

## Problem Set 6

### P4

a) for the isothermal reversible path

$$\begin{aligned}\Delta G &= \int_{P_i}^{P_f} V dP = nRT \ln \frac{P_f}{P_i} = nRT \ln \frac{V_i}{V_f} \\ &= 2.50 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{K}^{-1} \times 298 \text{ K} \times \ln \frac{10.0 \text{ L}}{50.0 \text{ L}} = -9.97 \times 10^3 \text{ J} \\ \Delta A &= - \int_{V_i}^{V_f} P dV = -nRT \ln \frac{V_f}{V_i} \\ &= -2.50 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{K}^{-1} \times 298 \text{ K} \times \ln \frac{50.0 \text{ L}}{10.0 \text{ L}} = -9.97 \times 10^3 \text{ J}\end{aligned}$$

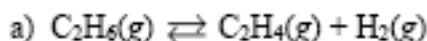
b) Because  $A$  and  $G$  are state functions, the answers are the same as to part (a) because the systems go between the same initial and final states,  $T, V_i \rightarrow T, V_f$ .  
 $\Delta G - \Delta A = \Delta H - \Delta U = \Delta(PV) = \Delta(nRT)$ . Therefore,  $\Delta G = \Delta A$  for an ideal gas if  $T$  is constant.

### P7

$$\begin{aligned}\Delta G_{\text{reaction}}^{\circ}(298.15 \text{ K}) &= \Delta G_f^{\circ}(\text{CO}_2, g) - \Delta G_f^{\circ}(\text{CO}, g) - \frac{1}{2} \Delta G_f^{\circ}(\text{O}_2, g) \\ &= -394.4 \times 10^3 \text{ J mol}^{-1} + 137.2 \times 10^3 \text{ J mol}^{-1} - 0 \\ &= -257.2 \times 10^3 \text{ J mol}^{-1} \\ \Delta H_{\text{reaction}}^{\circ}(298.15 \text{ K}) &= \Delta H_f^{\circ}(\text{CO}_2, g) - \Delta H_f^{\circ}(\text{CO}, g) - \frac{1}{2} \Delta H_f^{\circ}(\text{O}_2, g) \\ &= -393.5 \times 10^3 \text{ J mol}^{-1} + 110.5 \times 10^3 \text{ J mol}^{-1} - 0 \\ &= -283.0 \times 10^3 \text{ J mol}^{-1} \\ \Delta G_{\text{reaction}}^{\circ}(T_2) &= T_2 \left[ \frac{\Delta G_{\text{reaction}}^{\circ}(T_1)}{T_1} + \Delta H_{\text{reaction}}^{\circ}(T_1) \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \right] \\ \Delta G_{\text{reaction}}^{\circ}(650 \text{ K}) &= 650 \text{ K} \times \left[ \frac{-257.2 \times 10^3 \text{ J mol}^{-1}}{298.15 \text{ K}} - 283.0 \times 10^3 \text{ J mol}^{-1} \times \left( \frac{1}{650 \text{ K}} - \frac{1}{298.15 \text{ K}} \right) \right] \\ &= -226.8 \times 10^3 \text{ J mol}^{-1}\end{aligned}$$

**P9**

- a) Calculate  $K_p$  at 1000 K.  
 b) If  $\Delta H^\circ_{\text{reaction}} = 137.0 \text{ kJ mol}^{-1}$ , calculate the value of  $K_p$  at 298.15 K.  
 c) Calculate  $\Delta G^\circ_{\text{reaction}}$  for this reaction at 298.15 K.



$$K_p = \frac{(P_{\text{C}_2\text{H}_4} / P^\circ) \times (P_{\text{H}_2} / P^\circ)}{P_{\text{C}_2\text{H}_6} / P^\circ}$$

The partial pressure of each component,  $P_i$ , is  $P_i = x_i P_{\text{total}}$  and  $P_{\text{total}} = 1 \text{ atm}$ .

