Chemistry 217
Problem Set 6 Solutions

6.1 10 mol of H_2 and 2 mol O_2 at 298 K and 1 bar

$$\Delta S^\circ = -R\left(n_1 \ln Y_1 + n_2 \ln Y_2\right)$$

$$Y_1 = \frac{n_1}{n_1+n_2}, \quad Y_2 = \frac{n_2}{n_1+n_2}$$

$$\Delta S^\circ = -8.314\ \mathrm{J.K^{-1}.mol^{-1}}\left(10\ \mathrm{mol}\times\ln\frac{10}{12} + 2\ \mathrm{mol}\times\ln\frac{2}{12}\right) = 44.95\ \mathrm{J.K^{-1}}$$

6.2 (a) $S = n_A\bar{S}_A + n_B\bar{S}_B + n_C\bar{S}_C$

$$= n_A\bar{S}_A^o + n_B\bar{S}_B^o + n_C\bar{S}_C^o - R(n_A \ln Y_A + n_B \ln Y_B + n_C \ln Y_C) - \left((n_A + n_B + n_C)R\ln\left(\frac{P}{P^\circ}\right)\right)$$

(b) $S = \left[n_A\bar{S}_A + n_B\bar{S}_B\right] + n_C\bar{S}_C$

$$= \left[n_A\bar{S}_A^o + n_C\bar{S}_C^o - R(n_A \ln Y_A + n_C \ln Y_C) - \left((n_A + n_C)R\ln\left(\frac{P_I}{P^\circ}\right)\right)\right] + n_B\bar{S}_B$$

$$= n_I\left[r_A\bar{S}_A^o + r_C\bar{S}_C^o - R(r_A \ln r_A + r_C \ln r_C) - \left(R\ln\left(\frac{P_I}{P^\circ}\right)\right)\right] + n_B\bar{S}_B$$

$$n_I = n_A + n_C, \quad P_I = P_A + P_C$$

(c) $S = n_I\bar{S}_I + n_B\bar{S}_B = n_t\left[Y_I\bar{S}_I + Y_B\bar{S}_B\right]$

$$= n_t\left[Y_I\bar{S}_I^o - Y_I R\ln\left(\frac{P_I}{P^\circ}\right) + Y_B\bar{S}_B^o - Y_B R\ln\left(\frac{P_B}{P^\circ}\right)\right]$$

$$= n_t\left[Y_I\bar{S}_I^o + Y_B\bar{S}_B^o - R(Y_I \ln Y_I + Y_B \ln Y_B) - R\ln\left(\frac{P}{P^\circ}\right)\right]$$

Rearranging the above equation can lead to equation (a)

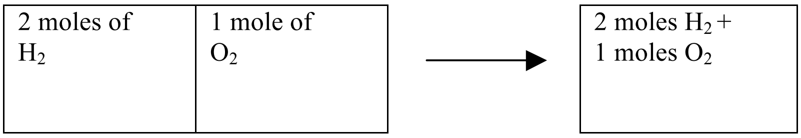
6.3

(a) $\Delta G_{mix} = RT\left(y_1 \ln y_1 + y_2 \ln y_2\right)$

$$= \left(8.314\ \mathrm{J.K^{-1}.mol^{-1}}\right)\left(298.15\ \mathrm{K}\right)\left(0.8\ln 0.8 + 0.2\ln 0.2\right) = -1239\ \mathrm{J.mol^{-1}}$$

$$\Delta S_{mix} = -R\left(y_1 \ln y_1 + y_2 \ln y_2\right) = 4.159\ \mathrm{J.K^{-1}.mol^{-1}}$$

(b) 25°C, 1.00 bar



$$\Delta H_{H_2} = 0$$

$$H_2\text{:}\ \Delta S_{mix} = \int \frac{dq_{rev}}{T} = -\int \frac{dw}{T} = \int \frac{PdV}{T} = \int \frac{nR}{V} dV = nR\ln \frac{V_f}{V_i}$$

$$= (2\ \mathrm{mol})(8.314\ \mathrm{J.K^{-1}.mol^{-1}})\ln\left(\frac{3}{2}\right) = 6.74\ \mathrm{J.K^{-1}}$$

$$\Delta H_{O_2} = 0$$

$$O_2\text{:}\ \Delta S_{mix} = 1\times(8.314)\ln\left(\frac{3}{1}\right) = 9.13\ \mathrm{J.K^{-1}}$$

$$\Delta S_{mix} = \Delta S_{mix,H_2} + \Delta S_{mix,O_2} = 15.9\ \mathrm{J.K^{-1}}$$

