

### Tutorial Sheet 7: Thermodynamics of phase equilibrium

1. The *Clapeyron* equation is used to represent the melting, sublimation and vaporisation lines. For two arbitrary phases A and B, it is written as:

$$\frac{dP}{dT} = \frac{L}{T(v_A - v_B)}$$

(a) Consider the melting (or fusion) equilibrium line in a typical phase diagram. For ice and water at 0°C, the specific volumes and the latent heat are given by:

$$v_{\text{ice}} = 1.09 \times 10^{-3} \text{ m}^3/\text{kg} \quad v_{\text{water}} = 1.00 \times 10^{-3} \text{ m}^3/\text{kg} \quad L_{\text{melt}} = 333 \text{ kJ/kg}$$

Calculate the change of saturated pressure with melting temperature in bar/K. What does this finding tell you about the melting line on the *PT* diagram?

(b) Consider now the boiling equilibrium line in a typical phase diagram. At a temperature of 100°C the saturated vapour pressure of water is 1.01325 bar. For liquid water and water vapour at these conditions, the specific volumes and the latent heat are given by:

$$v_{\text{vap}} = 1.673 \text{ m}^3/\text{kg} \quad v_{\text{water}} = 1.04 \times 10^{-3} \text{ m}^3/\text{kg} \quad L_{\text{boil}} = 2257 \text{ kJ/kg}$$

Calculate the change of saturated pressure with boiling temperature in bar/K. How does this compare with the gradient obtained in question (a)?

(c) Use the calculated gradient in question (b) (assume it is a constant) to estimate the boiling point of water at an absolute pressure of 2 bar. Is this a reasonable estimate? Compare with the value calculated using the Clausius-Clapeyron equation (assuming negligible liquid molar volume and ideal vapour):

$$\frac{dP}{dT} = \frac{LP}{RT^2}$$

2. 150 moles of benzene are held in a closed container of volume  $V = 1 \text{ m}^3$  at a pressure of 1 atm. Under these conditions, benzene separates into a liquid and a vapour phase in equilibrium with each other. The molar volume of liquid benzene is  $9.6 \times 10^{-5} \text{ m}^3/\text{mol}$ .

(a) If the vapour pressure ( $P^{\text{sat}}$ ) of benzene is given by the Antoine equation below, with pressure in bar and temperature in K, calculate the boiling temperature of benzene at 1 atm.

$$\ln(P^{\text{sat}}) = 10.882 - \frac{3823.79}{T - 1.461}$$

(b) Calculate the mole fraction of vapour in the system. Assume that the vapour phase behaves as an ideal gas.

# CP203 - Thermodynamics Tutorial Solutions Week 7

## Group 17

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1.

a)

$$\begin{aligned}\frac{\partial P}{\partial T} &= \frac{L}{T} \frac{1}{(V_a - V_b)} \\ &= \frac{333}{T} \frac{1}{(10^{-3} - 1.09 \times 10^{-3})} \\ &= \frac{333}{273.15(10^{-3} - 1.09 \times 10^{-3})} \\ &= -13545.67 \text{ kPa K}^{-1}\end{aligned}$$

$$\boxed{\frac{\partial P}{\partial T} = -135.5 \text{ Bar K}^{-1}}$$

Because the answer is negative, the pressure will decrease as temperature increases. This indicates that the density of liquid water is greater than that of ice which we know to be true because ice floats.

b)

$$\begin{aligned}\frac{\partial P}{\partial T} &= \frac{L}{T} \frac{1}{(V_a - V_b)} \\ &= \frac{2257}{T} \frac{1}{(1.673 - 1.04 \times 10^{-3})} \\ &= \frac{2257}{373.15(1.673 - 1.04 \times 10^{-3})} \\ &= 3.618 \text{ kPa K}^{-1}\end{aligned}$$

$$\boxed{\frac{\partial P}{\partial T} = 0.0362 \text{ Bar K}^{-1}}$$

This is a much smaller gradient than that of part a. This is because gas is much more compressible than liquid or solid and hence a much smaller pressure change is needed to change the temperature.

c)

$$\begin{aligned}P &= mT + c \\ 1.01325 &= 0.0362(373.15) + c \\ c &= 1.01325 - 0.0362(373.15) \\ c &= -12.495 \\ P &= 0.0362 T - 12.495 \\ T &= \frac{P + 12.495}{0.0362} \\ T &= \frac{2 + 12.495}{0.0362} \\ \boxed{T} &= 400 \text{ K}\end{aligned}$$

This is assuming linearity which is not the case and hence the answer will not be accurate. Using a differential equation we can find a more accurate value. This is shown below:

$$\begin{aligned}
\frac{dP}{dT} &= \frac{LP}{RT^2} \\
\frac{1}{LP} dP &= \frac{1}{RT^2} dT \\
\frac{1}{L} \int \frac{1}{P} dP &= \frac{1}{R} \int \frac{1}{T^2} dT \\
\frac{1}{L} \cdot \ln\left(\frac{P_2}{P_1}\right) &= -\frac{1}{R} \left[\frac{1}{T}\right]_{T_1}^{T_2} \\
-\frac{R}{L} \cdot \ln\left(\frac{P_2}{P_1}\right) &= \left[\frac{1}{T}\right]_{T_1}^{T_2} \\
\frac{1}{T_2} &= -\frac{R}{L} \cdot \ln\left(\frac{P_2}{P_1}\right) + \frac{1}{T_1} \\
T_2 &= \left(-\frac{R}{L} \cdot \ln\left(\frac{P_2}{P_1}\right) + \frac{1}{T_1}\right)^{-1} \\
T_2 &= \left(-\frac{8.3145}{40626} \cdot \ln\left(\frac{2}{1.01325}\right) + \frac{1}{393.15}\right)^{-1} \\
\boxed{T_2} &= 393.59 \text{ K}
\end{aligned}$$

This value is more accurate than the linear model because we calculate it using integration which doesn't assume that the relationship is linear. Note that the units of  $L$  have been changed to be consistent with the units of the gas constant meaning that we have multiplied the value by the molecular weight of water. This allows for a dimensionless ratio.

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**2.**  
a)

$$\begin{aligned}
\ln(P^{\text{sat}}) &= 10.882 - \frac{3823.79}{T - 1.461} \\
\frac{3823.79}{T - 1.461} &= 10.882 - \ln(P^{\text{sat}}) \\
T &= \frac{3823.79}{10.882 - \ln(P^{\text{sat}})} + 1.461 \\
T &= \frac{3823.79}{10.882 - \ln(1.01325)} + 1.461 \\
T &= 353.27 \text{ K} \\
\boxed{T} &= 80.12^\circ\text{C}
\end{aligned}$$

This lines up with the empirical data obtained from the internet. Part b is shown below:

b)

$$Pv_v = RT$$

$$v_v = \frac{RT}{P}$$

$$v_v = \frac{8.3145 \cdot 352.27}{1.01325 \times 10^5}$$

$$v_v = 0.029$$

$$v_t = x_L v_L + x_v v_v$$

$$v_t = x_L v_L + (1 - x_L) v_v$$

$$v_t = v_v - v_v x_L + v_L x_L$$

$$v_t - v_v = v_L x_L - v_v x_L$$

$$v_t - v_v = (v_L - v_v) x_L$$

$$x_L = \frac{v_t - v_v}{(v_L - v_v)}$$

$$x_v = 1 - x_L$$

$$x_v = 1 - \frac{\frac{1}{150} - 0.029}{(9.6 \times 10^{-5} - 0.029)}$$

$$\boxed{x_v = 0.227}$$