

### Chapter 20 Problems: Chemical Equilibrium

1. Determine  $\Delta_r G^\circ$  at 298.2 K for the reaction:  $\text{AgCl (s)} \rightleftharpoons \text{Ag}^+ \text{(aq)} + \text{Cl}^- \text{(aq)}$ . The  $K_{\text{sp}}$  for AgCl is  $1.8 \times 10^{-10}$ .

*Answer:* Using  $\Delta_r G^\circ = -RT \ln K_a$ :

$$\Delta_r G^\circ = -8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1} (298.2 \text{ K}) \ln 1.8 \times 10^{-10} = 55.63 \pm 0.13 \text{ kJ mol}^{-1}$$

assuming  $K_{\text{sp}} = 1.8 \times 10^{-10} \pm 0.1 \times 10^{-10}$ . Using significant figure rules you would expect only two significant figures in the result.

2. Nitrogen dioxide forms a dimer in the equilibrium:  $2 \text{NO}_2 \text{(g)} \rightleftharpoons \text{N}_2\text{O}_4 \text{(g)}$ . The standard state reaction Gibbs energy for the dimerization of  $\text{NO}_2$  is  $-4.77 \text{ kJ mol}^{-1}$  at 298.2 K. In a reaction mixture, the partial pressure of  $\text{NO}_2$  is 0.332 bar and of  $\text{N}_2\text{O}_4$  is 0.986 bar. Is the reaction at equilibrium, and if not what is the spontaneous direction for the reaction?

*Answer:* The plan is to calculate the equilibrium constant from  $\Delta_r G^\circ$  and then calculate the reaction quotient,  $Q$ , and compare.

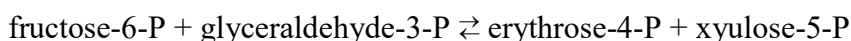
The equilibrium constant is given by:

$$K_p = e^{-\Delta_r G^\circ / RT} = e^{-(-4.77 \times 10^3 \text{ J mol}^{-1}) / (8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.2 \text{ K})} = 6.848$$

The reaction quotient is:  $Q = \frac{P_{\text{N}_2\text{O}_4} / P^\circ}{(P_{\text{NO}_2} / P^\circ)^2} = \frac{0.986}{0.332^2} = 8.945$

Finally,  $Q > K_p$ ; the reaction is not at equilibrium and the spontaneous direction is to the left, towards increased reactant,  $\text{NO}_2$ .

3. Under standard conditions, one of the steps in the photosynthetic production of glucose does not occur spontaneously:



where  $\Delta_r G^\circ = +6.28 \text{ kJ mol}^{-1}$  at 298.2 K. The “P” indicates the phosphorylated form of the sugar; fructose-6-P is fructose-6-phosphate. Can this reaction take place spontaneously in a chloroplast where the concentrations are:  $[\text{fructose-6-P}] = 53.0 \times 10^{-5} \text{ M}$ ,  $[\text{glyceraldehyde-3-P}] = 3.20 \times 10^{-5} \text{ M}$ ,  $[\text{erythrose-4-P}] = 2.00 \times 10^{-5} \text{ M}$ , and  $[\text{xyulose-5-P}] = 2.10 \times 10^{-5} \text{ M}$ ?

*Answer:* The prime for  $\Delta_r G^\circ$  indicates  $\text{pH} = 7$ , the “biochemist’s standard state.” The reaction Gibbs energy under non-standard state conditions is given by Eq. 20.1.10:

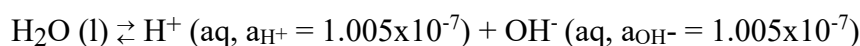
$$\Delta_r G = \Delta_r G^\circ + RT \ln Q = \Delta_r G^\circ + RT \ln \left( \frac{[\text{erythrose-4-P}]/c^\circ [\text{xyulose-5-P}]/c^\circ}{[\text{fructose-6-P}]/c^\circ [\text{glyceraldehyde-3-P}]/c^\circ} \right)$$

where  $c^\circ = 1 \text{ M}$ , the standard state concentration. Substituting the given values:

$$\begin{aligned} \Delta_r G &= +6.28 \text{ kJ mol}^{-1} + 8.314 \text{ J K}^{-1} \text{ mol}^{-1} (1 \text{ kJ}/1000 \text{ J})(298.15 \text{ K}) \ln \left( \frac{(2.00 \times 10^{-5})(2.10 \times 10^{-5})}{(53.0 \times 10^{-5})(3.20 \times 10^{-5})} \right) \\ &= +6.28 - 9.17 \text{ kJ mol}^{-1} = -2.89 \text{ kJ mol}^{-1} \end{aligned}$$

The reaction is spontaneous under these conditions.

4. At 298.15 K the  $\Delta_r G^\circ$  for the dissociation of water to  $\text{H}^+$  and  $\text{OH}^-$  is  $79.89 \text{ kJ mol}^{-1}$ . Calculate  $\Delta_r G$  for the reaction conditions specified below.

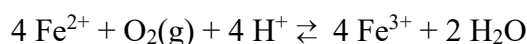


*Answer:* The reaction Gibbs energy under non-standard state conditions is given by Eq. 20.1.10:

$$\begin{aligned} \Delta_r G &= \Delta_r G^\circ + RT \ln Q = \Delta_r G^\circ + RT \ln[(a_{\text{H}^+})(a_{\text{OH}^-})] \\ &= 79.89 \text{ kJ/mol} + 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} (1 \text{ kJ}/1000 \text{ J})(298.15 \text{ K}) \ln(1.010 \times 10^{-14}) \\ &= 79.89 - 79.888 \text{ kJ mol}^{-1} = 0 \end{aligned}$$

The reaction conditions correspond to  $\text{pH} = 7.00$ , which is the equilibrium state for pure water at 298.15 K:  $K_w = 1.01 \times 10^{-14}$  at 298.15 K on a molal concentration basis. The reaction Gibbs energy at equilibrium should be zero.

5. In rivers and lakes, bacteria catalyze the oxidation of Fe(II) to Fe(III):



with  $\Delta_r G^\circ(\text{Fe}^{2+}) = -78.90 \text{ kJ mol}^{-1}$ ,  $\Delta_r G^\circ(\text{Fe}^{3+}) = -4.70 \text{ kJ mol}^{-1}$ , and  $\Delta_r G^\circ(\text{H}_2\text{O}) = -237.13 \text{ kJ mol}^{-1}$ . Calculate the reaction Gibbs energy for  $m_{\text{Fe}^{2+}} = 1.00 \times 10^{-6} \text{ m}$ ,  $m_{\text{Fe}^{3+}} = 1.00 \times 10^{-5} \text{ m}$ ,  $P_{\text{O}_2} = 0.200 \text{ bar}$ ,  $m_{\text{H}^+} = 1.00 \times 10^{-6} \text{ m}$  at 298.15 K (neglect activity coefficients).

*Answer:* The standard state reaction Gibbs energy is given by  $\Delta_r G^\circ = [\Sigma \text{products}] - [\Sigma \text{reactants}]$ :

$$\begin{aligned} \Delta_r G^\circ &= [2(-237.13 \text{ kJ mol}^{-1}) + 4(-4.70 \text{ kJ mol}^{-1})] - [4(-78.90 \text{ kJ mol}^{-1}) + (0) + 4(0)] \\ &= -177.46 \text{ kJ mol}^{-1} \end{aligned}$$

The reaction Gibbs energy under non-standard state conditions is given by Eq. 20.1.10:

$$\Delta_r G = \Delta_r G^\circ + RT \ln Q = \Delta_r G^\circ + RT \ln \left( \frac{(m_{\text{Fe}^{3+}}/m^\circ)^4}{(m_{\text{Fe}^{2+}}/m^\circ)^4 (P_{\text{O}_2}/P^\circ) (m_{\text{H}^+}/m^\circ)^4} \right)$$

where  $m^\circ = 1 \text{ m}$ , the standard state concentration. Substituting the given values:

$$\Delta_r G = -177.46 + 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} (1 \text{ kJ}/1000 \text{ J})(298.15 \text{ K}) \ln \left( \frac{(1.00 \times 10^{-5})^4}{(1.00 \times 10^{-6})^4 (0.200)(1.00 \times 10^{-6})^4} \right)$$

$$= -177.46 \text{ kJ mol}^{-1} + 163.80 \text{ kJ mol}^{-1} = -13.66 \text{ kJ mol}^{-1}$$

Note that the reaction pH can have a large influence of the spontaneity for redox reactions if the stoichiometric coefficient for the  $\text{H}^+$  ion is large, as it is in this case.

6. The equilibrium constant for the dissociation  $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g})$  is  $K_p = 0.146$  at 298.2 K. Assume that the initial amount of  $\text{N}_2\text{O}_4$  is 0.300 mol with no initial  $\text{NO}_2$ . Find the equilibrium partial pressures for the dissociation assuming that the reaction is run under constant pressure conditions at (a) 0.500 bar and at (b) 5.00 bar. (c). Does the shift in equilibrium position with applied pressure agree with LeChâtelier's Principle?

*Answer:* The plan is to set up a table to calculate the mole fractions and partial pressures of  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$  based on the extent of the reaction,  $\xi$ . The equilibrium expression is then constructed in terms of  $\xi$ , and the expression is solved for  $\xi$ . This problem is very similar to Example 20.2.1.

Let the initial moles of  $\text{N}_2\text{O}_4$  be "a." The total moles at equilibrium will be:

$$n_{\text{tot}} = (a - \xi) + 2 \xi = a + \xi \quad 1$$

Next, a table for the moles of each reactant and product is constructed. Then the mole fractions using  $Y_i = n_i/n_{\text{tot}}$  and the equilibrium partial pressures using Dalton's Law of pressures,  $P_i = Y_i P$ , are calculated:

	$\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g})$		
moles	$a - \xi$	$2\xi$	
$Y_i$	$\frac{a - \xi}{a + \xi}$	$\frac{2\xi}{a + \xi}$	
$P_i$	$\frac{a - \xi}{a + \xi} P$	$\frac{2\xi}{a + \xi} P$	2

where  $P$  is the total applied pressure. The equilibrium expression (law of mass action) is:

$$K_p = \frac{(P_{\text{NO}_2}/P^\circ)^2}{P_{\text{N}_2\text{O}_4}/P^\circ} = \frac{\left(\frac{2\xi}{a + \xi}\right)^2}{\left(\frac{a - \xi}{a + \xi}\right)} (P/P^\circ) = \frac{4\xi^2}{(a + \xi)(a - \xi)} (P/P^\circ) = \frac{4\xi^2}{a^2 - \xi^2} (P/P^\circ) \quad 3$$

Notice the similarity to Eq. 20.2.7. To solve for the extent, divide both sides of the last equation by  $(P/P^\circ)$ :

$$\frac{4\xi^2}{a^2 - \xi^2} = \frac{K_p}{(P/P^\circ)} = K_x \quad 4$$

The last equality results since  $K_p = K_x (P/P^\circ)^{\Delta n_g}$  with  $\Delta n_g = 1$  for this dissociation. The solution to Eq. 4 is:

$$\xi = \left(\frac{K_x}{4 + K_x}\right)^{1/2} a \quad 5$$

(a). For  $P = 0.5$  bar:  $K_x = 0.292$  and  $\xi = \left(\frac{0.292}{4+0.292}\right)^{1/2} 0.300 \text{ mol} = 0.07825 \text{ mol}$

which gives a degree of dissociation of  $\alpha = \xi/n_{\text{tot}} = 0.261$ . The partial pressures using Eqs. 2 are:

$$P_{\text{N}_2\text{O}_4} = \frac{a - \xi}{a + \xi} P = \frac{0.300 - 0.07825}{0.300 + 0.07825} P = 0.2931 \text{ bar}$$

and  $P_{\text{NO}_2} = \frac{2\xi}{a + \xi} P = \frac{2(0.07825)}{0.300 + 0.07825} P = 0.2069 \text{ bar}$

(b). For  $P = 5.00$  bar:  $K_x = 0.0292$  and  $\xi = \left(\frac{0.0292}{4+0.0292}\right)^{1/2} 0.300 \text{ mol} = 0.02554 \text{ mol}$

which gives a degree of dissociation of  $\alpha = \xi/n_{\text{tot}} = 0.085$ . The partial pressures using Eqs. 2 are:

$$P_{\text{N}_2\text{O}_4} = \frac{a - \xi}{a + \xi} P = \frac{0.300 - 0.02554}{0.300 + 0.02554} P = 4.215 \text{ bar}$$

and  $P_{\text{NO}_2} = \frac{2\xi}{a + \xi} P = \frac{2(0.02554)}{0.300 + 0.02554} P = 0.7845 \text{ bar}$

(c). For a reaction with  $\Delta_r n_g = 1$ , the equilibrium extent should decrease with an increase in pressure, thus favoring the side of the reaction with the fewer moles of gas. The decrease in the degree of dissociation with pressure for this problem shows the expected result.

7. Calculate the equilibrium partial pressures at 298.2 K for the dimerization of  $\text{NO}_2$ :  
 $2 \text{NO}_2 (\text{g}) \rightleftharpoons \text{N}_2\text{O}_4 (\text{g})$ . The standard state reaction Gibbs energy for the dimerization of  $\text{NO}_2$  is  $-4.77 \text{ kJ mol}^{-1}$  at 298.2 K. Assume the initial amount of  $\text{NO}_2$  is 0.300 moles at a constant total pressure of 1.00 bar. [Hint: you may use successive approximations to solve for the equilibrium position.]

