

Name: Solutions

**Problem 1:** The excess Gibbs energy for the system chloroform (1) / ethanol (2) at 55°C is described by the Margules equation:

$$\frac{G^E}{RT} = (1.42x_1 + 1.42x_2)x_1x_2$$

$\begin{matrix} A_{21} & A_{12} \\ \swarrow & \searrow \end{matrix}$

The vapor pressures of chloroform and ethanol at 55°C are:

$$P_1^{\text{sat}} = 82.37 \text{ kPa and } P_2^{\text{sat}} = 37.31 \text{ kPa.}$$

$$\begin{cases} A_{12} = A_{21} = 1.42 \\ x_1 = x_2 = 0.5 \end{cases} \Rightarrow \boxed{\gamma_1 = \gamma_2}$$

What is the bubble point pressure for an equimolar mixture of chloroform and ethanol? What is the composition of the first bubble that forms?

$$\gamma_1 = \exp[A_{12}x_1^2] = \exp[(1.42)(0.5)^2] = 1.4262$$

$$P_{\text{bubble}} = \sum x_i \gamma_i P_i^{\text{sat}} = x_1 \gamma_1 P_1^{\text{sat}} + x_2 \gamma_2 P_2^{\text{sat}} = x_1 \gamma_1 (P_1^{\text{sat}} + P_2^{\text{sat}})$$

$$P_{\text{bubble}} = (0.5)(1.4262)(82.37 + 37.31) = \boxed{85.344 \text{ kPa}}$$

This is impossible since it is not b/w  $P_1^{\text{sat}}$  and  $P_2^{\text{sat}}$

**Problem 2:** True / false  $y_1 = \frac{x_1 \gamma_1 P_1^{\text{sat}}}{P_{\text{bubble}}} = \frac{(0.5)(1.4262)(82.37)}{(85.344)} = \boxed{0.688}$

"A" values were poorly chosen.

(a) Non-ideal vapors in equilibrium with ideal solutions have negative deviations from Raoult's Law: True

(b) Thermodynamically, when liquids split (e.g., oil and water), these are still described as a single liquid phase: False

(c) Heats of solution are always exothermic: False

Useful equation:  $\ln \gamma_1 = Ax_2^2$