L-V Equilibrium in a Binary System

A. Ideal Solution Theory (Raoult’s Law)

1. \( P_{i,\text{id}} = x_{i,\ell} P_i^*(T) \)  
   \( x = \text{mole fraction; } \ell = \text{liq.; } * = \text{pure; } \)
   \( i = A \text{ or } B \text{ for binary system.} \)

2. Typically used for mixtures of volatile components.

3. Far less reliable than ideal gas theory for gases.

4. BUT, R’s Law does hold for component A when \( x_{A,\ell} \to 1 \).

5. Then \textit{Henry’s Law} holds for other component:
   \( P_B = k_{H,B} x_{B,\ell} \) (as \( x_{A,\ell} \to 1 \))

B. Real Solution

1. \( P_i = a_i P_i^*(T) \), with \( a_i = \gamma_i x_{i,\ell} \)  
   \([\text{activity & act. coef.}]\)

2. \( \gamma_i \to 1 \) as \( x_{i,\ell} \to 1 \), so \( a_i \to x_{i,\ell} \).

3. This is called \textit{Convention I} in Levine.

4. Vapor: \( P_i = x_{i,v} P \) (Dalton’s Law of Partial \( P \)s)
C. Deviations from Ideality

1. Accommodated by activity coefficient “fudge factor.”
2. Distinguish *positive* and *negative deviations*.
3. Extreme → *azeotropes*, compound formation, *immiscibility*. 
D. Experiment

1. Use refractive index to determine mixture compositions.

2. Prepare calibration curve by measuring RI for several (8-10) prepared samples. (Start with 6 and expand.)

3. Starting with mixture on vacuum line, establish \( \ell - v \) equilibrium, measuring \( P \) and capturing \( \sim 2 \) L of vapor in storage bulb.

4. Transfer vapor to sample cell by freezing out with liq N\(_2\).

5. Measure RI for both samples -- but allow to warm to room \( T \) first. (The composition of the \( \ell \) sample changes with vaporization.)

6. Try to get results for 6 mixtures, plus both pure components (\( P^* \) only); but 4 mixtures will suffice if pressed for time.

7. In the estimation of \( \gamma_A \) and \( \gamma_B \), data noise tends to be amplified; follow the fitting procedures and use your smooth fitted curves for this determination.