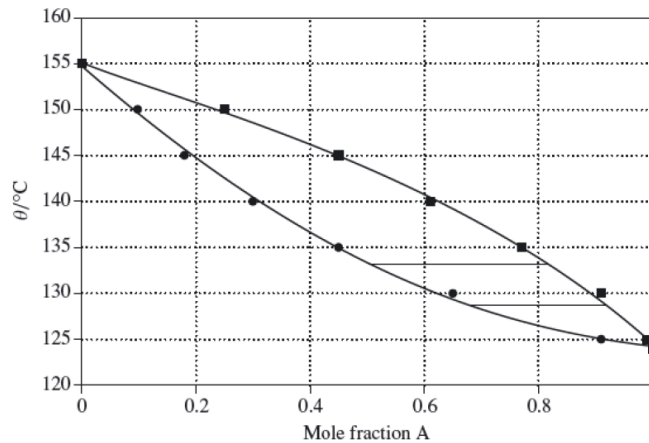


Exercise

- 5C.1(b)** Add the boiling point of A to the table at $x_A = y_A = 1$ and the boiling point of B at $x_B = y_B = 0$. Plot the boiling temperatures against liquid mole fractions and the same boiling temperatures against vapour mole fractions on the same plot.

The phase diagram is shown in Figure 5C.1. The phase boundary curves are polynomial fits to the data points.

Figure 5C.1

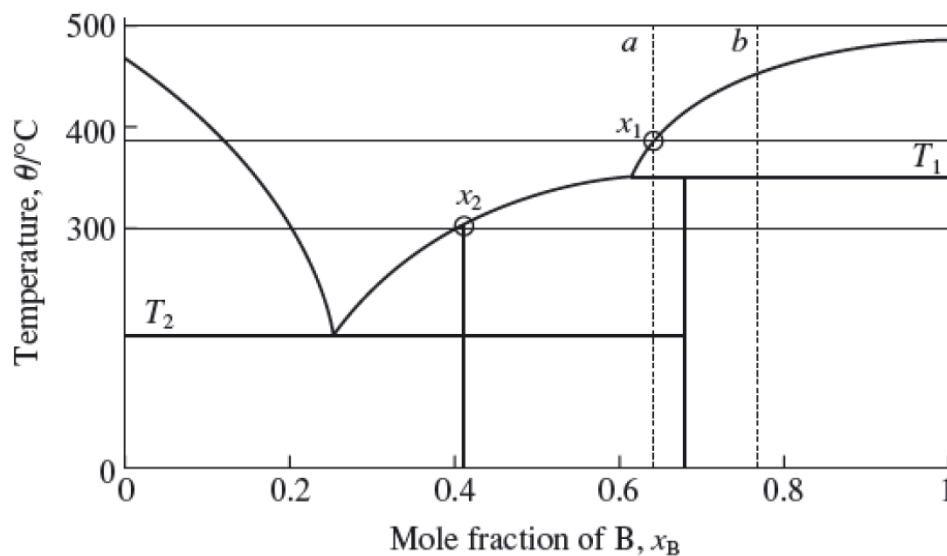


- (i) Find $x_A = 0.50$ on the lower curve and draw a horizontal tie line to the upper curve. The mole fraction at that point is $y_A = 0.82$.

- (ii) Find $x_A = 0.67$ (i.e., $x_B = 0.33$) on the lower curve and draw a horizontal tie line to the upper curve. The mole fraction at that point is $y_A = 0.91$ (i.e., $y_B = 0.09$).

- 5C.6(b)** Refer to Figure 5C.5. Dotted horizontal lines have been drawn at the relevant temperatures.

Figure 5C.5



(i) At 500°C, the phase diagram shows a single liquid phase at all compositions, so **B is soluble in A in all proportions**.

(ii) At 390°C, solid B exists in equilibrium with a liquid whose composition is circled and labeled x_1 on Figure 5.11. That composition is $x_B = x_1 = \boxed{0.63}$.

(iii) At point x_2 , two phases coexist: solid AB_2 and a liquid mixture of A and B with mole fraction $x_B = x_2 = 0.41$. Although the liquid does not contain any AB_2 units, we can think of the liquid as a mixture of dissociated AB_2 in A. Call the amount (moles) of the compound n_c and that of free A n_a . Thus, the amount of A (regardless of whether free or in the compound) is

$$n_A = n_a + n_c,$$

and the amount of B is

$$n_B = 2n_c.$$

The mole fraction of B is

$$x_B = x_2 = \frac{n_B}{n_A + n_B} = \frac{2n_c}{(n_a + n_c) + 2n_c} = \frac{2n_c}{n_a + 3n_c}$$

Rearrange this relationship, collecting terms in n_c on one side and n_a on the other:

$$n_a x_2 = n_c(2 - 3x_2).$$

The mole ratio of compound to free A is given by

$$\frac{n_c}{n_a} = \frac{x_2}{2 - 3x_2} = \frac{0.41}{2 - 3 \times 0.41} = \boxed{0.53}.$$

5E.1(b) Let A = water and B = solute.

$$a_A = \frac{p_A}{p_A^*} \quad [5E.2] = \frac{0.02239 \text{ atm}}{0.02308 \text{ atm}} = \boxed{0.9701}$$

$$\gamma_A = \frac{a_A}{x_A} \quad [5E.4] \quad \text{and} \quad x_A = \frac{n_A}{n_A + n_B}$$

$$n_A = \frac{920 \text{ g}}{18.02 \text{ g mol}^{-1}} = 51.1 \text{ mol} \quad n_B = \frac{122 \text{ g}}{241 \text{ g mol}^{-1}} = 0.506 \text{ mol}$$

$$\text{So} \quad x_A = \frac{51.1}{51.1 + 0.506} = 0.990 \quad \text{and} \quad \gamma_A = \frac{0.9701}{0.990} = \boxed{0.980}$$

