

Finally, the entropy of the solution is obtained by summing the partial molar entropies in proportion to the mole fraction of each component

$$S = \sum_i \bar{S}_i = \sum_i x_i S_i - R \sum_i x_i \ln x_i.$$

The last result is eq. (11.3). This ideal-solution entropy reflects the fact that a solution can exist in more microscopic states than a pure fluid because in addition to arranging molecules in space and assigning energy to them, we have the additional freedom to assign a molecule to species  $i$  or  $j$ . As we discussed in Chapter 4, more microstates means higher entropy.

### Example 11.2: Separation Work

Calculate the amount of work needed to separate into pure components a solution that contains n-heptane (1) and n-octane (2) with  $x_1 = 0.3$ , at 40 °C, 5 bar.

**Solution** The ideal work for separation is equal to the lost work of mixing:

$$W_{\text{ideal}} = T_0 \Delta S_{\text{mix}} - \Delta H_{\text{mix}}.$$

We treat the solution as ideal since the components are chemically similar. The enthalpy of mixing in this case is 0. The entropy of mixing of the ideal solution is  $\Delta S_{\text{mix}} = -R(x_1 \ln x_1 + x_2 \ln x_2)$ . With  $x_1 = 0.3$ ,  $x_2 = 0.7$ , we find  $\Delta S_{\text{mix}} = +0.611R = +5.08 \text{ J/mol K}$ . For ideal solutions the entropy of mixing is always positive. The lost work then is

$$W_{\text{ideal}} = (300)(5.08) - 0 = 1523.6 \text{ J/mol}.$$

We notice that the temperature (40 °C) and pressure (5 bar) of the system do not enter in the calculation. This is because the entropy and enthalpy of mixing in ideal solutions are independent of temperature and pressure.

## 11.2 Fugacity in Ideal Solution

and

The key problem is to calculate the phase diagram of ideal solution band for this we first need an expression for fugacity. We start with the basic relationship between fugacity and chemical potential in eq. (10.18). Taking state  $A$  to be component  $i$  in ~~solution~~, and state  $B$  the pure component at the same temperature and pressure, we have

ideal solution

$$\ln \frac{f_i^{\text{id}}}{f_{i,\text{pure}}} = \frac{\mu_i^{\text{id}} - G_i}{RT} = \ln x_i,$$

where we use eq. (11.9) to write the result on the far right. Solving for  $f_i$  we obtain the following simple expression:

$$f_i^{\text{id}} = x_i f_{i,\text{pure}}. \quad (11.10)$$

This states that the fugacity of component in ideal solution is the product of the pure-component fugacity, and the mol fraction of component in solution. This equation is known as the Lewis-Randall rule and is the basis for VLE calculations with ideal solutions.

For the fugacity of pure liquid at the temperature and pressure of the solution we use the Poynting equation, which relates this fugacity to the fugacity of the saturated liquid at same temperature:

$$f_{i,\text{pure}} = \phi_i^{\text{sat}} P_i^{\text{sat}} \exp \left( \frac{P - P_i^{\text{sat}}}{RT} V_i^L \right), \quad [7.16]$$

where  $P_i^{\text{sat}}$  is the saturation pressure,  $\phi_i^{\text{sat}}$  is the fugacity coefficient of the saturated pure component, and  $V_i^L$  is the molar volume of the pure liquid. Then, the fugacity in ideal solution takes the form,

$$f_i^{\text{id}} = x_i \phi_i^{\text{sat}} P_i^{\text{sat}} \exp \left( \frac{P - P_i^{\text{sat}}}{RT} V_i^L \right). \quad (11.11)$$

Here, except for the mol fraction, all other properties in the right-hand side refer to pure liquid  $i$ .

### Example 11.3: Fugacity in Ideal Solution

Calculate the fugacity of water in a water/acetic acid solution at 25 °C, 1 bar,  $x_w = 0.42$ . Assume that these components form an ideal solution.

**Solution** From the Lewis-Randall rule,  $f_w = x_w f_w^{\text{pure}}$ , where  $f_w^{\text{pure}}$  is the fugacity of pure water at 25 °C, 1 bar. At this state, water is a compressed liquid. We calculate the fugacity using the Poynting factor:

$$f_w^{\text{pure}} = P_w^{\text{sat}} \phi_w^{\text{sat}} \exp \left[ \frac{P - P_w^{\text{sat}}}{RT} V_w^L \right].$$

The saturation pressure of water at 25 °C is  $P_w^{\text{sat}} = 0.03166$  bar. This value is so much smaller than the critical pressure that the fugacity coefficient  $\phi_w^{\text{sat}}$  can be safely approximated as unity. Using the molar volume of water,  $V_w^L = 1.003 \times 10^{-3} \text{ m}^3/\text{kg} = 18.05 \times 10^{-6} \text{ m}^3/\text{mol}$ , the Poynting factor is 1.00071. The fugacity of pure water is  $f_w^{\text{pure}} = 0.03166$  bar and its fugacity in the solution is

$$f_w = x_w f_w^{\text{pure}} = (0.42)(0.03166) = 0.0133 \text{ bar}.$$

**Comments** The calculation demonstrates ~~that the approximations in Raoult's law are generally justified~~ for pressures around ambient.

