Problem Set 5 Solutions

1. Thoroughly state and solve a problem analogous to the problem that was solved in class where we used NaF as the material of interest. Be sure to include the references (not from our books – use another source – e.g., “Smithells Metals Reference Book” referenced in complete form or some other reference) for the material and vapor pressure data you chose and a sketch of a fully labeled Pressure versus Temperature equilibrium phase diagram. State and justify any assumptions you. You are the instructor, so include a complete and understandable posed question and solution to your problem.

- Pose question with stated materials system - 2pt
- Vapor pressures with units and with complete reference - 2pts
- Sketch of pressure versus temperature diagram - 5pts
- State and justify any assumptions - 2pts
- Find all parameters that was found with NaF with complete solutions:
  - T_{tp} & P_{tp} (2pts)
  - T_{normal, boil} (1pts)
  - All \Delta H_{c->v} (4pts)
  - \Delta H_{s->L} (2pts)
  - All \Delta C_{c->v} (4pts)
  - \Delta C_{s->L} (2pts)
- Total points: ~26

Note: This is a suggestion only. It is up to the discretion of the grader.
2. At the normal boiling temperature of iron, $T_b = 3330\, \text{K}$, the rate of change of the vapor pressure of liquid iron with temperature is $3.72 \times 10^{-3} \, \text{atm/K}$. Calculate the molar latent heat of boiling of iron at 3330 K.

At the normal $T_b$ of Fe, $T_b = 3330\, \text{K}$, the rate of change of the vapor pressure of liquid Fe with temp is $\frac{dP}{dT} = 3.72 \times 10^{-3} \, \text{atm/K}$. Calculate the molar latent heat of boiling of Fe, $\Delta H^\circ_v$, at $T = 3330\, \text{K}$.

\[
\frac{dP}{dT} = \frac{\Delta H}{RT^2} \Rightarrow \frac{dP}{dT} = \frac{\Delta H_P}{RT^2}
\]

\[
\frac{dP}{dT} = \frac{\Delta H}{RT^2} \Rightarrow \frac{\Delta P}{\Delta T} = \frac{\Delta H}{RT^2} \cdot P
\]

Assume that $P = 1\, \text{atm}$

\[
\Delta H = \frac{RT^2}{P} \frac{\Delta P}{\Delta T} = \frac{(0.08206 \, \text{atm} \cdot \text{L/mol} \cdot \text{K}) (3330\, \text{K})^2}{1 \, \text{atm}} \times (3.72 \times 10^{-3} \, \text{atm} \cdot \text{K})
\]

\[
= 3385.03 \, \text{atm} \cdot \text{L} \times 101.325 \, \frac{\text{J}}{\text{atm} \cdot \text{L}}
\]

\[
= 342,988 \, \text{J}
\]
3. Measurements of the saturated vapor pressure of liquid NdCl₅ give 0.3045 atm at 478 K and 0.9310 at 520 K. Calculate the normal boiling temperature of NdCl₅. Assume that the curve fitting equation for the vapor pressure (in atm) of NdCl₅ is given by:

\[
\ln[p] = \frac{A_L}{T} + C_L
\]

Approach 1:
Substitute into \( \ln P \) and get \( C_L \):

\[
C_L = \ln P - \frac{U_C}{T_C} \\
= \ln 0.3045 - \frac{-66.14}{478} \\
= 12.65
\]

For \( T_b \):

\[
\ln (1) = 0 = \frac{-66.14}{T_b} + 12.65
\]

Solving:

\[
T_b = \frac{66.14}{12.65} = 5.23 K
\]
Approach 2:

\[
\text{What is } T_b \text{?}
\]

Use vapor pressure Eqns:

\[
\ln p = \frac{-A}{T} + B
\]