By definition,  $P^\circ = 1 \text{ atm}$ .

$$K_p = \frac{0.26 \times 0.26}{0.48} = 0.1408$$

$$\begin{aligned} \text{b) } \ln K_p(1000 \text{ K}) &= \ln K_p(298.15 \text{ K}) - \frac{\Delta H^\circ_{\text{reaction}}}{R} \left( \frac{1}{1000 \text{ K}} - \frac{1}{298.15 \text{ K}} \right) \\ \ln K_p(298.15 \text{ K}) &= \ln K_p(1000 \text{ K}) + \frac{137.0 \times 10^3 \text{ J}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}} \times \left( \frac{1}{1000 \text{ K}} - \frac{1}{298.15 \text{ K}} \right) = -40.75 \\ K_p(298.15 \text{ K}) &= 2.00 \times 10^{-18} \end{aligned}$$

$$\begin{aligned} \text{c) } \Delta G^\circ_{\text{reaction}} &= -RT \ln K_p \\ \Delta G^\circ_{\text{reaction}}(298.15 \text{ K}) &= -8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K} \times (-40.75) = 101 \text{ kJ mol}^{-1} \end{aligned}$$

**P13**

$$K_p = \frac{P_{\text{NH}_3} / P^\circ}{(P_{\text{H}_2} / P^\circ)^{3/2}}$$

$$P_{\text{total}} = 1 \text{ atm} = P_{\text{NH}_3} + P_{\text{H}_2}$$

At 700 K,

$$1 \text{ atm} = 2.165 P_{\text{H}_2} + P_{\text{H}_2} = 3.165 P_{\text{H}_2}$$

$$P_{\text{H}_2} = 0.316 \text{ atm}, \quad P_{\text{NH}_3} = 0.684 \text{ atm}$$

$$K_p(700 \text{ K}) = \frac{0.684}{(0.316)^{3/2}} = 3.85$$

At 800 K,

$$1 \text{ atm} = 1.083 P_{H_2} + P_{H_2} = 2.083 P_{H_2}$$

$$P_{H_2} = 0.480 \text{ atm}, P_{NH_3} = 0.520 \text{ atm}$$

$$K_p(800 \text{ K}) = \frac{0.520}{(0.480)^{3/2}} = 1.56$$

b) Assume that  $\Delta H_{\text{reaction}}^\circ$  is independent of temperature

$$\ln \frac{K_p(800 \text{ K})}{K_p(700 \text{ K})} = \frac{-\Delta H_{\text{reaction}}^\circ}{R} \left( \frac{1}{800 \text{ K}} - \frac{1}{700 \text{ K}} \right)$$

$$\Delta H_{\text{reaction}}^\circ = \frac{-R \ln \frac{K_p(800 \text{ K})}{K_p(700 \text{ K})}}{\left( \frac{1}{800 \text{ K}} - \frac{1}{700 \text{ K}} \right)} = -42.1 \text{ kJ mol}^{-1}$$

$$\Delta G_{\text{reaction}}^\circ(700 \text{ K}) = -RT \ln K_p(700 \text{ K}) = -7.81 \text{ kJ mol}^{-1}$$

$$\Delta G_{\text{reaction}}^\circ(800 \text{ K}) = -RT \ln K_p(800 \text{ K}) = -2.91 \text{ kJ mol}^{-1}$$

$$\Delta S_{\text{reaction}}^\circ(700 \text{ K}) = \frac{\Delta H_{\text{reaction}}^\circ - \Delta G_{\text{reaction}}^\circ(700 \text{ K})}{700 \text{ K}} = 60.1 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Delta S_{\text{reaction}}^\circ(800 \text{ K}) = 52.6 \text{ J mol}^{-1} \text{ K}^{-1}$$

