# Montogue

## QUIZ CE104
## Liquid–Liquid Equilibrium and Miscibility Gaps
### Lucas Montogue

## ▶▶ PROBLEMS

### ▶ Problem 1 (Dahm & Visco, 2015, w/ permission)

Given the 1-parameter Margules equation, plot the molar Gibbs free energy of mixing as a function of $x_1$ for three temperatures: 325 K, 300.7 K, and 250 K on the same plot. Determine if there is a miscibility gap at each of the three temperatures. For this study, let the product of the Margules parameter ($A$) and $RT$ be equal to 5000 J/mol.

### ▶ Problem 2 (Dahm & Visco, 2015, w/ permission)

You have liquid-liquid equilibrium data for several normal alkanes in water at 25°C provided in the table below. What would be a reasonable prediction for the amount of $n$-decane ($C_{10}H_{22}$) in the aqueous phase and the infinite dilution activity coefficient of $n$-decane in water at 25°C? In the following, the aqueous-rich phase is $\alpha$ and the organic rich phase is $\beta$.

| $n$-alkane | $x_{alkane}^{\alpha}$ | $x_{water}^{\beta}$ |
|---|---|---|
| Pentane | $1.10 \times 10^{-5}$ | $6.20 \times 10^{-4}$ |
| Hexane | $2.40 \times 10^{-6}$ | $6.10 \times 10^{-4}$ |
| Heptane | $5.30 \times 10^{-7}$ | $6.00 \times 10^{-4}$ |
| Octane | $1.0 \times 10^{-7}$ | $6.10 \times 10^{-4}$ |
| Nonane | $1.90 \times 10^{-8}$ | $6.20 \times 10^{-4}$ |

**A)** $x_{decane}^{\alpha} = 8.49 \times 10^{-10}$ and $(\gamma_1^{\alpha})_{decane} = 2.43 \times 10^{8}$

**B)** $x_{decane}^{\alpha} = 8.49 \times 10^{-10}$ and $(\gamma_1^{\alpha})_{decane} = 9.18 \times 10^{8}$

**C)** $x_{decane}^{\alpha} = 5.45 \times 10^{-9}$ and $(\gamma_1^{\alpha})_{decane} = 2.43 \times 10^{8}$

**D)** $x_{decane}^{\alpha} = 5.45 \times 10^{-9}$ and $(\gamma_1^{\alpha})_{decane} = 9.18 \times 10^{8}$

### ▶ Problem 3 (Dahm & Visco, 2015, w/ permission)

Consider the 1-butanol (1) + water (2) system. The parameters for this liquid mixture at 50°C using the 2-parameter Margules equation are $A_{12}$ = 2.61 and $A_{21}$ = 1.25. Determine whether this system will split into two phases and, if so, what will be the composition of each phase.

**α)** The system has a miscibility gap.

**β)** The system does not have a miscibility gap.

**γ)** There is not enough information.

### ▶ Problem 4 (Dahm & Visco, 2015, w/ permission)

Using the double-tangency method, determine if the following systems, as defined by their Margules equation parameter values, will exhibit a miscibility gap. If so, identify the composition of the coexisting phases.

| System 1 | System 2 | System 3 | System 4 |
|---|---|---|---|
| $A_{12}$ = 2.5 | $A_{12}$ = 1.2 | $A_{12}$ = 3.3 | $A_{12}$ = 2.0 |
| $A_{21}$ = 3.0 | $A_{21}$ = 3.0 | $A_{21}$ = 0.3 | $A_{21}$ = 1.4 |
| **α)** Has a MG. | **α)** Has a MG. | **α)** Has a MG. | **α)** Has a MG. |
| **β)** Does not have. | **β)** Does not have. | **β)** Does not have. | **β)** Does not have. |

## ► Problem 5

A mixture of water (1) and butanol (2) forms a miscibility gap at 92°C. What is the composition at the miscibility gap? The van Laar parameters for this system are $L_{12} = 1.27$ and $L_{21} = 3.98$.

**A)** $x_1^\alpha = 0.218$ and $x_1^\beta = 0.625$
**B)** $x_1^\alpha = 0.218$ and $x_1^\beta = 0.981$
**C)** $x_1^\alpha = 0.434$ and $x_1^\beta = 0.625$
**D)** $x_1^\alpha = 0.434$ and $x_1^\beta = 0.981$

## ► Problem 6

The infinite dilution activity coefficients for the 1-butanol (1) + $p$-xylene (2) mixture at 333.15 K are $\gamma_1^\infty = 7.2360$ and $\gamma_2^\infty = 4.9720$. Will the 2-parameter Margules equation predict a miscibility gap for this system at this temperature? If so, what is the composition?

**A)** $x_1^\alpha = 0.306$ and $x_1^\beta = 0.527$
**B)** $x_1^\alpha = 0.306$ and $x_1^\beta = 0.921$
**C)** $x_1^\alpha = 0.603$ and $x_1^\beta = 0.527$
**D)** $x_1^\alpha = 0.603$ and $x_1^\beta = 0.921$
**E)** There is no miscibility gap.

## ► Problem 7

The infinite dilution activity coefficients for the methanol (1) + $n$-heptane (2) mixture at 30°C are $\gamma_1^\infty = 84.20$ and $\gamma_2^\infty = 35.10$. You know that this system shows a miscibility gap at this temperature ($x_1^\alpha = 0.167$, $x_1^\beta = 0.884$). Will the 2-parameter Margules equation predict a miscibility gap for this system? If so, what is the composition of the equilibrium phases and how do they compare with the experimental data?

**A)** $x_1^\alpha = 0.0133$ and $x_1^\beta = 0.577$
**B)** $x_1^\alpha = 0.0133$ and $x_1^\beta = 0.966$
**C)** $x_1^\alpha = 0.165$ and $x_1^\beta = 0.577$
**D)** $x_1^\alpha = 0.165$ and $x_1^\beta = 0.966$
**E)** The Margules equation does not predict a miscibility gap.

## ► Problem 8

At 10°C, $n$-pentane (1) + water (2) shows a miscibility gap. The composition of the phases in equilibrium are as follows: $x_1^\alpha = 0.00107$ and $x_2^\beta = 0.0184$, where "$\alpha$" is for the water-rich phase and "$\beta$" is for the organic-rich phase. Estimate the pressure and composition where this system would show vapor-liquid-liquid equilibrium at this temperature.

**Note:** The coefficients $A$, $B$, and $C$ for $n$-pentane and water in the Antoine equation are listed below.

$$\log_{10} P^{\text{sat}} / \text{mmHg} = A - \frac{B}{T/^\circ\text{C} + C}$$

| Compound | $A$ | $B$ | $C$ |
|---|---|---|---|
| $n$-Pentane | 6.85296 | 1064.84 | 233.01 |
| Water | 8.01195 | 1698.785 | 231.04 |

## ► Problem 9

Estimate the pressure and composition for VLLE of a diethyl ether (1) + water (2) system at 35°C. Assume the liquid can be modeled by the 2-parameter Margules equation where $A_{12} = 4.62$ and $A_{21} = 3.35$. The vapor pressure of diethyl ether and water at the temperature of interest are 0.966 bar and 0.0577 bar, respectively.

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# ▶▶ SOLUTIONS

## P.1 ▶ *Solution*

The 1-parameter Margules equation is

$$\frac{\overline{G}^E}{RT} = Ax_1x_2$$

To determine the molar Gibbs free energy of mixing, we write

$$\frac{\Delta \overline{G}_{mix}}{RT} = \frac{\overline{G}^E}{RT} + x_1 \ln(x_1) + x_2 \ln(x_2)$$

$$\therefore \frac{\Delta \overline{G}_{mix}}{RT} = Ax_1x_2 + x_1 \ln(x_1) + x_2 \ln(x_2)$$

Multiplying through by $RT$ gives

$$\Delta \overline{G}_{mix} = ARTx_1x_2 + RTx_1 \ln(x_1) + RTx_2 \ln(x_2)$$

According to the problem statement, $ART = 5000$ J/mol. In addition, $R = 8.314$ J/mol·K and the first temperature value $T = 325$ K. The equation above then becomes

$$\Delta \overline{G}_{mix} = 5000x_1(1-x_1) + 8.314 \times 325x_1 \ln(x_1) + 8.314 \times 325(1-x_1)\ln(1-x_1)$$

$$\therefore \Delta \overline{G}_{mix} = 5000x_1(1-x_1) + 2700x_1 \ln(x_1) + 2700(1-x_1)\ln(1-x_1) \quad (I)$$

