

Chapter 4 Homework Solutions

$$\begin{aligned} 4.1 \quad \Delta\mu &= \int_{T_1}^{T_2} -S_m dT = -S_m [T_2 - T_1] \\ &= (-53 \text{ J / mol} \cdot \text{K}) [473 \text{ K} - 373 \text{ K}] = -5300 \text{ J / mol} = -5.3 \text{ kJ / mol} \end{aligned}$$

$$\begin{aligned} 4.2 \quad \Delta\mu &= \int_{T_1}^{T_2} -S_m dT = \int_{T_1}^{T_2} -(a + bT) dT = -\int_{T_1}^{T_2} a dT - \int_{T_1}^{T_2} bT dT \\ &= -a [T_2 - T_1] - b \left[\frac{T_2^2}{2} - \frac{T_1^2}{2} \right] \\ &= -(1.5 \text{ J / mol}) [363 \text{ K} - 298 \text{ K}] - (0.23 \text{ J / mol} \cdot \text{K}^2) \left[\frac{363^2}{2} - \frac{298^2}{2} \right] \\ &= -98 \text{ J / mol} - 4940 \text{ J / mol} = -5038 \text{ J / mol} = -5.0 \text{ kJ / mol} \end{aligned}$$

$$4.3 \quad p_1 = 1. \text{ bar} = 100 \text{ kPa} , p_2 = 1000 \text{ bar} = 100,000 \text{ kPa}$$

The Molar Volume of benzene is:

$$\begin{aligned} V_m &= \frac{M}{\rho} = \frac{78 \text{ g / mol}}{0.88 \text{ g / cm}^3} = 88.6 \text{ cm}^3 / \text{mol} \cdot \frac{1 \text{ L}}{1000 \text{ cm}^3} = 0.0886 \text{ L / mol} \\ \Delta\mu &= \int_{p_1}^{p_2} V_m dp = V_m [p_2 - p_1] = (0.0886 \text{ L / mol}) [100,000 \text{ kPa} - 100 \text{ kPa}] \\ &= 8850 \text{ J / mol} = 8.9 \text{ kJ / mol} \end{aligned}$$

$$4.4 \quad n = 1 \text{ mol} , T = 25 \text{ }^\circ\text{C} = 298 \text{ K} , p_1 = 1 \text{ bar} = 100 \text{ kPa} , p_2 = 20 \text{ bar} = 2000 \text{ kPa}$$

$$\begin{aligned} V_m &= \frac{RT}{p} \\ \Delta\mu &= \int_{p_1}^{p_2} V_m dp = \int_{p_1}^{p_2} \frac{RT}{p} dp = RT \ln \left(\frac{p_2}{p_1} \right) \\ &= (8.31 \text{ J / mol} \cdot \text{K}) (298 \text{ K}) \ln \left(\frac{2000}{100} \right) = 7420 \text{ J / mol} = 7.4 \text{ kJ / mol} \end{aligned}$$

Note: Even though the pressure increase is a factor of 1,000 for liquid benzene (HW 4.4), vs. only a factor of 20 for CH₄(g), the Chemical Potential changes for both the liquid and gas are comparable. This is because gases have much higher Molar Volumes, with consequently greater changes in $\Delta\mu$ over the same range of pressures.

4.5 $T_1 = T_b^\circ = 6^\circ\text{C} = 279\text{ K}$, $T_2 = 15.0^\circ\text{C} = 288.0\text{ K}$, $P_1 = 1\text{ bar} = 100\text{ kPa}$, $P_2 = ?$

$$V_m(\text{liq}) = \frac{78\text{ g/mol}}{0.88\text{ g/cm}^3} = 88.6\text{ cm}^3/\text{mol} \quad V_m(\text{sol}) = \frac{78\text{ g/mol}}{0.95\text{ g/cm}^3} = 82.1\text{ cm}^3/\text{mol}$$

$$\Delta V_m = V_m(\text{liq}) - V_m(\text{sol}) = 88.6 - 82.1 = 6.5\text{ cm}^3/\text{mol} \cdot \frac{1\text{ L}}{1000\text{ cm}^3} = 6.5 \times 10^{-3}\text{ L/mol}$$

$$\Delta T = 288\text{ K} - 279\text{ K} = 9.0\text{ K}$$

$$\Delta_{\text{fus}}H = 9.80\text{ kJ/mol} \cdot \frac{10^3\text{ J}}{1\text{ kJ}} = 9.80 \times 10^3\text{ J/mol} \cdot \frac{1\text{ kPa} \cdot \text{L}}{1\text{ J}} = 9.80 \times 10^3\text{ kPa} \cdot \text{L/mol}$$

$$\frac{\Delta p}{\Delta T} = \frac{\Delta_{\text{fus}}H}{T\Delta V_m} \rightarrow \Delta p = \frac{\Delta_{\text{fus}}H}{T\Delta V_m} \cdot \Delta T$$

$$\Delta p = \frac{9.8 \times 10^3\text{ kPa} \cdot \text{L}}{(279\text{ K})(6.5 \times 10^{-3}\text{ L/mol})} \cdot (9.0\text{ K}) = 4.86 \times 10^4\text{ kPa} \cdot \frac{1\text{ bar}}{100\text{ kPa}}$$

$$= 486\text{ bar} = p_2 - 1\text{ bar} \approx p_2 \approx 490\text{ bar}$$

Solution with alternate units

In the PP presentation, we worked a similar problem on the melting point of benzene, using units of L-bar.

One can also work this problem using L-atm. In this case, one would convert $\Delta_{\text{fus}}H$ from kJ/mol to L-atm/mol.

4.6 $\Delta_{\text{fus}}H = 6.01\text{ kJ/mol} = 6.01 \times 10^3\text{ J/mol} = 6.01 \times 10^3\text{ kPa} \cdot \text{L/mol}$

$$T = 0^\circ\text{C} = 273\text{ K}$$

$$V_m(\text{liq}) = \frac{18\text{ g/mol}}{1.00\text{ g/cm}^3} = 18\text{ cm}^3/\text{mol} \quad V_m(\text{sol}) = \frac{18\text{ g/mol}}{0.92\text{ g/cm}^3} = 19.6\text{ cm}^3/\text{mol}$$

$$\Delta V_m = V_m(\text{liq}) - V_m(\text{sol}) = 18.0 - 19.6 = -1.6\text{ cm}^3/\text{mol} \cdot \frac{1\text{ L}}{1000\text{ cm}^3} = -1.6 \times 10^{-3}\text{ L/mol}$$

$$\Delta p = 1.0 \times 10^5\text{ kPa} - 100\text{ kPa} = 0.999 \times 10^5\text{ kPa} \approx 1.0 \times 10^5\text{ kPa}$$

$$\frac{\Delta p}{\Delta T} = \frac{\Delta_{\text{fus}}H}{T\Delta V_m} = \frac{6.01 \times 10^3\text{ kPa} \cdot \text{L/mol}}{273\text{ K}(-1.6 \times 10^{-3}\text{ L/mol})} = -13,800\text{ kPa/K}$$

$$\text{Therefore, } \Delta T = \frac{\Delta p}{-13,800\text{ kPa/K}} = \frac{1.0 \times 10^5\text{ kPa}}{-13,800\text{ kPa/K}} = -7.2\text{ K} = -7.2^\circ\text{C}$$

$$T_m = 0^\circ\text{C} + \Delta T = 0^\circ\text{C} - 7.2^\circ\text{C} = -7.2^\circ\text{C}$$

Note that, unlike benzene (Exer. 4.12a and most other substances, the melting point of ice under high pressure is lower than the normal melting point.

$$4.7 \quad V_m(sol) = 161.0 \text{ mL} / \text{mol} \frac{10^{-3} \text{ L}}{1 \text{ mL}} = 0.161 \text{ L} / \text{mol}$$

$$V_m(liq) = 163.3 \text{ mL} / \text{mol} \frac{10^{-3} \text{ L}}{1 \text{ mL}} = 0.1633 \text{ L} / \text{mol}$$

$$\Delta V_m = V_m(liq) - V_m(sol) = 0.1633 - 0.161 = 0.0023 \text{ L} / \text{mol}$$

$$p_1 = 1. \text{ atm} \quad p_2 = 100. \text{ atm}$$

$$\Delta p = p_2 - p_1 = 100 - 1 = 99 \text{ atm} \cdot \frac{101.3 \text{ kPa}}{1 \text{ atm}} = 1.00 \times 10^4 \text{ kPa}$$

$$T_1 = 350.75 \text{ K} \quad T_2 = 351.26 \text{ K}$$

$$\Delta T = T_2 - T_1 = 351.26 - 350.75 = 0.51 \text{ K}$$

$$\frac{\Delta p}{\Delta T} = \frac{\Delta_{fus} S}{\Delta V_m} \left(= \frac{\Delta_{fus} H}{T \Delta V_m} \right)$$

$$\Delta_{fus} S = \frac{\Delta p \cdot \Delta V_m}{\Delta T} = \frac{(1.00 \times 10^4 \text{ kPa})(0.0023 \text{ L} / \text{mol})}{0.51 \text{ K}} = 45.1 \text{ kPa} \cdot \text{L} / \text{mol} \cdot \text{K} \frac{1 \text{ J}}{1 \text{ kPa} \cdot \text{L}}$$

$$= 45.1 \text{ J} / \text{mol} \cdot \text{K}$$

$$\Delta_{fus} H = T \cdot \Delta_{fus} S = (350.75 \text{ K})(45.1 \text{ J} / \text{mol} \cdot \text{K}) = 15800 \text{ J} / \text{mol} = 15.8 \text{ kJ} / \text{mol}$$

$$4.8 \quad \Delta_{vap} H = 28.7 \text{ kJ} / \text{mol}$$

$$p_1 = 53.3 \text{ kPa} \text{ at } T_1 = 24. \text{ } ^\circ\text{C} = 297 \text{ K}$$

$$p_2 = 70.0 \text{ kPa} \text{ at } T_2 = ?$$

$$\ln(p_2 / p_1) = -\frac{\Delta_{vap} H}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right] \rightarrow \frac{1}{T_2} = \frac{1}{T_1} - \frac{R}{\Delta_{vap} H} \ln(p_2 / p_1)$$

$$\frac{1}{T_2} = \frac{1}{297 \text{ K}} - \frac{8.31 \times 10^{-3} \text{ kJ} / \text{mol} \cdot \text{K}}{28.7 \text{ kJ} / \text{mol}} \ln(70.0 / 53.3) = 0.003288 \text{ K}^{-1}$$

$$T_2 = \frac{1}{0.003288 \text{ K}^{-1}} = 301 \text{ K} = 31 \text{ } ^\circ\text{C}$$

- 4.9** $p_1 = 1.3 \text{ kPa}$ at $T_1 = 85.3 \text{ }^\circ\text{C} \approx 359 \text{ K}$
 $p_2 = 5.3 \text{ kPa}$ at $T_2 = 119.3 \text{ }^\circ\text{C} \approx 392 \text{ K}$

(a) Enthalpy of Vaporization

$$\ln(p_2 / p_1) = -\frac{\Delta_{\text{vap}}H}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right] \rightarrow \Delta_{\text{vap}}H = -\frac{R \ln(p_2 / p_1)}{\left[\frac{1}{T_2} - \frac{1}{T_1} \right]}$$

$$\Delta_{\text{vap}}H = -\frac{(8.31 \times 10^{-3} \text{ kJ/mol} \cdot \text{K}) \ln(5.3/1.3)}{\left[\frac{1}{392 \text{ K}} - \frac{1}{359 \text{ K}} \right]} = 49.8 \text{ kJ/mol}$$

(b) Normal Boiling Point

$T_3 = T_b^\circ = ?$ when $p_3 = 1 \text{ bar} = 100 \text{ kPa}$

$$\ln(p_3 / p_1) = -\frac{\Delta_{\text{vap}}H}{R} \left[\frac{1}{T_3} - \frac{1}{T_1} \right] \rightarrow \frac{1}{T_3} = \frac{1}{T_1} - \frac{R}{\Delta_{\text{vap}}H} \ln(p_3 / p_1)$$

$$\frac{1}{T_3} = \frac{1}{359 \text{ K}} - \frac{8.31 \times 10^{-3} \text{ kJ/mol} \cdot \text{K}}{49.8 \text{ kJ/mol}} \ln(100/1.3) = 0.002061 \text{ K}^{-1}$$

$$T_3 = \frac{1}{0.002061 \text{ K}^{-1}} = 485 \text{ K} - 273 = 212 \text{ }^\circ\text{C}$$

(c) Entropy of Vaporization at the Boiling Point

Question incorrectly asks for Enthalpy of Vaporization (which we already know)

$$\Delta_{\text{vap}}S = \frac{\Delta_{\text{vap}}H}{T_b^\circ} = \frac{49.8 \text{ kJ/mol}}{485 \text{ K}} = 0.103 \text{ kJ/mol} \cdot \text{K} \cdot \frac{10^3 \text{ J}}{1 \text{ kJ}} = 103 \text{ J/mol} \cdot \text{K}$$

- 4.10** $T_1 = T_b^\circ = 357 \text{ }^\circ\text{C} = 630 \text{ K}$, $p_1 = 1 \text{ bar} \cdot \frac{750 \text{ torr}}{1 \text{ bar}} = 750 \text{ torr}$

$T_2 = 250 \text{ }^\circ\text{C} = 523 \text{ K}$, $P_2 = 75 \text{ torr}$

$$\ln(p_2 / p_1) = -\frac{\Delta_{\text{vap}}H}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right] \rightarrow \Delta_{\text{vap}}H = -R \frac{\ln(p_2 / p_1)}{\left[\frac{1}{T_2} - \frac{1}{T_1} \right]}$$

$$\Delta_{\text{vap}}H = -(8.31 \text{ J/mol} \cdot \text{K}) \frac{\ln(75/750)}{\left[\frac{1}{523 \text{ K}} - \frac{1}{630 \text{ K}} \right]} = 58,920 \text{ J/mol} \approx 58.9 \text{ kJ/mol}$$