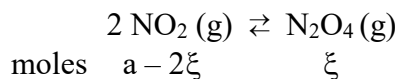
*Answer:* The plan is to set up a table to calculate the mole fractions and partial pressures of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  based on the extent of the reaction,  $\xi$ . The equilibrium expression is then constructed in terms of  $\xi$ , and the expression is solved for  $\xi$ . The equilibrium constant is given by:

$$K_p = e^{-\Delta_r G^\circ/RT} = e^{-(-4.77 \times 10^3 \text{ J mol}^{-1})/(8.314 \text{ J K}^{-1} \text{ mol}^{-1} 298.2 \text{ K})} = 6.848$$

Let the initial moles of  $\text{NO}_2$  be “a.” The total moles at equilibrium will be:

$$n_{\text{tot}} = (a - 2\xi) + \xi = a - \xi$$

Next, set up a table for the moles of each reactant and product, the mole fractions using  $Y_i = n_i/n_{\text{tot}}$ , and the equilibrium partial pressures using Dalton’s Law of pressures,  $P_i = Y_i P$ , with  $P$  the total pressure:



$$Y_i = \frac{a - 2\xi}{a - \xi} \quad \frac{\xi}{a - \xi}$$

$$P_i = \frac{a - 2\xi}{a - \xi} P \quad \frac{\xi}{a - \xi} P$$

The equilibrium expression (law of mass action) is:

$$K_p = \frac{P_{\text{N}_2\text{O}_4}/P^\circ}{(P_{\text{NO}_2}/P^\circ)^2} = \frac{\left(\frac{\xi}{a - \xi}\right)}{\left(\frac{a - 2\xi}{a - \xi}\right)^2} (P/P^\circ)^{-1} = \frac{\xi(a - \xi)}{(a - 2\xi)^2} (P/P^\circ)^{-1} = \frac{a\xi - \xi^2}{(a - 2\xi)^2} (P/P^\circ)^{-1} \quad 1$$

with  $P = 1$  bar specified in the problem. This expression can be solved exactly using the quadratic expression:

$$(4K+1)\xi^2 - (4K+1)a\xi + Ka^2 = 0 \quad \text{giving} \quad \xi = \left(1 \pm \sqrt{\frac{1}{4K+1}}\right) \frac{a}{2} = 0.1218 \text{ mol}$$

However, successive approximations is often more time efficient. Using the values given:

$$K_p = \frac{0.300 \xi - \xi^2}{(0.300 - 2\xi)^2} = 6.848 \quad 2$$

As a basis for successive approximations, we need to solve this last equation for  $\xi$  in terms that also involve  $\xi$ . Two examples will show the idea. Solving the last equation for  $\xi$ :

$$(0.300 - 2\xi)^2 = \frac{0.300 \xi - \xi^2}{6.848} \quad \text{or} \quad 0.300 \xi - \xi^2 = 6.848 (0.300 - 2\xi)^2 \quad 3$$

$$\text{giving: } \xi = \frac{1}{2} \left( 0.300 - \left( \frac{0.300 \xi - \xi^2}{6.848} \right)^{1/2} \right) \quad \text{or} \quad \xi = \sqrt{0.300 \xi - 6.848 (0.300 - 2\xi)^2} \quad 4$$

The next step is to guess an initial value. The extent of the reaction may vary from 0 to 0.300/2 moles. A short spreadsheet was written based on the first iteration formula in Eqs. 4 with an initial guess of 0.05 mol, below. The update formula for  $\xi$  in C8 is “=((\$C\$3-SQRT(B8\*(\$C\$3-B8)/\$C\$4))/2)”. The last column calculates the equilibrium constant using Eq. 2 with the updated value of  $\xi$  to check for accuracy. The approximation converges in three iterations. This update formula works for guesses from  $\xi = 1.0 \times 10^{-5}$  to 0.2999 mol. The range of initial guesses that leads, or converges, to the correct answer is called the convergence interval. Guesses outside the convergence interval either diverge or oscillate around the correct value.

A1	B	C	D
2			
3	a=	0.3	
4	Kp=	6.848	
5			
6	guess	updated	giving
7	extent	extent	Q
8	0.05	0.128638	12.0764
9	0.128638	0.121632	6.739764
10	0.121632	0.121857	6.852015
11	0.121857	0.121849	6.847854
12	0.121849	0.121849	6.848005

The second update formula from Eqs. 4 converges over the interval [0.115, 0.19]. Some rearrangements of Eq. 2 do not lead to update formulas that converge on the final result for any initial guess. The disadvantage of the successive approximations approach is that several rearrangements may need to be tried to find an update formula that converges rapidly.

For  $\xi = 0.1218$  mol the corresponding partial pressures are:

$$P_{\text{NO}_2} = \frac{a - 2\xi}{a - \xi} P = \left( \frac{0.300 - 2(0.1218)}{0.300 - 0.1218} \right) 1.00 \text{ bar} = 0.3164 \text{ bar}$$

$$P_{\text{N}_2\text{O}_4} = \frac{\xi}{a - \xi} P = \left( \frac{0.1218}{0.300 - 0.1218} \right) 1.00 \text{ bar} = 0.6835 \text{ bar}$$

Checking the final results against the equilibrium constant gives  $K_p = 0.6835/(0.3164)^2 = 6.838$

*Method 2:* A clever way to approach this problem is to first assume the reaction goes to completion, giving the moles of  $\text{N}_2\text{O}_4$  as 0.150 mol. Then reversing the reaction gives the form of a dissociation:  $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g})$  with  $K_p' = 1/K_p = 1/6.848 = 0.1460$ . Then using Problem 6 Eq. 3, above:

$$K_p' = K_x (P/P^\circ) = \frac{4 \xi^2}{a^2 - \xi^2} (P/P^\circ) = \frac{4 \xi^2}{0.150^2 - \xi^2} = 0.1460$$

where “a” is now the amount of  $\text{N}_2\text{O}_4$ . Solving for the extent at equilibrium for the new direction gives  $\xi = 0.0282$  mol, which results in the same final partial pressures as the more direct method.

8. Calculate the equilibrium partial pressures and the degree of dissociation for the reaction:



The equilibrium constant is  $K_p = 2.78$  at  $110^\circ\text{C}$ . Assume a constant total pressure of 0.500 bar with 2.00 moles of  $\text{SO}_2\text{Cl}_2$ , only, initially placed in the reaction vessel.

*Answer:* The plan is to note that the reaction is a  $\text{A}(\text{g}) \rightleftharpoons \text{B}(\text{g}) + \text{C}(\text{g})$  dissociation, for which Eq. 20.2.7 and 20.2.8 apply.

Since  $\Delta n_g = 1$  and  $K_p = K_x (P/P^\circ)^{\Delta n_g}$ ,  $K_x = 2.78/0.500 = 5.56$ . Using Eqs. 20.2.7 and 20.2.8 with the given parameters:

$$K_x = \frac{\xi^2}{2.00^2 - \xi^2} = 5.56 \quad \text{and} \quad \xi = \left( \frac{K_x}{1+K_x} \right)^{1/2} a = \left( \frac{5.56}{1+5.56} \right)^{1/2} 2.00 \text{ mol} = 1.841 \text{ mol}$$

We can check the result by substituting back in to calculate the resulting equilibrium constant given the extent of the reaction:

$$\text{check } K_x = \frac{\xi^2}{2.00^2 - \xi^2} = \frac{1.841^2}{2.00^2 - 1.841^2} = 5.55$$

which is close enough given round-off error. The degree of dissociation for this stoichiometry is then:

$$\alpha = \xi/a = 1.841/2.00 = 0.920$$

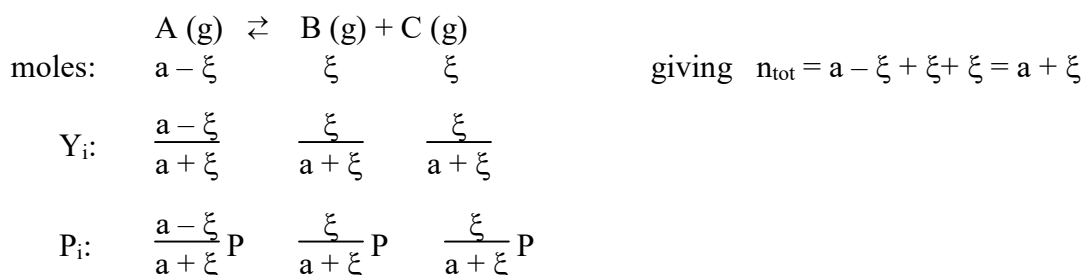
or 92% dissociated at equilibrium.

9. Consider a gas phase dissociation with the stoichiometry  $A(g) \rightleftharpoons B(g) + C(g)$ . (a). Show that the equilibrium expression can be directly expressed in terms of the degree of dissociation as:

$$K_p = \frac{\alpha^2}{1 - \alpha^2} (P/P^\circ) \quad \text{P20.9.1}$$

(b). Solve for the degree of dissociation.

*Answer:* At equilibrium:



where  $n_{\text{tot}}$  is the total moles of gases,  $P_i = Y_i P$ , and the total pressure is  $P$ . Substitution of the mole fractions into  $K_x$  gives:

$$K_p = \frac{(P_B/P^\circ)(P_C/P^\circ)}{(P_A/P^\circ)} = \frac{\left(\frac{\xi}{a + \xi}\right)\left(\frac{\xi}{a + \xi}\right)}{\left(\frac{a - \xi}{a + \xi}\right)} (P/P^\circ) = \frac{\xi^2}{a^2 - \xi^2} (P/P^\circ) \quad 1$$

This result is the corresponding expression to Example 20.2.1, in terms of pressures. Eq. 1 can be expressed in terms of the degree of dissociation. Divide the numerator and denominator by the initial amount of reactant squared,  $a^2$ . Then use the definition of the degree of dissociation for this reaction,  $\alpha = \xi/a$ :

$$K_p = \frac{(\xi/a)^2}{1 - (\xi/a)^2} (P/P^\circ) = \frac{\alpha^2}{1 - \alpha^2} (P/P^\circ) \quad 2$$

The total moles of gas is then determined by  $n_{\text{tot}} = a + \xi = a(1 + \alpha)$ .

(b). To solve for the degree of dissociation, divide both sides of the last equation by  $(P/P^\circ)$ :

$$\frac{\alpha^2}{1 - \alpha^2} = \frac{K_p}{(P/P^\circ)} = K_x \quad 3$$

The last equality results since  $K_p = K_x (P/P^\circ)^{\Delta n_g}$  with  $\Delta n_g = 1$  for this dissociation. The solution to Eq. 3 is:

$$\alpha = \left( \frac{K_x}{1+K_x} \right)^{1/2} \quad 4$$

10. For the reaction  $\text{H}_2\text{S}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \frac{1}{2} \text{S}_2(\text{g})$  the degree of dissociation of  $\text{H}_2\text{S}$  is 0.305 at  $1125^\circ\text{C}$  and 1.00 bar total pressure. Calculate  $K_p$  at  $1125^\circ\text{C}$ .

*Answer:* To determine the equilibrium expression for the reaction, let the initial moles of  $\text{H}_2\text{S}$  be “a” and the extent of the reaction be  $\xi$ . The total moles at equilibrium is:

$$n_{\text{tot}} = (a - \xi) + \xi + \frac{1}{2} \xi = a + \frac{1}{2} \xi$$

Next, set up a table for the moles of each reactant and product, the mole fractions using  $Y_i = n_i/n_{\text{tot}}$ , and the equilibrium partial pressures using Dalton’s Law of pressures,  $P_i = Y_i P$ , with  $P$  the total pressure:

	$\text{H}_2\text{S}(\text{g})$	$\rightleftharpoons$	$\text{H}_2(\text{g})$	$+$	$\frac{1}{2} \text{S}_2(\text{g})$
moles	$a - \xi$		$\xi$		$\frac{1}{2} \xi$
$Y_i$	$\frac{a - \xi}{a + \frac{1}{2} \xi}$		$\frac{\xi}{a + \frac{1}{2} \xi}$		$\frac{\frac{1}{2} \xi}{a + \frac{1}{2} \xi}$
$P_i$	$\frac{a - \xi}{a + \frac{1}{2} \xi} P$		$\frac{\xi}{a + \frac{1}{2} \xi} P$		$\frac{\frac{1}{2} \xi}{a + \frac{1}{2} \xi} P$

The equilibrium expression (law of mass action) then simplifies to:

$$K_p = \frac{(P_{\text{H}_2}/P^\circ) (P_{\text{S}_2}/P^\circ)^{1/2}}{(P_{\text{H}_2\text{S}}/P^\circ)} = \frac{\left( \frac{\xi}{a + \frac{1}{2} \xi} \right) \left( \frac{\frac{1}{2} \xi}{a + \frac{1}{2} \xi} \right)^{1/2} (P/P^\circ)^{1/2}}{\left( \frac{a - \xi}{a + \frac{1}{2} \xi} \right)} = \left( \frac{\xi}{a - \xi} \right) \left( \frac{\frac{1}{2} \xi}{a + \frac{1}{2} \xi} \right)^{1/2} (P/P^\circ)^{1/2}$$

Divide the numerator and denominator of each expression in parentheses by the initial moles of  $\text{H}_2\text{S}$  and then substitute the definition of the degree of dissociation,  $\alpha = \xi/a$ :

$$K_p = \left( \frac{\alpha}{1 - \alpha} \right) \left( \frac{\frac{1}{2} \alpha}{1 + \frac{1}{2} \alpha} \right)^{1/2} (P/P^\circ)^{1/2}$$

Substituting the given degree of dissociation:

$$K_p = \left( \frac{0.305}{1 - 0.305} \right) \left( \frac{\frac{1}{2} 0.305}{1 + \frac{1}{2} 0.305} \right)^{1/2} 1.00^{1/2} = (0.4388)(0.1323)^{1/2} = 0.160$$

11. The  $K_p$  and  $K_x$  based equilibrium expressions are convenient to use for reactions at constant pressure.  $K_c$  based expressions are convenient for reactions at constant volume. Consider dissociation with the stoichiometry:  $\text{A}(\text{g}) \rightleftharpoons \text{B}(\text{g}) + \text{C}(\text{g})$ . Set up the  $K_p$  expression in terms of the extent of the reaction,  $\xi$ , as in Example 20.2.1. Show that the  $K_p$  expression reduces to:



$$K_c = \frac{(x/c^\circ)^2}{c_{A0}/c^\circ - x/c^\circ}$$

where  $c_{A0}$  is the initial concentration of A and  $x$  is the final concentration of B and C. Assume the reaction is run at constant volume.