Proceeding similarly with a temperature $T = 300.7$ K gives

$$\Delta \overline{G}_{mix} = 5000x_1(1-x_1) + 8.314 \times 300.7x_1 \ln(x_1) + 8.314 \times 300.7(1-x_1)\ln(1-x_1)$$

$$\therefore \Delta \overline{G}_{mix} = 5000x_1(1-x_1) + 2500x_1 \ln(x_1) + 2500(1-x_1)\ln(1-x_1) \quad (II)$$

Finally, with $T = 250$ K, we get

$$\Delta \overline{G}_{mix} = 5000x_1(1-x_1) + 8.314 \times 250x_1 \ln(x_1) + 8.314 \times 250(1-x_1)\ln(1-x_1)$$

$$\therefore \Delta \overline{G}_{mix} = 5000x_1(1-x_1) + 2079x_1 \ln(x_1) + 2079(1-x_1)\ln(1-x_1) \quad (III)$$

We can now plot $\Delta \overline{G}_{mix}$ as a function of $x_1$ for the three temperature levels.
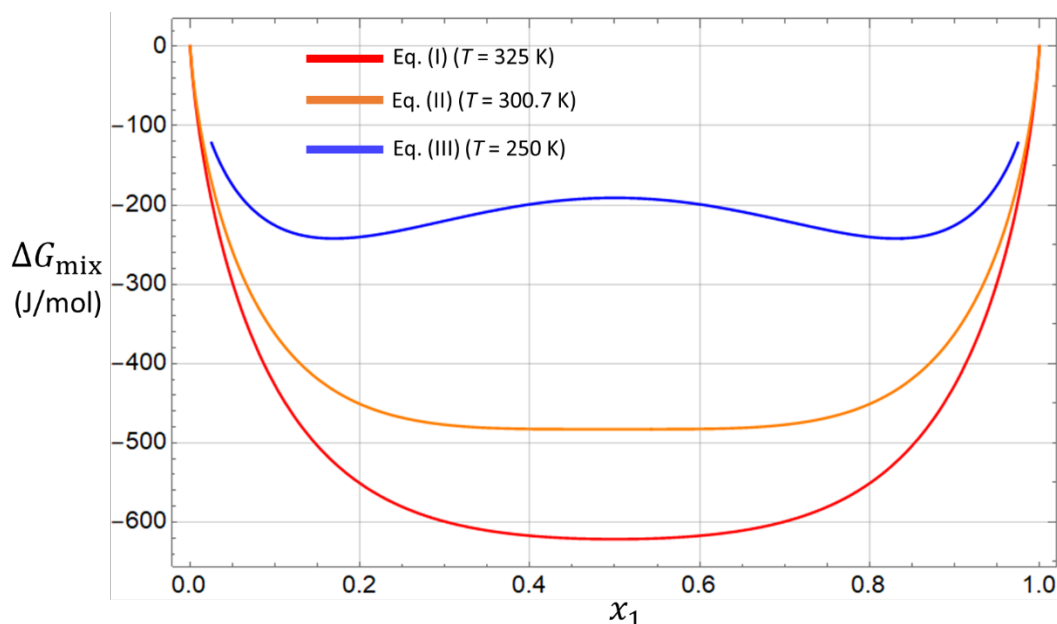


For $T = 250$ K, it is clear that a miscibility gap exists since there is a region where the curve is concave down. Likewise, the curve is always concave up at 325 K and hence no miscibility gap exists. The distinction is not clear for $T = 300.7$ K. However, we know a rule for the 1-parameter Margules equation: if $A < 2$ the mixture will be stable for all compositions. Given $A \times RT = 5000$ J/mol, we can calculate the $A$ values for the mixture at the three temperatures.

| $T$ (K) | $A$ |
|---------|-----|
| 250 | 5000/(8.314×250) = 2.41 |
| 300.7 | 2.0 |

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| 325 | 1.85 |
|---|---|

Thus, at 300.7 K the miscibility gap begins. Or, in other words, it is the point of the upper critical solution temperature (UCST). Note that we know it is the UCST because above that temperature (e.g., at 325 K) a single liquid phase exists.

## P.2 ➡ *Solution*

As suggested by Dahm and Visco, we denote the alkane as "1" and the water as "2." Since this system is virtually immiscible (as evidenced by the values of the mole fraction), it is reasonable to assume that the activity coefficient of water in the aqueous phase is 1.0 and that of the alkane in the organic phase is 1.0; i.e., $\gamma_2^{\alpha} = 1$, $\gamma_1^{\beta} = 1$. In view of these simplifications, the phase equilibrium relationships become

$$x_1^{\alpha}\gamma_1^{\alpha} = x_1^{\beta}\gamma_1^{\beta} \rightarrow x_1^{\alpha}\gamma_1^{\alpha} = x_1^{\beta}$$

$$\left(1 - x_1^{\alpha}\right)\gamma_2^{\alpha} = \left(1 - x_1^{\beta}\right)\gamma_2^{\beta} \rightarrow \left(1 - x_1^{\alpha}\right) = \left(1 - x_1^{\beta}\right)\gamma_2^{\beta}$$

Since we know all of the mole fractions, the two unknowns for these two equations are the activity coefficients of the dilute species in the concentrated species. For instance, consider pentane; in this case, $x_1^{\beta} = 1 - 6.20\times10^{-4}$ and $x_1^{\alpha} = 1.10\times10^{-5}$, so that

$$\gamma_1^{\alpha} = \frac{1 - 6.20\times10^{-4}}{1.10\times10^{-5}} = 90,900$$

Calculations for other composition values are summarized below.

| *n*-Alkane | No. of Carbons | 1 - $x_2^b$ | $x_1^a$ | $\gamma_1^a$ |
|---|---|---|---|---|
| Pentane | 5 | 0.99938 | 1.10E-05 | 9.09E+04 |
| Hexane | 6 | 0.99939 | 2.40E-06 | 4.16E+05 |
| Heptane | 7 | 0.99940 | 5.30E-07 | 1.89E+06 |
| Octane | 8 | 0.99939 | 1.00E-07 | 9.99E+06 |
| Nonane | 9 | 0.99938 | 1.90E-08 | 5.26E+07 |

Clearly, the solubility of the alkane in the aqueous phase decreases with increasing size of the alkane and the infinite dilution activity coefficient increases. A reasonable approach would be to plot the solubility of the alkane in the aqueous phase (the red column in the table above) as a function of carbon number (the blue column). Since the value of $\gamma_1^{\alpha}$ seems to be increasing dramatically as the carbon chain size increases, it seems reasonable to plot the solubility in a logarithmic scale. The plot in question is shown below.
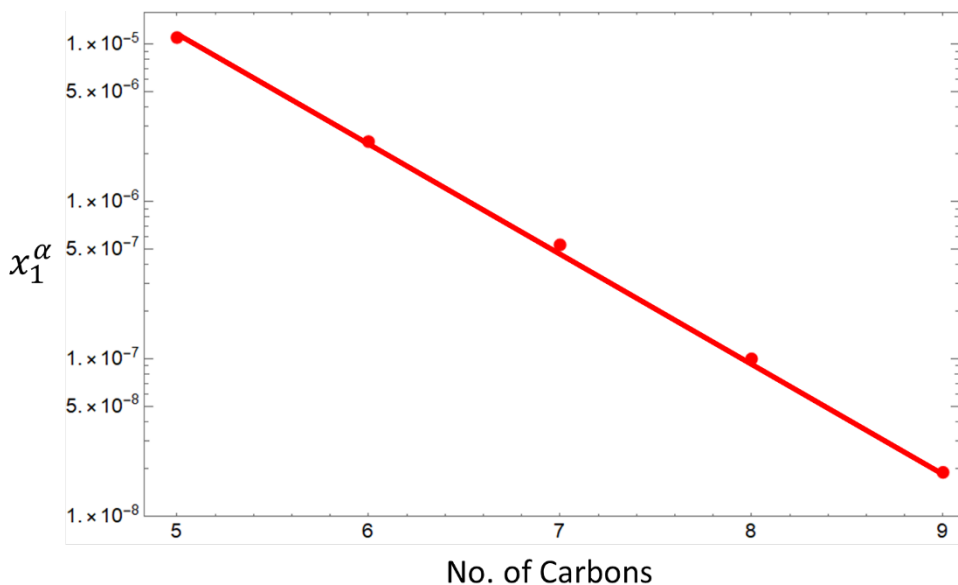


We can then fit the data to an exponential model by dint of Mathematica's *FindFit* function,

$$\text{FindFit}[\text{solub}, a * \text{Exp}[b * x], \{a, b\}, x]$$

This returns a fit of the form $0.0222\exp(-1.522\,x)$. Substituting $x = 10$ gives

