9.5

a) The interaction energy is

\[ u(x, y, z) = u(x_0, y_0, z_0) + \alpha \left( (x-x_0)^2 + (y-y_0)^2 \right) + \frac{\beta}{2} (z-z_0)^2 \]

\[ \frac{du}{dx} = \frac{\alpha}{2} (x-x_0) \quad \text{and} \quad \frac{d^2u}{dx^2} = \alpha = f(\text{force}) \quad \text{but} \quad \nu = \frac{1}{2\pi} \sqrt{\frac{\alpha}{m}} \quad \text{and similar for} \ y \ \text{and} \ z. \]

Therefore, the ground state energy is

\[ u_0 = u(x_0, y_0, z_0) + \frac{h}{2} (\nu_x + \nu_y + \nu_z) = u(x_0, y_0, z_0) + \frac{h}{4\pi \sqrt{m}} \left( 2\sqrt{\alpha} + \sqrt{\beta} \right) \]

b) So if there are \( M \) lattice sites and \( N \) adsorbed molecules

\[ Q(N, M, T) = \frac{M!}{N!(N-M)!} q^N \]

where \( q_{\text{ads}} = e^{-u(x_0, y_0, z_0)/kT} \)

\[ q_{\text{vib},x} q_{\text{vib},y} q_{\text{vib},z} = \left( \frac{e^{-\frac{h\nu_x}{kT}}}{1-e^{-\frac{h\nu_x}{kT}}} \right) \left( \frac{e^{-\frac{h\nu_y}{kT}}}{1-e^{-\frac{h\nu_y}{kT}}} \right) \left( \frac{e^{-\frac{h\nu_z}{kT}}}{1-e^{-\frac{h\nu_z}{kT}}} \right) = \left( \frac{e^{-\Theta_x/2T}}{1-e^{-\Theta_x/2T}} \right) \left( \frac{e^{-\Theta_y/2T}}{1-e^{-\Theta_y/2T}} \right) \left( \frac{e^{-\Theta_z/2T}}{1-e^{-\Theta_z/2T}} \right) \]

where \( \Theta_x = \frac{h\nu_x}{k} \) and \( \Theta_y = \frac{h\nu_y}{k} \)

\[ \Theta = \frac{h\nu_z}{k} = \frac{h}{2\pi \sqrt{m}} \sqrt{\frac{\beta}{m}} \]

c) To develop the adsorption isotherm, equate the chemical potential of the adsorbed molecules to those in an ideal gas. So the starting point is to calculate the chemical potential of the adsorbed molecules.

\[ \ln Q(N, M, T) = \ln M! - \ln N! - \ln (M-N)! + N \ln q_{\text{ads}} = \]

\[ = M \ln M - M \ln N + N \ln N - (M-N) \ln (M-N) + (M-N) + N \ln q_{\text{ads}} = \]

\[ = M \ln M - N \ln N - (M-N) \ln (M-N) + N \ln q_{\text{ads}} \]

\[ A = -kT \ln Q = -MkT \ln M + NkT \ln N + (M-N)kT \ln (M-N) - NkT \ln q_{\text{ads}} = \]

\[ \mu_{\text{ads}} = \left( \frac{\partial A}{\partial N} \right)_{M,T} = kT \ln N + kT - kT \ln (M-N) + kT \frac{M-N}{M-N} (1) - kT \ln q_{\text{ads}} = \]

\[ = kT \ln N - kT \ln (M-N) - kT \ln q_{\text{ads}} = \mu_{\text{gas}} = -kT \ln q_{\text{gas}} \]

\[ \frac{N}{M-N} = \frac{q_{\text{ads}}}{q_{\text{gas}}} \]