*Answer:* The total moles of gas in the reaction mixture is:  $n_{\text{tot}} = a - \xi + \xi + \xi = a + \xi$ . The concentration of a constituent in the reaction mixture is  $c_i = n_i/V$ , with  $n_i$  moles of constituent  $i$  and  $V$  the total volume. The total pressure is determined by the total moles of gas:

$$P = n_{\text{tot}} RT/V = (a + \xi) RT/V \quad 1$$

with the total volume  $V$  held constant. We next lay out the equilibrium state in terms of moles, mole fractions, and partial pressures. In the last step we substitute Eq. 1 for the total pressure and cancel the common factor:

moles:	$A(g) \rightleftharpoons$	$B(g) +$	$C(g)$
	$a - \xi$	$\xi$	$\xi$
X <sub>i</sub> :	$\frac{a - \xi}{a + \xi}$	$\frac{\xi}{a + \xi}$	$\frac{\xi}{a + \xi}$
P <sub>i</sub> :	$\frac{a - \xi}{a + \xi} (P/P^\circ)$	$\frac{\xi}{a + \xi} (P/P^\circ)$	$\frac{\xi}{a + \xi} (P/P^\circ)$
P <sub>i</sub> :	$\frac{a - \xi}{V} (RT/P^\circ)$	$\frac{\xi}{V} (RT/P^\circ)$	$\frac{\xi}{V} (RT/P^\circ)$

The  $K_p$  expression is then:

$$K_p = \frac{(P_B/P^\circ)(P_C/P^\circ)}{(P_A/P^\circ)} = \frac{(\xi/V)(\xi/V)}{(a - \xi)/V} (RT/P^\circ) \quad 3$$

Let  $c_{A0}$  be the initial concentration of A with  $c_{A0} = a/V$  and let  $x$  be the final concentration of B and C with  $x = \xi/V$ . Substitution of these definitions into Eq. 3 gives:

$$K_p = \frac{x^2}{c_{A0} - x} (RT/P^\circ) \quad 4$$

Multiply and divide through each concentration term by  $c^\circ$  and collect terms to ensure that the concentration based equilibrium constant is unitless:

$$K_p = \frac{(x/c^\circ)^2}{c_{A0}/c^\circ - x/c^\circ} (c^\circ RT/P^\circ) = K_c (c^\circ RT/P^\circ) \quad 5$$

Note that the result agrees with  $K_p = K_c (c^\circ RT/P^\circ)^{\Delta n_g}$  with  $\Delta n_g = 1$  for this reaction. Dividing Eq. 5 by  $(c^\circ RT/P^\circ)$ :

$$K_c = \frac{(x/c^\circ)^2}{c_{A0}/c^\circ - x/c^\circ} \quad 6$$

In other words, at constant volume, the position of equilibrium can be determined by solving the  $K_p$  or  $K_c$  expressions. Eq. 6 is the form for the equilibrium expression most commonly used in General Chemistry texts for this type of problem.

12. Calculate the equilibrium partial pressures and the degree of dissociation for the reaction:



The equilibrium constant is  $K_p = 2.78$  at  $110.^\circ\text{C}$ . Assume the reaction starts with 2.00 moles of  $\text{SO}_2\text{Cl}_2$ , only, initially placed in the reaction vessel with an initial pressure of 0.500 bar. Assume the reaction runs at constant volume (see Problem 8 for the constant pressure version of this problem).

*Answer:* The plan is to convert the initial amount of  $\text{SO}_2\text{Cl}_2$  to the equivalent concentration and then use  $K_c = (x/c^\circ)^2 / (c_{\text{A}0}/c^\circ - x/c^\circ)$ . [In General Chemistry, you allowed  $K_c$  to have units and then  $K_c = x^2 / (c_{\text{A}0} - x)$ .]

For the given conditions, the volume and initial concentration of  $\text{SO}_2\text{Cl}_2$  are:

$$V = n_{\text{SO}_2\text{Cl}_2} RT/P = 2.00 \text{ mol}(0.08314 \text{ L bar K}^{-1} \text{ mol}^{-1})(383.15 \text{ K})/0.500 \text{ bar} = 127.4 \text{ L}$$

$$c_{\text{A}0} = n_{\text{SO}_2\text{Cl}_2}/V = 2.00 \text{ mol}/127.4 \text{ L} = 0.01570 \text{ mol L}^{-1}$$

Then using concentrations at equilibrium:



$$c_i: \quad c_{\text{A}0} - x \quad \quad x \quad \quad x$$

$$K_c = \frac{(x/c^\circ)^2}{c_{\text{A}0}/c^\circ - x/c^\circ} \quad (x/c^\circ)^2 + K_c x/c^\circ - K_c c_{\text{A}0}/c^\circ = 0 \quad x/c^\circ = \frac{-K_c \pm \sqrt{K_c^2 + 4 K_c c_{\text{A}0}/c^\circ}}{2}$$

Using  $K_p = K_c (c^\circ RT/P^\circ)^{\Delta n_g}$  and  $\Delta n_g = 1$  for this reaction:

$$K_c = \frac{2.78 (1 \text{ bar})}{0.08314 \text{ L bar mol}^{-1}(383.15 \text{ K})(1 \text{ mol L}^{-1})} = 0.08726 = \frac{(x/c^\circ)^2}{0.01570 \text{ mol L}^{-1} - x/c^\circ}$$

$$x = 0.013585 \text{ mol L}^{-1}$$

$$c_{\text{SO}_2\text{Cl}_2} = (c_{\text{A}0} - x) = (0.01570 - 0.013585 \text{ mol L}^{-1}) = 0.00211 \text{ mol L}^{-1}$$

Giving the final amounts and partial pressures:

$$n_{\text{SO}_2\text{Cl}_2} = (c_{\text{A}0} - x) V = (0.00211 \text{ mol L}^{-1}) 127.4 \text{ L} = 0.2690 \text{ mol}$$

$$P_{\text{SO}_2\text{Cl}_2} = (c_{\text{A}0} - x) RT = 0.00211 \text{ mol L}^{-1}(0.08314 \text{ L bar K}^{-1} \text{ mol}^{-1})(383.15 \text{ K}) = 0.067 \text{ bar}$$

$$n_{\text{SO}_2} = n_{\text{Cl}_2} = x V = 1.73 \text{ mol}$$

$$P_{\text{SO}_2} = P_{\text{Cl}_2} = x RT = 0.433 \text{ bar}$$

The final pressure is  $P = P_{\text{SO}_2\text{Cl}_2} + P_{\text{SO}_2} + P_{\text{Cl}_2} = 0.933 \text{ bar}$  and the degree of dissociation is:

$$\alpha = n_{\text{SO}_2} / n_{\text{SO}_2\text{Cl}_2,0} = 1.73 \text{ mol}/2.00 \text{ mol} = 0.865$$

or equivalently:  $\alpha = (n_{\text{SO}_2}/V)/(n_{\text{SO}_2\text{Cl}_2,0}/V) = x/c_{\text{A}0} = 0.013585 \text{ mol L}^{-1}/0.01570 \text{ mol L}^{-1} = 0.865$ .

Notice that the degree of dissociation is less than Problem 8, with a constant total pressure. The smaller degree of dissociation for the constant volume process is consistent with LeChâtelier's Principle, given  $\Delta_r n_g = 1$  and the corresponding increase in pressure for this reaction. (See Problem 11 for more information on constant volume reactions.)

13. For the reaction  $\text{BeSO}_4(\text{s}) \rightleftharpoons \text{BeO}(\text{s}) + \text{SO}_3(\text{g})$ ,  $K_p = 1.71 \times 10^{-19}$  at 400.0 K and  $9.70 \times 10^{-11}$  at 600.0 K. (a). Predict, without doing the numerical calculation, if the reaction is endothermic or exothermic. (b). Calculate  $\Delta_r H^\circ$  for this temperature range and  $\Delta_r G^\circ$  and  $\Delta_r S^\circ$  at 400.0 K.

*Answer:* The plan is to use LeChâtelier's Principle for part (a) and the integrated form of the van 't Hoff equation for two data points, Eq. 20.1.28, for part (b). Then the thermodynamic parameters are calculated using  $\Delta_r G^\circ = -RT \ln K_p$  and  $\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ$  at 400.0 K.

(a). The equilibrium constant increases with temperature. In other words, the position of equilibrium shifts to the right, the forward direction, with an increase in temperature. The forward direction for the reaction, as written, must then be the endothermic direction.

(b). From Eq. 20.1.28, assuming  $\Delta_r H^\circ$  is constant over the temperature range:

$$\ln \frac{K_{p,T_2}}{K_{p,T_1}} = -\frac{\Delta_r H^\circ}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\ln \frac{9.70 \times 10^{-11}}{1.71 \times 10^{-19}} = -\frac{\Delta_r H^\circ}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \left( \frac{1}{600.0 \text{ K}} - \frac{1}{400.0 \text{ K}} \right)$$

$$\ln \frac{9.70 \times 10^{-11}}{1.71 \times 10^{-19}} = -\frac{\Delta_r H^\circ}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} (0.0016667 - 0.0025000)$$

$$20.156 = -\frac{\Delta_r H^\circ}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} (-8.333 \times 10^{-4} \text{ K}^{-1})$$

$$\Delta_r H^\circ = 2.011 \times 10^5 \text{ J mol}^{-1} = 201.1 \text{ kJ mol}^{-1}$$

Remember to carry at least one extra significant figure than allowed for the  $(1/T_2 - 1/T_1)$  term to avoid round-off error. The standard state reaction Gibbs energy and entropy at 400 K are then:

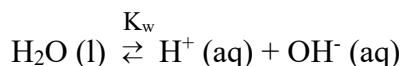
$$\Delta_r G^\circ = -RT \ln K_p = -8.3145 \text{ J K}^{-1} \text{ mol}^{-1} (400.0 \text{ K}) (1 \text{ kJ}/1000 \text{ J}) \ln 1.71 \times 10^{-19}$$

$$= 143.7 \text{ kJ mol}^{-1}$$

$$\Delta_r S^\circ = \frac{\Delta_r H^\circ - \Delta_r G^\circ}{T} = \frac{(201.1 \text{ kJ mol}^{-1} - 143.7 \text{ kJ mol}^{-1})(1000 \text{ J}/1 \text{ kJ})}{400.0 \text{ K}} = 144. \text{ J K}^{-1} \text{ mol}^{-1}$$

$$= 1.4 \times 10^2 \text{ J K}^{-1} \text{ mol}^{-1}$$

14. The autoprotolysis constant for water,  $K_w$ , is the equilibrium constant for the reaction:



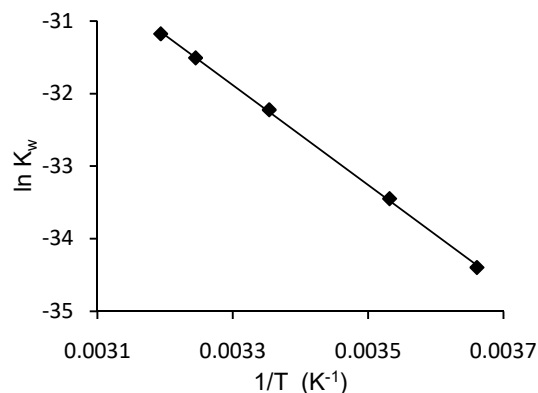
The temperature dependence for  $K_w$  is given in the table, below.<sup>1</sup> (a). Assume  $\Delta_r H^\circ$  is constant. Calculate  $\Delta_r H^\circ$  for this temperature range and  $\Delta_r G^\circ$  and  $\Delta_r S^\circ$  at 298.2 K. (b). Neutral pH is the pH that gives  $a_{H^+} = a_{OH^-}$ . Calculate the pH of a neutral solution at each temperature.

T (°C)	0.0	10.0	25.0	35.0	40.0
$K_w$	$1.15 \times 10^{-15}$	$2.97 \times 10^{-15}$	$1.01 \times 10^{-14}$	$2.07 \times 10^{-14}$	$2.88 \times 10^{-14}$

*Answer:* First, don't forget to convert to kelvins. Eq. 20.1.31 shows a plot of  $\ln K_w$  versus  $1/T$  gives a slope of  $-\Delta_r H^\circ/R$ :

$K_w$	T (K)	$1/T$ ( $K^{-1}$ )	$\ln K$
1.15E-15	273.15	0.003661	-34.399
2.97E-15	283.15	0.003532	-33.4502
1.01E-14	298.15	0.003354	-32.2262
2.07E-14	308.15	0.003245	-31.5086
2.88E-14	313.15	0.003193	-31.1784

slope	-6878.66	-9.18538	intercept
$\pm$	85.91525	0.292248	$\pm$
$r^2$	0.999532	0.033738	s(y)
F	6410.131	3	df
SSreg	7.296323	0.003415	SSresid



The corresponding  $\Delta_r H^\circ$  is:

$$\Delta_r H^\circ = -8.3145 \text{ J K}^{-1} \text{ mol}^{-1} (-6878.66 \text{ K}^{-1})(1\text{kJ}/1000 \text{ J}) = 57.2 \pm 0.7 \text{ kJ mol}^{-1}$$

From the data table at 298.15 K:

$$\begin{aligned} \Delta_r G^\circ &= -RT \ln K_w = -8.3145 \text{ J K}^{-1} \text{ mol}^{-1} (298.15 \text{ K}) (1\text{kJ}/1000 \text{ J}) \ln 1.01 \times 10^{-14} \\ &= 79.89 \text{ kJ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta_r S^\circ &= \frac{\Delta_r H^\circ - \Delta_r G^\circ}{T} = \frac{(57.2 \text{ kJ mol}^{-1} - 79.89 \text{ kJ mol}^{-1})(1000 \text{ J}/1 \text{ kJ})}{298.15 \text{ K}} \\ &= -76.1 \pm 2.3 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

Notice that there is noticeable upward curvature to the plot, showing that the reaction enthalpy is temperature dependent for this range of temperatures. A more accurate estimation of  $\Delta_r S^\circ$  would result from a curve fit to Eq. 20.1.36.