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$$\left(x_1^{\alpha}\right)_{\text{decane}} = 0.0222 \times \exp\left(-1.522 \times 10\right) = \boxed{5.45 \times 10^{-9}}$$

This is an overestimation of the experimental result $x_1^{\alpha} = 3.3 \times 10^{-9}$. We can proceed similarly with the activity coefficient; the plot in question, this time, is one of $\gamma_1^{\alpha}$ (the yellow column in the foregoing table) versus the number of carbons (the blue column).
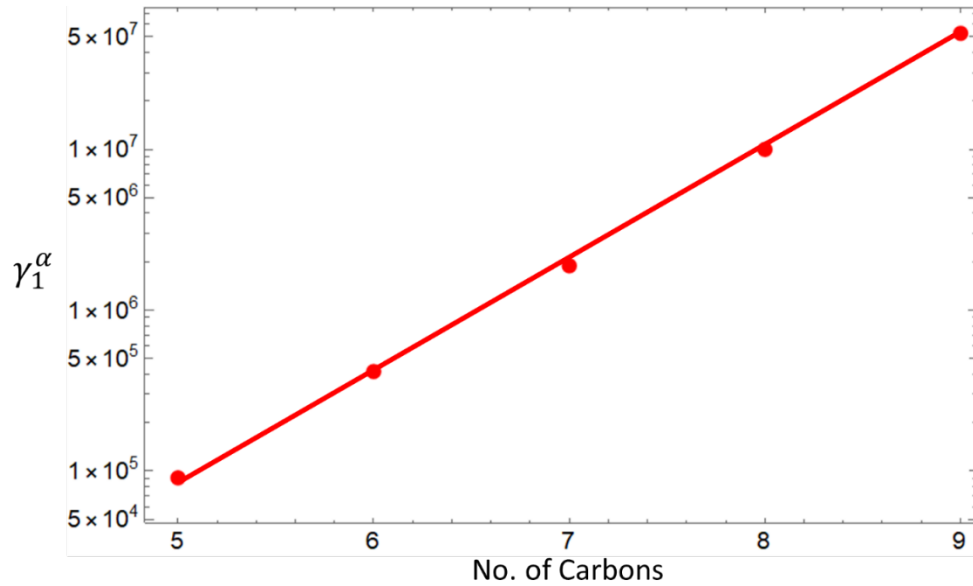


We apply the *FindFit* command a second time,

$$\text{FindFit}[\text{activity}, a * \text{Exp}[b * x], \{a, b\}, x]$$

This returns a fit of the form $16.964 \times \exp(1.661x)$. Substituting $x = 10$ yields

$$\left(\gamma_1^{\alpha}\right)_{\text{decane}} = 16.964 \exp\left(1.661 \times 10\right) = \boxed{2.43 \times 10^{8}}$$

The activity coefficient for $n$-decane has been established.

◆ The correct answer is **C**.

## P.3 ➡ *Solution*

The LLE equations are

$$x_1^{\alpha} \gamma_1^{\alpha} = x_1^{\beta} \gamma_1^{\beta}$$

$$\left(1 - x_1^{\alpha}\right)\gamma_2^{\alpha} = \left(1 - x_1^{\beta}\right)\gamma_2^{\beta}$$

We need activity coefficients to use these equations. The activity coefficients in the 2-parameter Margules equation are given by

$$\ln \gamma_1 = x_2^2 \left[ A_{12} + 2\left(A_{21} - A_{12}\right)x_1 \right]$$

$$\ln \gamma_2 = x_1^2 \left[ A_{21} + 2\left(A_{12} - A_{21}\right)x_2 \right]$$

We can then write

$$\ln \gamma_1^{\alpha} = \left(1 - x_1^{\alpha}\right)^2 \left[ 2.61 + 2\left(1.25 - 2.61\right)x_1^{\alpha} \right]$$

$$\therefore \ln \gamma_1^{\alpha} = \left(1 - x_1^{\alpha}\right)^2 \left(2.61 - 2.72 x_1^{\alpha}\right)$$

or, equivalently,

$$\gamma_1^{\alpha} = \exp\left[\left(1 - x_1^{\alpha}\right)^2 \left(2.61 - 2.72 x_1^{\alpha}\right)\right]$$

Likewise,

$$\ln \gamma_1^{\beta} = \left(1 - x_1^{\beta}\right)^2 \left[ 2.61 + 2\left(1.25 - 2.61\right)x_1^{\beta} \right]$$

$$\therefore \ln \gamma_1^{\beta} = \left(1 - x_1^{\beta}\right)^2 \left(2.61 - 2.72 x_1^{\beta}\right)$$

so that

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$$\gamma_1^\beta = \exp\left[\left(1-x_1^\beta\right)^2\left(2.61-2.72x_1^\beta\right)\right]$$

Proceeding similarly with $\gamma_2^\alpha$ and $\gamma_2^\beta$ gives, firstly,

$$\ln\gamma_2^\alpha = \left(x_1^\alpha\right)^2\left[1.25+2\left(2.61-1.25\right)\left(1-x_1^\alpha\right)\right]$$

$$\therefore \ln\gamma_2^\alpha = \left(x_1^\alpha\right)^2\left[1.25+2.72\left(1-x_1^\alpha\right)\right]$$

or, equivalently,

$$\gamma_2^\alpha = \exp\left\{\left(x_1^\alpha\right)^2\left[1.25+2.72\left(1-x_1^\alpha\right)\right]\right\}$$

The second result is

$$\ln\gamma_2^\beta = \left(x_1^\beta\right)^2\left[1.25+2\left(2.61-1.25\right)\left(1-x_1^\beta\right)\right]$$

$$\therefore \ln\gamma_2^\beta = \left(x_1^\beta\right)^2\left[1.25+2.72\left(1-x_1^\beta\right)\right]$$

so that

$$\gamma_2^\beta = \exp\left\{\left(x_1^\beta\right)^2\left[1.25+2.72\left(1-x_1^\beta\right)\right]\right\}$$

With the foregoing expressions for the activity coefficients, the LLE equations can be restated as

$$x_1^\alpha \exp\left[\left(1-x_1^\alpha\right)^2\left(2.61-2.72x_1^\alpha\right)\right] = x_1^\beta \exp\left[\left(1-x_1^\beta\right)^2\left(2.61-2.72x_1^\beta\right)\right]$$

$$\left(1-x_1^\alpha\right)\exp\left\{\left(x_1^\alpha\right)^2\left[1.25+2.72\left(1-x_1^\alpha\right)\right]\right\} = \left(1-x_1^\beta\right)\exp\left\{\left(x_1^\beta\right)^2\left[1.25+2.72\left(1-x_1^\beta\right)\right]\right\}$$

The two equations constitute a system of two nonlinear equations with two unknowns, $x_1^\alpha$ and $x_1^\beta$. One way to solve it is to apply Mathematica's *FindRoot* function,

```
FindRoot[{a * Exp[(1 − a)²(2.61 − 2.72a)] =
        = b * Exp[(1 − b)²(2.61 − 2.72b)], (1 − a) * Exp[a² * (1.25 + 2.72(1 − a))]
        == (1 − b) * Exp[b² * (1.25 + 2.72(1 − b))]}, {{a, 0.1}, {b, 1}}]
```

Note that we have used initial guesses such that $a \neq b$ in order to have the program return a solution different from the trivial result $x_1^\alpha = x_1^\beta$. Applying the code above, the solutions are found to be $x_1^\alpha = 0.119$ and $x_1^\beta = 0.601$. The fact that the program returned real composition (i.e., between 0 and 1) indicates the existence of a miscibility gap.

