Example Problem 7.1
Given the following expression for the internal energy of a system:

\[ U = \frac{V_0 \theta S^3}{R^2 NV} \]

Solution 7.1

a. 

\[ P = \left( \frac{\partial U}{\partial V} \right)_{S,N} = \frac{V_0 \theta S^3}{R^2 NV^2} \]

\[ T = \left( \frac{\partial U}{\partial S} \right)_{V,N} = \frac{V_0 \theta 3S^2}{R^2 NV} \]

\[ \mu = \left( \frac{\partial U}{\partial N} \right)_{S,V} = -\frac{V_0 \theta S^3}{R^2 VN^2} \]

b. Intensive quantities are independent of the size of a system. We know that \( N, S, \) and \( V \) are extensive quantities and additive. If one system is characterized by \( N, S, \) and \( V \) then \( \lambda \) systems joined together to form a supersystem are characterized by \( \lambda N, \lambda S, \) and \( \lambda V. \)

\[ P(\lambda) = \frac{V_0 \theta (\lambda S)^3}{R^2 \lambda N (\lambda V)^2} = \frac{V_0 \theta S^3}{R^2 NV^2} \]

\[ T(\lambda) = \frac{V_0 \theta 3(\lambda S)^2}{R^2 \lambda^2 NV} = \frac{V_0 \theta 3S^2}{R^2 NV} \]

\[ \mu(\lambda) = -\frac{V_0 \theta (\lambda S)^3}{R^2 \lambda V (\lambda N)^2} = -\frac{V_0 \theta S^3}{R^2 VN^2} \]

By inspection it is apparent that \( P, T, \) and \( \mu \) are independent of the size of the system.

c. 

\[ dU(S, N, V) = \left( \frac{\partial U}{\partial V} \right)_{S,N} dV + \left( \frac{\partial U}{\partial S} \right)_{V,N} dS + \left( \frac{\partial U}{\partial N} \right)_{S,V} dN \]

\[ dU(S, N, V) = -PdV + TdS + \mu dN \]

\[ dU(S, N, V) = -\frac{V_0 \theta S^3}{R^2 NV^2} dV + \frac{V_0 \theta 3S^2}{R^2 NV} dS - \frac{V_0 \theta S^3}{R^2 VN^2} dN \]
Example Problem 7.2

Pure nickel exists in two solid forms $\alpha$-Ni (fcc) and $\beta$-Ni (bcc) with the transition at $T_{a\rightarrow\beta} = 630K$ at atmospheric pressure. $\beta$-Ni melts at $T_m = 1728K$. The enthalpy of formation of $\alpha$-Ni at 298K is $\Delta H_{a,0} = 0J/mole$. The entropy of formation of $\alpha$-Ni at 298K is $\Delta S_{a,0} = 29.8J/moleK$. The heat capacities of the solid forms are given below. Calculate the enthalpy and entropy of transformation, $\Delta H_{a\rightarrow\beta}$ and $\Delta S_{a\rightarrow\beta}$, respectively, for the $\alpha \rightarrow \beta$ transition in terms of the given data and the enthalpy of $\beta$-Ni at the melting temperature, $\Delta H_{\beta,T_m}$.

\[
\overline{C}_{p,a} = 32.6 - 1.97 \cdot 10^{-3}T - 5.586 \cdot 10^5 \frac{1}{T^2}
\]
\[
\overline{C}_{p,\beta} = 29.7 + 4.18 \cdot 10^{-3}T - 9.33 \cdot 10^5 \frac{1}{T^2}
\]

Solution 7.2 This is an exercise in manipulating standard state information. We start by recognizing that at the equilibrium transformation temperature the molar Gibbs free energies of the $\alpha$ and $\beta$ phases, $\overline{G}_a(T_{a\rightarrow\beta})$ and $\overline{G}_\beta(T_{a\rightarrow\beta})$, respectively, are equal.

\[
\Delta \overline{G}_{a\rightarrow\beta} = \overline{G}_\beta - \overline{G}_a
\]
\[
\overline{G}_{a\rightarrow\beta} = \overline{G}_{a,0} + \int_{298}^{630} \overline{C}_{p,a} dT - \overline{G}_{\beta,1728} - \int_{1728}^{630} \overline{C}_{p,\beta} dT
\]
\[
\overline{G}_{a\rightarrow\beta} = 0J/mole + \int_{298}^{630} \left(32.6 - 1.97 \cdot 10^{-3}T - 5.586 \cdot 10^5 \frac{1}{T^2}\right) dT
\]
\[
-\overline{G}_{\beta,1728} - \int_{1728}^{630} \left(29.7 + 4.18 \cdot 10^{-3}T - 9.33 \cdot 10^5 \frac{1}{T^2}\right) dT
\]
\[
\overline{G}_{a\rightarrow\beta} = 9578J/mole - \overline{G}_{\beta,1728} + 370801J/mole
\]
\[
\overline{G}_{a\rightarrow\beta} = -46659J/mole - \overline{G}_{\beta,1728}
\]

We know that $\overline{G}_{a,630} = \overline{G}_{\beta,630}$ at atmospheric pressure. From this we find the following relation for the entropy of transformation.

\[
\Delta \overline{S}_{a\rightarrow\beta} = 0
\]
\[
\Delta \overline{G}_{a\rightarrow\beta} - 630 \Delta \overline{S}_{a\rightarrow\beta} = 0
\]
\[
\Delta \overline{S}_{a\rightarrow\beta} = \frac{-46659J/mole - \overline{G}_{\beta,1728}}{630}
\]

We expect both the entropy and enthalpy of transformation to be positive. From this they have the same sign and it is expected to be positive depending on $\overline{G}_{\beta,1728}$.