(b). From the equilibrium expression:  $K_w = (a_{H^+})(a_{OH^-})$ , or  $pK_w = \text{pH} + \text{pOH}$ . For a neutral solution  $\text{pH} = \text{pOH}$ . Neutral pH is then given by  $pK_w/2$ :

T (°C)	0.0	10.0	25.0	35.0	40.0
$K_w$	$1.15 \times 10^{-15}$	$2.97 \times 10^{-15}$	$1.01 \times 10^{-14}$	$2.07 \times 10^{-14}$	$2.88 \times 10^{-14}$
pH=pOH	7.47	7.26	7.00	6.84	6.77

Notice that a neutral solution at body temperature is not pH = 7.

15. In the last problem for the autoprotolysis of water, we assumed that the reaction enthalpy was temperature independent. Assume the temperature dependence of the reaction enthalpy is given by  $\Delta_r H_T^\circ = \Delta_r H_0^\circ + \Delta_r C_p T$ , with  $\Delta_r C_p = -186.6 \pm 2.7 \text{ J K}^{-1} \text{ mol}$ . The temperature dependence of  $\ln K$  is then just the first two terms of Eq. 20.1.36:

$$\ln K = -\frac{\Delta_r H_0^\circ}{RT} + \frac{\Delta_r C_p}{R} \ln T + c$$

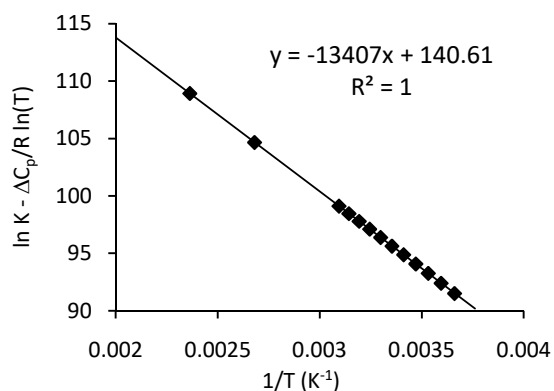
where  $c$  is a constant. Calculate  $\Delta_r H^\circ$ ,  $\Delta_r G^\circ$ , and  $\Delta_r S^\circ$  at 298.2 K. A more complete table for the autoprotolysis constant for water,  $K_w$ , is given in the table, below.<sup>1</sup> [Hint: subtract  $\Delta_r C_p \ln T$  from both sides of the above equation and plot  $(\ln K - \Delta_r C_p \ln T)$  along the vertical axis.]

T (°C)	0.0	5.0	10.0	15.0	20.0	25.0	30.0
$K_w$	$1.15 \times 10^{-15}$	$1.88 \times 10^{-15}$	$2.97 \times 10^{-15}$	$4.57 \times 10^{-15}$	$6.88 \times 10^{-15}$	$1.01 \times 10^{-14}$	$1.46 \times 10^{-14}$
T (°C)	35.0	40.0	45.0	50.0	100.0	150.0	
$K_w$	$2.07 \times 10^{-14}$	$2.88 \times 10^{-14}$	$3.94 \times 10^{-14}$	$5.31 \times 10^{-14}$	$5.43 \times 10^{-13}$	$2.3 \times 10^{-12}$	

*Answer:* As we did in the last problem, convert the temperature to kelvins and calculate  $\ln K_w$  at each temperature. Then subtract  $\Delta_r C_p \ln T$  from both sides of the above equation and plot  $(\ln K - \Delta_r C_p \ln T)$  along the vertical axis and  $1/T$  along the horizontal axis:

$$\ln K - \frac{\Delta_r C_p}{R} \ln T = -\frac{\Delta_r H_0^\circ}{RT} + c$$

T(°C)	K	T (K)	1/T	$\ln K - \Delta_r C_p / R \ln T$
0	1.15E-15	273.15	0.003661	91.505
5	1.88E-15	278.15	0.003595	92.404
10	2.97E-15	283.15	0.003532	93.261
15	4.57E-15	288.15	0.003475	94.085
20	6.88E-15	293.15	0.003411	94.880
25	1.01E-14	298.15	0.003354	95.643
30	1.46E-14	303.15	0.003299	96.385
35	2.07E-14	308.15	0.003245	97.101
40	2.88E-14	313.15	0.003193	97.793
45	3.94E-14	318.15	0.003143	98.462
50	5.31E-14	323.15	0.003095	99.110
100	5.43E-13	373.15	0.00268	104.664
150	2.30E-12	423.15	0.00236	108.930



slope	-13407.4	140.607	intercept
	6.72292	0.02186	
±	6	9	±
r <sup>2</sup>	0.99999	0.00850	s(y)
F	3977173	11	df
SSreg	287.982	0.00079	SSresid
	9	6	

The curve fit results give:

$$\Delta_r H^\circ = -R \text{ slope} = 111.48 \pm 0.05 \text{ kJ mol}^{-1}$$

The corresponding reaction enthalpy at room temperature is:

$$\begin{aligned} \Delta_r H_T^\circ &= \Delta_r H^\circ + \Delta_r C_p T = 111.48 \text{ kJ mol}^{-1} - 186.6 \text{ J K}^{-1} \text{ mol}^{-1} (298.15 \text{ K}) (1 \text{ kJ}/1000 \text{ J}) \\ &= 55.85 \pm 0.81 \text{ kJ mol}^{-1} \end{aligned}$$

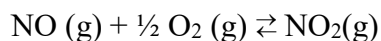
which matches the literature value of 55.84 kJ mol<sup>-1</sup>. From the K<sub>w</sub> table at 298.15 K:

$$\begin{aligned} \Delta_r G^\circ &= -RT \ln K_w = -8.3145 \text{ J K}^{-1} \text{ mol}^{-1} (298.15 \text{ K}) (1 \text{ kJ}/1000 \text{ J}) \ln 1.01 \times 10^{-14} \\ &= 79.89 \text{ kJ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta_r S^\circ &= \frac{\Delta_r H^\circ - \Delta_r G^\circ}{T} = \frac{(55.85 \text{ kJ mol}^{-1} - 79.89 \text{ kJ mol}^{-1})(1000 \text{ J}/1 \text{ kJ})}{298.15 \text{ K}} \\ &= -80.6 \pm 2.7 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

The literature value for the reaction entropy is -80.66 J K<sup>-1</sup> mol<sup>-1</sup>. The agreement of our values with the literature should be considered to be fortuitous given the parameter uncertainties.

16. In the atmosphere NO and NO<sub>2</sub> approach equilibrium (see Ch. 5 Problems 10-12):



Because NO and NO<sub>2</sub> are rapidly interconverted, the concentration of NO and NO<sub>2</sub> in the atmosphere are usually combined and quoted as [NO<sub>x</sub>]. The equilibrium constant is K<sub>p</sub> = 1.168 × 10<sup>5</sup> at 335.15 K and 4075. at 400.15 K. (a). Calculate the standard state reaction enthalpy at the average temperature, assuming the reaction enthalpy is constant over the temperature range. (b). Calculate the standard state reaction Gibbs energy and entropy at 335.15 K. (c). The molar constant pressure heat capacities are 29.844 J K<sup>-1</sup> mol<sup>-1</sup> for NO, 29.355 J K<sup>-1</sup> mol<sup>-1</sup> for O<sub>2</sub>, and 37.20 J K<sup>-1</sup> mol<sup>-1</sup> for NO<sub>2</sub>. Calculate Δ<sub>r</sub>H°, Δ<sub>r</sub>S°, and Δ<sub>r</sub>G° at 298.15 K.

*Answer:* The plan is to use Eq. 20.1.28 to solve for Δ<sub>r</sub>H° at the average temperature and Δ<sub>r</sub>G° = -RT ln K<sub>p</sub> to find Δ<sub>r</sub>G° at 335.15 K. Δ<sub>r</sub>S° at 335.15 K is calculated from Δ<sub>r</sub>G° = Δ<sub>r</sub>H° - T Δ<sub>r</sub>S°. Then Δ<sub>r</sub>C<sub>p</sub> is used with Eqs. 8.5.5 and 13.3.7 to find Δ<sub>r</sub>H° and Δ<sub>r</sub>S° at 298.15 K. Finally, Δ<sub>r</sub>G° at 298.15 K is calculated from Δ<sub>r</sub>G° = Δ<sub>r</sub>H° - T Δ<sub>r</sub>S°.

(a). Using the van 't Hoff equation for two data points, Eq. 20.1.28:

$$\ln \frac{K_{p,T_2}}{K_{p,T_1}} = -\frac{\Delta_r H^\circ}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\ln \frac{4075.}{1.168 \times 10^5} = -\frac{\Delta_r H^\circ}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} \left( \frac{1}{400.15 \text{ K}} - \frac{1}{335.15 \text{ K}} \right)$$

$$-3.3556 = -\frac{\Delta_r H^\circ}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} (0.00249906 - 0.00298374)$$

$$-3.3556 = -\frac{\Delta_r H^\circ}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} (-4.8468 \times 10^{-4} \text{ K}^{-1})$$

$$\Delta_r H^\circ = -5.7564 \times 10^4 \text{ J mol}^{-1} = -57.564 \text{ kJ mol}^{-1} \quad \text{at average temperature } 367.65 \text{ K}$$

(b). At 335.15 K:  $\Delta_r G^\circ = -RT \ln K_p$ :

$$\Delta_r G^\circ = -8.3145 \text{ J K}^{-1} \text{ mol}^{-1} (1 \text{ kJ}/1000 \text{ J})(335.15 \text{ K}) \ln 1.168 \times 10^5 = -32.515 \text{ kJ mol}^{-1}$$

$$\Delta_r S^\circ = \frac{\Delta_r H^\circ - \Delta_r G^\circ}{T} = \frac{(-57.564 \text{ kJ mol}^{-1} - (-32.515 \text{ kJ mol}^{-1}))(1000 \text{ J}/1 \text{ kJ})}{335.15 \text{ K}} = -74.742 \text{ J K}^{-1} \text{ mol}^{-1}$$

(c). The reaction change in heat capacity is:

$$\Delta_r C_p = [37.20] - [29.844 + \frac{1}{2} (29.355)] \text{ J K}^{-1} \text{ mol}^{-1} = -7.322 \text{ J K}^{-1} \text{ mol}^{-1}$$

The reaction enthalpy corrected to 298.15 K from the average temperature for the experiment is:

$$\begin{aligned} \Delta_r H_{298 \text{ K}}^\circ &= \Delta_r H_{367 \text{ K}}^\circ + \Delta_r C_p \Delta T \\ &= -57.564 \text{ kJ mol}^{-1} + (-7.322 \text{ J K}^{-1} \text{ mol}^{-1})(1 \text{ kJ}/1000 \text{ J})(298.15 \text{ K} - 367.65 \text{ K}) \\ &= -57.055 \text{ kJ mol}^{-1} \end{aligned}$$

The reaction entropy at 298.15 K corrected from 335.15 K is:

$$\begin{aligned} \Delta_r S_{298 \text{ K}}^\circ &= \Delta_r S_{367 \text{ K}}^\circ + \Delta_r C_p \ln(T_2/T_1) \\ &= -74.742 \text{ J K}^{-1} \text{ mol}^{-1} + (-7.322 \text{ J K}^{-1} \text{ mol}^{-1})(1 \text{ kJ}/1000 \text{ J}) \ln(298.15/335.15) \\ &= -74.742 + 0.8565 \text{ J K}^{-1} \text{ mol}^{-1} = -73.885 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

The final standard state reaction Gibbs energy is then:

$$\begin{aligned} \Delta_r G^\circ &= \Delta_r H^\circ - T \Delta_r S^\circ = -57.055 \text{ kJ mol}^{-1} - (298.15 \text{ K})(-73.885 \text{ J K}^{-1} \text{ mol}^{-1})(1 \text{ kJ}/1000 \text{ J}) \\ \Delta_r G^\circ &= -35.03 \text{ kJ mol}^{-1} \end{aligned}$$

17. The density at equilibrium for gas phase reaction mixtures can be used to calculate the equilibrium constant for the chemical reaction. Consider a gas phase dissociation with the stoichiometry  $A(g) \rightleftharpoons B(g) + C(g)$ , giving at equilibrium (see Problem 9):

$$K_p = \frac{\xi^2}{a^2 - \xi^2} (P/P^\circ) = \frac{(\xi/a)^2}{1 - (\xi/a)^2} (P/P^\circ) = \frac{\alpha^2}{1 - \alpha^2} (P/P^\circ) \quad (\text{P20.9.1})$$

Assume only A is initially placed in the reaction vessel. The total moles of gas is then determined by  $n_{\text{tot}} = a + \xi = a(1 + \alpha)$ . Now consider the density of the gas mixture. The total mass of the reaction mixture is constant,  $w = a \mathcal{M}_A$ , where  $\mathcal{M}_A$  is the molar mass of reactant A.

However, the total moles of gas changes as the reaction progresses, if  $\Delta_r n_g \neq 0$ . For a reaction at constant temperature and pressure, the change in moles of gas will cause a change in volume as the reaction progresses from the initial state. The density of the reaction gas mixture at equilibrium, assuming each constituent is ideal, is given by the ideal gas law:

$$d = w/V_{\text{eq}} = \frac{a \mathcal{M}_A}{n_{\text{tot}} RT/P} = \frac{a \mathcal{M}_A}{a(1 + \alpha) RT/P} = \frac{1}{1 + \alpha} \left( \frac{\mathcal{M}_A P}{RT} \right) \quad \text{P20.17.1}^\circ$$

$\text{COCl}_2$  dissociates according to the reaction:  $\text{COCl}_2(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + \text{Cl}_2(\text{g})$ . The density of the reaction mixture at equilibrium at 724. K and 1.00 bar total pressure is  $1.16 \text{ g L}^{-1}$ . Calculate the degree of dissociation,  $K_p$ , and  $\Delta_r G^\circ$  at 724. K.

*Answer:* The plan is to use Eq. P20.17.1 $^\circ$  to find  $\alpha$ , and then use Eq. 20.2.7 with  $K_p = K_x P/P^\circ$  and  $\alpha = \xi/a$  to find  $K_p$ . Finally  $\Delta_r G^\circ = -RT \ln K_p$ .