♦ The correct answer is **α.**

## P.4 ➡ *Solution*

**Part 1:** We are essentially looking for values of the independent variables $x_1^\alpha$ and $x_1^\beta$ where there is a double tangency in the curve of $\Delta\bar{G}/RT$ versus $x_1$. Since there are two unknowns, we need two equations. The first equation says that the value of the slope of $\Delta\bar{G}_{\text{mix}}/RT$ at both of these points needs to be the same (since they are on the same tangent line). In mathematical terms,

$$\left(\frac{\partial\left[\dfrac{\Delta\bar{G}_{\text{mix}}}{RT}\left(x_1^\alpha\right)\right]}{\partial x_1}\right)_{T,P} = \left(\frac{\partial\left[\dfrac{\Delta\bar{G}_{\text{mix}}}{RT}\left(x_1^\beta\right)\right]}{\partial x_1}\right)_{T,P} \quad \text{(I)}$$

Since any two points define a line, the second relationship is the equation for the tangent line defined by those two points. Mathematically,

$$\frac{\Delta\bar{G}_{\text{mix}}}{RT}\left(x_1^\alpha\right) - \frac{\Delta\bar{G}_{\text{mix}}}{RT}\left(x_1^\beta\right) = \left(\frac{\partial\left[\dfrac{\Delta\bar{G}_{\text{mix}}}{RT}\left(x_1^\alpha\right)\right]}{\partial x_1}\right)_{T,P}\left(x_1^\alpha - x_1^\beta\right) \quad \text{(II)}$$

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The equation for $\Delta\bar{G}_{\text{mix}}/RT$ is of course

$$\frac{\Delta\bar{G}_{\text{mix}}}{RT} = \frac{\bar{G}^E}{RT} + x_1 \ln(x_1) + x_2 \ln(x_2)$$

$$\therefore \frac{\Delta\bar{G}_{\text{mix}}}{RT} = x_1 x_2 \left(A_{21}x_1 + A_{12}x_2\right) + x_1 \ln(x_1) + x_2 \ln(x_2)$$

This can be restated as

$$\frac{\Delta\bar{G}_{\text{mix}}}{RT} = x_1(1-x_1)\times\left[A_{21}x_1 + A_{12}\times(1-x_1)\right] + x_1 \ln(x_1) + (1-x_1)\ln(1-x_1) \quad \text{(III)}$$

Deriving with respect to $x_1$, we obtain

$$\frac{\partial\left(\dfrac{\Delta\bar{G}_{\text{mix}}}{RT}(x_1)\right)}{\partial x_1} = \ln(x_1) - \ln(1-x_1) + A_{21}x_1(2-3x_1) + A_{12}\left(1-4x_1+3x_1^2\right)$$

Plugging this result into equation (I) yields

$$\ln(x_1^\alpha) - \ln(1-x_1^\alpha) + A_{21}x_1^\alpha(2-3x_1^\alpha) + A_{12}\left[1-4x_1^\alpha+3\left(x_1^\alpha\right)^2\right]$$

$$= \ln(x_1^\beta) - \ln(1-x_1^\beta) + A_{21}x_1^\beta(2-3x_1^\beta) + A_{12}\left[1-4x_1^\beta+3\left(x_1^\beta\right)^2\right]$$

so that, given $A_{12}$ = 2.5 and $A_{21}$ = 3.0,

$$\ln(x_1^\alpha) - \ln(1-x_1^\alpha) + 3.0x_1^\alpha(2-3x_1^\alpha) + 2.5\left[1-4x_1^\alpha+3\left(x_1^\alpha\right)^2\right]$$

$$= \ln(x_1^\beta) - \ln(1-x_1^\beta) + 3.0x_1^\beta(2-3x_1^\beta) + 2.5\left[1-4x_1^\beta+3\left(x_1^\beta\right)^2\right] \quad \text{(IV)}$$

In turn, we substitute into equation (II) to obtain

$$\frac{\Delta\bar{G}_{\text{mix}}}{RT}(x_1^\alpha) - \frac{\Delta\bar{G}_{\text{mix}}}{RT}(x_1^\beta) =$$

$$\left\{\ln(x_1^\alpha) - \ln(1-x_1^\alpha) + A_{21}x_1^\alpha(2-3x_1^\alpha) + A_{12}\left[1-4x_1^\alpha+3\left(x_1^\alpha\right)^2\right]\right\}(x_1^\alpha - x_1^\beta)$$

$$\therefore \frac{\Delta\bar{G}_{\text{mix}}}{RT}(x_1^\alpha) - \frac{\Delta\bar{G}_{\text{mix}}}{RT}(x_1^\beta) =$$

$$\left\{\ln(x_1^\alpha) - \ln(1-x_1^\alpha) + 3.0x_1^\alpha(2-3x_1^\alpha) + 2.5\left[1-4x_1^\alpha+3\left(x_1^\alpha\right)^2\right]\right\}(x_1^\alpha - x_1^\beta) \quad \text{(V)}$$

Note that $\Delta\bar{G}_{\text{mix}}/RT$ is given by equation (III). Equations (IV) and (V) constitute a system of two nonlinear equations with two unknowns. One way to solve it is via Mathematica's *FindRoot* function; letting $x_1^\alpha = a$ and $x_1^\beta = b$, we can apply the following code.

```
FindRoot[{Log[a] - Log[1 - a] + 3 * a * (2 - 3 a) + 2.5 (1 - 4 * a + 3 * a²) == Log[b] - Log[1 - b] + 3 * b * (2 - 3 b) + 2.5 (1 - 4 * b + 3 * b²),
    delGa - delGb == (Log[a] - Log[1 - a] + 3 * a * (2 - 3 a) + 2.5 (1 - 4 * a + 3 * a²)) * (a - b)}, {{a, 0.1}, {b, 0.8}}]
```

The initial guesses $x_1^\alpha$ = 0.1 and $x_1^\beta$ = 0.8 are arbitrary. The code above returns $x_1^\alpha$ = 0.127 and $x_1^\beta$ = 0.927. Since these are valid composition values (i.e., between zero and 1), we conclude that the system does exhibit a miscibility gap.

♦ The correct answer is **α.**

**Part 2:** With $A_{12}$ = 1.2 and $A_{21}$ = 3.0, equation (III) becomes

$$\frac{\Delta\bar{G}_{\text{mix}}}{RT} = x_1(1-x_1)\times\left[3.0x_1 + 1.2(1-x_1)\right] + x_1 \ln(x_1) + (1-x_1)\ln(1-x_1) \quad \text{(VI)}$$

while equation (IV) becomes

$$\ln(x_1^\alpha) - \ln(1-x_1^\alpha) + 3.0x_1^\alpha(2-3x_1^\alpha) + 1.2\left[1-4x_1^\alpha+3\left(x_1^\alpha\right)^2\right]$$

$$= \ln(x_1^\beta) - \ln(1-x_1^\beta) + 3.0x_1^\beta(2-3x_1^\beta) + 1.2\left[1-4x_1^\beta+3\left(x_1^\beta\right)^2\right] \quad \text{(VII)}$$

Lastly, equation (V) becomes

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$$\therefore \frac{\Delta \bar{G}_{\text{mix}}}{RT}\left(x_1^\alpha\right) - \frac{\Delta \bar{G}_{\text{mix}}}{RT}\left(x_1^\beta\right) =$$

$$\left\{\ln\left(x_1^\alpha\right) - \ln\left(1 - x_1^\alpha\right) + 3.0x_1^\alpha\left(2 - 3x_1^\alpha\right) + 1.2\left[1 - 4x_1^\alpha + 3\left(x_1^\alpha\right)^2\right]\right\}\left(x_1^\alpha - x_1^\beta\right) \text{ (VIII)}$$

Equations (VII) and (VIII) can be solved simultaneously with the following Mathematica code.

```
FindRoot[{Log[a] - Log[1-a] + 3*a*(2-3a) + 1.2 (1-4*a+3*a²) == Log[b] - Log[1-b] + 3*b*(2-3b) + 1.2 (1-4*b+3*b²),
    delGa - delGb == (Log[a] - Log[1-a] + 3*a*(2-3a) + 1.2 (1-4*a+3*a²)) * (a-b)}, {{a, 0.15}, {b, 0.9}}]
```

This returns $x_1^\alpha = 0.323$ and $x_1^\beta = 0.937$. Since these are valid composition values, we surmise that the system does present a miscibility gap.

♦ The correct answer is **α**.

