L-V Equilibrium in a Binary System

A. Ideal Solution Theory (Raoult's Law)

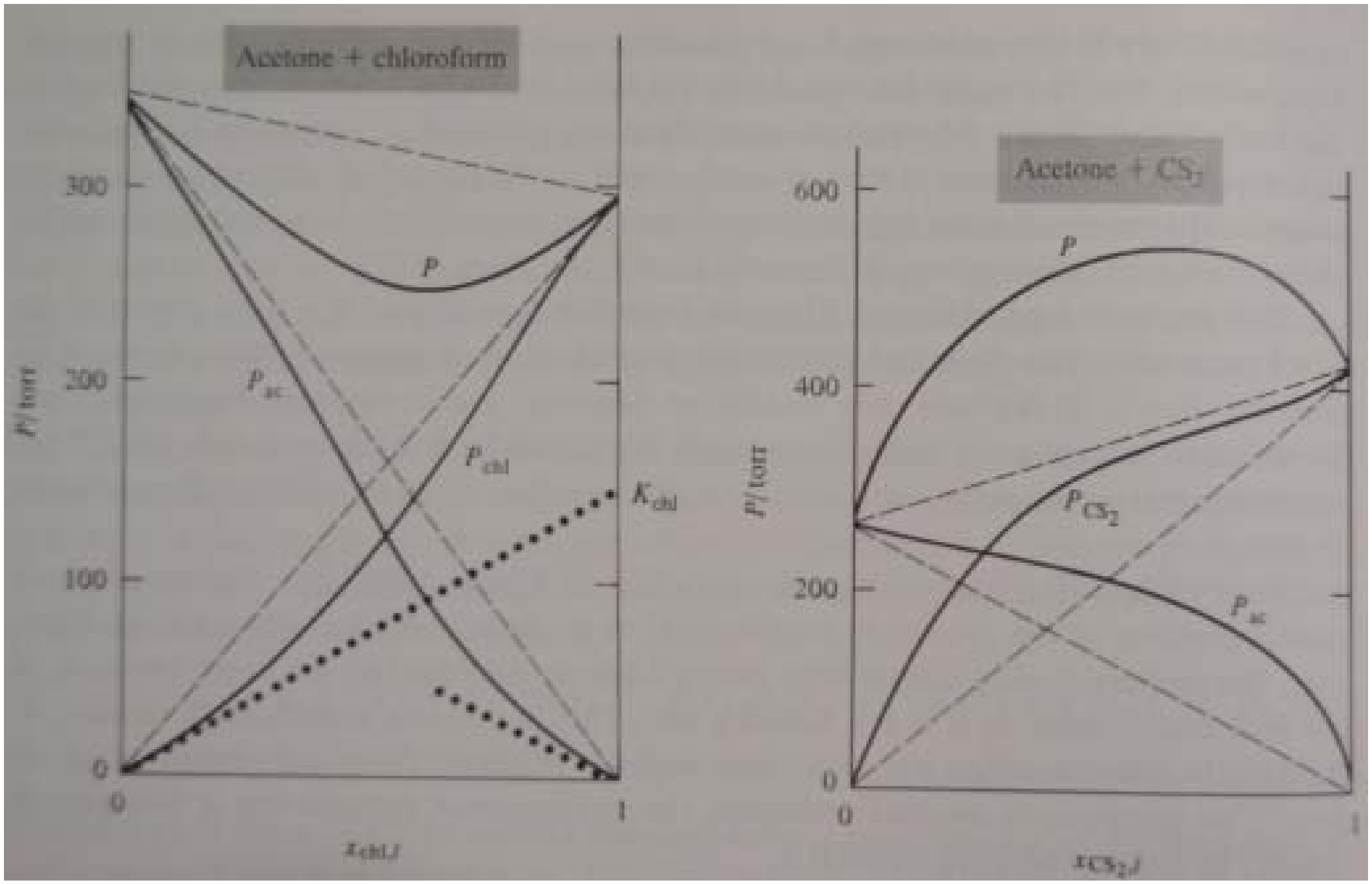
1. $P_{i,\text{id}} = x_{i,\ell}\, P_i^*(T)$ x = mole fraction; ℓ = liq.; * = pure; i = A or B for *binary* system.
2. Typically used for mixtures of volatile components.
3. Far less reliable than ideal gas theory for gases.
4. BUT, R's Law *does* hold for component A when $x_{\text{A},\ell} \to 1$.
5. Then *Henry's Law* holds for other component:
   $$P_\text{B} = k_{\text{H,B}}\, x_{\text{B},\ell} \quad (\text{as } x_{\text{A},\ell} \to 1)$$