Two Eqns & Two Unknowns

\[
\frac{\ln 0.345}{T_1} = \frac{A}{B} + B
\]

\[
\ln 0.931 = \frac{-A}{B} + B
\]

\[
D = \begin{pmatrix}
  a_1 & b_1 \\
  a_2 & b_2
\end{pmatrix} = \begin{pmatrix}
  \frac{\ln 0.345}{T_1} & 1 \\
  \frac{1}{T_1} & 1
\end{pmatrix} = \begin{pmatrix}
  -0.999 & 1 \\
  1 & 1
\end{pmatrix}
\]

\[
D_B = \frac{a_1}{a_2} \frac{b_1}{b_2} = \frac{\ln 0.345}{\ln 0.931} = \frac{\ln 0.345 - \ln 0.931}{\ln 1.000 - \ln 0.931} = 1.12
\]

\[
D_B = \frac{a_1}{a_2} \frac{b_1}{b_2} = \left| \frac{\ln 0.345}{\ln 0.931} \right| = \frac{\ln 0.345}{\ln 0.931} = \frac{-0.999 \ln 0.345 + \frac{1}{T_1} \ln 0.345}{\frac{1}{T_1} \ln 0.345 - 2.4 \times 10^{-3}}
\]

\[
A = \frac{D_B}{D} = \frac{1.12}{-1.69 \times 10^{-4}} = 6.61 \times 10^4
\]

\[
B = \frac{D_B}{D} = \frac{1.265}{-1.69 \times 10^{-4}} = 7.30 \times 10^4
\]

\[
\frac{A_0}{T_0} = \frac{-6.014}{12.65}
\]

\[
T_B = \frac{6.014}{12.65} = 472 \text{ K}
\]
4. In figure 1, we see that $\Delta H_{\text{phase}1 \to \text{phase}2} \neq f(T)$. Yet in figure 2, we see that $\Delta H_{\text{phase}1 \to \text{phase}2} = f(T)$ when thinking in terms of the Clausius and Clausius-Clapeyron relations. Use the concepts of the figures to answer why there is a difference? Sketch a series of plots to prove that both cases are correct.

Fig. 1 is somewhat misleading. Each $\Delta H$ is not a function of temperature or pressure at a set pressure and temperature. However, $\Delta H$ will have different values at different temperatures and pressures as long as the equilibrium line in the $P$ versus $T$ diagram (fig. 2) is not vertical.
5. Given that the volume change in mixing of a solution obeys the relation:

\[ \Delta V_{\text{mix}} = aX_1X_2^2 \left( \frac{\text{mL}}{\text{Mol}} \right) \text{ where } a = 2.7 \]

a. Derive expressions for the partial molar volumes of each of the components as a function of composition. Be sure to fully simplify your answers.

\[ \Delta \bar{B}_2 = \Delta B_{\text{mix}} + (1-X_2) \frac{d\Delta B_{\text{mix}}}{dX_2} \quad (8.28) \]

\[ \Delta \bar{B}_1 = \Delta B_{\text{mix}} + (1-X_1) \frac{d\Delta B_{\text{mix}}}{dX_1} \quad (8.29) \]

\[ \frac{d\Delta B_{\text{mix}}}{dX_2} = -(9.30)X_1X_2 = 1 \quad \Rightarrow \quad \frac{dX_1}{dX_2} = -1 \]

Also:

\[ \Delta B_{\text{mix}} = X_1 \Delta \bar{B}_1 + X_2 \Delta \bar{B}_2 \quad (8.24) \]

Expressing \( \Delta V_{\text{mix}} \): Let \( a=2.7 \)

\[ \Delta V_{\text{mix}} = 2.7 X_1 X_2^2 = a X_2^2 (-X_1) \]

\[ = a X_2^2 - a X_2^3 \]

\[ \therefore \frac{d\Delta V_{\text{mix}}}{dX_2} = 2aX_2 - 3aX_2^2 \]

And \( \frac{d\Delta V_{\text{mix}}}{dX_1} = - \frac{d\Delta V_{\text{mix}}}{dX_2} = 3aX_2^2 - 2aX_2 \)
\[ \Delta V_2 = \Delta B_{\text{mix}} + (1-X_2) \frac{\partial \Delta B_{\text{mix}}}{\partial X_2} \]
\[ = a X_2^2 - a X_2^3 + (1-X_2)(2a X_2 - 3a X_2^2) \]
\[ = a X_1 X_2^2 + X_2 (2a X_2 - 3a X_2^2) \]
\[ = a X_1 (X_2^2 + 2a X_2 - 3X_2^2) \]
\[ = a X_1 (2X_2 - 2X_2^2) \]
\[ = 2a X_1 X_2^2 (1 - X_2) \]
\[ = 2a X_1 X_2^2 \]

\[ \Delta V_1 = \Delta B_{\text{mix}} + (1-X_1) \left( -\frac{\partial \Delta B_{\text{mix}}}{\partial X_2} \right) \]
\[ = a X_1 X_2^2 + (1-X_1)(3a X_2^2 - 2a X_2) \]
\[ = a X_1 X_2^2 + a X_2^2 (3X_2 - 2) \]
\[ = a X_2^2 \left[ X_1 + 3X_2 - 2 \right] \]
\[ = a X_2^2 \left[ X_1 + 3(1-X_1) - 2 \right] \]
\[ = a X_2^2 \left[ 1 - 2X_1 \right] \]

Units in \( \frac{\text{mL}}{\text{Mol}} \)

b. Demonstrate that your result is correct by using it to compute \( \Delta V_{\text{mix}} \), demonstrating that the equation above is recovered.

\[ \text{Check: } \Delta V_{\text{mix}} = X_1 \Delta V_1 + X_2 \Delta V_2 \]
\[ = a X_2^2 X_1^2 (1 - 2X_1) + 2a X_1^2 X_2^2 \]
\[ = a X_2^2 X_1 \left[ 1 - 2X_1 + 2X_1 \right] \]
\[ = a X_2^2 X_1, \text{ which is correct} \]

Units in \( \frac{\text{mL}}{\text{Mol}} \)
c. Use the partial molar volumes computed in part a to demonstrate that the Gibbs-Duhem equation holds for properties in this system. Be sure to fully simplify your answers.

\[
\Delta V_{\text{mix}} = a x_1 x_2^2 \quad \Delta \bar{V}_1 = a x_2^2 (1 - 2x_1) \quad \Delta \bar{V}_2 = 2a x_2 x_2
\]

\[
\sum x_k d \Delta B_k = 0
\]

\[
\therefore x_1 d \Delta \bar{V}_1 + x_2 d \Delta \bar{V}_2 = 0 \quad (1)
\]

\[
d \Delta \bar{V}_1 = d [a x_2^2 (1 - 2x_1)]
\]
\[= 2ax_2 x_2 (1 - 2x_1) - 2a x_2^2 dx_1 \]
\[= 2a x_2 x_2 (1 - 2x_1) + 2a x_2^2 dx_2 \]
\[= 2a x_2 (1 - 2x_1 + x_2) dx_2 \quad (2)
\]

\[
d \Delta \bar{V}_2 = 2a x_2 dx_1^2 + 2a x_2^2 dx_2
\]

\[
= 4a x_2 x_2 dx_1 + 2a x_2 x_2 dx_2 \]
\[= 2ax_1 (x_1 - 2x_2) dx_2 \quad (3)
\]

Substitute Eqs. (2) and (3) into (1):

\[
x_1 2a x_2 (1 - 2x_1 + x_2) dx_2 + x_2 2a x_1 (x_1 - 2x_2) dx_2 = 0
\]

Divide by \( 2a x_2 dx_2 \):

\[
1 - 2x_1 + x_2 - 2x_2 = 0
\]
\[2 - 2(x_1 + x_2) = 0
\]
\[2 - 2 = 0
\]
\[0 = 0
\]

Gibbs-Duhem holds true

Units in \( \frac{\text{mL}}{\text{Mol}} \)
d. Plot $\Delta V_{mix}$ as a function of $X_2$ mathematical program labeling the plot thoroughly. Using Mathematica, the code and resulting plot is below. I plotted $\Delta V_{mix}$ over several values of $a$.

```
a: 0 to 10 plotted at 1 mL/mol increments
```

![Plot](image)

e. Comment and provide insight to your plot.
As $X_2$ of component 2 increases, the change in the volume of mixing increases and maximizes between values of 0.6 and 0.7 of $X_2$. This suggests that component 2 causes the solution to expand or become more active. This may be due to repulsion effects between and among components.

Extra:
Although I did not require you to plot as a function of $a$, I thought it might prove insightful. We observe as $a$ increases, the $\Delta V_{mix}$ increases. This statement seems self-evident since $a$ is positive and is stepped in positive values. A question that comes to mind is, physically, what does $a$ represent. More on this later in the semester.