**Part 3:** Given $A_{12} = 3.3$ and $A_{21} = 0.3$, equation (III) becomes

$$\frac{\Delta \bar{G}_{\text{mix}}}{RT} = x_1\left(1 - x_1\right) \times \left[0.3x_1 + 3.3\left(1 - x_1\right)\right] + x_1 \ln\left(x_1\right) + \left(1 - x_1\right)\ln\left(1 - x_1\right) \text{ (IX)}$$

Equation (IV), in turn, becomes

$$\ln\left(x_1^\alpha\right) - \ln\left(1 - x_1^\alpha\right) + 0.3x_1^\alpha\left(2 - 3x_1^\alpha\right) + 3.3\left[1 - 4x_1^\alpha + 3\left(x_1^\alpha\right)^2\right]$$

$$= \ln\left(x_1^\beta\right) - \ln\left(1 - x_1^\beta\right) + 0.3x_1^\beta\left(2 - 3x_1^\beta\right) + 3.3\left[1 - 4x_1^\beta + 3\left(x_1^\beta\right)^2\right] \text{ (X)}$$

Lastly, equation (V) is rewritten as

$$\therefore \frac{\Delta \bar{G}_{\text{mix}}}{RT}\left(x_1^\alpha\right) - \frac{\Delta \bar{G}_{\text{mix}}}{RT}\left(x_1^\beta\right) =$$

$$\left\{\ln\left(x_1^\alpha\right) - \ln\left(1 - x_1^\alpha\right) + 0.3x_1^\alpha\left(2 - 3x_1^\alpha\right) + 3.3\left[1 - 4x_1^\alpha + 3\left(x_1^\alpha\right)^2\right]\right\}\left(x_1^\alpha - x_1^\beta\right) \text{ (XI)}$$

Equations (X) and (XI) can be solved simultaneously with the following Mathematica code.

```
FindRoot[{Log[a] - Log[1-a] + 0.3*a*(2-3a) + 3.3 (1-4*a+3*a²) == Log[b] - Log[1-b] + 0.3*b*(2-3b) + 3.3 (1-4*b+3*b²),
    delGa - delGb == (Log[a] - Log[1-a] + 0.3*a*(2-3a) + 3.3 (1-4*a+3*a²)) * (a-b)}, {{a, 0.1}, {b, 0.8}}]
```

This returns $x_1^\alpha = 0.0331$ and $x_1^\beta = 0.646$. Recognizing that these are valid composition values, we surmise that the system does exhibit a miscibility gap.

♦ The correct answer is **α**.

**Part 4:** Given $A_{12} = 2.0$ and $A_{21} = 1.4$, equation (III) becomes

$$\frac{\Delta \bar{G}_{\text{mix}}}{RT} = x_1\left(1 - x_1\right) \times \left[1.4x_1 + 2.0\left(1 - x_1\right)\right] + x_1 \ln\left(x_1\right) + \left(1 - x_1\right)\ln\left(1 - x_1\right) \text{ (XII)}$$

Equation (IV), in turn, becomes

$$\ln\left(x_1^\alpha\right) - \ln\left(1 - x_1^\alpha\right) + 1.4x_1^\alpha\left(2 - 3x_1^\alpha\right) + 2.0\left[1 - 4x_1^\alpha + 3\left(x_1^\alpha\right)^2\right]$$

$$= \ln\left(x_1^\beta\right) - \ln\left(1 - x_1^\beta\right) + 1.4x_1^\beta\left(2 - 3x_1^\beta\right) + 2.0\left[1 - 4x_1^\beta + 3\left(x_1^\beta\right)^2\right] \text{ (XIII)}$$

Finally, equation (V) is rewritten as

$$\therefore \frac{\Delta \bar{G}_{\text{mix}}}{RT}\left(x_1^\alpha\right) - \frac{\Delta \bar{G}_{\text{mix}}}{RT}\left(x_1^\beta\right) =$$

$$\left\{\ln\left(x_1^\alpha\right) - \ln\left(1 - x_1^\alpha\right) + 1.4x_1^\alpha\left(2 - 3x_1^\alpha\right) + 2.0\left[1 - 4x_1^\alpha + 3\left(x_1^\alpha\right)^2\right]\right\}\left(x_1^\alpha - x_1^\beta\right) \text{ (XIV)}$$

Equations (XIII) and (XIV) can be solved simultaneously with the following Mathematica code.

```
FindRoot[{Log[a] - Log[1-a] + 1.4*a*(2-3a) + 2.0 (1-4*a+3*a²) == Log[b] - Log[1-b] + 1.4*b*(2-3b) + 2.0 (1-4*b+3*b²),
    delGa - delGb == (Log[a] - Log[1-a] + 1.4*a*(2-3a) + 2.0 (1-4*a+3*a²)) * (a-b)}, {{a, 0.1}, {b, 0.8}}]
```

The code above returns the trivial solution $a = b$. Changing the initial guess does not change this behavior. Thus, we surmise that this system does not exhibit a miscibility gap.

♦ The correct answer is **β**.

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## P.5 ➡ *Solution*

As usual, we begin with the two governing equations for LLE,

$$x_1^\alpha \gamma_1^\alpha = x_1^\beta \gamma_1^\beta$$

$$\left(1 - x_1^\alpha\right)\gamma_2^\alpha = \left(1 - x_1^\beta\right)\gamma_2^\beta$$

The activity coefficients, expressed in terms of the van Laar parameters, are

$$\ln \gamma_1 = L_{12}\left(1 + \frac{L_{12}x_1}{L_{21}x_2}\right)^{-2}$$

$$\ln \gamma_2 = L_{21}\left(1 + \frac{L_{21}x_2}{L_{12}x_1}\right)^{-2}$$

Accordingly,

$$\ln \gamma_1 = 1.27 \times \left(1 + \frac{1.27x_1}{3.98x_2}\right)^{-2} = 1.27 \times \left(1 + 0.319\frac{x_1}{x_2}\right)^{-2}$$

$$\ln \gamma_2 = 3.98 \times \left(1 + \frac{3.98x_2}{1.27x_1}\right)^{-2} = 3.98 \times \left(1 + 3.13\frac{x_2}{x_1}\right)^{-2}$$

or, equivalently,

$$\gamma_1 = \exp\left\{1.27\left[1 + 0.319\frac{x_1}{\left(1 - x_1\right)}\right]^{-2}\right\}$$

$$\gamma_2 = \exp\left\{3.98\left[1 + 3.13\frac{\left(1 - x_1\right)}{x_1}\right]^{-2}\right\}$$

Substituting in the initial equations, we have

$$x_1^\alpha \exp\left\{1.27\left[1 + 0.319\frac{x_1^\alpha}{\left(1 - x_1^\alpha\right)}\right]^{-2}\right\} = x_1^\beta \exp\left\{1.27\left[1 + 0.319\frac{x_1^\beta}{\left(1 - x_1^\beta\right)}\right]^{-2}\right\}$$

$$\left(1 - x_1^\alpha\right)\exp\left\{3.98\left[1 + 3.13\frac{\left(1 - x_1^\alpha\right)}{x_1^\alpha}\right]^{-2}\right\} = \left(1 - x_1^\beta\right)\exp\left\{3.98\left[1 + 3.13\frac{\left(1 - x_1^\beta\right)}{x_1^\beta}\right]^{-2}\right\}$$

Mathematica's *FindRoot* function can be used to establish the solutions to the system of nonlinear equations above. Needless to say, the user must provide a good initial guess at the values of $x_1^\alpha$ and $x_1^\beta$, otherwise the program will return the trivial solution $x_1^\alpha = x_1^\beta$. One way to obtain good initial guesses is to plot $\Delta \bar{G}_{\text{mix}}/RT$ versus $x_1$ and check for concavity and points of tangency. In the case at hand, $\Delta \bar{G}_{\text{mix}}/RT$ is given by

$$\frac{\Delta \bar{G}_{\text{mix}}}{RT} = x_1 x_2 \frac{L_{12}L_{21}}{L_{12}x_1 + L_{21}x_2} + x_1 \ln\left(x_1\right) + x_2 \ln\left(x_2\right)$$

$$\therefore \frac{\Delta \bar{G}_{\text{mix}}}{RT} = x_1\left(1 - x_1\right)\frac{1.27 \times 3.98}{1.27x_1 + 3.98\left(1 - x_1\right)} + x_1 \ln\left(x_1\right) + \left(1 - x_1\right)\ln\left(1 - x_1\right)$$

$$\therefore \frac{\Delta \bar{G}_{\text{mix}}}{RT} = x_1\left(1 - x_1\right)\frac{5.05}{3.98 - 2.71x_1} + x_1 \ln\left(x_1\right) + \left(1 - x_1\right)\ln\left(1 - x_1\right)$$

The plot is shown below.

