

## CHAPTER VII

### Energy Effects in Liquids

**Sensible Heat:**

$Q = m C_p (T_2 - T_1)$   
 use  $n$  if  $C_p$  is molar heat cap.  
 $C_p$  for liq,  $P C_{pv}$  for vap.

**Latent:**  $Q = n \Delta H_v$  or  $m \Delta H_v$



Trouton's rule:

$$\frac{\Delta H_v}{T_b} = 88 \frac{\text{kJ}}{\text{kmol K}}$$

where  $T_b$  is the normal boiling point

Clausius-Clapeyron Equation:

$$\ln P = -\frac{\Delta H_v}{RT} + C_0 \quad \text{where } P \text{ is in kPa and } T \text{ is in K}$$

$\ln \left( \frac{P_2}{P_1} \right) = \frac{\Delta H_v}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$

(i) Calculate  $\Delta H_v$  if the pairs  $(P_1, T_1)$  &  $(P_2, T_2)$  known  
 (ii) Calculate  $P_2$  or  $T_2$  if  $\Delta H_v$  and  $(P_1, T_1)$  given.

General vapour pressure correlation:  $\ln P = \frac{C_1}{T} + C_2$

where  $C_1$  and  $C_2$  are constants

### Equilibrium Pressure Above Liquid Mixtures

Relationship between bubble-point pressure and partial pressure:

$$P = \sum_{i=1}^c \bar{p}_i = \sum_{i=1}^c P_{vi} x_i$$

Find  $P_{tot}$  when  $x_i$  known.

Raoult's Law:

$$\bar{p}_i = P_{vi} x_i$$

Definition of  $\bar{p}_i$ :  
 $\bar{p}_i = y_i P_{tot}$

$$\bar{p}_i = y_i P = P_{vi} x_i$$

$$y_i = \frac{P_{vi} x_i}{P}$$

$$x_i = \frac{y_i P}{P_{vi}}$$

For a binary mixture:

$$y_i = \frac{P_{vi} x_i}{\sum_{i=1}^c P_{vi} x_i}$$

$$\sum x_i = 1 = \sum \frac{y_i P}{P_{vi}} = P \sum \frac{y_i}{P_{vi}} \Rightarrow P = \frac{1}{\sum \frac{y_i}{P_{vi}}}$$

$$y_1 = \frac{x_1}{x_1 + (\alpha_{21}) x_2} \quad \text{where} \quad \alpha_{21} = \left( \frac{P_{v2}}{P_{v1}} \right)$$

Find  $P_{tot}$  when  $y_i$  known

Henry's Law:

$$\bar{p}_i = y_i P = H_i x_i$$

Use this to find one of  $(y_i, x_i, \alpha_{21})$  when the remaining two are known. 1 = component 1, 2 = component 2

Remember:  $\sum y_i = \sum x_i = 1$

$P_{system} = P_{tot} = P_{bp} \text{ of liq } (x_1, x_2) = P_{dp} \text{ of vapour } (y_1, y_2)$

$P_{bp}$  = bubble-point pressure  
 $P_{dp}$  = dew point pressure

## Chapter 7 -Solution

## Final Exam W2012

The normal boiling point of n-pentane is 36.1°C. At a temperature of 75°C, the vapour pressure of n-pentane is 310.5 kPa. The latent heat of vaporization of benzene at its normal boiling point of 80.1°C is 30.7 MJ/kmol. You have been given a liquid mixture containing 10 mol% benzene (M=78 g/mol) and 90 mol% n-pentane (M= 72.15 g/mol). Use the information provided to answer the following questions:

- Determine the vapour pressure (in kPa) of pure n-pentane at 65°C.
- Estimate the vapour pressure (in kPa) of pure benzene at 65°C.
- Calculate the bubble point pressure (in kPa) of the liquid mixture at 65°C.
- Determine the composition of the vapour phase in equilibrium when the liquid mixture is at 65°C and at its bubble point pressure at this temperature.
- You now have 10 kg of pure liquid benzene at a temperature of 4°C at a pressure of 1 atm. Determine the total heat energy required (kJ) to boil the substance entirely to a vapour at 100°C. Note:  $C_{pL}$  for benzene is 134.8 kJ/kmol.K and  $C_{pv}$  for benzene is 82.4 kJ/kmol.K

a) Given, ( $T_1 = 36.1^\circ\text{C} = 309.25\text{ K}$ ,  $P_1 = 101.325\text{ kPa}$ )

and ( $T_2 = 75^\circ\text{C} = 348.15\text{ K}$ ,  $P_2 = 310.5\text{ kPa}$ )