Solving Eq. P20.17.1 $^\circ$  for the degree of dissociation gives:

$$\alpha = \left( \frac{\mathcal{M}_A P}{d RT} \right) - 1 = \left( \frac{98.91 \text{ g mol}^{-1} \cdot 1.00 \text{ bar}}{1.16 \text{ g L}^{-1} \cdot 0.08314 \text{ bar L K}^{-1} \text{ mol}^{-1} \cdot 724. \text{ K}} \right) - 1 = 0.4166$$

The equilibrium expression is then given by Eq. 20.2.7. Then,  $K_p = K_x (P/P^\circ)^{\Delta_r n_g}$  with  $\Delta_r n_g = 1$  for this dissociation. Substituting  $K_p = K_x P/P^\circ$ ,  $\alpha = \xi/a$  and  $P = 1.00 \text{ bar}$  gives:

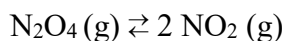
$$K_p = \frac{\alpha^2}{1 - \alpha^2} (P/P^\circ) = \frac{0.4166^2}{1 - 0.4166^2} = 0.2100$$

See Problem 9 and Eq. P20.9.1 for a complete derivation of this last equation.

$$\Delta_r G^\circ = -RT \ln K_p = -8.314 \text{ J K}^{-1} \text{ mol}^{-1} (724. \text{ K})(1 \text{ kJ}/1000 \text{ J}) \ln 0.2100 = 9.39 \text{ kJ mol}^{-1}$$

18. The density of an equilibrium mixture of  $\text{N}_2\text{O}_4(\text{g})$  and  $\text{NO}_2(\text{g})$ , at 1.00 bar pressure, is  $3.62 \text{ g L}^{-1}$  at  $15.^\circ\text{C}$ . Only  $\text{N}_2\text{O}_4$  was initially placed in the reaction vessel. Calculate  $K_p$  and  $\Delta_r G^\circ$  at  $15.^\circ\text{C}$ . [Hint: write the equilibrium expression in terms of the degree of dissociation.]

*Answer:* The reaction is the dissociation of  $\text{N}_2\text{O}_4$ :



See Problem 6 for the derivation of the equilibrium expression:

$$K_p = \frac{4\xi^2}{a^2 - \xi^2} (P/P^\circ) \quad 1$$

The degree of dissociation for this stoichiometry is  $\alpha = \xi/a$ . Dividing the numerator and denominator of the last equation by  $a^2$  gives:

$$K_p = \frac{4(\xi/a)^2}{1 - (\xi/a)^2} (P/P^\circ) = \frac{4\alpha^2}{1 - \alpha^2} (P/P^\circ) \quad 2$$



The total moles of gas is  $n_{\text{tot}} = a + \xi = a(1 + \alpha)$ . Now consider the density of the gas mixture. The total mass of the reaction mixture is constant,  $w = a \mathcal{M}_A$ , where  $\mathcal{M}_A$  is the molar mass of reactant A. The total moles of gas changes as the reaction progresses if  $\Delta n_g \neq 0$ , giving a change in volume. The density of the reaction gas mixture at equilibrium, assuming each constituent is ideal, is given by the ideal gas law,  $V_{\text{eq}} = n_{\text{tot}} RT/P$ :

$$d = w/V_{\text{eq}} = \frac{a\mathcal{M}_A}{n_{\text{tot}} RT/P} = \frac{a \mathcal{M}_A}{a(1 + \alpha) RT/P} = \frac{1}{1 + \alpha} \left( \frac{\mathcal{M}_A P}{RT} \right) \quad 3^\circ$$

where  $\mathcal{M}_A$  is the molar mass of reactant A,  $V_{\text{eq}}$  is the total volume at equilibrium, and  $P$  is the total applied pressure. Substituting in the given values and solving Eq. 3<sup>o</sup> for the degree of dissociation:

$$\alpha = \left( \frac{\mathcal{M}_A P}{d RT} \right) - 1 = \left( \frac{92.02 \text{ g mol}^{-1} 1.00 \text{ bar}}{3.62 \text{ g L}^{-1} 0.08314 \text{ bar L K}^{-1} \text{ mol}^{-1} 288.2 \text{ K}} \right) - 1 = 0.06082$$

The equilibrium constant is then given by Eq. 2 and  $P = 1.00 \text{ bar}$ :

$$K_p = \frac{4\alpha^2}{1 - \alpha^2} (P/P^\circ) = \frac{4(0.06082)^2}{1 - 0.06082^2} = 0.01485$$

$$\begin{aligned} \Delta_r G^\circ &= -RT \ln K_p = -8.314 \text{ J K}^{-1} \text{ mol}^{-1} (1 \text{ kJ}/1000\text{J})(288.2 \text{ K}) \ln 0.01485 \\ &= 10.1 \text{ kJ mol}^{-1} \end{aligned}$$

19. Create an Excel spreadsheet based on Eq. 20.1.21<sup>o</sup> to reproduce Figure 20.1.1. Assume the total pressure is constant at 1.00 bar and the standard state chemical potentials of A, B, C, and D are 6.24, 5.64, 2.78, and 2.22 kJ mol<sup>-1</sup>, respectively. Assume 1.00 mol for A and B initially, with no C and D.

*Answer:* The spreadsheet used to produce Figures 20.1.1 and 20.1.2 is shown below.

species		A	B	C	D							
chem.potential		6.24	5.64	2.78	2.22	kJ/mol						
stoichiometry		-1	-1	1	1							
initial mol		1	1	0	0	mol						
T=	298.2	K	R=	8.314	J/K/mol	RT=	2.4792	kJ/mol				
K <sub>p</sub> =	16.039		P <sub>tot</sub> =	1	bar							
$\xi$ (mol)	n <sub>A</sub>	n <sub>B</sub>	n <sub>C</sub>	n <sub>D</sub>	P <sub>A</sub>	P <sub>B</sub>	P <sub>C</sub>	P <sub>D</sub>	Q	$\Delta_r G$	G <sup>o</sup> (pure)	G (kJ)
0	1	1	0	0	0.5	0.5	0	0	0		11.88	8.443
0.1	0.9	0.9	0.1	0.1	0.45	0.45	0.05	0.05	0.0123	-17.775	11.192	6.143
0.2	0.8	0.8	0.2	0.2	0.4	0.4	0.1	0.1	0.0625	-13.754	10.504	4.586
0.3	0.7	0.7	0.3	0.3	0.35	0.35	0.15	0.15	0.1837	-11.081	9.816	3.350
0.4	0.6	0.6	0.4	0.4	0.3	0.3	0.2	0.2	0.4444	-8.890	9.128	2.354
0.5	0.5	0.5	0.5	0.5	0.25	0.25	0.25	0.25	1	-6.880	8.44	1.566
0.6	0.4	0.4	0.6	0.6	0.2	0.2	0.3	0.3	2.25	-4.870	7.752	0.978
0.7	0.3	0.3	0.7	0.7	0.15	0.15	0.35	0.35	5.4444	-2.679	7.064	0.598
0.8	0.2	0.2	0.8	0.8	0.1	0.1	0.4	0.4	16	-0.006	6.376	0.458
0.9	0.1	0.1	0.9	0.9	0.05	0.05	0.45	0.45	81	4.015	5.688	0.639
1	0	0	1	1	0	0	0.5	0.5			5	1.563

The top section specifies the reaction stoichiometry for  $A + B \rightleftharpoons C + D$ , the given chemical potentials, and the initial conditions. The chemical potentials give the standard state reaction Gibbs energy using Eq. 15.4.17 and the equilibrium constant using Eq. 20.1.14 as  $K_p = 16.0$ . The partial pressures are determined by Dalton's Law of partial pressures,  $P_i = Y_i P$ , and then:

$$Q = \frac{(P_C/P^\circ)(P_D/P^\circ)}{(P_A/P^\circ)(P_B/P^\circ)} \quad \Delta_r G = RT \ln(Q/K_p) \quad G^\circ(\text{pure}) = \sum n_i \mu_i^\circ$$

and the Gibbs energy for each value of  $\xi$  from Eq. 20.1.21°. Notice that the minimum occurs for  $\xi = 0.80$  where  $Q = K_p = 16.0$ .

20. Dissociations with the stoichiometries  $A \rightleftharpoons B + C$  and  $A \rightleftharpoons 2 B$  have significantly different equilibrium positions, given the same equilibrium constant and initial conditions. (a). First, assume the equilibrium constant for both reactions is  $K_p = 1.33$  and the initial moles of reactant is 1.00 mol, with no initial products at 1.00 bar total pressure. Calculate the degree of dissociation for each reaction. (b). Qualitatively sketch diagrams of the form in Figure 20.1.1 and discuss the effect of the entropy of mixing in determining the difference in equilibrium position for the two reaction stoichiometries. (See also Problems 6, 8, and 9.)

*Answer:* (a). Since  $\Delta_r n_g = 1$  for both reactions,  $K_p = K_x (P/P^\circ)^{\Delta_r n_g}$ . Given the total pressure of 1.00 bar,  $K_p = K_x$ . Using Eq. 20.2.8 with  $\alpha = \xi/a$ , the degree of dissociation for the reaction  $A \rightleftharpoons B + C$  is given by Problem 9 Eq. 4:

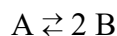
$$A \rightleftharpoons B + C \quad \alpha = \left( \frac{K_x}{1+K_x} \right)^{1/2} = \left( \frac{1.33}{1+1.33} \right)^{1/2} = 0.756$$

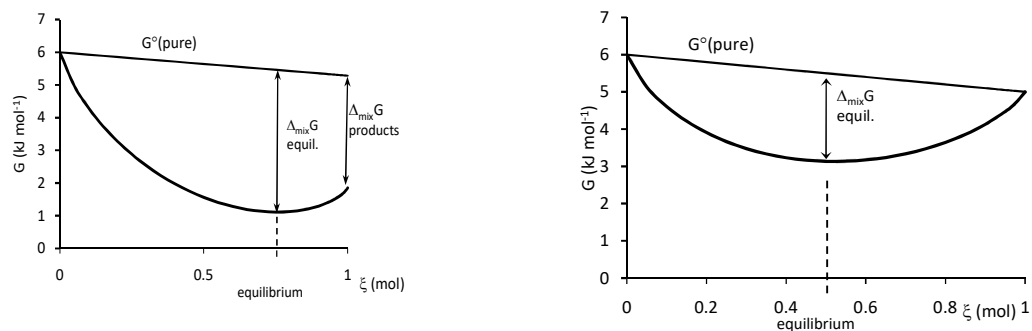
Using Problem 6 Eq. 5 for the reaction  $A \rightleftharpoons 2 B$ , the degree of dissociation is given by:

$$A \rightleftharpoons 2 B \quad \alpha = \left( \frac{K_x}{4+K_x} \right)^{1/2} = \left( \frac{1.33}{4+1.33} \right)^{1/2} = 0.500$$

The extent of the reaction is significantly less for the stoichiometry  $A \rightleftharpoons 2 B$ . Why does this difference occur, even though the equilibrium constants are the same and  $\Delta_r n_g = 1$  for both reactions?

(b). The difference in extent results because the reaction  $A \rightleftharpoons B + C$  has a favorable entropy and Gibbs energy of mixing for the products, while  $A \rightleftharpoons 2 B$  does not. Since both reactions have the same equilibrium constant, the standard state reaction Gibbs energies are the same,  $\Delta_r G^\circ = -RT \ln K_p$ . Sketches for the Gibbs energy versus reaction extent, corresponding to Figure 20.1.1, for the two reactions are shown below. Neither case has entropy of mixing for the reactants. There is a favorable entropy and Gibbs energy of mixing for intermediate reaction extents, so that the reactions don't run to completion in either case. The favorable entropy of mixing for the products pulls the position of equilibrium further to the right towards products for the  $A \rightleftharpoons B + C$  case.





A rough sketch for this problem is sufficient; however, see the next problem for the Excel spreadsheet used to construct these figures.

21. Derive an expression for the Gibbs energy for the dissociation  $A \rightleftharpoons B + C$  as a function of the extent of the reaction. Your derivation will parallel Eqs. 20.1.16-20.1.21°, but for the new stoichiometry. Create an Excel spreadsheet based on your expression to produce a plot similar to Figure 20.1.1. Assume the total pressure is constant at 1.00 bar and the standard state chemical potentials of A, B, and C are 6.00, 2.95, and 2.34 kJ mol<sup>-1</sup>, respectively. Assume 1.00 mol for A initially, with no B and C.