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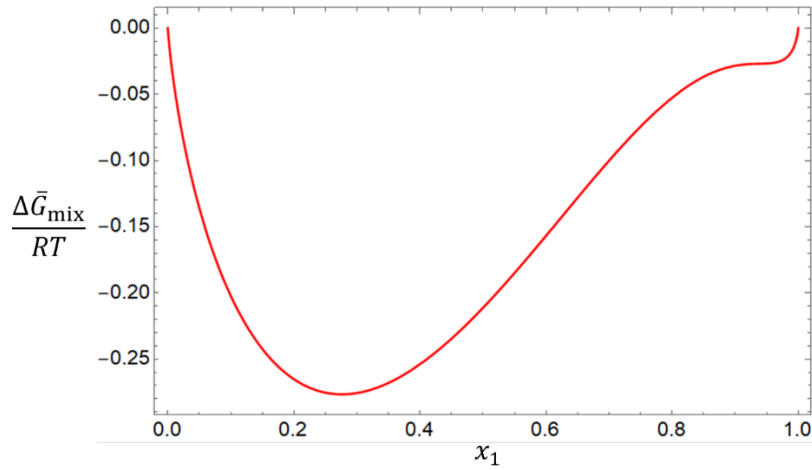
Clearly, the plot has a double tangency. From the shape of the graph, we can suggest compositions $x_1^\alpha = 0.3$ and $x_1^\beta = 0.95$. Accordingly, we enter the LLE equations and apply Mathematica's *FindRoot* command,

```
FindRoot[{a * Exp[1.27 (1 + (0.319 a)/(1 - a))^-2] == b * Exp[1.27 (1 + (0.319 * b)/(1 - b))^-2],
(1 - a) * Exp[3.98 * (1 + (3.13 * (1 - a))/a)^-2] == (1 - b) * Exp[3.98 * (1 + (3.13 (1 - b))/b)^-2]}, {{a, 0.3}, {b, 0.95}}]
```

This code returns $a = x_1^\alpha = 0.434$ and $b = x_1^\beta = 0.981$. The composition of the miscibility gap has been determined.

♦ The correct answer is **D**.

## P.6 ➡ *Solution*

Equipped with the infinite dilution activity coefficients, we can easily determine the $A$ parameters in the 2-parameter Margules equation,

$$\ln \gamma_1^\infty = A_{12} \to A_{12} = \ln(7.2360)$$
$$\therefore A_{12} = 1.98$$
$$\ln \gamma_2^\infty = A_{21} \to A_{21} = \ln(4.9720)$$
$$\therefore A_{21} = 1.60$$

In view of the Margules equation, we write

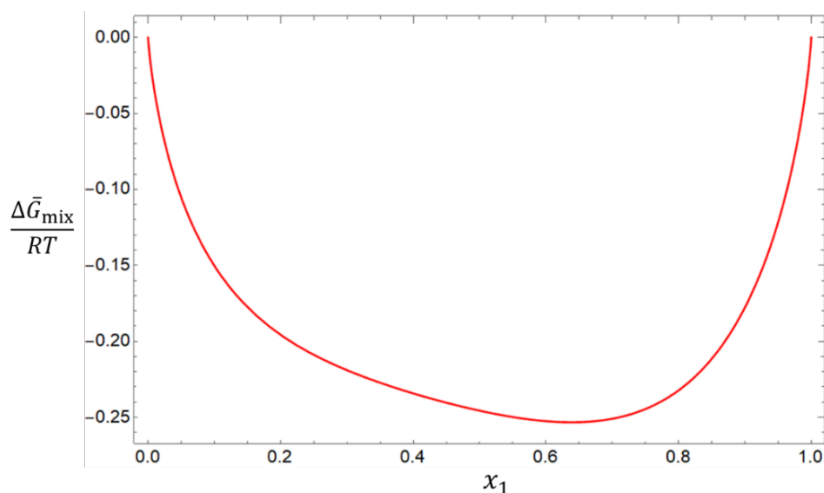$$\frac{\overline{G}^E}{RT} = x_1 x_2 \left(A_{21}x_1 + A_{12}x_2\right)$$

so that

$$\frac{\Delta \overline{G}_{\text{mix}}}{RT} = \frac{\overline{G}^E}{RT} + x_1 \ln(x_1) + x_2 \ln(x_2)$$

$$\therefore \frac{\Delta \overline{G}_{\text{mix}}}{RT} = x_1 x_2 \left(A_{21}x_1 + A_{12}x_2\right) + x_1 \ln(x_1) + x_2 \ln(x_2)$$

Noting that $x_2 = 1 - x_1$ and substituting numerical values, we have

$$\frac{\Delta \overline{G}_{\text{mix}}}{RT} = x_1(1 - x_1)\left[1.60x_1 + 1.98(1 - x_1)\right] + x_1 \ln(x_1) + (1 - x_1)\ln(1 - x_1)$$

A graph of $\Delta \overline{G}_{\text{mix}}/RT$ versus $x_1$ will reveal if a miscibility gap exists. The plot in question is shown below.



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Clearly, this function is always concave up, and hence we conclude that there is no miscibility gap for this system.

♦ The correct answer is **E**.

## P.7 ➡ Solution

Given the infinite dilution activity coefficients, we can easily establish the $A$ parameters in the 2-parameter Margules equation,

$$\ln \gamma_1^\infty = A_{12} \to A_{12} = \ln(84.20)$$
$$\therefore A_{12} = 4.43$$

$$\ln \gamma_2^\infty = A_{21} \to A_{21} = \ln(35.10)$$
$$\therefore A_{21} = 3.56$$

Recalling that, from the 2-parameter Margules equation,

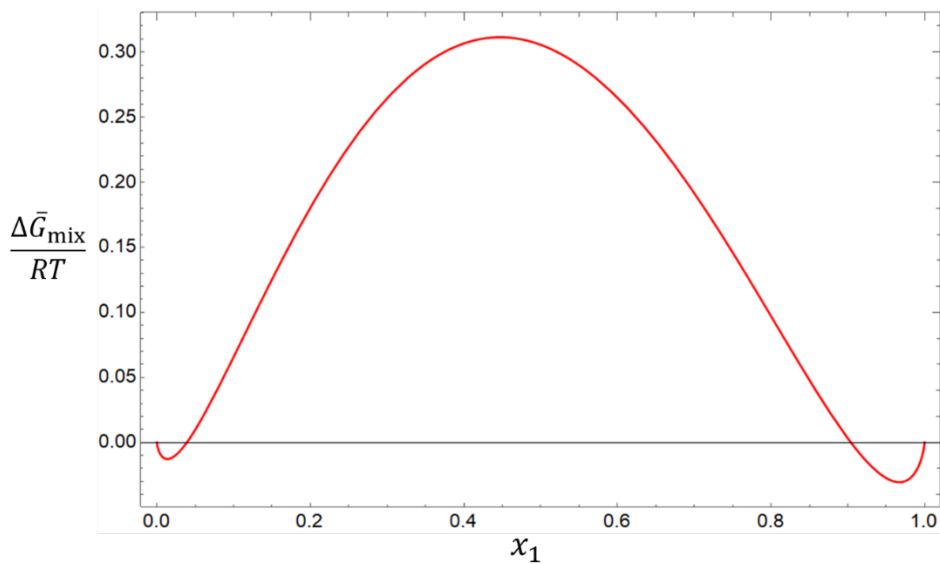$$\frac{\bar{G}^E}{RT} = x_1 x_2 \left( A_{21} x_1 + A_{12} x_2 \right)$$

it follows that

$$\frac{\Delta\bar{G}_{\text{mix}}}{RT} = \frac{\bar{G}^E}{RT} + x_1 \ln(x_1) + x_2 \ln(x_2)$$

$$\therefore \frac{\Delta\bar{G}_{\text{mix}}}{RT} = x_1 x_2 \left( A_{21} x_1 + A_{12} x_2 \right) + x_1 \ln(x_1) + x_2 \ln(x_2)$$

Noting that $x_2 = 1 - x_1$ and substituting numerical values, we have

$$\frac{\Delta\bar{G}_{\text{mix}}}{RT} = x_1 (1 - x_1) \left[ 3.56 x_1 + 4.43(1 - x_1) \right] + x_1 \ln(x_1) + (1 - x_1) \ln(1 - x_1)$$

A plot of $\Delta\bar{G}_{\text{mix}}/RT$ versus $x_1$ will reveal if a miscibility gap exists. The graph is shown in continuation.



