

Problems: P6.30**HW8A Practice for Second Exam Friday (02/29/08)**

Problem 6.30 embodies many of the points that we need to learn about solving for the equilibrium. Monday's Lecture we will do this problem in class. This is an excellent problem to practice for the second exam.

P6.30) Assume that a sealed vessel at constant pressure of 1 bar initially contains 2.00 mol of $\text{NO}_2(\text{g})$. The system is allowed to equilibrate with respect to the reaction $2 \text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$. The number of moles of $\text{NO}_2(\text{g})$ and $\text{N}_2\text{O}_4(\text{g})$ at equilibrium is $2.00 - 2\xi$ and ξ , respectively, where ξ is the extent of reaction. The symbol ξ , X_i , is used in the text and means the same as the symbol X used in the lectures and in the notes; it is the extent of advancement

- Derive an expression for the entropy of mixing as a function of ξ .
- Graphically determine the value of ξ for which ΔS_{mixing} has its maximum value.
- Write an expression for G_{pure} as a function of ξ . Use Equation (6.34) to obtain values of G_m° for NO_2 and N_2O_4 .
- Plot $G_{\text{mixture}} = G_{\text{pure}} + \Delta G_{\text{mixing}}$ as a function of ξ for $T = 298 \text{ K}$ and graphically determine the value of ξ for which G_{mixture} has its minimum value. Is this value the same as for part (b)?

The answer appears at the end, so don't peek. Work the problem and the additional parts below before you look.

Additional questions about problem 6.30 to consider. For all of these following questions assume the same initial conditions as specified in problem 6.30.

- When computing $\Delta G_{\text{rxn}}^\circ$, provide a qualitative explanation for the sign of the enthalpy and the entropy that go into this number. $\Delta G_{\text{rxn}}^\circ = \Delta H_{\text{rxn}}^\circ - T \Delta S_{\text{rxn}}^\circ$.
- Before plotting the part b) above, explain what range of values ξ or X can take on, based on the initial amounts of material present before equilibrium is achieved.
- By comparison with part d), in which G_{mixture} is plotted as a function of ξ or X , plot $\ln(Q)$ as a function of ξ . Why do we plot the log of Q and not Q ? Why can't we plot the function for the starting point where $\xi = 0$?
- Plot ΔG_{rxn} as a function of ξ and compare the minimum in G_{mixture} with the zero value of ΔG_{rxn} .
- Compare and contrast ΔG_{rxn} and $\Delta G_{\text{rxn}}^\circ$, as to their dependence on ξ .
- Is the system in equilibrium when there is one mole of dimer and one mole of monomer? Why? What is the value of ξ at this point?
- Is it possible for ξ to equal 1.5 moles?
- Is it possible for there to be .75 moles of dimer and .75 moles of monomer (regardless of K_p)?

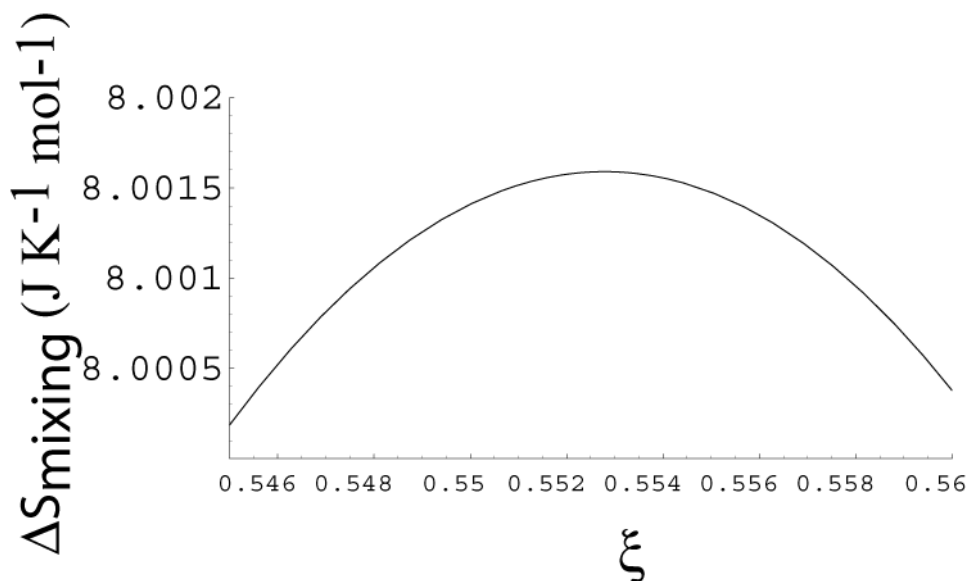
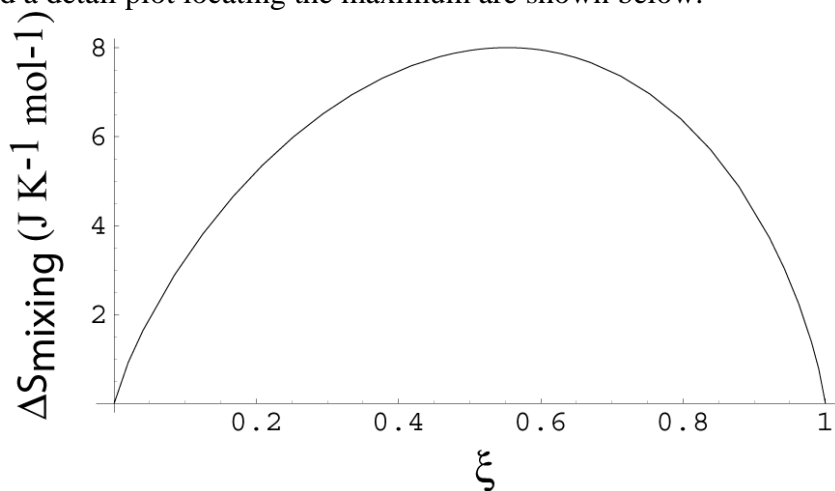
- 9) What pressure should be applied to make the system be in equilibrium with one mole of dimer and one mole of monomer?
- 10) In general, should an increase in pressure produce more monomer or dimer and why?
- 11) Will an increase in the temperature produce more monomer or dimer and why?
- 12) The dissociation and association reaction is called forming a homodimer because the two molecules that form a single molecule are the same. Compare the expression for Q above with the case where one forms a heterodimer, where $A + B \rightleftharpoons A \cdot B$. If the K_p is the same for both the homo and heterodimer reactions and the heterodimer begins with 1 mole of A and 1 mole of B will the partial pressure (or number of moles) of the heterodimer at equilibrium be greater or less than the number of moles of the homodimer at equilibrium, and why?
- 13) What is the optimum concentration of species in the case of the homodimer reaction to give the largest mixing entropy? (From part a) above) Compare this to the optimum concentration of species in the case of heterodimer. How do the optimum values change and why?

a) Derive an expression for the entropy of mixing as a function of ξ .

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

$$= -(2.00 - \xi) R \left(\frac{2.00 - 2\xi}{2.00 - \xi} \ln \frac{2.00 - 2\xi}{2.00 - \xi} + \frac{\xi}{2.00 - \xi} \ln \frac{\xi}{2.00 - \xi} \right)$$

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

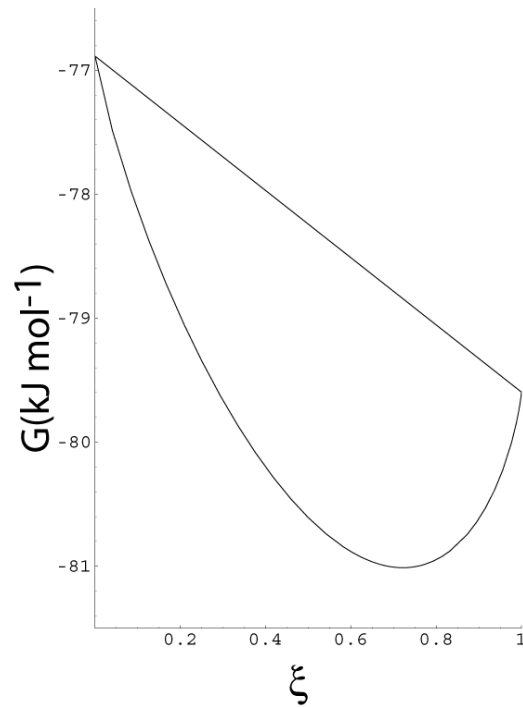


The value of ξ at the maximum is $\xi = 0.55$.

c) Write an expression for G_{pure} as a function of ξ .

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

d) Plot $\Delta G_{\text{reaction}} = G_{\text{pure}} + \Delta G_{\text{mixing}}$ as a function of ξ for $T = 298 \text{ K}$ and graphically determine the value of ξ for which $\Delta G_{\text{reaction}}$ 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 ξ relative to the ΔS vs ξ curve for mixing because of the contribution of G_{pure} to $\Delta G_{\text{reaction}}$.