Find:  $P = ?$  when  $T = 65^\circ\text{C}$  using  $\ln(P_2/P_1) = \frac{\Delta H_v}{R} (1/T_1 - 1/T_2)$

First, develop the P-T relationship by determining  $\Delta H_v$

$$\ln \left( \frac{310.5}{101.325} \right) = \frac{\Delta H_v}{R} \left( \frac{1}{309.25} - \frac{1}{348.15} \right)$$

$$\Rightarrow \frac{\Delta H_v}{R} = 1.1198507 / 0.0003613 = 3099.5\text{ K}$$

Then, applying the same equation between ( $T_1 = 309.25$ ,  $P_1 = 101.325$ ) and ( $T_2 = 65^\circ\text{C} = 338.15\text{ K}$ ,  $P_2$ ) we get,

$$\ln \left( \frac{P_2}{101.325} \right) = 3099.5\text{ K} \left( \frac{1}{309.25} - \frac{1}{338.15} \right) = 0.8566$$

$$\Rightarrow P_2 = 238.63\text{ kPa}$$

b) Given  $\Delta H_{v, \text{benzene}} = 30.7 \times 10^3\text{ kJ/kmol}$

and at  $P_1 = 101.325\text{ kPa}$ ,  $T_1 = T_b = 353.25\text{ K}$

Apply the same relationship for benzene for the condition  
 $T_2 = 65^\circ\text{C} = 338.15\text{ K}$

$$\ln \frac{P_2}{P_1} = \frac{\Delta H_v}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad (2)$$

$$\Rightarrow \ln \frac{P_2}{P_1 = 101.325 \text{ kPa}} = \frac{30.7 \times 10^3 \text{ kJ/mol}}{8.314 \text{ kJ/mol}\cdot\text{K}} \times \left( \frac{1}{353.25 \text{ K}} - \frac{1}{338.25 \text{ K}} \right)$$

$$= 3692.5668 (-0.000125536)$$

$$= -0.46355$$

$$\Rightarrow \frac{P_2}{101.325 \text{ kPa}} = \exp(-0.46355) = 0.629047$$

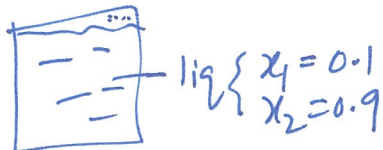
$$\Rightarrow P = 63.74 \text{ kPa} \text{ (vap pr. of benzene at } 65^\circ\text{C)}$$

c) Given liquid mixture : 10 mol% benzene (1) + 90 mol% n-pentane (2)

Given temp :  $T = 65^\circ\text{C}$

Determine :  $P_{bp}$  for liq mixture at  $65^\circ\text{C}$

We do the following experiment : Take certain amount of this mixture inside a variable-volume container and set the pressure such that just only the 1st drop of bubble is observed at  $65^\circ\text{C}$ . At equilibrium. The liquid composition at equilibrium is same as the liquid composition of the given liquid.



We know at equilib :

$$P_{total} = P_{bp} \text{ of liq mix } (x_1 = 0.1, x_2 = 0.9) = P_{bp} \text{ of vapor } (y_1, y_2)$$

$$P_{total} = \sum x_i P_{vi} = x_1 P_{v1} + x_2 P_{v2} = 0.1 \times 63.74 + 0.9 \times 238.428$$

$$= 220.94 \text{ kPa}$$

$$\text{So, } P_{bp} = 220.94 \text{ kPa}$$

d) Vapor composition :