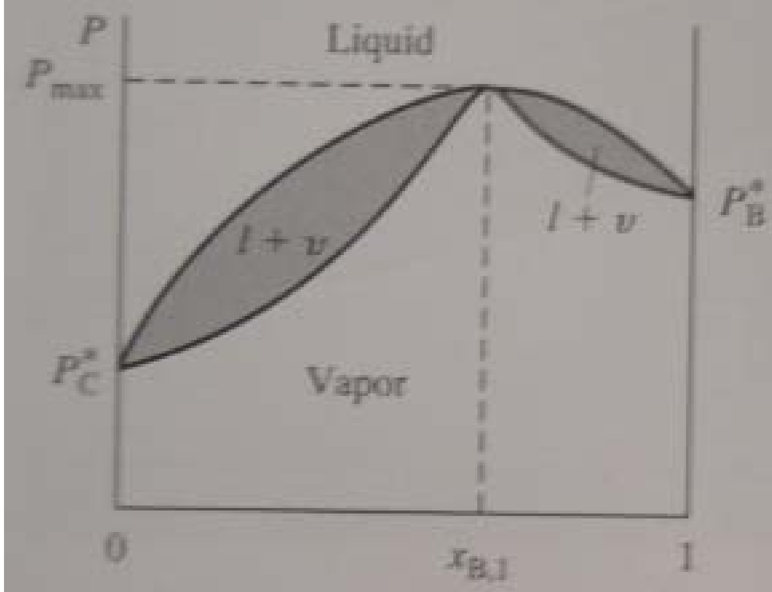
B. Real Solution

1. $P_i = a_i\, P_i^*(T)$, with $a_i = \gamma_i\, x_{i,\ell}$ [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 *Convention I* in Levine.
4. Vapor: $P_i = x_{i,v}\, P$ (Dalton's Law of Partial Ps)

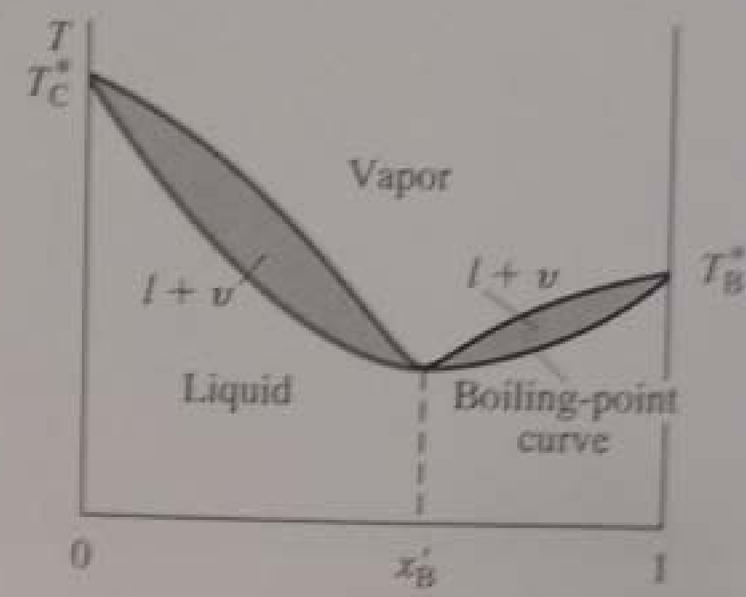
C. Deviations from Ideality

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




P
P_{max}
Liquid
$l + v$
$l + v$
P_C^*
Vapor
P_B^*
0
$x_{B,1}$
1

(a)


T
T_C^*
Vapor
$l + v$
$l + v$
T_B^*
Liquid
Boiling-point curve
0
x_B'
1

(b)

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 ℓ-*v* equilibrium, measuring *P* and capturing ~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 ℓ 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 γ_A and γ_B, data noise tends to be amplified; follow the fitting procedures and use your smooth fitted curves for this determination.