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} = 0 - 298.15\ \mathrm{K}\times 15.9\ \mathrm{J.K^{-1}} = -4740\ \mathrm{J}$$

6.4. EU & Al-Ghoul, Chapter 7

Problem 1 :

$$V = 1.00294 + 0.0194m + 0.00214m^{3/2} + 2.7\times10^{-6} m^{5/2}$$

$$\overline{V}_{NaCl} = \left(\frac{\partial V}{\partial m_{NaCl}}\right)_{T,P,n_{water}} = 0.0164 + 0.00321m^{1/2} + 6.75\times10^{-6} m^{3/2}\ (L)$$

$$\overline{V}_{water} = -\frac{n_{NaCl}\overline{V}_{NaCl}}{n_{Water}} = -\frac{n_{NaCl}M_{water}\overline{V}_{NaCl}}{m_{water}}$$

$$= -m\times M_{water}\times10^{-3}\times\overline{V}_{NaCl} = -0.018m\times\overline{V}_{NaCl}$$

$$\Rightarrow \overline{V}_{water} = -2.952\times10^{-4} m - 5.778\times10^{-5} m^{3/2} - 1.215\times10^{-7} m^{5/2}\ (L)$$

Problem 2 **:**

$$V_{Total} = n_{water}\overline{V}_{water} + n_{ethanol}\overline{V}_{ethanol}$$

$$\Rightarrow \overline{V}_{ethanol} = \frac{V_{Total} - n_{water}\overline{V}_{water}}{n_{ethanol}} = \frac{0.06816 - 1.158\times0.01698}{0.842} = 0.057 L.mol^{-1}$$

Problem 3 :

$$V_{m_{H_2O}} = \frac{M_{H_2O}}{d_{H_2O}} = \frac{1.802\times10^{-2}}{0.997} = 1.81\times10^{-2}\,L.mol^{-1}$$

$$\frac{V_{m_{H_2O}}}{\overline{V}_{H_2O}} = \frac{1.81\times10^{-2}}{1.70\times10^{-2}} = 1.06$$

$$V_{m_{ethanol}} = \frac{M_{ethanol}}{d_{ethanol}} = \frac{4.602\times10^{-2}}{0.7852} = 5.861\times10^{-2}\,L.mol^{-1}$$

$$\frac{V_{m_{ethanol}}}{\overline{V}_{ethanol}} = \frac{5.86\times10^{-2}}{5.7\times10^{-2}} = 1.03$$

Problem 4 :

According to the Gibbs—Duhem equation for a single component:

$$SdT - VdP = -nd\mu$$

$$\Rightarrow S = V\left(\frac{\partial P}{\partial T}\right)_V - n\left(\frac{\partial \mu}{\partial T}\right)_V$$

$$\left(\frac{\partial S}{\partial T}\right)_V = V\left(\frac{\partial^2 P}{\partial T^2}\right)_V - n\left(\frac{\partial^2 \mu}{\partial T^2}\right)_V$$

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V \Rightarrow \frac{C_V}{T} = \left(\frac{\partial S}{\partial T}\right)_V$$

$$\frac{C_V}{T} = V\left(\frac{\partial^2 P}{\partial T^2}\right)_V - n\left(\frac{\partial^2 \mu}{\partial T^2}\right)_V \Rightarrow \frac{C_V}{V} = T\left[\left(\frac{\partial^2 P}{\partial T^2}\right)_V - \frac{n}{V}\left(\frac{\partial^2 \mu}{\partial T^2}\right)_V\right]$$

$$\Rightarrow C_V = T\left[\left(\frac{\partial^2 P}{\partial T^2}\right)_V - n\left(\frac{\partial^2 \mu}{\partial T^2}\right)_V\right]$$

6.5 Plot ln(P/KPa) vs. 1000/T

(a) $$\text{slope} = -2.34\times10^3\text{K} = \frac{\Delta H_{vap}}{(2.303)(8.314\text{J.K}^{-1}.\text{mol}^{-1})}$$

$$\Delta H_{vap} = 44.8\text{kJ.mol}^{-1}$$

(b) $$\ln\left(\frac{12.3}{100}\right) = \frac{44800}{8.3145}\left(\frac{1}{T} - \frac{1}{373.15}\right)$$

$$T = \frac{1}{\left(\frac{83145}{44800}\right)\ln\left(\frac{112.3}{100}\right) + \left(\frac{1}{373.15}\right)} = 370.18\text{K} = 97.03°\text{C}$$