Raoult's law :  $y_i P_{tot} = x_i P_{vi}$

$$y_i = \frac{x_i P_{vi}}{P_{tot}}$$

With ref. to part (c),

$$y_1 = \frac{(0.1)(63.74)}{220.94} = 0.029 = y_{\text{benzene}}$$

$$y_2 = 1 - y_1 = 0.971 = y_{\text{pentane}}$$

e) Heat requirement :

liq benzene ( $4^\circ\text{C}$ )  $\xrightarrow{Q_1}$  sat liq  $80.1^\circ\text{C}$   $\xrightarrow{Q_2}$  sat vap  $80.1^\circ\text{C}$   $\xrightarrow{Q_3}$  superheated vapor at  $100^\circ\text{C}$

$$Q_p = Q_1 + Q_2 + Q_3 = n [C_{pL} \Delta T_1 + \Delta H_v + C_{pV} \Delta T_2]$$

$$= 5461 \text{ KJ} \quad (n = m/M = 10/78 = 0.1282 \text{ kmol})$$



### Final Exam Winter 2015

A liquid mixture is formed by mixing 20 kg of n-hexane ( $C_6H_{14}$ ) and 80 kg of n-octane ( $C_8H_{18}$ ). The molar masses of n-hexane and n-octane are 86 kg/kmol and 114 kg/kmol respectively. The data available for the two liquids are shown in the table below:

Temperature ( $^{\circ}C$ )	Vapor Pressure (mmHg)	
	n-hexane	n-octane
50 (1)	405.6 (1)	50.3 (1)
100 (2)	1844.4 (2)	351.1 (2)

- Calculate the mole fraction of n-hexane and n-octane in the liquid.
- Estimate the latent heat of vaporization of pure n-octane (kJ/kg).
- Estimate the boiling point of pure n-octane at 200 mm Hg (in  $^{\circ}C$ ).
- The liquid mixture (20 kg n-hexane and 80 kg n-octane) is maintained at  $80^{\circ}C$ . Calculate the following:
  - Equilibrium (total) pressure (in mmHg)
  - Estimate the composition of the vapor in equilibrium with liquid

a)  $n = m/M$   
 1 = hexane, 2 = octane  
 $n_1 = 20/86 = 0.2326 \text{ kmol}$   
 $n_2 = 80/114 = 0.7018 \text{ kmol}$   
 $x_1 = n_1/n_{tot} = 0.25$   
 $x_2 = n_2/n_{tot} = 0.75$

b) Given ( $P_1 = 50.3 \text{ mmHg}$  at  $T_1 = 50^{\circ}C = 323.15 \text{ K}$ ) and  
 ( $P_2 = 351.1 \text{ mmHg}$  at  $T_2 = 100^{\circ}C = 373.15 \text{ K}$ ).

Find  $\Delta H_v$

$$\ln(P_2/P_1) = \frac{\Delta H_v}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \Rightarrow \frac{\Delta H_v}{R} = \frac{\ln(P_2/P_1)}{\frac{1}{T_1} - \frac{1}{T_2}}$$

$$= \frac{\ln(351.1/50.3)}{\frac{1}{323.15 \text{ K}} - \frac{1}{373.15 \text{ K}}}$$

$$= 4686 \text{ K}$$

So,  $\Delta H_v = (R)(4686 \text{ K}) = \frac{4686 \text{ K} \cdot 8.314 \text{ kJ}}{1 \text{ kmol} \cdot \text{K}} \cdot \frac{1 \text{ kmol}}{114 \text{ kg}}$   
 $= 341.74 \text{ kJ/kg}$

c) Find  $T_b = T_2$  at  $P_2 = 200 \text{ mm Hg}$ .

Known:  $T_1 = 50^\circ\text{C} = 323.15 \text{ K}$  at  $P_1 = 50.3 \text{ mm Hg}$   
and  $\Delta H_v/R = 4686 \text{ K}$

$$\text{Therefore, } \ln \frac{200}{50.3} = 4686 \text{ K} \left[ \frac{1}{323.15 \text{ K}} - \frac{1}{T_2 \text{ (K)}} \right]$$

$$\Rightarrow 2.9456 \times 10^{-4} = \frac{1}{323.15} - \frac{1}{T_2}$$

$$\Rightarrow T_2 = 357.146 \text{ K} \approx 84^\circ\text{C}$$

d) Given: vapor & liquid coexist, find  $P, x_1, y_2$   
 $T = 80^\circ\text{C}, x_1, x_2 = 353.15 \text{ K}$   
 $x_1 = 0.25$   
 $x_2 = 0.75$