The usual way of reporting adsorption isotherms is as fractional coverage (the fraction of the total adsorption sites \( M \) with adsorbed molecules). That is, the fractional coverage is
Therefore, the fractional coverage is
\[
\frac{N}{M} = \left( \frac{q_{\text{ads}}}{q_{\text{gas}}} \right) - \frac{1}{1 + \frac{q_{\text{gas}}}{q_{\text{ads}}}}
\]

Now \( q_{\text{ads}} \) is independent of pressure, while in the gas (assuming it is ideal) so that
\[
q_{\text{gas}} = \left( \frac{2\pi mkT}{h^2} \right)^{3/2}
\]
\[
V = \left( \frac{2\pi mkT}{h^2} \right)^{3/2} \frac{N_{\text{gas}} kT}{P}
\]

Putting everything together, we then have for the fractional coverage that
\[
\frac{N}{M} = \frac{\left( \frac{q_{\text{ads}}}{q_{\text{gas}}} \right)}{\left( 1 + \frac{q_{\text{gas}}}{q_{\text{ads}}} \right)} = \frac{1}{1 + e^{-\frac{2\pi mkT}{h^2}}} \frac{\left( \frac{2\pi mkT}{h^2} \right)^{3/2} \frac{N_{\text{gas}} kT}{P}}{e^{-\Theta_{2}/T}}
\]

This form of the isotherm is referred to as a Langmuir isotherm. As the pressure becomes larger, the denominator decreases in value, so the extent of adsorption (that is, fractional coverage), increases as would be expected. The temperature dependence is a bit harder to discern, but a careful analysis shows that as the temperature increases, the denominator increases in value, so the extent of adsorption decreases, again as expected.
9.6

This is for copper

\[ \text{TT} := 100 \quad \theta := 500 \quad \text{Guessed value of } \theta \]

Reduced heat capacity at 100 K

\[ \text{Cpr} := \frac{16.108}{8.314} \]

given

\[ \text{Cpr} = 3 \left( \frac{\theta}{\text{TT}} \right)^2 \frac{\exp \left( \frac{-\theta}{\text{TT}} \right)}{\left( 1 - \exp \left( \frac{-\theta}{\text{TT}} \right) \right)^2} \]

\[ \theta := \text{find}(\theta) \quad \theta = 234.032 \]

\[ i := 1, 2, \ldots, 11 \quad T_i := 100 + 100i \]

\[ \text{Cp}_i := 3 \left( \frac{\theta}{T_i} \right)^2 \frac{\exp \left( \frac{-\theta}{T_i} \right)}{\left( 1 - \exp \left( \frac{-\theta}{T_i} \right) \right)^2} \]

\[ \text{TT} = 1200 \]

\[ \text{CpT} := 8.314 \begin{bmatrix} 3 \left( \frac{\theta}{\text{TT}} \right)^2 \frac{\exp \left( \frac{-\theta}{\text{TT}} \right)}{\left( 1 - \exp \left( \frac{-\theta}{\text{TT}} \right) \right)^2} \end{bmatrix} \]

\[ \text{CpT} = 24.863 \]
9.9 a) Einstein model

Silver

\[ M = 107.87 \quad T_T := 830 \quad \Theta_E := 215.0806 \]
\[ k := 1.3807 \times 10^{-23} \quad \Theta_{E_T} := \frac{\Theta_E}{T_T} \quad \mu_e := 1 \]
\[ \ln(n_{\text{sub}}) = \ln(2.955 \times 10^{-7}) \quad \text{at } 830 \text{ K} \]