*Answer:* The initial amount of the reactant is  $n_{A0}$ . Assume that we start with only reactant so that  $n_{B0} = 0$  and  $n_{C0} = 0$ . From the stoichiometry for this example, the mole amounts are:

$$n_A = n_{A0} - \xi, \quad n_B = \xi, \quad n_C = \xi \quad 1$$

The Gibbs energy at any point during the reaction is just the sum of the Gibbs energies for each product and reactant:

$$G = n_A \mu_A + n_B \mu_B + n_C \mu_C \quad (\text{cst. T\&P}) \quad 2$$

$$G = n_A \left[ \mu_A^\circ + RT \ln \left( \frac{P_A}{P^\circ} \right) \right] + n_B \left[ \mu_B^\circ + RT \ln \left( \frac{P_B}{P^\circ} \right) \right] + n_C \left[ \mu_C^\circ + RT \ln \left( \frac{P_C}{P^\circ} \right) \right] \quad (\text{cst. T\&P, ideal gas}) \quad 3^\circ$$

The partial pressures are expressed in terms of the mole fractions using Dalton's Law of partial pressures,  $P_i = Y_i P$ , with  $P$  the total pressure,  $Y_i = n_i/n$ , and  $n = \sum n_i$ . Collecting terms, as we did for Eqs. 20.1.17-20.1.19, gives:

$$G = (n_A \mu_A^\circ + n_B \mu_B^\circ + n_C \mu_C^\circ) + n_A RT \ln Y_A + n_B RT \ln Y_B + n_C RT \ln Y_C + n_A RT \ln \left( \frac{P}{P^\circ} \right) + n_B RT \ln \left( \frac{P}{P^\circ} \right) + n_C RT \ln \left( \frac{P}{P^\circ} \right) \quad (\text{cst. T\&P, ideal gas}) \quad 4^\circ$$

Using Eq. 20.1.20,  $n = n_A + n_B + n_C$ , and  $G^\circ(\text{pure}) = (n_A \mu_A^\circ + n_B \mu_B^\circ + n_C \mu_C^\circ)$ , we can simplify Eq. 4° to:

$$G = G^\circ(\text{pure}) + nRT (Y_A \ln Y_A + Y_B \ln Y_B + Y_C \ln Y_C) + nRT \ln\left(\frac{P}{P^\circ}\right)$$

(cst. T&P, ideal gas) 5°

The spreadsheet used to produce Figures 20.1.1 and 20.1.2 is shown below, but with the new stoichiometry and chemical potentials.

species		A	B	C		$\Delta_r G^\circ$			
chem.potential		6	2.95	2.34	kJ/mol	-0.71	kJ/mol		
stoichiometry		-1	1	1					
initial mol		1	0	0	mol				
T	298.2	K	R	8.31	J/K/mol		RT=	2.47923	kJ/mol
$K_p =$	1.332		$P_{\text{tot}} =$	1.00	bar				
$\xi$ (mol)	$n_A$	$n_B$	$n_C$	$P_{\text{tot}}$	$P_A$	$P_B$	$P_C$	$G^\circ(\text{pure})$	G (kJ)
0	1	0	0	1	1	0	0	6.000	6
0.1	0.9	0.1	0.1	1.1	0.818	0.091	0.091	5.929	4.292
0.2	0.8	0.2	0.2	1.2	0.667	0.167	0.167	5.858	3.277
0.3	0.7	0.3	0.3	1.3	0.538	0.231	0.231	5.787	2.531
0.4	0.6	0.4	0.4	1.4	0.429	0.286	0.286	5.716	1.971
0.5	0.5	0.5	0.5	1.5	0.333	0.333	0.333	5.645	1.559
0.6	0.4	0.6	0.6	1.6	0.25	0.375	0.375	5.574	1.281
0.65	0.35	0.65	0.65	1.65	0.212	0.394	0.394	5.539	1.191
0.7	0.3	0.7	0.7	1.7	0.176	0.412	0.412	5.503	1.133
0.75	0.25	0.75	0.75	1.75	0.143	0.429	0.429	5.468	1.110
0.8	0.2	0.8	0.8	1.8	0.111	0.444	0.444	5.432	1.126
0.9	0.1	0.9	0.9	1.9	0.053	0.474	0.474	5.361	1.296
0.985	0.015	0.985	0.985	1.99	0.008	0.496	0.496	5.301	1.697
1	0	1	1	2	0	0.5	0.5	5.290	1.853

The top section specifies the reaction stoichiometry for  $A \rightleftharpoons B + C$ , the given chemical potentials, and the initial conditions. The chemical potentials give the standard state reaction Gibbs energy using Eq. 15.4.17 and the equilibrium constant using Eq. 20.1.14° as  $K_p = 1.33$ . The partial pressures are determined by Dalton's Law of partial pressures,  $P_i = Y_i P$ , and then:

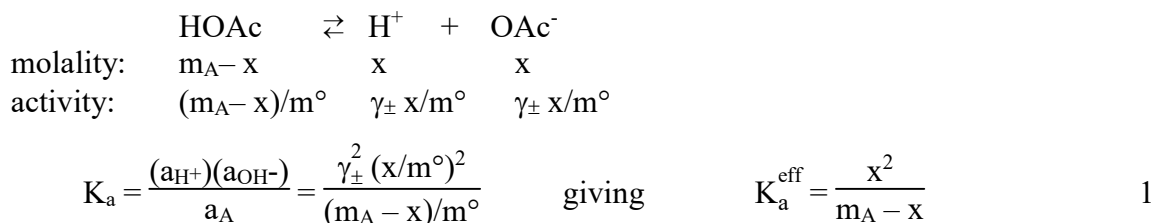
$$G^\circ(\text{pure}) = \sum n_i \mu_i^\circ = (n_A \mu_A^\circ + n_B \mu_B^\circ + n_C \mu_C^\circ)$$

The Gibbs energy for each value of  $\xi$  is determined from Eq. 5. Notice that the minimum occurs for  $\xi \cong 0.75$  as shown in Problem 20a. The plot of the Gibbs energy is shown in Problem 20.

22. Calculate the pH and degree of dissociation of 0.100 m acetic acid in water at 25°C using the Debye-Hückel approximation and  $K_a = 1.75 \times 10^{-5}$ . (The acid dissociation constant is determined on a molal basis. Neglect the autoprotolysis of water.) Compare to the degree of dissociation calculated neglecting activity coefficients.

*Answer:* The dissociation is given by:  $\text{HOAc}(\text{aq}) \rightleftharpoons \text{H}^+ + \text{OAc}^-$ . Assume that the activity coefficient for undissociated acetic acid is one, since acetic acid is neutral. The analytical (nominal, undissociated) concentration of the weak acid is  $m_A$ . The activities for the ions are

$a_{\text{H}^+} = \gamma_{\pm} m_{\text{H}^+}/m^\circ$  and  $a_{\text{OAc}^-} = \gamma_{\pm} m_{\text{OAc}^-}/m^\circ$ . However, by the 1:1 stoichiometry and neglecting the autoprotolysis of water,  $m_{\text{H}^+} = m_{\text{OAc}^-}$ . Let  $x = m_{\text{H}^+} = m_{\text{OAc}^-}$ . The value of  $x$  is the extent of the reaction measured as a molality. The acid dissociation reaction is:



where for convenience, we define the effective equilibrium constant as  $K_{\text{a}}^{\text{eff}} = K_{\text{a}}/\gamma_{\pm}^2 m^\circ$ . Solving for  $x$  gives:

$$x^2 + K_{\text{a}}^{\text{eff}} x - K_{\text{a}}^{\text{eff}} m_{\text{A}} = 0 \qquad x = \frac{-K_{\text{a}}^{\text{eff}} \pm \sqrt{(K_{\text{a}}^{\text{eff}})^2 + 4 K_{\text{a}}^{\text{eff}} m_{\text{A}}}}{2} \quad 2$$

Neglecting activity coefficients,  $K_{\text{a}}^{\text{eff}} \approx K_{\text{a}}$  and using the given values:

$$x = \frac{-1.75 \times 10^{-5} \pm \sqrt{(1.75 \times 10^{-5})^2 + 4(1.75 \times 10^{-5})(0.100)}}{2} = 1.314 \times 10^{-3} \text{ m} \quad (\text{ideal}) \quad 3^\circ$$

Only the positive root gives a positive concentration. The Debye-Hückel approximation depends on the ionic strength. However, the exact concentration of the ions is not known. However, since the degree of dissociation is so small, the activity coefficients will be close to one. We can use the ion concentrations that we calculate neglecting activity coefficients to approximate the ionic strength. Using the definition of ionic strength, Eq. 19.4.22:

$$I = \frac{1}{2} \sum z_i^2 \frac{m_i}{m^\circ} = \frac{1}{2} [(1)^2 m + (-1)^2 m]/m^\circ = m/m^\circ = 1.314 \times 10^{-3} \quad 4$$

This result is expected for a uni-positive:uni-negative electrolyte:  $I = m/m^\circ$ . The mean ionic activity coefficient is calculated using Eq. 19.4.23:

$$\begin{array}{l} \ln \gamma_{\pm} = -1.171 |z_+ z_-| I^{1/2} = -1.171 |(1)(-1)| (1.314 \times 10^{-3})^{1/2} = -0.04245 \quad 5 \\ \text{or } \log \gamma_{\pm} = -0.509 |z_+ z_-| I^{1/2} = -0.509 |(1)(-1)| (1.314 \times 10^{-3})^{1/2} = -0.01845 \quad 6 \end{array}$$

giving  $\gamma_{\pm} = 0.9584$  and  $K_{\text{a}}^{\text{eff}} = K_{\text{a}}/\gamma_{\pm}^2 m^\circ = 1.75 \times 10^{-5}/(0.9584)^2 = 1.905 \times 10^{-5} \text{ m}$ . The molal extent using Eq. 2 is:

$$x = \frac{-1.905 \times 10^{-5} \pm \sqrt{(1.905 \times 10^{-5})^2 + 4(1.905 \times 10^{-5})(0.100)}}{2} = 1.371 \times 10^{-3} \text{ m} \quad 7$$

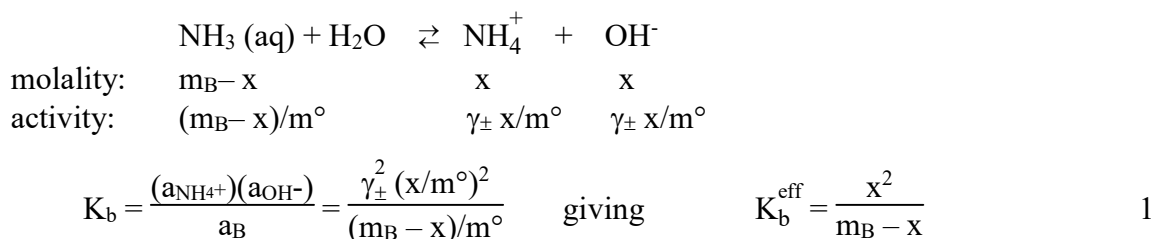
Given that  $x = m_{\text{H}^+}$ , the pH is calculated from the activity:

$$\begin{array}{l} a_{\text{H}^+} = \gamma_{\pm} m_{\text{H}^+}/m^\circ = 0.9584 (1.371 \times 10^{-3}) = 1.314 \times 10^{-3} \\ \text{pH} = -\log a_{\text{H}^+} = 2.88 \end{array}$$

and the degree of dissociation is:  $\alpha = x/m_{\text{A}} = 0.0137$  or 1.37% dissociated. The degree of dissociation neglecting activity coefficients, using Eq. 3°, is  $\alpha = 0.0131$  for a 4% error.

23. Calculate the pH and degree of hydrolysis of 0.100 m ammonia in water at 25°C using the Debye-Hückel approximation and  $K_b = 1.78 \times 10^{-5}$ . (The hydrolysis constant is determined on a molal basis. Neglect the autoprotolysis of water.) Compare to the degree of hydrolysis calculated neglecting activity coefficients.

*Answer:* The hydrolysis is given by:  $\text{NH}_3(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$ . Assume that the activity coefficient for ammonia is one, since ammonia is neutral. The analytical (nominal, undissociated) concentration of the weak base is  $m_B$ . The activities for the ions are  $a_{\text{NH}_4^+} = \gamma_{\pm} m_{\text{NH}_4^+}/m^\circ$  and  $a_{\text{OH}^-} = \gamma_{\pm} m_{\text{OH}^-}/m^\circ$ . However, by the 1:1 stoichiometry and neglecting the autoprotolysis of water,  $m_{\text{NH}_4^+} = m_{\text{OH}^-}$ . Let  $x = m_{\text{NH}_4^+} = m_{\text{OH}^-}$ . The value of  $x$  is the extent of the reaction measured as a molality. The hydrolysis reaction is:



where for convenience, we define the effective equilibrium constant as  $K_b^{\text{eff}} = K_b/\gamma_{\pm}^2 m^\circ$ . Solving for  $x$  gives:

$$x^2 + K_b^{\text{eff}} x - K_b^{\text{eff}} m_B = 0 \qquad x = \frac{-K_b^{\text{eff}} \pm \sqrt{(K_b^{\text{eff}})^2 + 4 K_b^{\text{eff}} m_B}}{2} \quad 2$$

Neglecting activity coefficients,  $K_b^{\text{eff}} \approx K_b$  and using the given values:

$$x = \frac{-1.78 \times 10^{-5} \pm \sqrt{(1.78 \times 10^{-5})^2 + 4(1.78 \times 10^{-5})(0.100)}}{2} = 1.325 \times 10^{-3} \text{ m} \quad (\text{ideal}) \quad 3^\circ$$

Only the positive root gives a positive concentration. The Debye-Hückel approximation depends on the ionic strength. However, the exact concentration of the ions is not known. However, since the degree of hydrolysis is so small, the activity coefficients will be close to one. We can use the ion concentrations that we calculate neglecting activity coefficients to approximate the ionic strength, Eq. 3°. Using the definition of ionic strength, Eq. 19.4.22:

$$I = \frac{1}{2} \sum z_i^2 \frac{m_i}{m^\circ} = \frac{1}{2} [(1)^2 m + (-1)^2 m]/m^\circ = m/m^\circ = 1.325 \times 10^{-3} \quad 4$$

This result is expected for a uni-positive:uni-negative electrolyte:  $I = m/m^\circ$ . The mean ionic activity coefficient is calculated using Eq. 19.4.23:

$$\begin{array}{l} \ln \gamma_{\pm} = -1.171 |z_+ z_-| I^{1/2} = -1.171 |(1)(-1)| (1.325 \times 10^{-3})^{1/2} = -0.04263 \quad 5 \\ \text{or} \quad \log \gamma_{\pm} = -0.509 |z_+ z_-| I^{1/2} = -0.509 |(1)(-1)| (1.325 \times 10^{-3})^{1/2} = -0.01853 \quad 6 \end{array}$$

giving  $\gamma_{\pm} = 0.9583$  and  $K_b^{\text{eff}} = K_a/\gamma_{\pm}^2 m^{\circ} = 1.78 \times 10^{-5}/(0.9583)^2 = 1.938 \times 10^{-5}$  m. The molal extent is:

$$x = \frac{-1.938 \times 10^{-5} \pm \sqrt{(1.938 \times 10^{-5})^2 + 4(1.938 \times 10^{-5})(0.100)}}{2} = 1.382 \times 10^{-3} \text{ m} \quad 7$$

Given that  $x = m_{\text{OH}^-}$  the pOH is calculated from the activity:

$$a_{\text{OH}^-} = \gamma_{\pm} m_{\text{OH}^-}/m^{\circ} = 0.9583 (1.382 \times 10^{-3}) = 1.324 \times 10^{-3}$$

$$\text{pOH} = -\log a_{\text{OH}^-} = 2.878 \quad \text{and} \quad \text{pH} = 13.995 - 2.878 = 11.12$$

and the degree of hydrolysis is:  $\alpha = x/m_B = 0.0138$  or 1.38%. The degree of hydrolysis neglecting activity coefficients, using Eq. 3°, is  $\alpha = 0.0132$  for a 4% error.

