

Problem Set 4, sample solutions

2012
April 2,
①

$$\textcircled{1} \quad P_{\text{total}}^{\text{vap}} = x_{\text{brn}}^{\text{sol}} P_{\text{brn}}^* + x_{\text{tot}}^{\text{sol}} P_{\text{tot}}^* = 5.09 \text{ kPa}$$

$$x_{\text{tot}}^{\text{vap}} = x_{\text{tot}}^{\text{sol}} P_{\text{tot}}^* = 2.68 \text{ kPa}$$

$$x_{\text{tot}}^{\text{vap}} = \frac{P_{\text{tot}}^{\text{vap}}}{P_{\text{tot}}} = 0.526$$

② Raoult's equation

$$\frac{dP}{dT} = \frac{\Delta H_m}{T \Delta V_m}$$

↙ two ways ↘

a) since changes are very small:

$$\frac{dP}{dT} \approx \frac{\Delta P}{\Delta T} = \frac{\Delta H_m^{\text{fus}}}{T \Delta V_m^{\text{fus}}}$$

b) integrate - this is of course more precise

$$\Delta P = P_2 - P_1 = \frac{\Delta H_m^{\text{fus}}}{\Delta V_m^{\text{fus}}} \ln \frac{T_2}{T_1}$$

For 1 g (there are extensive properties, but we take a ratio!)

$$\Delta H = 79.9 \text{ cal}$$

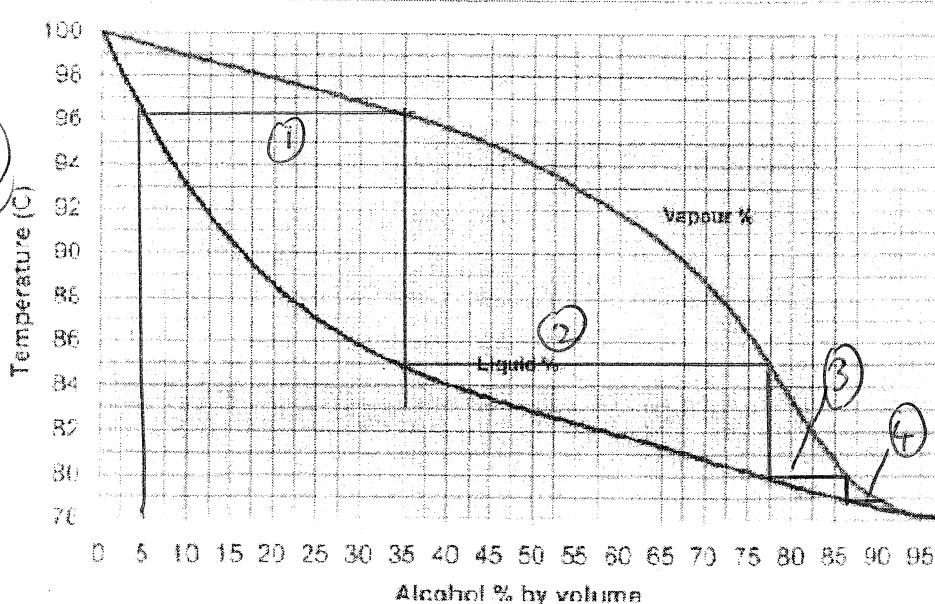
$$\Delta V = \frac{1g}{1,000 \text{ g cm}^{-3}} - \frac{1g}{0.97 \text{ g cm}^{-3}} \quad (\text{fusion}) \\ = -0.0905(1) \text{ cm}^3$$

