Question 10

A. Assuming a linear boundary between vapor and solid, use the Clausius-Clapeyron equation

$$\begin{aligned}\frac{dP}{dT} &= \frac{s^V - s^S}{v^V - v^S} \\ &= \frac{9.1562 - (-1.2210)}{206.132 - 0.0010908} \\ &= 0.0503[kPa/K]\end{aligned}$$

Find the y-intercept, b:

$$\begin{aligned}b &= 0.6113 - 0.0503(273.16) \\ &= -13.128648[kPa]\end{aligned}$$

Plug in the temperature, -6 C:

$$\begin{aligned}P &= 0.0503(273.15 - 6) - 13.128648 \\ &= 0.317645[KPa]\end{aligned}$$

since $0.4375 > 0.317645$, the system is in the solid phase.

B. Assuming a linear boundary between liquid and solid, use the Clausius-Clapeyron equation

$$\begin{aligned}\frac{dP}{dT} &= \frac{s^L - s^S}{v^L - v^S} \\ &= \frac{0 - (-1.2210)}{0.001000 - 0.0010908} \\ &= -13447.137[kPa/K]\end{aligned}$$

Find the y-intercept, b:

$$\begin{aligned}b &= 0.6113 + 13447.137(273.16) \\ &= 3.67E6[kPa]\end{aligned}$$

Plug in the temperature, -6 C:

$$\begin{aligned}P &= -13447.137(273.15 - 6) + 3.67E6 \\ &= 77597.35[KPa]\end{aligned}$$

An increase of 77597.03 KPa is needed.

C.

$$\begin{aligned}Pressure &= \frac{Force}{Area} \\ 77597350 &= \frac{100 * 9.81}{0.250(width)} \\ width &= 0.00005[m]\end{aligned}$$

In making such a calculation, we have assumed the linear dependence of saturation pressure on temperature, which in reality may not be the case.

Question 11

A. Solve for T,P:

$$\begin{aligned} 15.16 - \frac{3063}{T} &= 18.70 - \frac{3754}{T} \\ T &= 195.198[K] \\ P &= 59535.9[Pa] \end{aligned}$$

B. Latent heat for solid to vapour:

$$q_{VS} = T(s^V - s^S)$$

Using

$$\frac{dP}{dT} = \frac{s^V - s^S}{v^V - v^S}$$

We write

$$q_{VS} = (v^V - v^S)T\frac{dP}{dT} = T(s^V - s^S)$$

where

$$\frac{dP}{dT} = \frac{3754P_r e^{18.7} e^{-3754/T}}{T^2}$$

Noting $v^V >> v^L >> v^S$ and $v^V = \frac{RT}{P}$

$$\begin{aligned} q_{VS} &= v^V \frac{3754P_r e^{18.7} e^{-3754/T}}{T} \\ &= \frac{R}{P} 3754P_r e^{18.7} e^{-3754/T} \\ &= 31212.5[J/mol] \end{aligned}$$

Latent heat for liquid to vapour:

$$\begin{aligned} q_{VL} &= v^V \frac{3063P_r e^{15.16} e^{-3063/T}}{T} \\ &= \frac{R}{P} 3063P_r e^{15.16} e^{-3063/T} \\ &= 25467.1[J/mol] \end{aligned}$$

C. Latent heat for solid to liquid:

$$\begin{aligned} q_{VS} &= T(s^V - s^S) \\ q_{VL} &= T(s^V - s^L) \\ q_{LS} &= q_{VS} - q_{VL} = T(s^L - s^S) \\ &= 31212.5 - 25467.1 = 5746.4[J/mol] \end{aligned}$$

Question 13

A. The contraints

$$\Delta(V_c + V_R) = 0$$
$$\Delta(N_{ic}) = 0$$
$$\Delta(U_c + U_R) = 0$$

Assume that the solvent's volume does not change (incompressible) as it changes from a pure liquid to a weak solution, we have

$$\begin{aligned}\Delta(V_c) &= V_B^i - V_B^f + V_A^i - V_A^f \\ &= V_A^i = V_A^i(T, P)\end{aligned}$$

B. Apply the second postulate $\Delta S_c + \Delta S_R \geq 0$ and relying upon the assumption that the change in entropy is due solely to the dissolution of A into B, we write

$$\begin{aligned}\Delta S_c &= S_B^i - S_B^f + S_A^i - S_A^f \\ &= S_A^i - S_A^f = N_2 R \frac{\ln U^{3/2} V_A^i(T, P)}{N_2^{5/2}}\end{aligned}$$