24. The  $K_{\text{sp}}$  for  $\text{PbCl}_2$  in water is  $1.70 \times 10^{-5}$ . (a). Calculate the solubility of  $\text{PbCl}_2$  in pure water. (b). Show that the solubility of a 1:2 electrolyte with charges  $z_+ = 2$  and  $z_- = -1$  in a  $m$ -molal solution of  $\text{NaNO}_3$  (or other uni-positive : uni-negative non-participating electrolyte) is given by:

$$m_s = 10^{0.509|z_+ z_-|} (m/m^{\circ})^{1/2} \left( \frac{K_{\text{sp}}}{4} \right)^{1/3}$$

Use the Debye-Hückel approximation at 25°C for the activity coefficients. Calculate the solubility of  $\text{PbCl}_2$  in 0.100 m  $\text{KNO}_3$ .

*Answer:* The dissolution is  $\text{PbCl}_2(\text{s}) \rightleftharpoons \text{Pb}^{2+}(\text{aq}) + 2 \text{Cl}^{-}(\text{aq})$ . Assume  $\text{PbCl}_2$  is the only source of  $\text{Cl}^{-}$  ions, giving  $m_{\text{Cl}^{-}} = 2 m_{\text{Pb}^{2+}} = 2m_s$ . The equilibrium expression is given by:

$$K_{\text{sp}} = (a_{\text{Pb}^{2+}})(a_{\text{Cl}^{-}})^2 = \gamma_{\pm}^3 (m_{\text{Pb}^{2+}}/m^{\circ})(m_{\text{Cl}^{-}}/m^{\circ})^2 = \gamma_{\pm}^3 (m_s/m^{\circ})(2 m_s/m^{\circ})^2 = 4 \gamma_{\pm}^3 (m_s/m^{\circ})^3 \quad 1$$

(a). For  $\text{PbCl}_2$  in pure water, first assume the activity coefficient is equal to one:

$$m_s \cong (1.70 \times 10^{-5}/4)^{1/3} m^{\circ} = 0.01620 \text{ m} \quad (\text{ideal}) \quad 2^{\circ}$$

We can use this concentration to approximate the ionic strength:

$$I = \frac{1}{2} \sum z_i^2 \frac{m_i}{m^{\circ}} = \frac{1}{2} [(2)^2 m_s + (-1)^2 2 m_s]/m^{\circ} = 3 m_s/m^{\circ} = 0.04859 \quad 3$$

and the mean-ionic activity coefficient for  $\text{PbCl}_2$  is:

$$\log \gamma_{\pm} = -0.509 |z_+ z_-| I^{1/2} = \log \gamma_{\pm} = -0.509 |(2)(-1)| (0.04859)^{1/2} = 0.5965 \quad 4$$

The solubility in pure water is  $m_s = \left( \frac{K_{\text{sp}}}{4\gamma_{\pm}^3} \right)^{1/3} m^{\circ} \cong \left( \frac{1.70 \times 10^{-5}}{4(0.5965)^3} \right)^{1/3} \cong 0.0272 \text{ m} \quad 5$

For more accurate calculations this new estimate of the solubility should be used in the spirit of successive approximations to calculate a new ionic strength, activity coefficient, and then more accurate solubility. Given that  $K_{\text{sp}}$  is uncertain to 6%, our current result is sufficient for comparison with part b.

(b). Assume that the ionic strength is dominated by the non-participating electrolyte. For a

uni-positive : uni-negative electrolyte the ionic strength is given by the molality,  $I = m/m^\circ$ . The Debye-Hückel approximation correspondingly gives the activity coefficient of the sparingly soluble salt as:

$$\log \gamma_{\pm} = -0.509 |z_+ z_-| I^{1/2} \quad \text{giving} \quad \gamma_{\pm} = 10^{-0.509|z_+ z_-| (m/m^\circ)^{1/2}} \quad 6$$

$$\text{Solving for the solubility gives: } m_s = \left( \frac{K_{sp}}{4\gamma_{\pm}^3} \right)^{1/3} = 10^{0.509|z_+ z_-| (m/m^\circ)^{1/2}} \left( \frac{K_{sp}}{4} \right)^{1/3} \quad 7$$

For the specific case of  $\text{PbCl}_2$  (s) in 0.100 m  $\text{KNO}_3$ ,  $I = 0.100$ :

$$m_s = 10^{0.509|(2)(-1)| (0.100)^{1/2}} \left( \frac{K_{sp}}{4} \right)^{1/3} m^\circ = (2.098)(0.01620 \text{ m}) = 0.0340 \text{ m} \quad 8$$

or 210% of the ideal solubility, Eq. 2°, and 125% of the solubility in pure water, Eq. 5. The corresponding mean ionic activity coefficient in 0.100 m  $\text{KNO}_3$  works out to  $\gamma_{\pm} = 10^{-0.509|(2)(-1)| (0.100)^{1/2}} = 0.309$ .

25. The  $K_{sp}$  for  $\text{PbCl}_2$  in aqueous solution is  $1.70 \times 10^{-5}$  on a molal basis at 298.15 K. (a). Calculate the  $K_{sp}$  of  $\text{PbCl}_2$  in pure water on a molarity concentration basis. (b). Calculate the  $K_{sp}$  of  $\text{PbCl}_2$  on a molarity basis in a 0.200-M solution of  $\text{KNO}_3$ , assuming a very dilute solution. The density of 0.200 M  $\text{KNO}_3$  is  $0.9905 \text{ g mL}^{-1}$ .

*Answer:* (a). For the solubility equilibrium  $\text{PbCl}_2$  (s)  $\rightleftharpoons$   $\text{Pb}^{2+}$  (aq) + 2  $\text{Cl}^-$  (aq):  $\Delta_r v = [1 + 2] - [0] = 3$ , since the reactant is a solid. The solution is dilute, which allows the use of Eq. 20.3.12. Assume the solution density is the density of pure water at the same temperature,  $d_{\text{H}_2\text{O}}^{25} = 0.99705 \text{ g mL}^{-1}$ , Table 2.2.1:

$$K_c = K_m (d_{\text{soln}}/1 \text{ g mL}^{-1})^{\Delta_r v} = 1.70 \times 10^{-5} (0.99705)^3 = 1.685 \times 10^{-5}$$

or only a 0.9% change.

(b). However, for the solubility in 0.200 M  $\text{KNO}_3$ :

$$K_c = K_m (d_{\text{soln}}/1 \text{ g mL}^{-1})^{\Delta_r v} = 1.70 \times 10^{-5} (0.9905)^3 = 1.652 \times 10^{-5}$$

for a 3% difference.

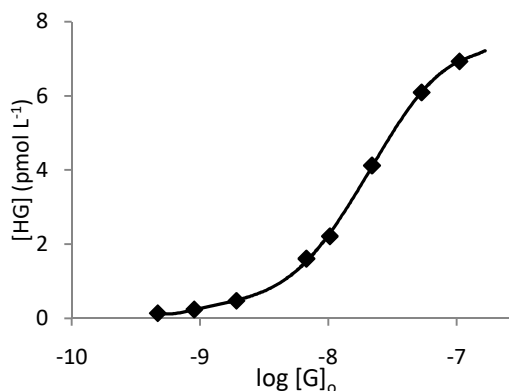
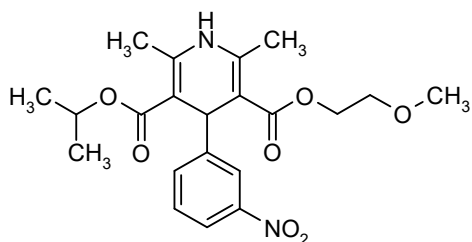
26. The hydrolysis of ammonia is given by:  $\text{NH}_3$  (aq) +  $\text{H}_2\text{O}$   $\rightleftharpoons$   $\text{NH}_4^+$  +  $\text{OH}^-$  with  $K_b = 1.78 \times 10^{-5}$  at 25°C on a molal basis. Calculate  $K_b$  on a molarity concentration basis. The density of 0.100 M ammonia is  $0.994 \text{ g mL}^{-1}$  at 25°C

*Answer:* For the hydrolysis  $\Delta_r v = [1 + 1] - [1] = 1$ , since water is kept on a mole fraction basis with  $X_{\text{H}_2\text{O}} \cong 1$ . Use of Eq. 20.3.12 with the solution density gives only a 0.6% difference in equilibrium constants:



$$K_c = K_m (d_{\text{soln}}/1 \text{ g ml}^{-1})^{\Delta_r v} = 1.78 \times 10^{-5} (0.994) = 1.769 \times 10^{-5}$$

27. Nimodipine is a dihydropyridine calcium channel blocker that was developed for the treatment of high blood pressure:



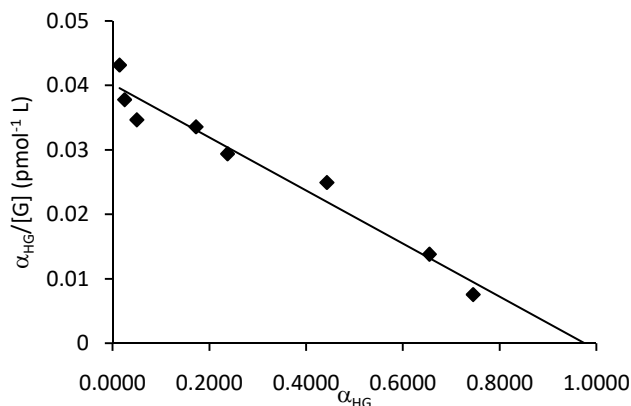
This class of calcium channel blockers are antagonists that block the flow of  $\text{Ca}^{2+}$  ions out of cardiac muscle cells. A receptor site for nimodipine is found in the plasma membrane of striated muscle tissue, or sarcolemma. Isolated sarcolemma membranes were used in a binding study with tritium-labeled nimodipine. Tritiated-nimodipine was incubated with the purified membranes in the absence of  $\text{Ca}^{2+}$  ion and then filtered. The concentration of bound nimodipine was determined by liquid scintillation counting of the membranes trapped on the filters. Consider the membrane bound protein receptor as the host and nimodipine as the guest. The concentration of bound guest as a function of the total concentration of guest is given in the table below.<sup>2</sup> The effective concentration of the host membrane receptors is  $[\text{H}]_0 = 9.3 \pm 0.4 \text{ pmol L}^{-1}$ .

$[\text{G}]_0$ (pmol L <sup>-1</sup> )	0.468	0.9	1.92	6.75	10.3	21.9	53.4	105.4
$[\text{HG}]$ (pmol L <sup>-1</sup> )	0.134	0.234	0.468	1.606	2.21	4.12	6.09	6.93

*Answer:* The plan is to determine the association constant from the Scatchard plot using Eq. 20.5.14. The free guest concentration is given by solving the mass balance:  $[\text{G}] = [\text{G}]_0 - [\text{HG}]$ . The degree of association for the host is given by  $\alpha_{\text{HG}} = [\text{HG}]/[\text{H}]_0$ . A spreadsheet was developed to calculate  $[\text{G}]$ ,  $\alpha_{\text{HG}}$ , and  $\alpha_{\text{HG}}/[\text{G}]$  to form the Scatchard plot:

		$[\text{H}]_0 =$	9.3	pmol L <sup>-1</sup>
$[\text{G}]_0$ (pmol L <sup>-1</sup> )	$[\text{HG}]$ (pmol L <sup>-1</sup> )	$[\text{G}]$ (pmol L <sup>-1</sup> )	$\alpha_{\text{HG}}$	$\alpha_{\text{HG}}/[\text{G}]$ (pmol <sup>-1</sup> L)
0.468	0.134	0.334	0.0144	0.04314
0.9	0.234	0.666	0.0252	0.03778
1.92	0.468	1.452	0.0503	0.03466
6.75	1.606	5.144	0.1727	0.03357
10.3	2.21	8.09	0.2376	0.02937
21.9	4.12	17.78	0.4430	0.02492
53.4	6.09	47.31	0.6548	0.01384
105.4	6.93	98.47	0.7452	0.00757

slope	-0.0411598	0.0401616	intercept
$\pm$	0.003408	0.0013577	$\pm$
$r^2$	0.9605001	0.0026033	s(y)
F	145.89902	6	df
SS <sub>regression</sub>	0.0009888	4.0664E-05	SS <sub>residual</sub>

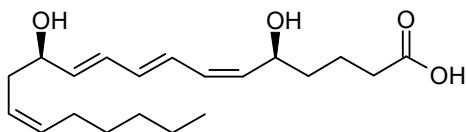


The association constant determined by the slope is  $0.0412 \text{ pmol}^{-1} \text{ L}$  or:

$$K = 0.0412 \text{ pmol}^{-1} \text{ L} \left( \frac{1000 \text{ pmol}}{1 \text{ nmol}} \right) = 41.2 \text{ nmol}^{-1} \text{ L} = 41.2 \pm 3.4 \text{ nM}^{-1}$$

Even though the effective host concentration is very uncertain, you can verify by changing  $[H]_0$  that the association constant that is determined from the slope is unaffected by the value of the total host concentration. The intercept should also give the association constant, but the value is strongly dependent on the total host concentration.

28. Leukotriene- $B_4$  is important in activating the inflammatory response:<sup>3</sup>



Developing leukotriene- $B_4$  antagonists may be helpful in managing chronic obstructive pulmonary disease, severe asthma, rheumatoid arthritis, inflammatory bowel disease, and cystic fibrosis. A receptor site for leukotriene- $B_4$  is a membrane bound protein in polymorphonuclear leukocytes, PMNLs. Isolated PMNL membranes were used in a binding study with radio-iodine labeled leukotriene- $B_4$ . The leukotriene was incubated with the purified membranes and then filtered. The concentration of bound leukotriene was determined by liquid scintillation counting of the membranes trapped on the filters. Consider the membrane bound protein receptor as the host and leukotriene- $B_4$  as the guest. The concentration of bound guest as a function of the total concentration of guest is given in the table below.<sup>3</sup> The effective concentration of the host membrane receptors is  $[H]_0 = 33 \pm 12 \text{ pmol L}^{-1}$ .

