vapor pressure at the temperature T, T is the temperature in Kelvins, A is 7641.5 K for acetone, 7500.5 K for chloroform; and B is 8.0172×10^7 Torr for acetone, 5.4335×10^7 Torr for chloroform. The composition of the liquid having a boiling point at this temperature may be found using the equation:

$$P = x_{1,liquid} P_1^*(T) + x_{2,liquid} P_2^*(T)$$

where P is the total (ambient) pressure. The vapor composition at this temperature is found by diving the partial pressure of each component by the total pressure. The ideal solution boiling point diagram is constructed from a series of such calculations. The final graph will show the boiling point diagram for the nonideal solution, using activity coefficients determined at the azeotrope. Because the compositions of the liquid and vapor are identical at the azeotrope, the activity coefficients are given by the equation:

$$\gamma_i = \frac{P}{P_i^*(T)}$$

The van Laar coefficients (A_1 and A_2) may be calculated from the activity coefficients and composition of the azeotrope:

$$\frac{A_2}{A_1} = \frac{(x_{1,liquid}^2 \, log\gamma_1)}{(x_{2,liquid}^2 \, log\gamma_2)}$$

$$A_2 = (1 + \frac{A_2 x_{2,liquid}}{A_1 x_{1,liquid}})^2 \, log\gamma_2$$

and,

$$A_1 = A_2/(A_2/A_1)$$

A liquid composition is chosen, and the activity coefficients calculated from that. Find the temperature at which the ambient pressure is given by the equation:

$$P = \gamma_1 x_{1,liquid} P_1^*(T) + \gamma_2 x_{2,liquid} P_2^*(T)$$

then determine the vapor composition from:

$$x_{i,vapor} = \gamma_i x_{i,liquid} \frac{P_i^*(T)}{P}$$