6.6 For $C_{10}H_8$, P_{vap} (359K) = 1.3 × 10^{-2}bar
P_{vap} (392K) = 5.3 × 10^{-2}bar

(a) Using the Clausius-Clapeyron equation (6.14 in S&A)

$$\ln\left(\frac{P_2}{P_1}\right)=\frac{\Delta\overline{H}_{vap}\left(T_2-T_1\right)}{RT_1T_2}$$

$$\Delta\overline{H}_{vap}=\frac{RT_1T_2}{T_2-T_1}\ln\left(\frac{P_2}{P_1}\right)=\frac{8.314JK^{-1}mol^{-1}(359K)(392K)}{392K-359K}\ln\left(\frac{5.3\times10^{-2}\,bar}{1.3\times10^{-2}\,bar}\right)=50kJ.mol^{-1}$$

Use the Clausius-Clapeyron again but

$$P_{vap}\left(T_b\right)=1atm=1.013bar=\frac{49900kJ.mol^{-1}\left(T_b-359K\right)}{8.314J.K^{-1}.mol^{-1}T_b359K}$$

$$\frac{T_b-359K}{T_b}=0.26053$$

$$T_b=\frac{358.95K}{1-0.26053}=485K$$

$$\Delta\overline{S}_{vap}=\frac{\Delta\overline{H}_{vap}}{T_b}=\frac{49.9kJ.mol^{-1}}{485K}=102.9J.K^{-1}.mol^{-1}$$

(b) At the triple point, $T_t=353.65K$

$$\ln\frac{P_t}{1.3\times10^{-2}\,bar}=\frac{\Delta\overline{H}_{vap}\left(T_t-359K\right)}{T_t-359K}=\frac{50000J.mol^{-1}\left(-5.35K\right)}{8.315J.K^{-1}.mol^{-1}\left(353.65K-359K\right)}=-0.25233$$

$$P_t=1.3\times10^{-2}\,bar\cdot e^{-0.25233}=0.01010bar=0.0101bar$$

(c) $P_{sub}=1.3\times10^{-3}\,bar$ $@T_{sub}=325.7K$

$P_t=0.0101bar$ $@T_t=353.65K$

$$\ln\left(\frac{P_{sub}}{P_t}\right)=\frac{\Delta\overline{H}_{sub}}{R}\left(\frac{T_{sub}-T_t}{T_{sub}T_t}\right)$$

$$\Delta\overline{H}_{sub}=R\left(\frac{T_{sub}T_t}{T_{sub}-T_t}\right)\ln\left(\frac{P_{sub}}{P_t}\right)=\left(8.314J.K^{-1}.mol^{-1}\right)\left(\frac{325.7K\times353.65K}{325.7K-353.65K}\right)\ln\left(\frac{1.3\times10^{-3}}{0.0101}\right)$$

$$=70kJ.mol^{-1}$$

$$\Delta\overline{H}_{fus}+\Delta\overline{H}_{vap}=\Delta\overline{H}_{sub}$$

$$\Delta\overline{H}_{fus}=\Delta\overline{H}_{sub}-\Delta\overline{H}_{vap}$$

$$\Delta\overline{H}_{fus}=20kJ.mol^{-1}$$

(d) $P_{C_{10}H_8}(s)=1.00g.cm^{-3}$, $P_{C_{10}H_8}(l)=0.98g.cm^{-3}$

Clapeyron equation

$$\frac{dP}{dT} = \frac{\Delta\overline{H}_{fus}}{T\Delta\overline{V}}$$

$$\int_{P_1}^{P_2} dP = \frac{\Delta\overline{H}_{fus}}{\Delta\overline{V}} \int_{T_1}^{T_2} \frac{dT}{T}$$

$$\Delta P = \frac{\Delta\overline{H}_{fus}}{\Delta\overline{V}} \ln\left(\frac{T_2}{T_1}\right)$$

$$T_2 = T_1 e^{\frac{\Delta P \Delta\overline{V}}{\Delta\overline{H}_{fus}}}$$

$$\frac{dP}{dT} = \frac{\Delta\overline{H}_{fus}}{T}\left(\frac{1}{\frac{m}{P(l)} - \frac{m}{P(s)}}\right) = \frac{\Delta\overline{H}_{fus}}{T}\left(\frac{m}{0.0204 g.cm^{-3}}\right)$$

so $\frac{dP}{dT} > 0 \Rightarrow \frac{\Delta P}{\Delta T} > 0$ and $\Delta P > 0$

$\Delta T > 0$ or $T > 80.5°C$

6.7 (a) Find T_2

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H}{R}\left(\frac{T_2 - T_1}{T_2 T_1}\right)$$

$$\Delta H_{vap} = 92 J.mol^{-1},\ T_1 = 2K,\ P_1 = 0.032 bar,\ P_2 = 10^{-3} bar$$

$$\ln\left(\frac{10^{-3} bar}{0.032 bar}\right) = \frac{92 J.mol^{-1}}{8.314 J.K^{-1}.mol^{-1}}\left(\frac{T_2 - 2}{2T_2}\right)$$

$$-0.3132 = \frac{T_2 - 2}{2T_2}$$

$$T_2 = 1.23K$$

(b) $4 J.min^{-1},\ \Delta H_{vap} = 92 J.mol^{-1}$

$$\frac{4}{92} = 0.04 mol.min^{-1} He(g)$$

Use ideal gas eq'n: PV = nRT; V = nRT/P

$$V = \frac{(0.04\text{mol.min}^{-1})(0.08314\text{L.bar.K}^{-1}.\text{mol}^{-1})(300\text{K})}{10^{-3}\text{bar}} = 997.68\text{L.min}^{-1}$$

6.8 (a) Sarin: Vapor pressure = 0.00387bar at 298K

The boiling point at 1bar is 158°C = 431.15K

$$\Delta H_{vap} = \frac{RT_1T_2}{(T_2 - T_1)}\ln\left(\frac{P_2}{P_1}\right) = \frac{(8.314)(298\text{K})(431.15\text{K})}{(133.15\text{K})}\ln\left(\frac{1.01325\text{bar}}{0.00387\text{bar}}\right) = 44666\text{J.mol}^{-1}$$

VX: Vapor pressure = 9.33 × 10^{-7}bar at 298K

Boiling point at 1bar is 298°C = 571.15K

$$\Delta H_{vap} = \frac{(8.314)(298\text{K})(571.15\text{K})}{(273.15\text{K})}\ln\left(\frac{1.01325\text{bar}}{9.33\times10^{-7}\text{bar}}\right) = 71999\text{J.mol}^{-1}$$

(b) Test Trouton's Rule

Sarin: $\Delta S_{vap} = \frac{\Delta H_{vap}}{T_b}$

$$\Delta S_{vap} = \frac{44666\text{J.mol}^{-1}}{431.15\text{K}} = 103.599\text{J.K}^{-1}.\text{mol}^{-1}$$

VX: $\Delta S_{vap} = \frac{71999\text{J.mol}^{-1}}{571.15\text{K}} = 126.0597\text{J.K}^{-1}.\text{mol}^{-1}$

(c) Change the unit for mg/m^3 to g/l

$$3\times10^{-6}\text{mg.m}^{-3} = 3\times10^{-9}\text{mg.l}^{-1} = 3\times10^{-12}\text{g.l}$$

For Sarin: $2\times10^{-14}\text{mol.l}^{-1}$

$$\frac{n}{V} = 2\times10^{-14}\,\mathrm{mol.l^{-1}}$$

$$\frac{P}{RT} = \frac{n}{V}$$

$$P = \left(2\times10^{-14}\,\mathrm{mol.l^{-1}}\right)(8.314)(431.15\,\mathrm{K}) = 7.17\times10^{-11}\,\mathrm{bar}$$

then use :

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_{vap}}{R}\left(\frac{T_2 - T_1}{T_2T_1}\right) \text{ to find } T_1,\ T_2 = 298\mathrm{K},\ \ P_2 = 0.00387\mathrm{bar}$$

$$\ln\left(\frac{0.00387\,\mathrm{bar}}{7.17\times10^{-11}\,\mathrm{bar}}\right) = \frac{44666\,\mathrm{J.mol^{-1}}}{8.314}\left(\frac{298 - T_1}{298T_1}\right)$$

$$0.003313 = \frac{298 - T_1}{298T_1}$$

$$0.9875T_1 = 298 - T_1 \Rightarrow T_1 = 149.93\mathrm{K}$$

For VX: $1\times10^{-14}\,\mathrm{mol.l^{-1}}$

VX: $\frac{n}{V} = 1\times10^{-14}\,\mathrm{mol.l^{-1}}$

$$\frac{P}{RT} = \frac{n}{V},\quad P = 4.749\times10^{-11}\,\mathrm{bar}$$

$$\ln\left(\frac{9.33\times10^{-7}\,\mathrm{bar}}{4.749\times10^{-11}\,\mathrm{bar}}\right) = \frac{71999\,\mathrm{J.mol^{-1}}}{8.314}\left(\frac{298 - T_1}{298T_1}\right) \Rightarrow T_1 = 222.36\mathrm{K}$$