(a) $T_2 = 271.7 \text{ K}$
 $(\Delta T = -1.43 \text{ K})$

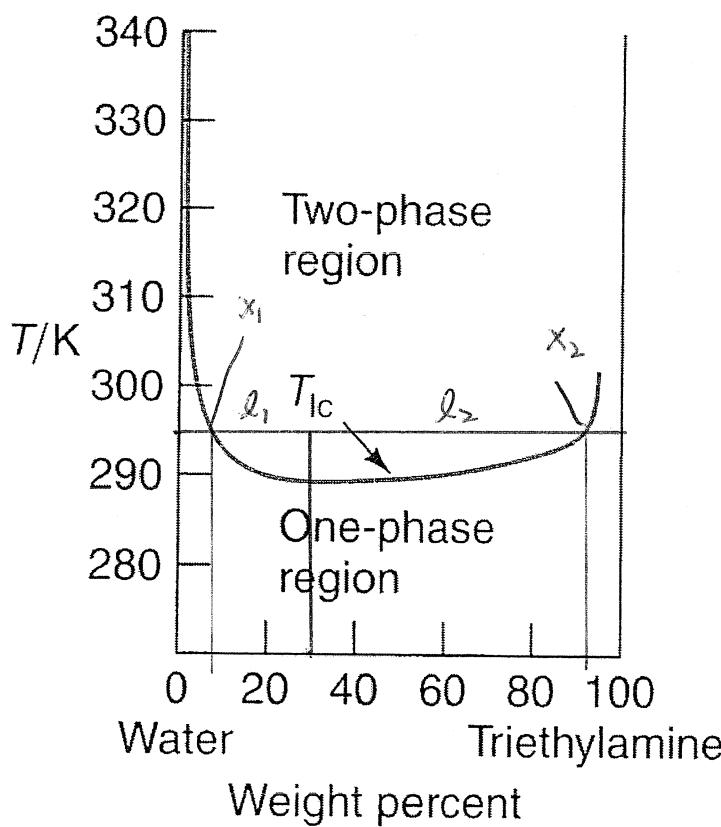
(b) $\ln \frac{T_2}{T_1} = -0.00546$
 $T_2 = 271.7 \text{ K}$

(nearly identical results)

DISTILLATION TEMPERATURE AND CONCENTRATION RELATIONSHIP



reached by distillation of a less-alcohol-rich mixture.)



Starting with a 5.0% ethanol by volume solution (a typical value for beer or cider), what is the minimum number of steps required in a fractional distillation to reach a solution that contains at least 90.0% (by volume) of ethanol?
(Note the azeotrope concentration of 95.6% alcohol:
This is the limit that can be

6. (a) From the phase diagram to the left (water-triethylamine), determine the ratio of the masses of the phases present at 295K, for a mixture containing 30.0 wt % triethylamine.
(b) What are the respective compositions of the phases?
(Figure copied from Laidler, Meiser, Sanctuary, Physical Chemistry, 4th edition.)

(a) Lever rule:

$$\frac{m_1}{m_2} = \frac{l_2}{l_1} \approx 0.36 \quad (\text{inversely: } 2.8)$$

(b) $x_1 \approx 7\%$
 $x_2 \approx 93\%$

3. Phase change

4 marks

Calculate the boiling point of water at 98.7kPa (a typical barometric pressure at 275m altitude)?

you may need some overall of info following
At standard conditions (373.15K; 1.00 atm), the heat of vaporization is 2258Jg⁻¹ (that's Joule per gram); the molar volume of liquid water is 18.78 cm³ mol⁻¹, and the molar volume of water vapor is 30.199 dm³ mol⁻¹. The molar mass of water is 18.015 g mol⁻¹.

gas-phase involved: Clapeyron eq if applicable

$$\frac{d \ln P}{dT} = \frac{\Delta H_m}{RT^2}$$

$$d \ln P = \frac{\Delta H_m}{R} \frac{dT}{T^2} - \text{integrate} -$$

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

$$P_1 = 1.00 \text{ atm} = 1.01325 \times 10^5 \text{ Pa}$$

$$P_2 = 98.7 \times 10^3 \text{ Pa}$$

$$T_1 = 373.15 \text{ K}$$

$$\begin{aligned} \text{need } \Delta H_m : \quad \Delta H_m &= \Delta H(\text{mass}) \cdot M \\ &= 2258 \text{ J g}^{-1} \cdot 18.015 \text{ g/mol} \\ &= 40.68 \text{ kJ mol}^{-1} \end{aligned}$$

$$T_2 = 372.40 \text{ K}$$