

Example 10.1 Binary system acetonitrile(1)/nitromethane(2) conforms closely to Raoult's law. Vapor pressures for the pure species are given by the following Antoine equations:

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$$\ln P_1^{\text{sat}}/\text{kPa} = 14.2724 - \frac{2,945.47}{T - 49.15}$$

$$\ln P_2^{\text{sat}}/\text{kPa} = 14.2043 - \frac{2,972.64}{T - 64.15}$$

- (a) Prepare a graph showing  $P$  vs.  $x_1$  and  $P$  vs.  $y_1$  for a temperature of  $75^\circ\text{C}$ .  
 (b) Prepare a graph showing  $t$  vs.  $x_1$  and  $t$  vs.  $y_1$  for a pressure of  $70$  kPa.

(a) Given  $T \uparrow$  (75°C) and  $x_1$  find  $P$  and  $y_1$  (BUBLP)

Raoult's law:  $y_i P = x_i P_i^{\text{sat}}$

$$y_i = \frac{x_i P_i^{\text{sat}}}{P} \quad , \quad \sum_i y_i = 1$$

$$\Rightarrow 1 = \sum_i \frac{x_i P_i^{\text{sat}}}{P} \quad \text{solve for } P$$

$$P = \sum_i x_i P_i^{\text{sat}} \Rightarrow P = x_1 P_1^{\text{sat}} + x_2 P_2^{\text{sat}}$$

$$x_2 = 1 - x_1 \Rightarrow P = P_2^{\text{sat}} + (P_1^{\text{sat}} - P_2^{\text{sat}}) x_1 \quad \textcircled{1}$$

$$\text{Since } P \text{ is known} \Rightarrow y_1 = \frac{x_1 P_1^{\text{sat}}}{P_2^{\text{sat}} + (P_1^{\text{sat}} - P_2^{\text{sat}}) x_1} \quad \textcircled{2}$$

$$P_1^{\text{sat}} (75^\circ\text{C}) = 83.21 \text{ kPa}$$

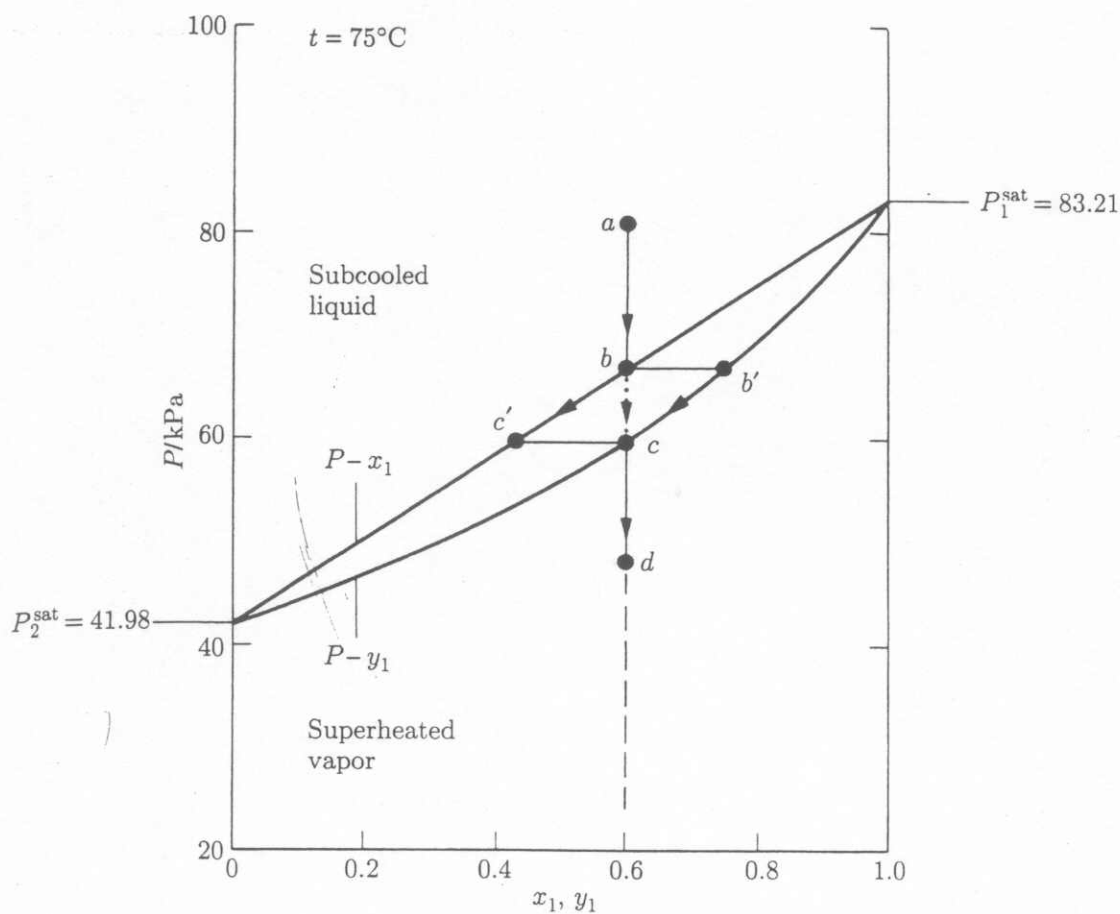
$$P_2^{\text{sat}} (75^\circ\text{C}) = 41.98 \text{ kPa}$$