Given

\[ \ln(n_{\text{sub}}) = \frac{\mu_e}{T_T} + 3 \ln(1 - \exp(-\Theta_{E_T})) + \ln\left[1.88 \times 10^{20} \cdot k \cdot M^{1.5} \cdot (T_T)^{2.5}\right] \]

\[ \mu_e := \text{Find}(\mu_e) \quad \mu_e = -2.316 \times 10^4 \]

\[ \text{PP}(T) := \exp\left[\frac{\mu_e}{T} - 3 \ln\left(1 - \exp\left(-\frac{\Theta_E}{T}\right)\right)\right] + \ln\left[1.88 \times 10^{20} \cdot k \cdot M^{1.5} \cdot (T_T)^{2.5}\right] \]

\[ \text{PP}(1224) = 2.132 \times 10^{-3} \quad \text{PP}(830) = 2.955 \times 10^{-7} \]

\[ t := 0, 0.2, 0.4, 0.6, 0.8, 1.0 \quad T_T := 830 + 20i \quad \text{recipT}_i := \frac{1}{T_i} \]

\[ P_i := \exp\left[\frac{\mu_e}{T_i} - 3 \ln\left(1 - \exp\left(-\frac{\Theta_E}{T_i}\right)\right)\right] + \ln\left[1.88 \times 10^{20} \cdot k \cdot M^{1.5} \cdot (T_i)^{2.5}\right] \]

[Graph showing the relationship between P and 1/T]
Heat of sublimation-Einstein model

\[ \Delta H_{HE}(TTT) := -\mu_e + \frac{-3}{1 - \exp\left[-\left(\frac{\Theta E}{TTT}\right)^{-3}\right]} \left(\frac{\Theta E}{TTT}\right) \exp\left[-\left(\frac{\Theta E}{TTT}\right)\right] = 5.8.314 \cdot TTT \]

\[ \Delta H_{HE}(830) = 3.45 \times 10^4 \]

\[ \Delta H_{i} := -b \cdot 8.314 \cdot c \cdot 8.314 \cdot T_i \]

\[ \Delta H(830) = 2.882 \times 10^5 \]

Results are not very good, as expected by the error in the sublimation pressures.
b) Debye model

\[
\mu \text{D} := -100
\]

\[
\begin{align*}
\text{GG}(z) & := \int_0^z x^2 \ln(1 - e^{-x}) \, dx \left( \frac{3}{z^3} \right) \\
& \quad \text{at } 830 \, K \\
\text{lns}ub & := \text{ln} \left( 2.955 \times 10^{-7} \right)
\end{align*}
\]

Given

\[
\text{lns}ub = \frac{\mu \text{D}}{T_i} + 3 \cdot \text{GG} \left( \frac{\Theta \text{D}}{T_i} \right) + \text{ln} \left[ 1.88 \times 10^{-20} \cdot k \cdot M^1.5 \cdot (T_i)^{2.5} \right] \\
\text{PlnP}_i := \text{ln}(P_i)
\]

\[
\mu \text{D} := \text{Find}(\mu \text{D})
\]

\[
\begin{align*}
\mu \text{D} & := -2.283 \times 10^4 \\
\text{PP}(\text{TR}) & := \exp \left[ \frac{\mu \text{D}}{\text{TR}} + 3 \cdot \text{GG} \left( \frac{\Theta \text{D}}{\text{TR}} \right) + \text{ln} \left[ 1.88 \times 10^{-20} \cdot k \cdot M^1.5 \cdot (\text{TR})^{2.5} \right] \right] \\
\text{PP}(1224) & = 1.903 \times 10^{-3} \\
\text{PP}(830) & = 2.955 \times 10^{-7}
\end{align*}
\]
Heat of Sublimation, Debye Model (Problem 9.11)

\[
FF(z) := \int_0^z \frac{x^3}{1 - e^{-z}} \frac{e^{-x}}{x} \, dx \left(\frac{3}{z^3}\right)
\]

\[
\Delta H_{H_D}(T_{TT}) = -\mu_D - 3 \cdot 8.314 \cdot FF\left(\frac{\Theta_D}{T_{TT}}\right) + 2.5 \cdot 8.314 \cdot T_{TT}
\]

\[
\Delta H_{D_t} := -b \cdot 8.314 + c \cdot 8.314 \cdot T_{T_t}
\]

\[
\Delta H(298.15) = 2.898 \times 10^5
\]

Results are not very good, as expected by the error in the sublimation pressures.

c) Results for the calculated sublimation pressures at the specified temperatures are found directly in Parts a and b solutions.
10.1

\[ G_{ex} = \delta \delta_1 \delta_2 = \delta \delta_1 \delta_2 \]

There are two equivalent solutions.

