Experiment 5

LIQUID-VAPOR EQUILIBRIA IN A TWO COMPONENT SYSTEM

In this experiment a boiling point-composition diagram is constructed for one of the following pairs of liquids.

- Cyclohexane-Ethanol
- Cyclohexane-Ethylacetate
- Ethanol-Ethylacetate
- Methanol-Ethylacetate

Solutions of various compositions are refluxed at atmospheric pressure and the boiling point and vapor composition are determined, from which activity coefficients in the liquid phase can be calculated. The heat of mixing will be estimated by invoking the regular solution model.

Theory

For real solutions following a Raoult's law convention, the partial pressure of each component in the equilibrium vapor is

\[ p_i = \gamma_i X_i p_i^\circ \]

where \( \gamma_i \) is the activity coefficient, \( X_i \) is the mole fraction in the liquid phase, and \( p_i^\circ \) is the vapor pressure of pure "i" at that temperature. The vapor phase will be assumed to be an ideal gas mixture, which means that the mole fraction in the vapor is given by \( Y_i = p_i / P_{\text{total}} \).

The molar Gibbs free energy of mixing of a binary solution is

\[ \Delta G_{\text{mix}} = RT(X_1 \ln \gamma_1 X_1 + X_2 \ln \gamma_2 X_2) \]

A reasonable assumption for small molecules of about the same size is that the molar entropy of mixing is that of an ideal solution.

\[ \Delta S_{\text{mix}} = -R(X_1 \ln X_1 + X_2 \ln X_2) \]

This is called a regular solution. The molar heat of mixing is then found by the following standard relation.

\[ \Delta H_{\text{mix}} = \Delta G_{\text{mix}} + T \Delta S_{\text{mix}} \]
Without some such assumption of a model, the heat of mixing cannot be obtained from boiling point-composition data at one pressure.

**Technique**

A gas chromatograph (GC) is used to determine the composition of the vapor phase. Our GCs have megabore (0.53mm) columns. The liquid phase is carbowax (DB-5; hydrogen bonding and very polar). Your instructor will set the flow rate and temperature settings and also instruct you in the use of the computer routine that will be used to accumulate your data.

Sampling is done with a 5 or 10 microliter syringe. Generally 0.5 to 1 µL is the proper sample size. The larger the sample, the poorer the peak resolution and the more likely the detector saturation will occur. The syringes are fragile and expensive and should be handled with care.

The refluxing apparatus consists of a small boiling flask, condenser, heating mantle (controlled by a variable transformer mounted on the utility island), and a thermometer whose bulb is wrapped in cotton thread. When equilibrium is established, as indicated by a constant thermometer reading, a sample of the vapor is withdrawn by inserting the syringe needle through the rubber septum into the small pool of condensate just below.

**Experimental Procedure**

In order to map out the variation of the boiling point as a function of mole fraction in solutions of the binary mixture it is necessary to either prepare a set of solutions at various concentrations or to follow an *in situ* method. First pipette 15 ml of component A into the boiling flask, assembly the apparatus and determine the boiling point of the pure substance. Then add a small amount of component B through the top of the condenser using an appropriate volumetric pipette. Because the liquid is already hot it will not take long for the new solution to boil. However, allow the temperature to re-equilibrate at the new boiling point and for the condensed vapors to rinse several volumes through the trap beneath the septum. Then a sample of the condensed vapors may be withdrawn for GC analysis. Using the known volumes, densities and molecular weights the mole fraction of the liquid phase can be calculated. Continue to add aliquots of component B through the condenser in steps, determining the boiling point and withdrawing a sample at each step, until the mole fraction is near 0.5. (The added volumes should be chosen to give 5 or 6 even steps between a mole fraction of 0 and 0.5.) Then disassemble the apparatus, discard the solution and repeat the process starting with 15 ml of the pure B.

A second set of about 6-8 solutions should be prepared for the calibration of the gas chromatograph. The concentrations should be more or less evenly spaced between 0 and 1 mole fraction but it is not necessary to inject the pure components. Each injection should yield
two peaks that are completely resolved (no overlap) on the chromatogram. The computer output will give peak areas. For a calibration curve plot mole fraction of component A versus peak area function (defined as the area of the peak for A divided by the sum of the area of the two peaks).

Plot boiling point versus mole fraction of both liquid and vapor to give the usual liquid-vapor phase diagram. You may wish to try one or two more solutions to pin down the phase diagram more accurately. Record the barometric pressure.

**Treatment of Data**

Calculate the activity coefficients of each component in each solution from the relations, \( p_i = Y_i p = \gamma_i X_i p^o \). Then calculate the Gibbs free energy of mixing and the enthalpy of mixing from the regular solution assumption. Plot \( \gamma_1 \) and \( \gamma_2 \) versus \( X_2 \) one graph, and \( \Delta G \) and \( \Delta H \) versus \( X_2 \) on a second graph.

Below are the vapor pressure formulas of the various pure components. You will need these to calculate the vapor pressures of the pure components at the temperature of the boiling points of the mixtures.

Vapor pressures near the normal b.p.:

\[
\ln P(\text{torr}) = A - \frac{B}{T^\circ K}
\]

<table>
<thead>
<tr>
<th>Component</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclohexane</td>
<td>17.406</td>
<td>3812.5</td>
</tr>
<tr>
<td>Ethylacetate</td>
<td>18.623</td>
<td>4200.0</td>
</tr>
<tr>
<td>Ethanol</td>
<td>21.1375</td>
<td>5099.7</td>
</tr>
<tr>
<td>Methanol</td>
<td>20.646</td>
<td>4734.8</td>
</tr>
</tbody>
</table>

**Illustrative Problem**

For a certain benzene-ethanol solution we have, \( P = 750 \text{ torr}, T = 68.3^\circ C \), Wt % benzene = 52.02 in the liquid and 62.90 in the vapor, \( p^o(68.3^\circ C) = 520.5 \text{ torr} \) for benzene and 504.1 torr for ethanol. Calculate \( \Delta G \) and \( \Delta H \) of mixing per mole of solution.

**Answer:**

\[
\begin{align*}
X_{\text{benz}} &= 0.390, \quad Y_{\text{benz}} 0.500 \\
\gamma_{\text{benz}} &= 1.847, \quad \gamma_{\text{EtOH}} = 1.220 \\
\Delta G &= -875 \text{ J/mol}, \quad \Delta H = 1024 \text{ J/mol}
\end{align*}
\]