As can be seen, the function has a double tangency. To establish the composition of the system, we must solve the phase equilibrium problem

$$x_1^\alpha \gamma_1^\alpha = x_1^\beta \gamma_1^\beta$$

$$\left(1 - x_1^\alpha\right) \gamma_2^\alpha = \left(1 - x_1^\beta\right) \gamma_2^\beta$$

The activity coefficients can be expressed as

$$\ln \gamma_1 = x_2^2 \left[ A_{12} + 2\left( A_{21} - A_{12} \right) x_1 \right]$$

$$\ln \gamma_2 = x_1^2 \left[ A_{21} + 2\left( A_{12} - A_{21} \right) x_2 \right]$$

so that, given the $A$ parameters, we have

$$\ln \gamma_1 = \left(1 - x_1\right)^2 \left[ 4.43 + 2 \times (3.56 - 4.43) x_1 \right] = \left(1 - x_1\right)^2 \left( 4.43 - 1.74 x_1 \right)$$

$$\ln \gamma_2 = x_1^2 \left[ 3.56 + 2 \times (4.43 - 3.56)(1 - x_1) \right] = x_1^2 \left[ 3.56 + 1.74(1 - x_1) \right]$$

Accordingly,

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$$\gamma_1 = \exp\left[\left(1-x_1\right)^2\left(4.43-1.74x_1\right)\right]$$

$$\gamma_2 = \exp\left\{x_1^2\left[3.56+1.74\left(1-x_1\right)\right]\right\}$$

Substituting in the LLE equations gives

$$x_1^\alpha \exp\left[\left(1-x_1^\alpha\right)^2\left(4.43-1.74x_1^\alpha\right)\right] = x_1^\beta \exp\left[\left(1-x_1^\beta\right)^2\left(4.43-1.74x_1^\beta\right)\right]$$

$$\left(1-x_1^\alpha\right)\exp\left\{\left(x_1^\alpha\right)^2\left[3.56+1.74\left(1-x_1^\alpha\right)\right]\right\} = \left(1-x_1^\beta\right)\exp\left\{\left(x_1^\beta\right)^2\left[3.56+1.74\left(1-x_1^\beta\right)\right]\right\}$$

Solving the equation above, we get $x_1^\alpha = 0.0133$ and $x_1^\beta = 0.966$. Note that using infinite dilution coefficient values to parametrize the model, while predicting a miscibility gap, identifies a larger gap than what is seen experimentally. This has mainly to do with using the infinite dilution values to parametrize the model.

♦ The correct answer is **B**.

## P.8 ➡ *Solution*

The equations that model VLLE are

$$x_1^{L1}\gamma_1^{L1} = x_1^{L2}\gamma_1^{L2} \quad \text{(I)}$$

$$\left(1-x_1^{L1}\right)\gamma_2^{L1} = \left(1-x_1^{L2}\right)\gamma_2^{L2} \quad \text{(II)}$$

$$x_1^{L1}\gamma_1^{L1}P_1^{\text{sat}} = y_1 P \quad \text{(III)}$$

$$\left(1-x_1^{L2}\right)\gamma_2^{L2}P_2^{\text{sat}} = \left(1-y_1\right)P \quad \text{(IV)}$$

Here, let "$\alpha$" be L1 and "$\beta$" be L2. The system has a very large miscibility gap, so we can use the compositions to help estimate the infinite dilution coefficients and then establish the parameters for a 2-parameter Margules equation. Indeed, if we assume that the activity coefficient of $n$-pentane in the organic phase is 1 and that of water in the aqueous phase is 1, equations (I) and (II) simplify to

$$x_1^{L1}\gamma_1^{L1} = x_1^{L2}\gamma_1^{L2} \to x_1^\alpha \gamma_1^\alpha = x_1^\beta \quad \text{(V)}$$

and

$$\left(1-x_1^{L1}\right)\gamma_2^{L1} = \left(1-x_1^{L2}\right)\gamma_2^{L2} \to \left(1-x_1^\alpha\right) = \left(1-x_1^\beta\right)\gamma_2^\beta \quad \text{(VI)}$$

Since we know that $x_1^\alpha = 0.00107$ and $x_2^\beta = 0.0184$, we can easily compute the activity coefficients,

$$x_1^\alpha \gamma_1^\alpha = x_1^\beta \to \gamma_1^\alpha = \frac{x_1^\beta}{x_1^\alpha}$$

$$\therefore \gamma_1^\alpha = \frac{1-0.000184}{0.0000107} = 93,440$$

$$1-x_1^\alpha = \left(1-x_1^\beta\right)\gamma_2^\beta \to \gamma_2^\beta = \frac{1-x_1^\alpha}{1-x_1^\beta}$$

$$\therefore \gamma_2^\beta = \frac{1-0.0000107}{0.000184} = 5434$$

Equipped with these quantities, the Margules equation parameters follow as

$$\ln \gamma_1^\infty = A_{12} = \ln\left(93,440\right) = 11.45$$

$$\ln \gamma_2^\infty = A_{21} = \ln\left(5434\right) = 8.60$$

so that, appealing to the activity coefficient expressions, we have

$$\ln \gamma_1 = x_2^2\left[A_{12}+2\left(A_{21}-A_{12}\right)x_1\right]$$

$$\therefore \ln \gamma_1 = \left(1-x_1\right)^2\left[11.45+2\left(8.60-11.45\right)x_1\right]$$

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$$\therefore \ln \gamma_1 = \left(1 - x_1\right)^2 \left(11.45 - 5.7x_1\right)$$

$$\therefore \gamma_1 = \exp\left[\left(1 - x_1\right)^2 \left(11.45 - 5.7x_1\right)\right]$$

and

$$\ln \gamma_2 = x_1^2 \left[A_{21} + 2\left(A_{12} - A_{21}\right)x_2\right]$$

$$\therefore \ln \gamma_2 = x_1^2 \left[8.60 + 2\left(11.45 - 8.60\right)\left(1 - x_1\right)\right]$$

$$\therefore \ln \gamma_2 = x_1^2 \left[8.60 + 5.7\left(1 - x_1\right)\right]$$

$$\therefore \gamma_2 = \exp\left\{x_1^2 \left[8.60 + 5.7\left(1 - x_1\right)\right]\right\}$$

Substituting these results into equation (V) brings to

$$x_1^\alpha \gamma_1^\alpha = x_1^\beta$$

$$\therefore x_1^\alpha \exp\left[\left(1 - x_1^\alpha\right)^2 \left(11.45 - 5.7x_1^\alpha\right)\right] = x_1^\beta \quad \text{(VII)}$$

Likewise, we substitute into equation (VI) to obtain

$$\left(1 - x_1^\alpha\right) = \left(1 - x_1^\beta\right)\gamma_2^\beta$$

$$\therefore \left(1 - x_1^\alpha\right) = \left(1 - x_1^\beta\right)\exp\left\{\left(x_1^\beta\right)^2 \left[8.60 + 5.7\left(1 - x_1^\beta\right)\right]\right\} \quad \text{(VIII)}$$

Next, we substitute into equation (III),

$$x_1^\alpha \gamma_1^\alpha P_1^{\text{sat}} = y_1 P$$

$$\therefore x_1^\alpha \exp\left[\left(1 - x_1^\alpha\right)^2 \left(11.45 - 5.7x_1^\alpha\right)\right] P_1^{\text{sat}} = y_1 P$$

The vapor pressure of $n$-pentane at the temperature of interest is

$$\log_{10} P^{\text{sat}} = 6.85296 - \frac{1064.84}{10 + 233.01} \rightarrow P^{\text{sat}} = 295.9 \text{ mmHg}$$

$$\therefore P_1^{\text{sat}} = 0.395 \text{ bar}$$

so that

$$x_1^\alpha \exp\left[\left(1 - x_1^\alpha\right)^2 \left(11.45 - 5.7x_1^\alpha\right)\right] \times 0.395 = y_1 P \quad \text{(IX)}$$

Lastly, we substitute into equation (IV) to find

$$\left(1 - x_1^\beta\right)\gamma_2^\beta P_2^{\text{sat}} = \left(1 - y_1\right)P$$

$$\therefore \left(1 - x_1^\beta\right)\exp\left\{\left(x_1^\beta\right)^2 \left[8.60 + 5.7\left(1 - x_1^\beta\right)\right]\right\} P_2^{\text{sat}} = \left(1 - y_1\right)P$$

The vapor pressure of water at the temperature of interest is

$$\log_{10} P^{\text{sat}} = 8.01195 - \frac{1698.785}{10 + 231.04} \rightarrow P^{\text{sat}} = 9.21 \text{ mmHg}$$

$$\therefore P_2^{\text{sat}} = 0.0123 \text{ bar}$$

so that

$$\left(1 - x_1^\beta\right)\exp\left\{\left(x_1^\beta\right)^2 \left[8.60 + 5.7\left(1 - x_1^\beta\right)\right]\right\} \times 0.0123 = \left(1 - y_1\right)P \quad \text{(X)}$$

Equations (VII), (VIII), (IX) and (X) constitute a system of four nonlinear equations with four unknowns, namely $x_1^\alpha$, $x_1^\beta$, $y_1$, and $P$. The equations are repeated below for convenience.