The values of  $\Delta S_{\text{reaction}}^\circ$  at 700 K and 800 K are nearly the same because

$$|\Delta G_{\text{reaction}}^\circ| \ll |\Delta H_{\text{reaction}}^\circ|$$

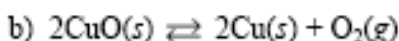
$$\begin{aligned} \text{c) } \ln K_p(298.15 \text{ K}) &= \ln K_p(700 \text{ K}) - \frac{\Delta H_{\text{reaction}}^\circ}{R} \left( \frac{1}{298.15 \text{ K}} - \frac{1}{700 \text{ K}} \right) \\ &= \ln 3.85 + \frac{42.1 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}} \times \left( \frac{1}{298.15 \text{ K}} - \frac{1}{700 \text{ K}} \right) = 11.1 \end{aligned}$$

$$\Delta G_{\text{reaction}}^\circ(298.15 \text{ K}) = -RT \ln K_p(298.15 \text{ K})$$

$$= -8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K} \times 11.1 = -27.5 \text{ kJ mol}^{-1}$$

**P15**

$$\begin{aligned}
 \text{a) } \int_{T_0}^{T_f} d \ln K_p &= \frac{1}{R} \int_{T_0}^{T_f} \frac{\Delta H_{\text{reaction}}^\circ}{T^2} dT \\
 \ln K_p(T_f) - \ln K_p(T_0) &= \frac{1}{R} \int_{T_0}^{T_f} \frac{\Delta H_{\text{reaction}}^\circ + \Delta C_p(T - T_0)}{T^2} dT \\
 &= \frac{\Delta H_{\text{reaction}}^\circ(T_0)}{R} \times \int_{T_0}^{T_f} \frac{dT}{T^2} + \frac{\Delta C_p}{R} \int_{T_0}^{T_f} \frac{dT}{T} - \frac{\Delta C_p T_0}{R} \int_{T_0}^{T_f} \frac{dT}{T^2} \\
 &= \frac{-\Delta H_{\text{reaction}}^\circ(T_0)}{R} \left( \frac{1}{T_f} - \frac{1}{T_0} \right) + \frac{\Delta C_p}{R} \ln \frac{T_f}{T_0} + \frac{\Delta C_p T_0}{R} \left( \frac{1}{T_f} - \frac{1}{T_0} \right)
 \end{aligned}$$



$$\Delta H_{\text{reaction}}^\circ(T_0) = 2 \times 157 \times 10^3 \text{ J mol}^{-1} = 314 \times 10^3 \text{ J mol}^{-1}$$

$$\Delta C_p = 2C_{p,m}(\text{Cu}, s) + C_{p,m}(\text{O}_2, g) - 2C_{p,m}(\text{CuO}, s)$$

$$= (2 \times 24.4 + 29.4 - 2 \times 42.3) \text{ J K}^{-1} \text{ mol}^{-1}$$

$$= -6.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\begin{aligned}
 \ln K_p(1200 \text{ K}) &= -\frac{2 \times 130 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K}} \\
 &\quad - \frac{2 \times 157 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \left( \frac{1}{1200 \text{ K}} - \frac{1}{298.15 \text{ K}} \right) - \frac{6.4 \text{ J K}^{-1} \text{ mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \ln \frac{1200 \text{ K}}{298.15 \text{ K}} \\
 &\quad - \frac{6.4 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}} \left( \frac{1}{1200 \text{ K}} - \frac{1}{298.15 \text{ K}} \right)
 \end{aligned}$$

$$\ln K_p(1200 \text{ K}) = -10.1818$$

$$K_p(1200 \text{ K}) = \frac{P_{\text{O}_2}}{P^\circ} = 3.78 \times 10^{-5}$$

$$P_{\text{O}_2} = 3.78 \times 10^{-5} \text{ bar}$$

c) This is equivalent to setting  $\Delta C_p = 0$ . Neglecting the last two terms in the calculation above gives  $\ln K_p = -9.6884$  and  $P_{\text{O}_2} = 6.20 \times 10^{-5} \text{ bar}$ .