that the Poynting correction is generally negligible



### 11.3 VLE in Ideal Solution–Raoult’s Law

To perform VLE calculations with ideal solutions, we begin with the equilibrium condition that requires the fugacity of component  $i$  to be the same in the liquid and in the vapor:

$$f_i^V = f_i^L.$$

For the fugacity of the liquid we use eq. (11.11); for the fugacity of the component in the vapor we use the general expression,  $f_i^V = y_i \phi_i^V P$ . Combining these expressions, the equilibrium criterion now takes the form,

$$y_i \phi_i^V P = x_i \phi_i^{\text{sat}} P_i^{\text{sat}} \exp \left[ \frac{P - P_i^{\text{sat}}}{RT} V_i^L \right]. \quad (11.12)$$

Here,  $\phi_i^V$  is the fugacity coefficient of component  $i$  in the vapor, not to be confused with  $\phi_i^{\text{sat}}$ , which refers to the *saturated pure* component  $i$  at the same temperature. This result takes a much simpler form if pressure is relatively low. Then, the Poynting correction can be neglected and the fugacity coefficients may be set to 1. With these simplifications, eq. (11.12) becomes

$$y_i P = x_i P_i^{\text{sat}}. \quad (11.13)$$

This is known Raoult’s law and requires only the saturation pressure of the pure components. The assumptions that make this simple equation valid are that the total pressure and the saturation pressure of component  $i$  be sufficiently low. Raoult’s law should be understood as a shortcut for quick calculations.

In a binary mixture, Raoult’s law gives

$$y_1 P = x_1 P_1^{\text{sat}}, \quad (11.14)$$

$$y_2 P = x_2 P_2^{\text{sat}}. \quad (11.15)$$

These two equations, along with the normalization conditions for the mol fractions,

$$\begin{aligned} x_1 + y_1 &= 1, \\ y_1 + y_2 &= 1, \end{aligned}$$

constitute four equations that relate the following six variables:

$$\{x_1, x_2, y_1, y_2, P, T\}.$$

Temperature appears implicitly in the saturation pressure of pure component, which is assumed to be known as a function of temperature, usually via the Antoine equation, or some similar temperature-dependent expression. The six unknowns and four equations result in two degrees of freedom.<sup>2</sup> The typical problems are

2. The same result is reached through application of the phase rule: with two components ( $N = 2$ ) and two phases ( $\pi = 2$ ), the degrees of freedom are  $\mathcal{F} = N + 2 - \pi = 2$ .



**Table 11-1:** Classification of VLE Problems

|                               | Knowns                         | Unknowns                       |
|-------------------------------|--------------------------------|--------------------------------|
| Bubble $P$                    | $T, x_i$                       | $P, y_i$                       |
| Bubble $T$                    | $P, x_i$                       | $T, y_i$                       |
| Dew $P$                       | $T, y_i$                       | $P, x_i$                       |
| <del>Dew <math>T</math></del> | <del><math>P, y_i</math></del> | <del><math>T, x_i</math></del> |
| Flash                         | $P, T$                         | $x_i, y_i$                     |

classified as “bubble  $T$  or  $P$ ,” “dew  $T$  or  $P$ ,” or “flash.” These classifications were introduced in Chapter 9 and are summarized again in Table 11-1. Solution strategies for performing these calculations are outlined below.

**Bubble  $P$  Calculation** Following the designation of VLE problems introduced in Chapter 10, in the bubble  $P$  problem we know temperature and the composition of the liquid and seek pressure and the composition of the vapor. Adding eqs. (11.14) and (11.15) to eliminate the unknown vapor fractions we obtain the bubble pressure of the solution:

$$P = x_1 P_1^{\text{sat}} + x_2 P_2^{\text{sat}}. \quad (11.16)$$

The vapor mol fractions are then calculated from eqs. (11.14) and (11.15):

$$y_1 = \frac{x_1 P_1^{\text{sat}}}{P}, \quad y_2 = \frac{x_2 P_2^{\text{sat}}}{P}, \quad (11.17)$$

where  $P$  is the bubble pressure calculated above. Notice that according to eq. (11.16), the bubble pressure of an ideal solution is an average of the saturation pressures of the pure components.

**Bubble  $T$  Calculation** In this case we know liquid composition and total pressure, and seek to calculate vapor composition and temperature. Again we add eqs. (11.14) and (11.15) to eliminate the unknown vapor fractions:

$$P = x_1 P_1^{\text{sat}} + x_2 P_2^{\text{sat}}. \quad [11.16]$$

In this equation, the unknown is temperature, which appears implicitly in the saturation pressure through an equation such as the Antoine. Because this is a nonlinear equation in  $T$ , it requires a numerical solution. Once temperature is known, the saturation pressures are calculated and the vapor mole fractions are obtained as before, using

$$y_1 = \frac{x_1 P_1^{\text{sat}}}{P}, \quad y_2 = \frac{x_2 P_2^{\text{sat}}}{P}. \quad [11.17]$$

**Dew  $P$  Calculation** Here the knowns are temperature and the composition of the vapor, and we seek to calculate pressure and the composition of liquid. We begin by solving eqs. (11.14) and (11.15) for the unknown mol fractions: