

NORTH CAROLINA STATE UNIVERSITY
Department of Chemistry
Take-home Quiz 5
CH 431
Physical Chemistry I

Solutions

1. Calculate a two-component composition/ pressure phase diagram for methanol and ethanol at 300 K. The enthalpy of vaporization of methanol is $\Delta_{\text{vap}}H^\circ = 35.3 \text{ kJ/mol}$ and the enthalpy of vaporization of ethanol is $\Delta_{\text{vap}}H^\circ = 43.5 \text{ kJ/mol}$. The boiling points of methanol and ethanol are 337.2 K and 352 K, respectively. Assuming component 1 is ethanol and component 2 is methanol,

a. Calculate the vapor pressure of each liquid at 300 K.

Solution: Use the Clausius-Clapeyron equation.

For ethanol the vapor pressure at 300 K is:

$$\begin{aligned} P_2 &= P_1 \exp \left\{ \frac{\Delta_{\text{vap}}H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \right\} \\ &= (1 \text{ bar}) \exp \left\{ \frac{43500 \text{ J/mol}}{8.31 \text{ J/mol-K}} \left(\frac{1}{352} - \frac{1}{300} \right) \right\} \\ &= 0.0759 \text{ bar} = 58 \text{ torr} \end{aligned}$$

For methanol the vapor pressure at 300 K is:

$$\begin{aligned} P_2 &= P_1 \exp \left\{ \frac{\Delta_{\text{vap}}H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \right\} \\ &= (1 \text{ bar}) \exp \left\{ \frac{35300 \text{ J/mol}}{8.31 \text{ J/mol-K}} \left(\frac{1}{337.2} - \frac{1}{300} \right) \right\} \\ &= 0.209 \text{ bar} = 159 \text{ torr} \end{aligned}$$

So $P_{\text{methanol}}^* = 159 \text{ torr}$ and $P_{\text{ethanol}}^* = 58 \text{ torr}$

- b. Calculate the total vapor pressure of a methanol/ethanol mixture at $x_2 = x_{\text{methanol}} = 0.0, 0.2, 0.4, 0.6, 0.8, \text{ and } 1.0$.

$$\begin{aligned} P_{\text{total}} &= x_1 P_1^* + x_2 P_2^* = x_{\text{ethanol}} P_{\text{ethanol}}^* + x_{\text{methanol}} P_{\text{methanol}}^* \\ &= P_{\text{ethanol}}^* + x_{\text{methanol}} (P_{\text{methanol}}^* - P_{\text{ethanol}}^*) \\ &= 58 + 101 x_{\text{methanol}} \end{aligned}$$

x_{methanol}	P_{total}
1.0	159
0.8	139
0.6	118.6
0.4	98.4
0.2	78.2
0.0	58

- c. Calculate the total vapor pressure of a methanol/ethanol mixture at $y_2 = y_{\text{methanol}} = 0.0, 0.2, 0.4, 0.6, 0.8, \text{ and } 1.0$.

Solution:

From Dalton's law: $P_2 = y_2 P_{\text{total}}$

So $P_{\text{total}} = x_2 P_2^* / y_2$

$P_{\text{total}} = (1 - x_2) P_1^* + x_2 P_2^*$

So

$$x_2 = \frac{P_{\text{total}} - P_1^*}{P_2^* - P_1^*}$$

and therefore

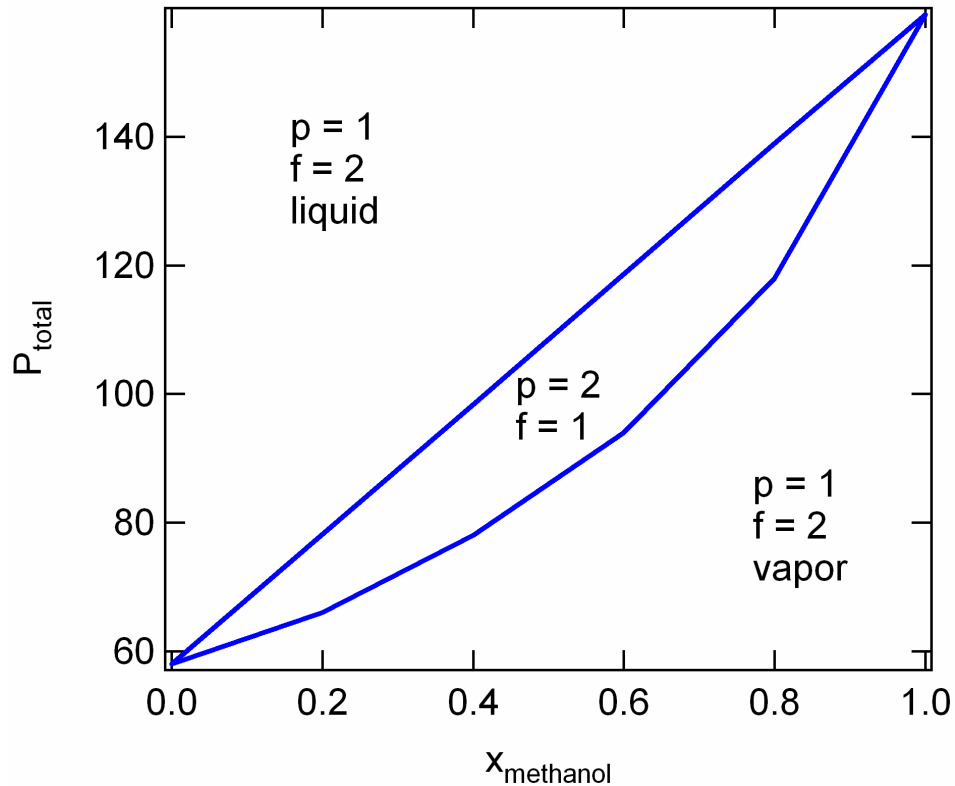
$$P_{\text{total}} (P_2^* - P_1^*) - P_{\text{total}} \left(\frac{P_2^*}{y_2} \right) = - \left(\frac{P_1^* P_2^*}{y_2} \right)$$

$$P_{\text{total}} \left(\frac{P_2^* y_2}{y_2} - \frac{P_2^*}{y_2} - P_1^* \right) = - \left(\frac{P_1^* P_2^*}{y_2} \right)$$

$$P_{\text{total}} = \left(\frac{P_1^* P_2^*}{\left(P_1^* y_2 - P_2^* (y_2 - 1) \right)} \right)$$

y_{methanol}	P_{total}
1.0	159
0.8	118
0.6	94
0.4	78
0.2	66
0.0	58

- d. Draw the two-component composition (z_{methanol})/pressure diagram. Label the number of phases (p) and degrees of freedom (f) from the Gibbs phase rule in each region of the diagram.



- e. For $z_2 = 0.5$ calculate the vapor pressure above the solution when it begins to boil.

Solution:

When the solution begins to boil it is still essentially all in the liquid phase. Thus,

$$P_{\text{total}} = x_1 P_1^* + x_2 P_2^* = x_{\text{ethanol}} P_{\text{ethanol}}^* + x_{\text{methanol}} P_{\text{methanol}}^* \\ = 0.5(58 \text{ torr}) + 0.5(159 \text{ torr}) = 108.5 \text{ torr}$$

- f. For $z_2 = 0.5$ calculate the vapor pressure above the solution when the last drop of solution is vaporized.

Solution:

$$P_{\text{total}} = \frac{P_1^* P_2^*}{\left(P_1^* y_2 - P_2^* (y_2 - 1) \right)} \\ = \frac{58(159)}{\left(58(0.5) - 159(0.5) \right)} \text{ torr} \\ = 90.3 \text{ torr}$$

- g. Using the lever rule determine the composition and the relative amount of both liquid and vapor when the vapor pressure is the average of the vapor pressure in parts e. and f.. In other words determine x_2 , y_2 , and $n^{\text{liquid}}/n^{\text{vapor}}$ when the vapor pressure is halfway between the pressure in parts e. and f.

Solution: the average vapor pressure is 99.4 torr. Assuming $z = 0.5$ we can determine x_2 and y_2 at this vapor pressure and apply the lever rule.

$$x_2 = \frac{P_{\text{total}} - P_1^*}{P_2^* - P_1^*} = \frac{99.4 - 58}{159 - 58} = 0.41$$

and

$$y_2 = \frac{P_2}{P_{\text{total}}} = \frac{x_2 P_2^*}{P_{\text{total}}} = \frac{0.41(159)}{99.4} = 0.654$$

Using the lever rule:

$$\frac{n_{\text{vapor}}}{n_{\text{liquid}}} = \frac{z - x_2}{y_2 - z} = \frac{0.5 - 0.41}{0.65 - 0.5} = 0.73$$

2. Given the following data construct a phase diagram for H_2O .

$T_{\text{fus}} = 273.15 \text{ K}$	$\Delta_{\text{fus}}H = 6.0 \text{ kJ/mol}$
$T_{\text{vap}} = 373.15 \text{ K}$	$\Delta_{\text{vap}}H = 40.65 \text{ kJ/mol}$
$\rho_{\text{ice}} = 0.917 \text{ gm/cm}^3$	$\rho_{\text{water}} = 1.000 \text{ gm/cm}^3$
$C_p(\text{water}) = 75.3 \text{ J/mol}\cdot\text{K}$	$C_p(\text{vapor}) = 33.6 \text{ J/mol}\cdot\text{K}$
Triple point $T = 273.16 \text{ K}$	$P = 0.006 \text{ bar}$
Critical point $T_c = 647.3 \text{ K}$	$P_c = 218 \text{ bar}$

- a. In reality $\Delta_{\text{vap}}H$ is a function of temperature. Therefore, the Clapeyron equation is not accurate over a wide temperature range. To illustrate this point we consider the critical point. We know that $\Delta_{\text{vap}}H$ should approach zero as we approach the critical point. Using the temperature dependence of $\Delta_{\text{vap}}H$ estimate the critical temperature based on the known $\Delta_{\text{vap}}H$ at the normal boiling point of water. How large is the error? Now using the experimental critical temperature and $\Delta_{\text{vap}}H$ at 373.15 K estimate the critical pressure. Is your estimate better or worse than your estimate of the critical temperature?

Solution: estimate of the critical temperature.

$$\Delta_{\text{vap}}H(T_c) = \Delta_{\text{vap}}H(T_{\text{boil}}) + \Delta_{\text{vap}}C_p(T_c - T_{\text{boil}})$$

$$\begin{aligned} \text{where } \Delta_{\text{vap}}C_p &= C_p(\text{vapor}) - C_p(\text{water}) \\ &= (33.6 - 75.3) \text{ J/mol-K} \\ &= -41.7 \text{ J/mol-K} \end{aligned}$$

At the critical point $\Delta_{\text{vap}}H(T_c) = 0$

$$\begin{aligned} T_c &= T_{\text{boil}} - \frac{\Delta_{\text{vap}}H(T_{\text{boil}})}{\Delta_{\text{vap}}C_p} \\ &= 373 \text{ K} + \frac{40,650 \text{ J/mol}}{41.7 \text{ J/mol-K}} \\ &= 1347 \text{ K} \end{aligned}$$

The calculated value is ~ 700 K too high since the true critical temperature is given as 647.3 K.

The critical pressure can be estimated using the Clausius-Clapeyron equation.

$$\frac{\Delta_{\text{vap}}H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) = \ln \left(\frac{P_2}{P_1} \right)$$

or

$$\begin{aligned} P_2 &= P_1 \exp \left\{ \frac{\Delta_{\text{vap}}H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \right\} \\ &= (1 \text{ bar}) \exp \left\{ \frac{40,650 \text{ J/mol}}{8.31 \text{ J/mol-K}} \left(\frac{1}{373} - \frac{1}{674} \right) \right\} \\ &= 349 \text{ bar} \end{aligned}$$

This value can be compared with the experimental value of 218 bar. This value too is an overestimate (because we have not taken into account the fact that $\Delta_{\text{vap}}H$ is temperature dependent and is decreasing with temperature).

- b. Starting with the experimental triple point temperature and pressure calculate the temperature of fusion at 1 bar. How large is the error compared to experiment?

Solution: To calculate the temperature of fusion at 1 bar of pressure we use the Clapeyron equation.

$$\frac{\Delta_{fus}H}{\Delta V} \ln\left(\frac{T_2}{T_1}\right) = P_2 - P_1$$

$$T_2 = T_1 \exp\left\{\frac{\Delta P \Delta V}{\Delta_{fus}H}\right\}$$

$$= (273.16 \text{ K}) \exp\left\{\frac{(1 \text{ bar} - 0.006 \text{ bar})(-0.0016 \text{ L/mol})}{60 \text{ L-bar/mol}}\right\}$$

$$= 273.15 \text{ K (exact agreement)}$$

- c. Calculate the solid-liquid coexistence curve by calculating the pressure at the following temperatures 273.14, 273, and 272.3 using the normal melting point as a reference point.

Solution:

For the solid liquid line we use

$$P = P^* + \Delta_{fus}H/\Delta_{fus}V \ln(T/T^*)$$

$$\text{We need } \Delta_{fus}V = V^l - V^s = M/\rho^l - M/\rho^s = M(1/\rho^l - 1/\rho^s)$$

$$\Delta_{fus}V = 18 \text{ gm/mole}(1/1.00 - 1/0.917)\text{cm}^3/\text{gm}(1\text{L}/1000\text{cm}^3) = -0.0016 \text{ L/mole}$$

In order to obtain units of bar for the second term we must convert $\Delta_{fus}H$ to L bar/mole.

$$\Delta_{fus}H = 6,000 \text{ J/mol} = 60 \text{ L bar/mol}$$

$$\Delta_{fus}H/\Delta_{fus}V = 60 \text{ L bar/mol}/(-0.0016 \text{ L/mol}) = 37,500 \text{ bar}$$

Starting at the triple point

$$P = 0.006 - 37,500 \ln(T/273.16)$$

$$P = 1.0 - 37,500 \ln(T/273.15)$$

T	P
273.16	0.006
273.15	1.0
273.14	2.37
273.13	3.74
273.12	5.11
273.11	6.5
273.10	7.8
273.05	14.7
273.0	21.5
272.9	35.3
272.8	49.0
272.7	62.8
272.6	76.5
272.5	90.4
272.4	104.0
272.3	117.8

- d. Calculate the solid-vapor coexistence curve by calculating the pressure at the following temperatures 270, 260, and 240 K using triple point data as a reference point.

Solution:

The solid-vapor coexistence curve

$$P = P^* \exp\left\{ \frac{\Delta_{\text{vap}}H}{R} \left[\frac{1}{T^*} - \frac{1}{T} \right] \right\}$$

$$P = 0.006 \exp\left\{ \frac{46,650 \text{ J/mol}}{8.314 \text{ J/mol}\cdot\text{K}} \left[\frac{1}{273.16} - \frac{1}{T} \right] \right\}$$

$$P = 0.006 \exp\left\{ 5,610 \text{ K} \left[\frac{1}{273.16} - \frac{1}{T} \right] \right\}$$

T	P
273.16	0.006
270.0	0.0047
260.0	0.0021
240.0	2.2e-4
220.0	4.1e-5

- e. Calculate the liquid-vapor coexistence curve by calculating the pressure at the following temperatures 280, 310, 340, 373.15, 450, 600, 647.3. The reference point and magnitude of $\Delta_{\text{vap}}H$ depends on temperature. The critical point temperature and pressure and $\Delta_{\text{vap}}H$ estimated at the critical temperature are to be used to the 600 K and T_c points. The $\Delta_{\text{vap}}H$ calculated at the freezing point of water and triple point data are to be used below 340 K. From 340 K to 450 K use the data from the normal boiling point of water as the reference.

Solution:

The liquid vapor phase curve is given by

But in reality $\Delta_{\text{vap}}H$ is a function of temperature so let's calculate $\Delta_{\text{vap}}H$ at 273 K

$$\Delta_{\text{vap}}H(273.15) = \Delta_{\text{vap}}H(373.15) + \Delta C_p(273.15 - 373.15)$$

$$\Delta_{\text{vap}}H(273.15) = 40,650 \text{ J/mol} + (-42.1 \text{ J/mol}\cdot\text{K})(-100 \text{ K})$$

$$\Delta_{\text{vap}}H(273.15) = 44,860 \text{ J/mol}$$

$$P = P^* \exp\left\{ \frac{\Delta_{\text{vap}}H}{R} \left[\frac{1}{T^*} - \frac{1}{T} \right] \right\}$$

$$P = 0.006 \exp\left\{ \frac{44,860 \text{ J/mol}}{8.314 \text{ J/mol}\cdot\text{K}} \left[\frac{1}{273.16} - \frac{1}{T} \right] \right\}$$

$$P = 0.006 \exp\left\{ 5,390 \left[\frac{1}{273.16} - \frac{1}{T} \right] \right\}$$

Up to about 330 K

Above 330 K we used

$$P = 1.0 \exp\left\{ \frac{40,650 \text{ J/mol}}{8.314 \text{ J/mol}\cdot\text{K}} \left[\frac{1}{373.15} - \frac{1}{T} \right] \right\}$$

$$P = 1.0 \exp\left\{ 4,900 \text{ K} \left[\frac{1}{373.15} - \frac{1}{T} \right] \right\}$$

Above 500 K we used

$$\Delta_{\text{vap}}H(500.0) = \Delta_{\text{vap}}H(373.15) + \Delta C_p(500.0 - 373.15)$$

$$\Delta_{\text{vap}}H(500.0) = 40,650 \text{ J/mol} + (-42.1 \text{ J/mol}\cdot\text{K})(500.0 - 373.15)\text{K}$$

$$\Delta_{\text{vap}}H(500.0) = 35,300 \text{ J/mol}$$

$$P = 1.0 \exp \{35,300 \text{ J/mol}/8.314 \text{ J/mol}\cdot\text{K} [1/373.15 - 1/T]\}$$

$$P = 1.0 \exp \{4,250 \text{ K} [1/373.15 - 1/T]\}$$

Above 600 K we used

$$\Delta_{\text{vap}}H(600.0) = \Delta_{\text{vap}}H(373.15) + \Delta C_p(600.0 - 373.15)$$

$$\Delta_{\text{vap}}H(600.0) = 40,650 \text{ J/mol} + (-42.1 \text{ J/mol}\cdot\text{K})(600.0 - 373.15)\text{K}$$

$$\Delta_{\text{vap}}H(600.0) = 31,100 \text{ J/mol}$$

$$P = 1.0 \exp \{31,100 \text{ J/mol}/8.314 \text{ J/mol}\cdot\text{K} [1/373.15 - 1/T]\}$$

$$P = 218 \exp \{3,740 \text{ K} [1/647.3 - 1/T]\}$$

T	P
273.16	0.006
280.0	0.01
290.0	0.019
300.0	0.035
310.0	0.062
320.0	0.107
330.0	0.180
340.0	0.277
350.0	0.419
360.0	0.618
370.0	0.849
373.15	1.0
380.0	1.26
400.0	2.41
450.0	9.4
500.0	39.7
600.0	138.0
647.3	218.0

- f. Plot the three curves on a P vs. T plot and on a log(P) vs. log(T) plot. Include the triple point on the plot.

