Thermodynamics of Materials 3.00
Example Problems for Week 7

Example Problem 7.1

Given the following expression for the internal energy of a system:

a. *Calculate the three corresponding equations of state*

b. *Show that they are zero order homogeneous (T, P, μ are intensive)*

c. *Write down the differential form of the internal energy, dU.*

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

Solution 7.1

a.

$$-\left(\frac{\partial U}{\partial V}\right)_{S,N} = P = \frac{V_0\theta}{R^2}\frac{S^3}{N}\frac{1}{V^2}$$
$$\left(\frac{\partial U}{\partial S}\right)_{V,N} = T = \frac{V_0\theta}{R^2}\frac{3S^2}{NV}$$
$$\left(\frac{\partial U}{\partial N}\right)_{S,V} = \mu = -\frac{V_0\theta}{R^2}\frac{S^3}{V}\frac{1}{N^2}$$

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 λ systems joined together to form a supersystem are characterized by λN, λS, and λV.

$$P(\lambda) = \frac{V_0\theta}{R^2}\frac{(\lambda S)^3}{\lambda N}\frac{1}{(\lambda V)^2} = \frac{V_0\theta}{R^2}\frac{S^3}{N}\frac{1}{V^2}$$
$$T(\lambda) = \frac{V_0\theta}{R^2}\frac{3(\lambda S)^2}{\lambda^2 NV} = \frac{V_0\theta}{R^2}\frac{3S^2}{NV}$$
$$\mu(\lambda) = -\frac{V_0\theta}{R^2}\frac{(\lambda S)^3}{\lambda V}\frac{1}{(\lambda N)^2} = -\frac{V_0\theta}{R^2}\frac{S^3}{V}\frac{1}{N^2}$$

By inspection it is apparent that P, T, and μ are independent of the size of the system.

c.

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

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

$$dU(S,N,V) = -\frac{V_0\theta}{R^2}\frac{S^3}{N}\frac{1}{V^2}dV + \frac{V_0\theta}{R^2}\frac{3S^2}{NV}dS - \frac{V_0\theta}{R^2}\frac{S^3}{V}\frac{1}{N^2}dN$$

Example Problem 7.2

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

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

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 α and β phases, $\overline{G}_\alpha(T_{\alpha\to\beta})$ and $\overline{G}_\beta(T_{\alpha\to\beta})$, respectively, are equal.

$$\Delta\overline{H}_{\alpha\to\beta} = \overline{H}_\beta - \overline{H}_\alpha$$
$$\overline{H}_{\alpha\to\beta} = \overline{H}_{\alpha,0} + \int_{298}^{630} \overline{C}_{p,\alpha} dT - \overline{H}_{\beta,1728} - \int_{1728}^{630} \overline{C}_{p,\beta} dT$$

$$\begin{aligned}\overline{H}_{\alpha\to\beta} = 0J/mole &+ \int_{298}^{630} \left(32.6 - 1.97 \cdot 10^{-3}T - 5.586 \cdot 10^5 \frac{1}{T^2}\right) dT \\ -\overline{H}_{\beta,1728} &- \int_{1728}^{630} \left(29.7 + 4.18 \cdot 10^{-3}T - 9.33 \cdot 10^5 \frac{1}{T^2}\right) dT\end{aligned}$$

$$\overline{H}_{\alpha\to\beta} = 9578J/mole - \overline{H}_{\beta,1728} + 370801J/mole$$
$$\overline{H}_{\alpha\to\beta} = -46659J/mole - \overline{H}_{\beta,1728}$$

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

$$\Delta\overline{G}_{\alpha\to\beta} = 0$$
$$\Delta\overline{H}_{\alpha\to\beta} - 630\Delta\overline{S}_{\alpha\to\beta} = 0$$
$$\Delta\overline{S}_{\alpha\to\beta} = \frac{-46659J/mole - \overline{H}_{\beta,1728}}{630}$$

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 $\overline{H}_{\beta,1728}$.