

10.40 Thermodynamics
Problem Set 10

Fall 2003

 Problem 15.31 Text

Solution:

- (a) At equilibrium along the solid-vapor coexistence curve

$$\left(\frac{dP}{dT}\right)_{S-V} = \frac{\Delta H_{\text{sub}}}{T\Delta V_{\text{sub}}} = \frac{H^V - H^S}{T(V^V - V^S)} \quad (1)$$

Assume

- 1) $V^V \gg V^S$
- 2) Vapor is ideal, $V^V = RT/P$
- 3) $\Delta H_{\text{sub}} = \text{constant}$

Then, Eq. (1) reduces to

$$\left(\frac{d \ln P_{vp}}{d(1/T)}\right)_{S-V} = \frac{-\Delta H_{\text{sub}}}{R} \quad (2)$$

From the information given in the problem,

$$\Delta H_{\text{sub}} = (3115)(R) = (3115)(8.314) = 25,898 \text{ J/mol} \quad (3)$$

Now to estimate the vapor pressure of liquid CO₂, assume:

$$4) \Delta H_{vap} = H^V - H^L \text{ and } \Delta H_{fus} = H^L - H^S \text{ are constant}$$

Then

$$\Delta H_{vap} = \Delta H_{sub} - \Delta H_{fus} = 25,898 - 8330 = 17,568 \text{ J/mol} \quad (4)$$

and we can write the Clausius-Clapeyron equation for *L-V* equilibrium, similar to Eq. (3) as:

$$\left(\frac{d \ln P_{vp}}{d(1/T)} \right)_{L-V} = \frac{-\Delta H_{vap}}{R} \quad (5)$$

Matching the vapor pressure at the triple point and integrating to find P_{vp} at $T = 273 \text{ K}$, we get

$$P_{vp}^{L-V}(T = -56.2^\circ\text{C}) = P_{vp}^{S-V}(T = -56.2^\circ\text{C}) = \exp\left[\frac{-3115}{216.8} + 16\right] = 5.1137 \text{ bar}$$

$$\ln \frac{P_{vp}(T)}{P_{vp}(-56.2^\circ\text{C})} = \frac{-\Delta H_{vap}}{R} \left(\frac{1}{T} - \frac{1}{216.8} \right) = \frac{-17,568}{8.314} \left[\frac{1}{T} - \frac{1}{216.8} \right] \quad (6)$$

At $T = 273 \text{ K}$, using Eq. (6)

$$P_{vp}(273 \text{ K}) = 38.02 \text{ bar} \quad (7)$$

(b) With CO₂ as the solvent, the phase equilibrium criteria are

$$\hat{f}_{\text{CO}_2}^L = \hat{f}_{\text{CO}_2}^V \quad (8)$$

if the solute has low volatility

$$\hat{f}_{\text{CO}_2}^V \approx f_{\text{CO}_2}^V(\text{pure CO}_2) \quad (9)$$

Using a differential approach expanding $d \ln \hat{f}_i$ in each phase as a function of T , P , and x_{CO_2} (liquid only) we get with $C = \text{CO}_2$ as a subscript:

$$\frac{-(\bar{H}_C^L - H_C^V)}{RT^2} dT + \frac{(\bar{V}_C^L - V_C^V)}{RT} dP + \left(\frac{d \ln \hat{f}_C^L}{d x_c} \right)_{T,P} dx_c = 0 \quad (10)$$

In general

$$\hat{f}_c^L = \gamma_c x_c f_c^L \quad (11)$$

but as a first approximation we can assume an ideal solution with $\gamma_c = 1.0$ and $\bar{H}_c^L = H_c^L$ we can further assume that the vapor phase is an ideal gas with $V_c^V \gg V_c^L$. Now Eq. (10) simplifies to:

$$\frac{\Delta H_{vap}}{RT^2} dT - \frac{dP}{P} + d \ln x_c = 0 \quad (12)$$

integrating, over appropriate limits from $x_c = 1$ to x_c

$$\ln \left[\frac{P_{vp,c}(x_c, T)}{P_{vp,c}(x_c = 1, T_o)} \right] = \frac{-\Delta H_{vap}}{R} \left[\frac{1}{T} - \frac{1}{T_o} \right] + \ln x_c \quad (13)$$

With $x_c = 1 - x_s$ ($s = \text{contaminant}$), at $T = T_o$ we can estimate the decrease in vapor pressure:

$$\begin{aligned} P_{vp,c}(x_c, T_o) &= P_{vp,c}(T_o) (1 - x_s) \\ P_{vp,c}(x_c, T_o) - P_{vp,c}(T_o) &= \Delta P_{vp} = -x_s P_{vp,c} \end{aligned} \quad (14)$$

so the decrease is linear in mole fraction for an ideal solution. For values of x_s that are small ≤ 0.01 this is a very reasonable approximation. The integral approach using Eq. (15-97) as a starting point will give the same result.