$$\Rightarrow P = 41.98 + 41.23 X_1$$

SEE eq. (1)

$$y_1 = \frac{83.21 X_1}{(41.98 + 42.23 X_1)}$$

| $x_1$ | $y_1$  | $P/\text{kPa}$ |
|-------|--------|----------------|
| 0.0   | 0.0    | 41.98          |
| 0.2   | 0.3313 | 50.23          |
| 0.4   | 0.5692 | 58.47          |
| 0.6   | 0.7483 | 66.72          |
| 0.8   | 0.8880 | 74.96          |
| 1.0   | 1.0    | 83.21          |



**Figure** Raoult's law.

$Pxy$  diagram for acetonitrile(1)/nitromethane(2) at  $75^\circ\text{C}$  as given by

(6) Given  $P = 70 \text{ kPa}$  and  $y_1$ , find  $T$  &  $x_1$  (DEWT) (3)

Raoult's law:  $y_i P = x_i P_i^{\text{sat}}$

$$x_i = y_i P / P_i^{\text{sat}}, \quad \sum_i x_i = 1$$

$$\Rightarrow 1 = \frac{y_1 P}{P_1^{\text{sat}}} + \frac{y_2 P}{P_2^{\text{sat}}}, \quad P = 70 \text{ kPa.}$$
$$y_2 = 1 - y_1$$

rearrange,

$$\Rightarrow \left( \frac{y_1}{P_1^{\text{sat}}} + \frac{1 - y_1}{P_2^{\text{sat}}} \right) 70 - 1 = 0$$