The excess Gibbs energy for the regular solution model is the following:

\[ G_{ex} = \chi N x_1 x_2 = \chi \left( \frac{N_1 N_2}{N_1 + N_2} \right) \]

The activity coefficient for component \( i \) is calculated from knowledge of \( G_{ex} \)

\[ kT \ln(\gamma_i) = \left( \frac{\partial [N G_{ex}]}{\partial N_i} \right)_{T,P} = \left( \frac{\partial G_{ex}}{\partial N_i} \right)_{T,P} \]

For the regular solution model this yields the following activity coefficient expressions:

\[ k_{k_k}(\gamma_1) = \delta x_2^2 \]

Assuming two liquid phases coexist, the following must be satisfied:

\[ x_1^l \gamma_1^l = x_1^u \gamma_1^u \]

This yields the following set of equations:

\[ \ln(\gamma_1) = \frac{\chi x_2^2}{kT} \]

\[ \ln(\gamma_2) = \frac{\chi x_1^2}{kT} \]
At any given $T$ and $\chi$ in the two phase region, these equations will yield a solution for $x_1^I$ and $x_1^{II}$. Because of the exponential terms there is no easy way to combine the two equations into one. Thus, the two equations together constitute the analytic expression for the compositions of the coexisting liquid phases.

**Drawing the phase boundary requires solving for the stability bound.** From classical thermodynamics we know that a phase is only stable if $\partial^2 G / \partial x_1^2 > 0$. Thus, finding the composition phase boundary requires solving for where $\frac{\partial}{\partial x_1}\left(\frac{\partial^2 G}{\partial x_1^2}\right) = N_{Av}\left(\frac{\partial^2 G}{\partial x_1^2}\right) = 0$.

$$G = G^{IM} + G^{ex} = x_1 G_1 + (1 - x_1) G_2 + kT x_1 \ln(x_1) + kT (1 - x_1) \ln(1 - x_1) + \chi x_1 (1 - x_1)$$

Setting this last equation equal to zero yields the following equation:

$$\frac{\chi}{kT} = \frac{2}{x_1 x_2} = \frac{2}{x_1 (1 - x_1)}$$

This is a bit complex to solve because $x_1$ cannot be easily isolated. Thus, just do it numerically. Note that because this equation is second order in $x_1$, there are two values of $x_1$ that satisfy each value of $\chi/kT$. Also, $x_1$ is bounded, while $\chi/kT$ is not. Thus, even though the problem indicates that $\chi/kT$ should be the independent variable, it is easier to specify values of $x_1$ and then find the corresponding values of $\chi/kT$. 

$$x_1^I \exp \left[ \frac{\chi (x_2^I)^2}{kT} \right] = x_1^{II} \exp \left[ \frac{\chi (x_2^{II})^2}{kT} \right]$$
As $\chi$ becomes very large, the two compounds become insoluble in one another. If phase I is chosen as the phase rich in component 1, and phase II the phase rich in component 2, then $x_1^I \approx x_2^I \approx 1$. Thus, the equations from part a) reduce to the following:

$$(1) \exp \left[ \frac{\chi(0)^2}{kT} \right] = x_1^I \exp \left[ \frac{\chi(1)^2}{kT} \right] \quad \text{and} \quad x_2^I \exp \left[ \frac{\chi(1)^2}{kT} \right] = (1) \exp \left[ \frac{\chi(0)^2}{kT} \right]$$

$\Rightarrow \quad x_1^I = x_2^I = \frac{1}{\exp[\chi/kT]} = \exp \left[ -\frac{\chi}{kT} \right]$