**P16**

$$\left(\frac{\partial A/T}{\partial T}\right)_V = \frac{1}{T} \left(\frac{\partial A}{\partial T}\right)_V - \frac{A}{T^2} = -\frac{S}{T} - \frac{A}{T^2} = -\frac{A+TS}{T^2} = -\frac{U}{T^2}$$

$$\left(\frac{\partial A/T}{\partial 1/T}\right)_V = \left(\frac{\partial A/T}{\partial T}\right)_V \left(\frac{\partial T}{\partial 1/T}\right)_V = \frac{\left(\frac{\partial A/T}{\partial T}\right)_V}{\left(\frac{\partial 1/T}{\partial T}\right)_V} = -T^2 \left(\frac{\partial A/T}{\partial T}\right)_V = U$$

At constant  $V$ ,

$$\int_{T_1}^{T_2} d\left(\frac{\Delta A}{T}\right) = \int_{T_1}^{T_2} d\left(\frac{\Delta U}{T}\right)$$

$$\frac{\Delta A(T_2)}{T_2} \approx \frac{\Delta A(T_1)}{T_1} + \Delta U(T_1) \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

**P18**

$$\Delta G_{\text{mixing}} = nRT \sum_i x_i \ln x_i$$

$$= (7.00 \text{ mol}) \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K} \times \left( \frac{2.25}{7.00} \ln \frac{2.25}{7.00} + \frac{3.00}{7.00} \ln \frac{3.00}{7.00} + \frac{1.75}{7.00} \ln \frac{1.75}{7.00} \right)$$

$$= -18.6 \times 10^3 \text{ J}$$

$$\Delta S_{\text{mixing}} = -nR \sum_i x_i \ln x_i$$

$$= -(7.00 \text{ mol}) \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times \left( \frac{2.25}{7.00} \ln \frac{2.25}{7.00} + \frac{3.00}{7.00} \ln \frac{3.00}{7.00} + \frac{1.75}{7.00} \ln \frac{1.75}{7.00} \right)$$

$$= 62.5 \text{ J K}^{-1}$$

P21

$$\ln K_p(T_f) = \ln K_p(298.15\text{K}) - \frac{\Delta H_{\text{reaction}}^\circ}{R} \left( \frac{1}{T_f} - \frac{1}{298.15\text{K}} \right)$$

$$\begin{aligned} \Delta H_{\text{reaction}}^\circ &= \Delta H_f^\circ(\text{CO}_2, g) + \Delta H_f^\circ(\text{H}_2, g) - \Delta H_f^\circ(\text{H}_2\text{O}, l) - \Delta H_f^\circ(\text{CO}, g) \\ &= -393.5 \times 10^3 \text{J mol}^{-1} + 0 + 285.8 \times 10^3 \text{J mol}^{-1} + 110.5 \times 10^3 \text{J mol}^{-1} = 2.80 \times 10^3 \text{J mol}^{-1} \end{aligned}$$

$$\begin{aligned} \frac{1}{T_f} &= \frac{1}{298.15\text{K}} - \frac{R}{\Delta H_{\text{reaction}}^\circ} \ln \frac{K_p(T_f)}{K_p(298.15\text{K})} \\ &= \frac{1}{298.15\text{K}} - \frac{8.314\text{JK}^{-1}\text{mol}^{-1}}{2.80 \times 10^3 \text{J mol}^{-1}} \times \ln \frac{5.00 \times 10^3}{3.32 \times 10^3} = 2.1382 \times 10^{-3} \text{K}^{-1} \end{aligned}$$

$$T_f = 468\text{K}$$

Because the reaction is endothermic,  $K_p$  increases with temperature. As  $T \rightarrow \infty$ ,

$$\begin{aligned} \frac{1}{298.15\text{K}} - \frac{R}{\Delta H_{\text{reaction}}^\circ} \ln \frac{K_p(T_f \rightarrow \infty)}{K_p(298.15\text{K})} &= 0 \\ \ln \frac{K_p(T_f \rightarrow \infty)}{K_p(298.15\text{K})} &= \frac{\Delta H_{\text{reaction}}^\circ}{R \times 298.15\text{K}} = \frac{2.80 \times 10^3 \text{J mol}^{-1}}{8.314\text{JK}^{-1}\text{mol}^{-1} \times 298.15\text{K}} = 1.12957 \\ K_p(T_f \rightarrow \infty) &= 3.094 \times K_p(298.15\text{K}) = 3.094 \times 3.32 \times 10^3 = 1.03 \times 10^4 \end{aligned}$$

**P28**

- a) Obtain an expression for  $K_p$  in terms of the degree of advancement  $\xi$ .