express  $P_1^{\text{sat}}$  and  $P_2^{\text{sat}}$  as functions of  $T$

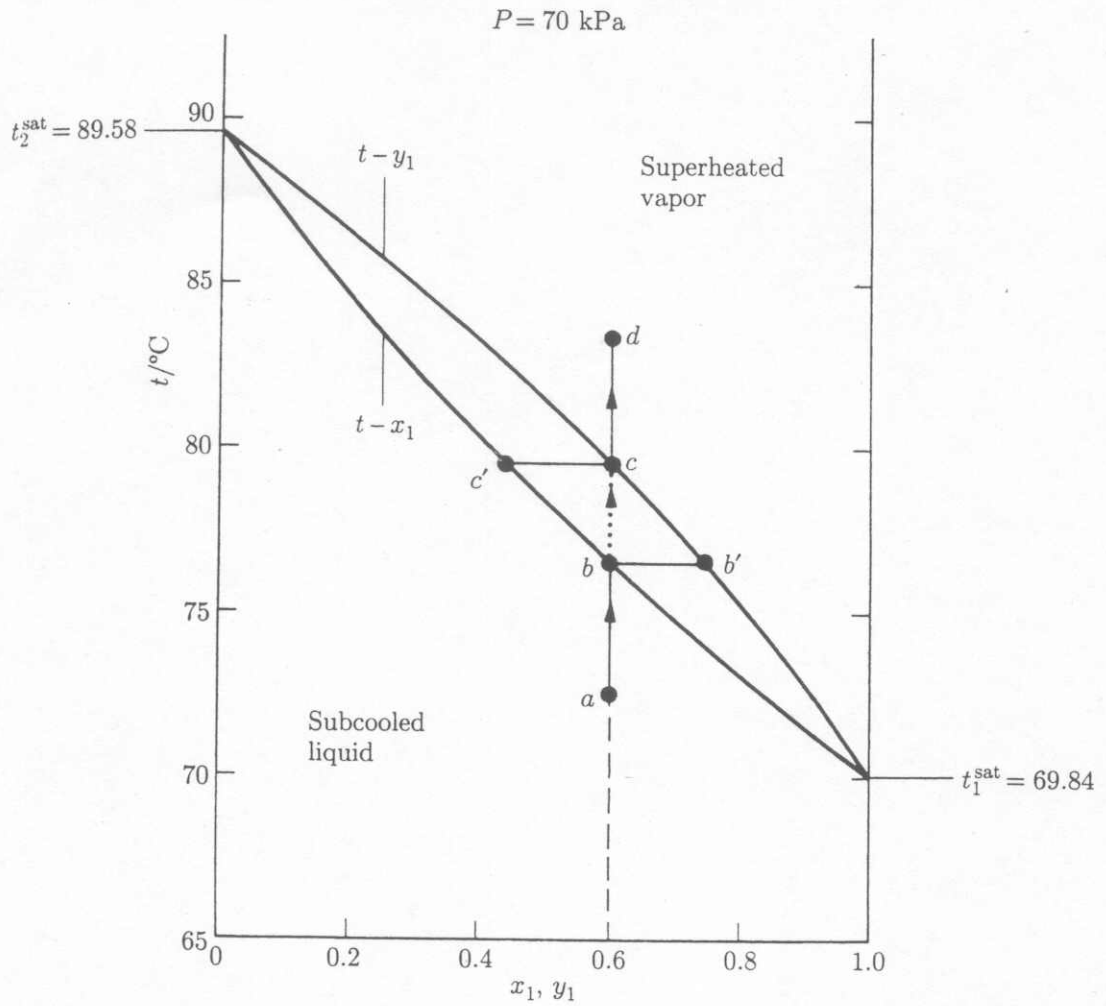
$$\left[ \frac{y_1}{1579154.3 \exp\left[-\frac{2945.47}{T+224}\right]} + \frac{1 - y_1}{1475193.9 \exp\left[\frac{-2972.64}{T+209}\right]} \right]$$

\*  $70 - 1 = 0$  ----- (3)  
given  $y_1$  calculate  $T$  by trail and error  
from above equation. Then,

$$x_1 = \frac{y_1 P}{P_1^{\text{sat}}} = \frac{70 y_1}{1579154.3 \exp\left[\frac{-2945.47}{T+224}\right]} \quad (4)$$

given  $y$  calculate  $T$  from (3) then calculate  
 $x_1$  from (4)

| $y_1$ | $x_1$ | T     |
|-------|-------|-------|
| 0.00  | 0.00  | 89.58 |
| 0.25  | 0.15  | 85.85 |
| 0.50  | 0.34  | 81.52 |
| 0.75  | 0.60  | 76.36 |
| 1.00  | 1.00  | 69.84 |



**Figure**  $t$ - $xy$  diagram for acetonitrile(1)/nitromethane(2) at 70 kPa as given by Raoult's law.