5E.2(b) From eqn 1A.8 (partial pressures) and y_A we can compute the partial pressures:

$$y_A = \frac{p_A}{p_A + p_B} = \frac{p_A}{101.3 \text{ kPa}} = 0.314$$

$$\text{So} \quad p_A = 101.3 \text{ kPa} \times 0.314 = 31.8 \text{ kPa}$$

$$\text{and} \quad p_B = 101.3 \text{ kPa} - 31.8 \text{ kPa} = 69.5 \text{ kPa}$$

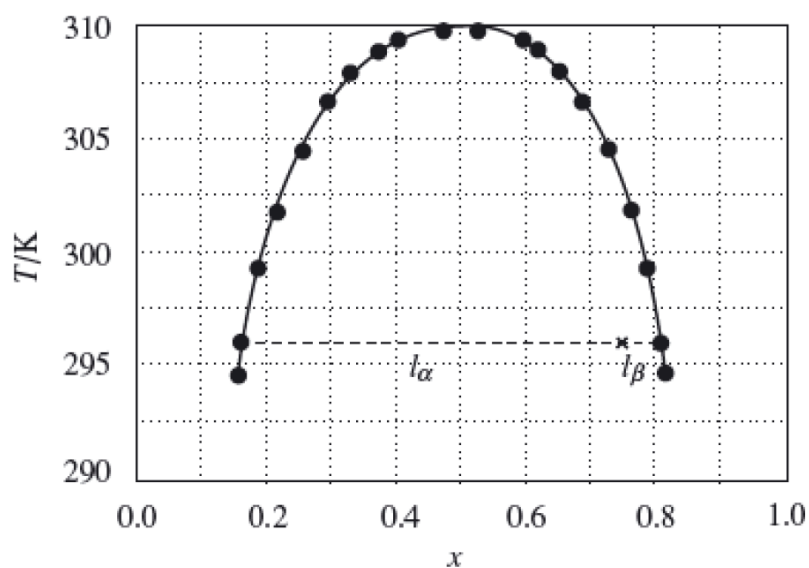
$$a_A = \frac{p_A}{p_A^*} \quad [5E.2] = \frac{31.8 \text{ kPa}}{73.0 \text{ kPa}} = \boxed{0.436} \quad \text{and} \quad a_B = \frac{p_B}{p_B^*} = \frac{69.5 \text{ kPa}}{92.1 \text{ kPa}} = \boxed{0.755}$$

$$\gamma_A = \frac{a_A}{x_A} \quad [5E.4] = \frac{0.436}{0.220} = \boxed{1.98} \quad \text{and} \quad \gamma_B = \frac{a_B}{x_B} = \frac{0.755}{0.780} = \boxed{0.967}$$

Problem

5C.2 (a) The phase diagram is shown in Figure 5C.10.

Figure 5C.10



(b) We need not interpolate data, for 296.0 K is a temperature for which we have experimental data. The mole fraction of *N,N*-dimethylacetamide in the heptane-rich phase (call the point α , at the left of the tie line) is 0.168 and in the acetamide-rich phase (β , at right) 0.804. The proportions of the two phases are in an inverse ratio of the distance their mole fractions are from the composition point in question, according to the lever rule. That is

$$n_\alpha / n_\beta = l_\beta / l_\alpha = (0.804 - 0.750) / (0.750 - 0.168) = \boxed{0.093}$$

The smooth curve through the data crosses $x = 0.750$ at $\boxed{302.5 \text{ K}}$, the temperature at which the heptane-rich phase will vanish.

$$5E.2 \quad \phi = -\frac{x_A}{x_B} \ln a_A = -\frac{\ln a_A}{r} \quad (a)$$

$$\text{Therefore, } d\phi = -\frac{1}{r} d \ln a_A + \frac{1}{r^2} \ln a_A dr$$

$$\text{and } d \ln a_A = \frac{1}{r} \ln a_A dr - r d\phi. \quad (b)$$

Now the Gibbs–Duhem equation [5A.12a], implies

$$x_A d\mu_A + x_B d\mu_B = 0.$$

Since $\mu = \mu^* + RT \ln a$,

$$x_A d \ln a_A + x_B d \ln a_B = 0.$$

$$\text{Therefore } d \ln a_B = -\frac{x_A}{x_B} d \ln a_A = -\frac{d \ln a_A}{r} = -\frac{1}{r^2} \ln a_A dr + d\phi \text{ [from (b)]}$$

$$= \frac{\phi}{r} dr + d\phi \text{ [from (a)]} = \phi d \ln r + d\phi$$

Subtract $d \ln r$ from both sides, to obtain

$$d \ln \frac{a_B}{r} = (\phi - 1) d \ln r + d\phi = \frac{(\phi - 1)}{r} dr + d\phi.$$

Integrate both sides of the equality from pure A (where $r = 0$) to an arbitrary composition:

$$\int d \ln \frac{a_B}{r} = \int \frac{(\phi - 1)}{r} dr + \int d\phi$$

The lower limit of the left-hand integral is:

$$\lim_{r \rightarrow 0} \ln \left(\frac{a_B}{r} \right) = \lim_{r \rightarrow 0} \ln \left(\frac{\gamma_B x_B}{r} \right) = \lim_{r \rightarrow 0} \ln(\gamma_B x_A) = \ln 1 = 0,$$

leaving the desired expression

$$\ln \frac{a_B}{r} = \boxed{\phi - \phi(0) + \int_0^r \left(\frac{\phi - 1}{r} \right) dr}$$