	$\text{NOCl(g)} \rightarrow$	$\text{NO(g)} +$	$1/2 \text{Cl}_2(\text{g})$
Initial number of moles	2.00	0	0
Moles present at equilibrium	$2.00 - \xi$	$\xi$	$1/2 \xi$
Mole fraction present at equilibrium	$\frac{2.00 - \xi}{2 + \frac{1}{2}\xi}$	$\frac{\xi}{2 + \frac{1}{2}\xi}$	$\frac{\frac{1}{2}\xi}{2 + \frac{1}{2}\xi}$
Partial pressure at equilibrium, $P_i = x_i P$	$\left( \frac{2.00 - \xi}{2 + \frac{1}{2}\xi} \right) P$	$\left( \frac{\xi}{2 + \frac{1}{2}\xi} \right) P$	$\left( \frac{\frac{1}{2}\xi}{2 + \frac{1}{2}\xi} \right) P$

We next express  $K_p$  in terms of  $\xi$  and  $P$ .

$$K_p(T) = \frac{\left( \frac{P_{\text{NO}}^{\text{eq}}}{P^\circ} \right) \left( \frac{P_{\text{Cl}_2}^{\text{eq}}}{P^\circ} \right)^{\frac{1}{2}}}{\left( \frac{P_{\text{NOCl}}^{\text{eq}}}{P^\circ} \right)} = \frac{\left( \frac{\xi}{2 + \frac{1}{2}\xi} \right) \frac{P}{P^\circ} \left[ \left( \frac{\frac{1}{2}\xi}{2 + \frac{1}{2}\xi} \right) \frac{P}{P^\circ} \right]^{\frac{1}{2}}}{\left( \frac{2.00 - \xi}{2 + \frac{1}{2}\xi} \right) \frac{P}{P^\circ}}$$

b)

$$K_p(T) = \frac{\left( \frac{\xi}{2 + \frac{1}{2}\xi} \right) \frac{P}{P^*} \left( \left( \frac{\frac{1}{2}\xi}{2 + \frac{1}{2}\xi} \right) \frac{P}{P^*} \right)^{\frac{1}{2}}}{\left( \frac{2.00 - \xi}{2 + \frac{1}{2}\xi} \right) \frac{P}{P^*}} = \frac{\xi \left( \frac{\xi}{2(2 + \xi/2)} \frac{P}{P^*} \right)^{\frac{1}{2}}}{2.00 - \xi}$$

$$\approx \frac{\frac{\xi P}{2P^*} \left( \frac{\xi}{4} \frac{P}{P^*} \right)^{\frac{1}{2}}}{\frac{P}{P^*}} = \frac{1}{4} \xi^{\frac{3}{2}} \left( \frac{P}{P^*} \right)^{\frac{1}{2}} \text{ if } \xi \ll 2$$



c) Calculate  $\xi$  and the degree of dissociation of NOCl in the above limit at 400 K and a pressure of 0.100 bar.