$$\begin{cases} x_1^{\alpha} \exp\left[(1-x_1^{\alpha})^2 (11.45-5.7x_1^{\alpha})\right] = x_1^{\beta} \\ (1-x_1^{\alpha}) = (1-x_1^{\beta})\exp\left\{(x_1^{\beta})^2\left[8.60+5.7(1-x_1^{\beta})\right]\right\} \\ x_1^{\alpha} \exp\left[(1-x_1^{\alpha})^2 (11.45-5.7x_1^{\alpha})\right] \times 0.395 = y_1 P \\ (1-x_1^{\beta})\exp\left\{(x_1^{\beta})^2\left[8.60+5.7(1-x_1^{\beta})\right]\right\} \times 0.0123 = (1-y_1) P \end{cases}$$

The equations can be solved with the lengthy Mathematica code

```
FindRoot[{a * Exp[(1 - a)^2 * (11.45 - 5.7 * a)] == b, (1 - a) == (1 - b) * Exp[b^2 * (8.60 + 5.7 (1 - b))],
  a * Exp[(1 - a)^2 * (11.45 - 5.7 * a)] * 0.395 == y * P, (1 - b) * Exp[b^2 * (8.60 + 5.7 (1 - b))] * 0.0123 == (1 - y) * P},
  {{a, 0.001}, {b, 0.99}, {P, 0.5}, {y, 0.95}}]
```

This returns $a = x_1^{L1} = 0.0000107$, $b = x_1^{L2} = 0.999816$, $P = 0.407$ bar, and $y = y_1 = 0.9698$. The pressure and composition of the vapor-liquid-liquid equilibrium in question have been determined.

## P.9 ➡ *Solution*

The equations that model VLLE, as was the case in Problem 8, are listed below.

$$x_1^{L1}\gamma_1^{L1} = x_1^{L2}\gamma_1^{L2} \quad \text{(I)}$$

$$(1-x_1^{L1})\gamma_2^{L1} = (1-x_1^{L2})\gamma_2^{L2} \quad \text{(II)}$$

$$x_1^{L1}\gamma_1^{L1}P_1^{\text{sat}} = y_1 P \quad \text{(III)}$$

$$(1-x_1^{L2})\gamma_2^{L2}P_2^{\text{sat}} = (1-y_1)P \quad \text{(IV)}$$

Let "$\alpha$" be L1 and "$\beta$" be L2. Given the Margules parameters, we can establish expressions for the activity coefficients,

$$\ln \gamma_1 = x_2^2\left[A_{12} + 2(A_{21}-A_{12})x_1\right]$$

$$\therefore \ln \gamma_1 = (1-x_1)^2\left[4.62 + 2(3.35-4.62)x_1\right]$$

$$\therefore \ln \gamma_1 = (1-x_1)^2(4.62-2.54x_1)$$

$$\therefore \gamma_1 = \exp\left[(1-x_1)^2(4.62-2.54x_1)\right]$$

and

$$\ln \gamma_2 = x_1^2\left[A_{21} + 2(A_{12}-A_{21})x_2\right]$$

$$\therefore \ln \gamma_2 = x_1^2\left[3.35 + 2(4.62-3.35)(1-x_1)\right]$$

$$\therefore \ln \gamma_2 = x_1^2\left[3.35 + 2.54(1-x_1)\right]$$

$$\therefore \gamma_2 = \exp\left\{x_1^2\left[3.35 + 2.54(1-x_1)\right]\right\}$$

Substituting into equation (I), it follows that

$$x_1^{\alpha}\gamma_1^{\alpha} = x_1^{\beta}\gamma_1^{\beta}$$

$$\therefore x_1^{\alpha}\exp\left[(1-x_1^{\alpha})^2(4.62-2.54x_1^{\alpha})\right] = x_1^{\beta}\exp\left[(1-x_1^{\beta})^2(4.62-2.54x_1^{\beta})\right] \quad \text{(V)}$$

Substituting into equation (II), in turn, gives

$$(1-x_1^{\alpha})\gamma_2^{\alpha} = (1-x_1^{\beta})\gamma_2^{\beta}$$

$$\therefore (1-x_1^{\alpha})\exp\left\{(x_1^{\alpha})^2\left[3.35+2.54(1-x_1^{\alpha})\right]\right\} = (1-x_1^{\beta})\exp\left\{(x_1^{\beta})^2\left[3.35+2.54(1-x_1^{\beta})\right]\right\} \quad \text{(VI)}$$

Then, substituting into equation (III),

$$x_1^{\alpha}\exp\left[(1-x_1^{\alpha})^2(4.62-2.54x_1^{\alpha})\right]P_1^{\text{sat}} = y_1 P$$

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At 35°C, the vapor pressure of diethyl ether is 0.966 bar. Accordingly,

$$x_1^\alpha \exp\left[\left(1-x_1^\alpha\right)^2\left(4.62-2.54x_1^\alpha\right)\right]\times 0.966 = y_1 P \quad \text{(VII)}$$

Lastly, we substitute into equation (IV) to obtain

$$\left(1-x_1^\beta\right)\gamma_2^\beta P_2^{\text{sat}} = \left(1-y_1\right)P$$

$$\therefore \left(1-x_1^\beta\right)\exp\left\{\left(x_1^\beta\right)^2\left[3.35+2.54\left(1-x_1^\beta\right)\right]\right\}P_2^{\text{sat}} = \left(1-y_1\right)P$$

At 35°C, the vapor pressure of water is 0.0577 bar. Thus,

$$\left(1-x_1^\beta\right)\exp\left\{\left(x_1^\beta\right)^2\left[3.35+2.54\left(1-x_1^\beta\right)\right]\right\}\times 0.0577 = \left(1-y_1\right)P \quad \text{(VIII)}$$

Equations (V), (VI), (VII), and (VIII) constitute a system of four nonlinear equations with four unknowns, namely $x_1^\alpha$, $x_1^\beta$, $y_1$, and $P$. The equations are repeated below for convenience.

$$\begin{cases} x_1^\alpha \exp\left[\left(1-x_1^\alpha\right)^2\left(4.62-2.54x_1^\alpha\right)\right] = x_1^\beta \exp\left[\left(1-x_1^\beta\right)^2\left(4.62-2.54x_1^\beta\right)\right] \\[2mm] \left(1-x_1^\alpha\right)\exp\left\{\left(x_1^\alpha\right)^2\left[3.35+2.54\left(1-x_1^\alpha\right)\right]\right\} = \left(1-x_1^\beta\right)\exp\left\{\left(x_1^\beta\right)^2\left[3.35+2.54\left(1-x_1^\beta\right)\right]\right\} \\[2mm] x_1^\alpha \exp\left[\left(1-x_1^\alpha\right)^2\left(4.62-2.54x_1^\alpha\right)\right]\times 0.966 = y_1 P \\[2mm] \left(1-x_1^\beta\right)\exp\left\{\left(x_1^\beta\right)^2\left[3.35+2.54\left(1-x_1^\beta\right)\right]\right\}\times 0.0577 = \left(1-y_1\right)P \end{cases}$$

The equations can be solved with the lengthy Mathematica code

```
FindRoot[{a * Exp[(1 - a)^2 (4.62 - 2.54 * a)] == b * Exp[(1 - b)^2 (4.62 - 2.54 * b)],
  (1 - a) * Exp[a^2 * (3.35 + 2.54 * (1 - a))] == (1 - b) * Exp[b^2 * (3.35 + 2.54 * (1 - b))], a * Exp[(1 - a)^2 * (4.62 - 2.54 * a)] * 0.966 == y * P,
  (1 - b) * Exp[b^2 * (3.35 + 2.54 * (1 - b))] * 0.0577 == (1 - y) * P}, {{a, 0.01}, {b, 0.95}, {P, 1}, {y, 0.9}}]
```

This returns $a = x_1^{L1} = 0.0107$, $b = x_1^{L2} = 0.9586$, $P = 0.987$ bar, and $y = y_1$ = 0.9421. The pressure and composition of the vapor-liquid-liquid equilibrium in question have been successfully calculated.

## ▶▶ ANSWER SUMMARY

| Problem 1 | | Open-ended pb. |
|-----------|-----|----------------|
| Problem 2 | | C |
| Problem 3 | | α |
| Problem 4 | 4.1 | α |
| | 4.2 | α |
| | 4.3 | α |
| | 4.4 | β |
| Problem 5 | | D |
| Problem 6 | | E |
| Problem 7 | | B |
| Problem 8 | | Open-ended pb. |
| Problem 9 | | Open-ended pb. |

## ▶▶ REFERENCES

- DAHM, K. and VISCO, D. (2015). *Fundamentals of Chemical Engineering Thermodynamics*. Stamford: Cengage Learning.

Got any questions related to this quiz? We can help! Send a message to contact@montogue.com and we'll answer your question as soon as possible.