Problem Set 4 Solutions

1. Chapter 7.4 in DeHoff discusses triple points. Starting with equations 7.43 and 7.44, DeHoff derives equation 7.46. Starting with equations 7.43 and 7.44, demonstrate whether or not you can derive equation 7.46. Do so by showing your full derivation.

Starting with equations 7.43 and 7.44 and assuming we are at the triple point, we obtain the following:

\[
P_T = A^S e^{-\frac{\Delta H_s}{RT}} \quad [\text{a}] \quad \text{For solid(s) vapor pressure}
\]

\[
P_T = A^V e^{-\frac{\Delta H_v}{RT}} \quad [\text{b}] \quad \text{For liquid vapor pressure}
\]

Equate equations [\text{a}] and [\text{b}], we have:

\[
A^S e^{-\frac{\Delta H_s}{RT}} = A^V e^{-\frac{\Delta H_v}{RT}}
\]

\[
\frac{A^S}{A^V} = e^{\frac{\Delta H_v - \Delta H_s}{RT}}
\]

\[
\ln \frac{A^S}{A^V} = \frac{\Delta H_v - \Delta H_s}{RT}
\]

Using [\text{a}]:

\[
P_T = A^S e^{-\frac{\Delta H_s}{RT}}
\]

\[
= A^S e^{-\frac{\Delta H_s}{RT}} \left( \frac{\Delta H_v - \Delta H_s}{RT} \right)
\]

\[
= A^S \left( \frac{\Delta H_v - \Delta H_s}{RT} \right)
\]

\[
= \frac{\Delta H_v - \Delta H_s}{RT}
\]

Now substitute into eqn[\text{b}]

What we see is that DeHoff obtained the correct \( P_T \).
2. Using the vapor pressure and temperature relationships for CaF$_2$($\alpha$), CaF$_2$($\beta$) and CaF$_2$(l), calculate:
   a. The temperatures and pressures of each of the triple points.
b. The normal boiling temperature

c. The molar latent heat of transformation for $\alpha \rightarrow \beta$ transformation.
d. The molar latent heat of melting.

\[
\begin{align*}
\frac{d\Delta H^\text{\text{v}}}{dt} &= \frac{50200}{T^2} - \frac{4.525}{T} = \frac{\Delta H^\text{\text{v}}}{RT^2} \\
\Rightarrow \Delta H^\text{\text{v}} &= R \left[ \frac{50200 - 4.525T}{T^2} \right] \\
\Delta H^\text{\text{v}} &= \Delta H^\text{\text{v}} + \Delta H^\text{\text{v}} \\
\Delta H^\text{\text{v}} &= \Delta H^\text{\text{v}} - \Delta H^\text{\text{v}} \\
&= 8.3144 (53780 - 50200) \\
&= 12765 \text{J}
\end{align*}
\]