Find:  $P, y_1, y_2$

Required:  $P_{v1}$  and  $P_{v2}$  at  $353.15 \text{ K}$

Hexane vap. pr: first determine  $\frac{\Delta H_v}{R}$

$$\ln \left( \frac{1844.4}{405.6} \right) = \frac{\Delta H_v}{R} \left( \frac{1}{323.15} - \frac{1}{373.15} \right)$$

$$\Rightarrow \frac{\Delta H_v}{R} = 3652.6 \text{ K}$$

$$\text{Then, } \ln \left( \frac{P_{v1}}{405.6} \right) = 3652.6 \text{ K} \left( \frac{1}{323.15 \text{ K}} - \frac{1}{353.15 \text{ K}} \right) = 0.9602$$

$$\Rightarrow P_{v1} = 1059.5 \text{ mm Hg} = \text{vap pr. of hexane at } 80^\circ\text{C}$$

Octane vap pr:

$$\ln \left( \frac{P_{v2}}{50.3} \right) = 4686 \text{ K} \left( \frac{1}{323.15 \text{ K}} - \frac{1}{353.15 \text{ K}} \right) = 1.2318$$

$$\Rightarrow P_{v2} = 172.41 \text{ mm Hg} = \text{vap. pr. of octane at } 80^\circ\text{C}$$

(i) Raoult's law:  $P_{\text{tot}} = x_1 P_{v1} + x_2 P_{v2} = 0.25 \times 1059.5 + 0.75 \times 172.41$   
(Tot pr. above liq mix)  $= 394.18 \text{ mm Hg}$

(ii) Composition: Raoult's law:  $y_i P_{\text{tot}} = x_i P_{vi} \Rightarrow y_i = \frac{x_i P_{vi}}{P_{\text{tot}}}$

$$y_1 = 0.25 \times 1059.5 / 394.18 = 0.612$$

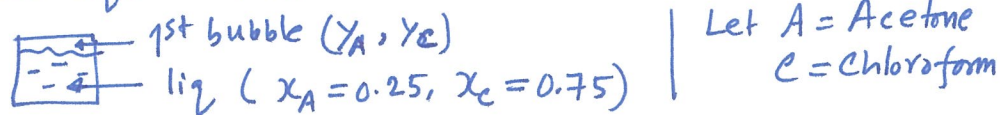
$$y_2 = 1 - y_1 = 0.328$$

## Final Exam W2016

A liquid binary mixture of acetone (25 mol%) and chloroform is at 60 kPa in a closed variable-volume container. Assume that both components follow Raoult's law. At 35°C, the vapor pressure of acetone is 46.3 kPa and the vapor pressure of chloroform is 36.4 kPa.

- The pressure in the container is now slowly reduced to the bubble point pressure of the liquid mixture at 35°C. Determine this pressure and the composition of the vapor in equilibrium.
- Determine the dew point pressure of a vapor mixture of acetone (25 mol%) and chloroform at 35°C and the composition of the liquid in equilibrium with the vapor at this conditions.
- The pressure of the container is now set to 38.6 kPa at 35°C. Determine the vapor and liquid compositions.
- The normal boiling point of acetone is 56°C. Estimate the latent heat of vaporization for acetone.

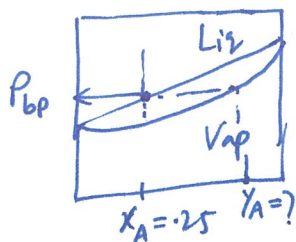
- a) At the bubble point (bp) pressure of the liquid, the liquid remains in equilibrium with the 1st bubble. The composition of the liquid after the bubble formation is considered to be the same of the original liquid mixture



at  $P_{tot} = P_{bp} \text{ of liq} = P_{dp} \text{ of vapor.}$

Given:  $T = 35^\circ\text{C}, x_A = 0.25, x_C = 0.75$

Find:  $P, y_A, y_B$



$P_{bp} \text{ of liq} = P_{tot} = \sum x_i P_{vi}$   
 $= x_A P_{vA} + x_C P_{vC} = 38.875 \text{ kPa}$

By Raoult's law:  $y_i P_{tot} = x_i P_{vi}$   
 $\Rightarrow y_i = x_i P_{vi} / P_{tot}$

Then,  $y_A = 0.25 \times 46.3 / 38.875 = 0.298$   
 $y_C = 1 - y_A = 0.702$

b) Solution 1:

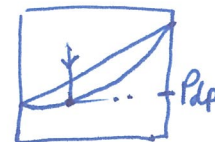
$P_{dp} \text{ of vapor} = P_{tot}$

Given,  $T = 35^\circ\text{C}, y_A = 0.25, y_C = 0.75$

Find:  $P_{tot}, x_A, x_C$

$x_A + x_C = 1$   
 $\Rightarrow \frac{y_A P_{tot}}{P_{vA}} + \frac{y_C P_{tot}}{P_{vC}} = 1 \Rightarrow P_{tot} \left( \frac{0.25}{46.3} + \frac{0.75}{36.4} \right) = 1$   
 $\Rightarrow P_{tot} = 38.456 \text{ kPa} = P_{dp}$

Then,  $x_A = y_A P_{tot} / P_{vA} = 0.25 \times 38.456 / 46.3 = 0.2076, y_C = 1 - y_A = 0.7924$





(b)

Alternatively,  
solution:

we know for comp 1:

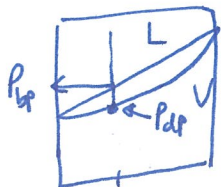
we know

$$y_1 = \frac{x_1}{x_1 + \alpha_{21}(1-x_1)}$$

$$y_{A \text{ or } C} = \frac{x_A}{x_A + \alpha_{CA}(1-x_A)}$$

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Then,  $y_A = 0.25 = \frac{x_A}{x_A + 0.7862(1-x_A)}$   $\alpha_{CA} = \frac{36.4}{46.3} = 0.7862$

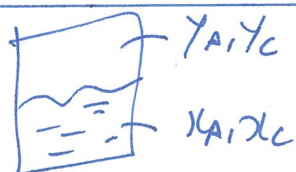


$$\Rightarrow 0.25 x_A + 0.1965 - 0.1965 x_A = x_A$$

$$\Rightarrow 0.1965 = 0.9465 x_A$$

$$\Rightarrow x_A = 0.2076 \quad x_C = 0.7924 \quad \left. \begin{array}{l} \text{Then, } P = 0.2076 \times 46.3 \\ \quad + 0.7924 \times 36.4 \\ = 38.455 \text{ kPa} \\ = P_{dp} \text{ of vapor.} \end{array} \right\}$$

(c)

 $T = 35^\circ\text{C}$  $P_{\text{tot}} = 38.6 \text{ kPa}$ T, P given. Find  $y_A, y_C, x_A, x_C$ .

4 equations are required for 4 unknowns.

(Two Raoult's law eq relations and  $y_A + y_C = x_A + x_C = 1$ .)

$$y_A = \frac{x_A P_{VA}}{P_{\text{tot}}} = x_A \left( \frac{46.3}{38.6} \right) = 1.199 x_A$$

$$y_C = 0.943 x_C$$

Now,  $y_A + y_C = 1$

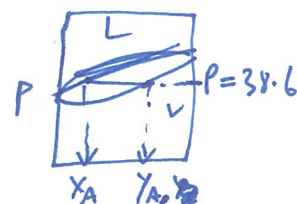
$$\Rightarrow 1.199 x_A + 0.943 x_C = 1$$

$$\Rightarrow 1.199 x_A + 0.943 (1 - x_A) = 1$$

$$\Rightarrow x_A = 0.223, \quad y_C = x_C = 0.777$$

$$y_A = 1.199 x_A = 0.267$$

$$y_C = 0.943 x_C = 0.733$$



d) We already know that  $P_{\text{vap}}$  of acetone at  $35^\circ\text{C}$  is  $46.3 \text{ kPa}$ .  
Given that at  $P = 101.325 \text{ kPa}$ ,  $T = T_b = 56^\circ\text{C} = 329.15 \text{ K}$

$$\ln \frac{P_2}{P_1} = \frac{\Delta H_v}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \Rightarrow \frac{\Delta H_v}{R} = \frac{\ln(P_2/P_1)}{1/T_1 - 1/T_2}$$

$$\Rightarrow \ln \frac{101.325}{46.3} = \frac{\Delta H_v}{R} \left[ \frac{1}{329.15 \text{ K}} - \frac{1}{308.15} \right] = \frac{\Delta H_v}{R}$$

$$\Rightarrow \frac{\Delta H_v}{R} = 3783.5 \text{ K} \Rightarrow \Delta H_v = 31.458 \frac{\text{kJ}}{\text{mol}}$$