$$\begin{aligned}\Delta G_{\text{reaction}}^{\circ} &= \Delta G_f^{\circ}(\text{NO}, g) - \Delta G_f^{\circ}(\text{NOCl}, g) = 87.6 \times 10^3 \text{ J mol}^{-1} - 66.1 \times 10^3 \text{ J mol}^{-1} \\ &= 21.5 \times 10^3 \text{ J mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta H_{\text{reaction}}^{\circ} &= \Delta H_f^{\circ}(\text{NO}, g) - \Delta H_f^{\circ}(\text{NOCl}, g) = 91.3 \times 10^3 \text{ J mol}^{-1} - 51.71 \times 10^3 \text{ J mol}^{-1} \\ &= 39.6 \times 10^3 \text{ J mol}^{-1}\end{aligned}$$

$$\ln K_p(T_f) = -\frac{\Delta G_{\text{reaction}}^{\circ}(298.15 \text{ K})}{R \times 298.15 \text{ K}} - \frac{\Delta H_{\text{reaction}}^{\circ}}{R} \left( \frac{1}{T_f} - \frac{1}{298.15 \text{ K}} \right)$$

$$\ln K_p(375 \text{ K}) = -\frac{25.00 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}} - \frac{38.54 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \times \left( \frac{1}{375 \text{ K}} - \frac{1}{298.15 \text{ K}} \right)$$

$$\ln K_p(375 \text{ K}) = -5.399$$

$$K_p(375 \text{ K}) = 4.52 \times 10^{-3}$$

$$K_p = \frac{1}{4} \xi^{\frac{3}{2}} \left( \frac{P}{P^{\circ}} \right)^{\frac{1}{2}}$$

$$\xi = \left[ 4K_p / \left( \frac{P}{P^{\circ}} \right)^{\frac{1}{2}} \right]^{\frac{2}{3}} = \left[ \frac{4 \times 4.52 \times 10^{-3}}{\sqrt{0.500}} \right]^{\frac{2}{3}} = 8.68 \times 10^{-2}$$

The degree of dissociation is  $\frac{\xi}{2-\xi} = 0.045$ .

d) Solve the expression derived in part (a) using a numerical equation solver for the conditions stated in the previous part. What is the relative error in  $\xi$  made using the approximation of part (b)?

Solving the expression of part (a) without approximations gives  $\xi = 8.49 \times 10^{-2}$ .

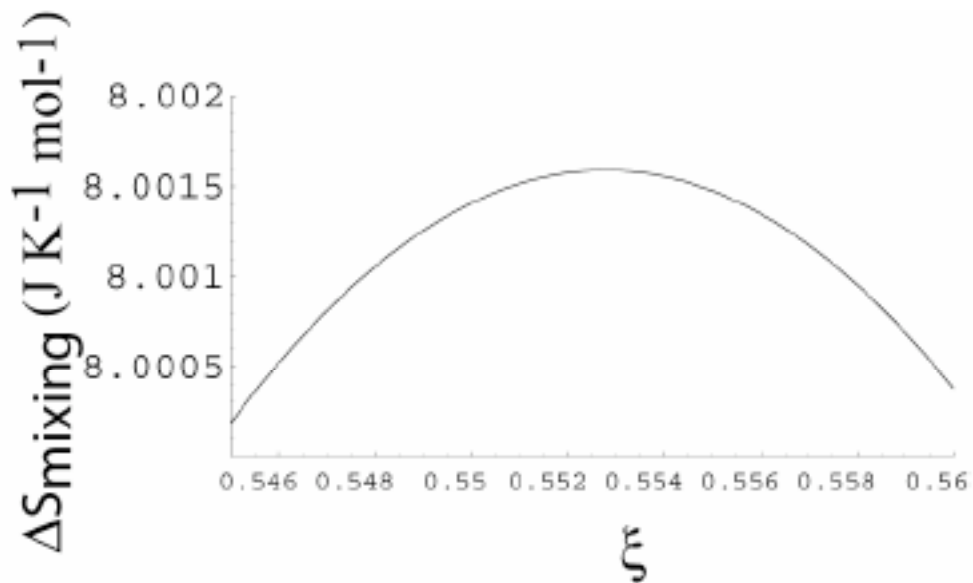
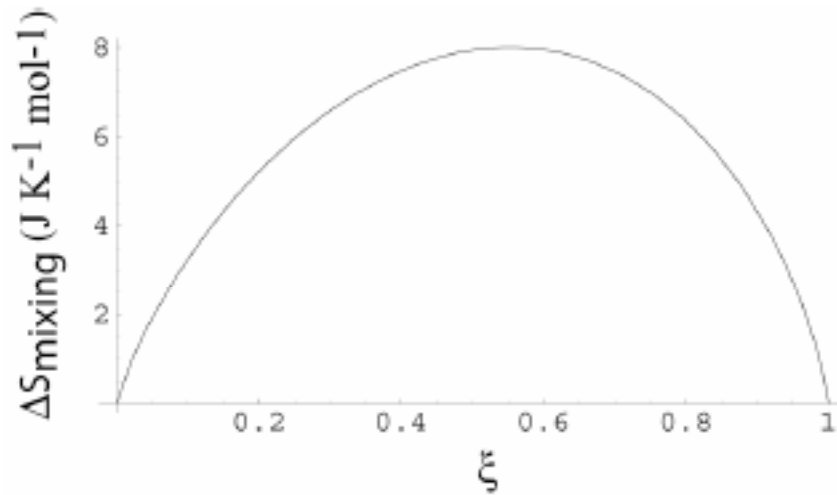
The relative error is  $\frac{8.68 \times 10^{-2} - 8.49 \times 10^{-2}}{8.49 \times 10^{-2}} = 2.2\%$ .

