HOMEWORK ASSIGNMENT 9

Problems Chapter 9

9-2

a) For an ideal gas

\[ S = \int \frac{dU}{T} + \int \frac{P}{T} dV = \int \frac{n c_v dT}{T} + \int \frac{n R}{V} dV \]

\[ = n c_v \ln \frac{T}{T_0} + n R \ln \frac{V}{V_0} + \text{const.} \]

\[ = S(T_0, V_0) + n c_v \ln \frac{T}{T_0} + n R \ln \frac{V}{V_0} \]

Then

\[ G = U + PV - TS \]

\[ = U(T_0) + n c_v (T - T_0) + n R T - T \left( S(T_0, V_0) + n c_v \ln \frac{T}{T_0} + n R \ln \frac{V}{V_0} \right) \]

and the chemical potential is

\[ \mu = \frac{G}{n} = u(T_0) + c_v (T - T_0) + RT - T \left( s(T_0, V_0) + c_v \ln \frac{T}{T_0} + R \ln \frac{V}{V_0} \right) \]

\[ = c_p T - c_v T \ln \frac{T}{T_0} - RT \ln \frac{V}{V_0} - T s(T_0, V_0) + u(T_0) - c_v T_0 \]

b) \[ \mu = c_p T - c_v T \ln \frac{T}{T_0} - RT \ln \frac{V}{V_0} - T s(T_0, V_0) + u(T_0) - c_v T_0 \]

\[ = c_p T - c_v T \ln \frac{T}{T_0} - RT \ln \frac{P}{P_0 T_0} - T s(T_0, V_0) + u(T_0) - c_v T_0 \]

\[ = RT \ln \frac{P}{P_0} + c_p T - c_v T \ln \frac{T}{T_0} - T s(T_0, \frac{n R T_0}{P_0}) + u(T_0) - c_v T_0 \]

\[ \mu (T, P) = \mu (T, P_0) + RT \ln \frac{P}{P_0} \]

9-8 Initially,

\[ P_A \frac{V}{2} = n_A RT, \quad P_N \frac{V}{2} = n_N RT \]

so

\[ n_A = n_N \frac{P_A}{P_N} = 1 \times \frac{1}{4} \]
a) After mixing the temperature remains the same and the pressure is the sum of the partial pressures (Dalton’s law)

\[ P = (n_A + n_N) \frac{RT}{V} = (n_A + n_N) \left( \frac{P_N}{2n_N} \right) \]

\[
= \left( 1 + \frac{1}{4} \right) \times \left( \frac{4}{2} \right) = 2.5
\]

b) The change in the Gibbs function is

\[ (G_A + G_N)_{\text{final}} - (G_A + G_N)_{\text{initial}} = (\mu_{A\text{final}} - \mu_{A\text{initial}}) n_A + (\mu_{B\text{final}} - \mu_{B\text{initial}}) n_B \]

But from 9-2 b) above, \( \mu \) has the form

\[ \mu_i = \mu_i(T, P_0) + RT \ln \frac{P_i}{P_0} = \mu_i(T, P_0) + RT \ln \frac{x_ip_i}{P_0} \]

where

\[ x_A = \frac{n_A}{n_A + n_B} = \frac{1}{1 + \frac{1}{4}} = 0.2, \quad x_B = \frac{n_B}{n_A + n_B} = 0.8 \]

Since \( T \) is the same for the initial and final states

\[ (G_A + G_N)_{\text{final}} - (G_A + G_N)_{\text{initial}} = RT n_A \left( \ln x_A + \ln \frac{P_{\text{final}}}{P_{\text{initial}}} \right) + RT n_B \left( \ln x_N + \ln \frac{P_{\text{final}}}{P_{\text{initial}}} \right) \]

\[ = RT (n_A + n_B) \left( x_A \ln x_A + x_N \ln x_N + x_A \ln \frac{P_{\text{final}}}{P_{\text{initial}}} + x_B \ln \frac{P_{\text{final}}}{P_{\text{initial}}} \right) \]

With the given initial conditions this is

\[ \Delta G = 8.31 \times 10^3 \times 300 \times \left( \frac{1}{4} + 1 \right) \]

\[ \times \left( 0.2 \ln 0.2 + 0.8 \ln 0.8 + 0.2 \ln \frac{2.5}{1} + 0.8 \ln \frac{2.5}{4} \right) \]

\[ = -2.16 \times 10^6 \]

c) The entropy change is

\[ \Delta S = - \left( \frac{\partial \Delta G}{\partial T} \right)_P = R \left( n_A \ln \frac{x_A P}{1} + n_B \ln \frac{x_B P}{4} \right) \]

\[ = - \frac{-2.16 \times 10^6}{300} = 7200 \]

9-10 Refer to figure 2.4 for a typical phase transition. The coexistence curves are characterized by the Clausius-Clapyron equation (section 8.7).
a) From the Clausius-Clapyron equation (8.28), which follows from \( dG = 0 \) for the phase transition

\[
\frac{dP}{dT} = \frac{S_1 - S_2}{V_1 - V_2}
\]

or

\[
\Delta S = \frac{dP}{dT} \Delta V, \quad \Delta S = S_1 - S_2, \quad \Delta V = V_1 - V_2
\]

This is the linear relationship of \( \Delta S \) to \( \Delta V \) asked for.

b) Since \( \Delta G = 0 \) and the initial and final values of \( T, P \) are the same

\[
\Delta G = 0 = \Delta (U + PV - TS) = \Delta U + P \Delta V - T \Delta S
\]

\[
\Delta U = T \Delta S - P \Delta V = T \Delta S \left( 1 - \frac{P \Delta V}{T \Delta S} \right)
\]

\[
= L \left( 1 - \frac{P \, dT}{T \, dP} \right) = L \left( 1 - \frac{d\ln T}{d \ln P} \right)
\]