**P30**

a) Derive an expression for the entropy of mixing as a function of  $\xi$ .

$$\Delta S_{\text{mixing}} = -nR \left( x_{\text{NO}_2} \ln x_{\text{NO}_2} + x_{\text{N}_2\text{O}_4} \ln x_{\text{N}_2\text{O}_4} \right)$$
$$= -(2.00 - \xi)R \left( \frac{2.00 - 2\xi}{2.00 - \xi} \ln \frac{2.00 - 2\xi}{2.00 - \xi} + \frac{\xi}{2.00 - \xi} \ln \frac{\xi}{2.00 - \xi} \right)$$

b) A plot and a detail plot locating the maximum are shown below.

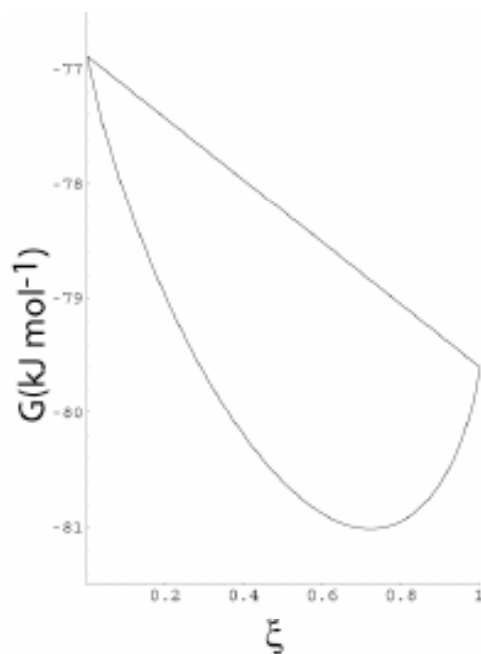


The value of  $\xi$  at the maximum is  $\xi = 0.55$ .

c) Write an expression for  $G_{pure}$  as a function of  $\xi$ .

$$\Delta G_{pure} = (2.00 - 2\xi)\Delta G_f^\circ(\text{NO}_2, g) + \xi\Delta G_f^\circ(\text{N}_2\text{O}_4, g)$$

d) Plot  $\Delta G_{reaction} = G_{pure} + \Delta G_{mixing}$  as a function of  $\xi$  for  $T = 298 \text{ K}$  and graphically determine the value of  $\xi$  for which  $\Delta G_{reaction}$  has its minimum value. Is this value the same as for part (b)?



The minimum is at  $\xi = 0.72$ . The minimum is shifted to higher values of  $\xi$  relative to the  $\Delta S$  vs  $\xi$  curve for mixing because of the contribution of  $G_{pure}$  to  $\Delta G_{reaction}$ .