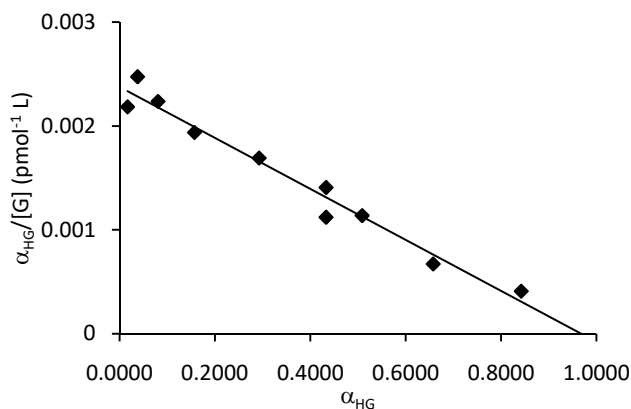
$[G]_0$ (pmol $L^{-1}$ )	8.33	16.7	38.7	86.4	183	322	401	464	1000	2080
$[HG]$ (pmol $L^{-1}$ )	0.56	1.26	2.66	5.19	9.67	14.3	14.3	16.8	21.7	27.8

*Answer:* The plan is to determine the association constant from the Scatchard plot using Eq. 20.5.14. The free guest concentration is given by solving the mass balance:  $[G] = [G]_o - [HG]$ . The degree of association for the host is given by  $\alpha_{HG} = [HG]/[H]_o$ . A spreadsheet was developed to calculate  $[G]$ ,  $\alpha_{HG}$ , and  $\alpha_{HG}/[G]$  to form the Scatchard plot:

		$[H]_o =$	33	$\mu\text{mol L}^{-1}$
$[G]_o$ ( $\mu\text{mol L}^{-1}$ )	$[HG]$ ( $\mu\text{mol L}^{-1}$ )	$[G]$ ( $\mu\text{mol L}^{-1}$ )	$\alpha_{HG}$	$\alpha_{HG}/[G]$ ( $\mu\text{mol}^{-1} \text{L}$ )
8.33	0.56	7.77	0.0170	0.00218
16.7	1.26	15.44	0.0382	0.00247
38.7	2.66	36.04	0.0806	0.00224
86.4	5.19	81.21	0.1573	0.00194
183	9.67	173.33	0.2930	0.00169
322	14.3	307.7	0.4333	0.00141
401	14.3	386.7	0.4333	0.00112
464	16.8	447.2	0.5091	0.00114
1000	21.7	978.3	0.6576	0.00067
2080	27.8	2052.2	0.8424	0.00041

The curve fit results are:

slope	-0.0024546	0.0023768	intercept
$\pm$	0.0001532	6.6721E-05	$\pm$
$r^2$	0.9697631	0.00012796	$s(y)$
F	256.57729	8	df
$SS_{\text{regression}}$	4.2011E-06	1.3099E-07	$SS_{\text{residual}}$



The association constant determined by the slope is  $0.00245 \mu\text{mol}^{-1} \text{L}$  or:

$$K = 0.00245 \mu\text{mol}^{-1} \text{L} \left( \frac{1000 \mu\text{mol}}{1 \text{ nmol}} \right) = 2.45 \text{ nmol}^{-1} \text{L} = 2.45 \pm 0.15 \text{ nM}^{-1}$$

Even though the effective host concentration is very uncertain, you can verify by changing  $[H]_o$  that the association constant that is determined from the slope is unaffected by the value of the total host concentration. The intercept should also give the association constant, but the value is strongly dependent on the total host concentration.

29. The organic dye eosin binds to the protein lysozyme. Binding to lysozyme quenches the fluorescence of the protein at  $340 \text{ nm}$ .<sup>4</sup> If  $I_H$  is the fluorescence intensity of the free form of lysozyme and  $I_{HG}$  is the fluorescence intensity of the bound form of the protein, then the observed intensity is the mole fraction weighted average:

$$I_{\text{obs}} = \alpha_H I_H + \alpha_{HG} I_{HG} = (1 - \alpha_{HG}) I_H + \alpha_{HG} I_{HG} = (I_{HG} - I_H) \alpha_{HG} + I_H \quad \text{P20.29.1}$$

where  $\alpha_H$  is the mole fraction of the free host protein,  $\alpha_H = n_H/(n_H + n_{HG}) = [H]/[H]_o$ , and  $\alpha_{HG}$  is the mole fraction of the guest-host complex,  $\alpha_{HG} = n_{HG}/(n_H + n_{HG}) = [HG]/[H]_o$ . Solving Eq. P20.29.1 for the degree of association gives:

$$\alpha_{HG} = \frac{[HG]}{[H]_o} = \frac{I_H - I_{obs}}{I_H - I_{HG}} \quad \text{P20.29.2}$$

The fluorescence intensity of free lysozyme in buffer alone is  $I_H = 1.541$ . The fluorescence intensity,  $I_{obs}$ , as a function of the concentration of eosin with  $[H]_o = 3.00 \times 10^{-6}$  M lysozyme in each solution is:<sup>4</sup>

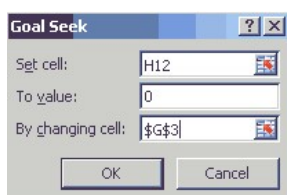
$[G]_o$ (M)	$5.00 \times 10^{-6}$	$10.0 \times 10^{-6}$	$20.0 \times 10^{-6}$	$50.0 \times 10^{-6}$
$I_{obs}$	1.198	1.064	0.855	0.494

The fluorescence intensities are relative and in arbitrary units, which makes fluorescence intensity effectively unitless. Calculate the association constant of eosin with lysozyme. Assume that the fluorescence of lysozyme is negligible in the bound form,  $I_{HG} \approx 0$ . [Hints: a Scatchard plot is not appropriate for this experiment, because the free eosin concentration is not known. There is only one unknown, so use of a curve fitting program is not necessary. Using “goal seek” in a spreadsheet format is useful for finding the optimum value for an adjustable parameter in a non-linear equation.]

*Answer:* The plan is to use Eq. 20.5.22 for calculating the degree of association. A spreadsheet is constructed and then “goal seek” is used to find the value of  $K[H]_o$  that best fits the data.

The spreadsheet is reproduced below. The raw data is in the first two columns. The guest-host ratio is then calculated,  $r = [G]_o/[H]_o$ , where the guest is eosin and the host is lysozyme. The degree of association is then determined from the fluorescence intensities:

$\alpha_{HG} = (I_H - I_{obs})/(I_H - I_{HG})$ . A value of  $K[H]_o$  is guessed. Eq. 20.5.22 is then used to calculate the fit value for the degree of association based on the guessed value of  $K[H]_o$ , in the fifth column. The formula is: “ $=((1+\$G\$3*(1+E6))-SQRT((1+\$G\$3*(1+E6))^2-4*\$G\$3^2*E6))/2/\$G\$3$ .” The last column is the squared residual  $(\alpha_{HG} - \alpha_{HG \text{ fit}})^2$ , which is used to judge the agreement of the experimental and modeled value based on the current guess for  $K[H]_o$ . The overall goodness of fit is determined by the sum of squared residuals in cell H12. The “goal seek” option under Data: What-if-analysis is then used to minimize the sum of squared residuals:



A1	B	C	D	E	F	G	H
2		$I_{HG} =$	0				
3		$[H]_o =$	$3.00 \times 10^{-6}$	M	$K[H]_o =$	0.141	
4							
5		$[G]_o$ (M)	$I_{obs}$	$r = [G]_o/[H]_o$	$\alpha_{HG}$	$\alpha_{HG \text{ fit}}$	residual <sup>2</sup>
6		0	1.541	0.0000	0.0000	0.0000	0
7		$5.00 \times 10^{-6}$	1.198	1.6667	0.2226	0.1739	0.002371
8		$1.00 \times 10^{-5}$	1.064	3.3333	0.3095	0.2996	9.878E-05
9		$2.00 \times 10^{-5}$	0.855	6.6667	0.4452	0.4664	0.0004529
10		$5.00 \times 10^{-5}$	0.494	16.6667	0.6794	0.6925	0.0001716
11							
12						$SS_{\text{residual}}$	3.095E-03
13						$s(y) =$	0.0278

The final optimized value is  $K[H]_o = 0.141$  or  $K = 4.70 \times 10^4$ . Biochemists often quote the results as dissociation constants and neglect to divide by the standard state concentrations in the equilibrium expression, which gives the dissociation constant with units:  $K_D = 1/K = 2.13 \times 10^{-5} = 21. \mu\text{M}$ . A standard goodness of fit criterion is the standard deviation of the y values,  $s_y$  or  $s(y)$ . The y values in this problem are the  $\alpha_{\text{HG}}$  values and  $s_y = \sqrt{SS_{\text{residual}}/(n-1)}$ . See the next problem for the error analysis.

30. Finding the optimum value for a single adjustable parameter in a non-linear equation is easily handled using the “goal seek” option in a spreadsheet, rather than using non-linear least squares curve fitting programs. However, the spreadsheet approach makes the determination of the uncertainty of the final fit value more involved than using non-linear least squares curve fitting algorithms. However, least squares curve fitting programs are often set up to fit two or more adjustable parameters, not just one parameter. The uncertainty for fitting procedures for a single parameter are easily handled using the following approach.

The general formula for propagation of errors for the two-parameter function  $f(x,y)$  is (Appendix 1):

$$\delta^2 f = \left( \frac{\partial f}{\partial x} \right)_y^2 \delta^2 x + \left( \frac{\partial f}{\partial y} \right)_x^2 \delta^2 y$$

Consider a non-linear function  $f(b,x)$ , with the adjustable parameter  $b$  and independent variable  $x$ . The adjustable parameter is often an equilibrium constant and the  $x$  variable is a concentration or a mole ratio (see the previous problem). Let the value of the measured observables at a series of  $x$  values be  $y_1 = f(b,x_1)$ ,  $y_2 = f(b,x_2)$ ,  $y_3 = f(b,x_3)$ , ... for  $n$  values of  $x$ . The  $y$  values are often absorbances, fluorescence intensities, or chemical shifts. The uncertain variables are the  $y_i$  values. The uncertainty in the fit parameter,  $b$ , is then given by:

$$\delta^2 b = \left( \frac{\partial b}{\partial y_1} \right)^2 \delta^2 y_1 + \left( \frac{\partial b}{\partial y_2} \right)^2 \delta^2 y_2 + \dots$$

with the sum over all  $n$  data points. If we assume that the derivatives are all approximately equal, then the last equation reduces to:

$$\delta^2 b \approx \left( \frac{\partial b}{\partial y} \right)^2 \sum_{i=1}^n \delta^2 y_i \quad \text{or} \quad \left( \frac{\delta^2 b}{n-1} \right) \approx \left( \frac{\partial b}{\partial y} \right)^2 \left( \frac{\sum_{i=1}^n \delta^2 y_i}{n-1} \right)$$

Dividing both sides of the equation by  $n-1$  converts the uncertainties to variances,  $s_b$  and  $s_y$ . Taking the square root and inverting the derivative gives:

$$s_b \approx \frac{1}{\left( \frac{\partial y}{\partial b} \right)} s_y$$

where  $(\partial y/\partial b)$  is approximately evaluated numerically as the change in a typical  $y$  value for a small change in the fit parameter:

$$\left(\frac{\partial y}{\partial b}\right) = \frac{f(b+\delta b, x) - f(b, x)}{\delta b}$$

where  $x$  is a typical  $x$ -value and  $\delta b$  is a small change in the fit parameter. The derivative is easily calculated by finding the  $y$ -value for the optimal  $b$ -value,  $f(b, x)$ , and then changing  $b$  by a small amount and finding the new  $y$ -value,  $f(b+\delta b, x)$ .

Using these last two equations, find the uncertainty in the association constant for the previous fluorescence quenching problem.

*Answer:* For the last problem the  $y_i$  values are the experimental  $\alpha_{HG}$  values. The adjustable parameter is  $b = K[H]_o$ . The  $x$  values are the eosin concentrations. Focus on data point 3 for  $x = 2.00 \times 10^{-5}$  M eosin as a typical value, in the spreadsheet in the last problem. The fit value for  $\alpha_{HG,3}$  is 0.4664 with  $b = K[H]_o = 0.141$ . Now change  $b$  to 0.142. The new value of  $\alpha_{HG,3}$  is 0.4681. The derivative is then:

$$\left(\frac{\partial y}{\partial b}\right) = \frac{f(b+\delta b, x) - f(b, x)}{\delta b} = \frac{0.4681 - 0.4664}{0.001} = 1.70$$

The standard deviation of the  $y$  values from spreadsheet cell H13 is  $s_y = 0.0278$ , at the optimum value for  $K[H]_o = 0.141$ . The estimate for the uncertainty in the variable parameter  $b = K[H]_o$  is then:

$$\delta b \approx \frac{1}{\left(\frac{\partial y}{\partial b}\right)} s_y = \frac{1}{1.70} (0.0278) = 0.0164 \quad \text{or} \quad \frac{0.0164}{0.141} 100\% = 11.6\%$$

Giving the uncertainty in the association constant as  $K = 4.7 \times 10^4 \pm 0.5 \times 10^4$ . The dissociation constant is  $K_D = 1/K = 2.13 \times 10^{-5} \pm 0.25 \times 10^{-5}$ .

31. NMR is an important technique for measuring formation constants in guest-host chemistry. For example, if a given proton in the host shows a chemical shift difference between the free and bound forms, then the chemical shift of the proton is strongly concentration dependent. The dependence is due to changes in the mole fractions of the free and bound forms. Assume the reactions are rapid on the NMR time scale:  $\text{rate} > 1/\nu_o$  with  $\nu_o$  the resonance frequency. If  $\delta_H$  is the chemical shift of the free form of the host and  $\delta_{HG}$  is the chemical shift of the bound form of the host, then the observed chemical shift is the mole fraction weighted average, assuming the reactions are rapid:

$$\delta_{\text{obs}} = \alpha_H \delta_H + \alpha_{HG} \delta_{HG}$$

where  $\alpha_H$  is the mole fraction of the free host,  $\alpha_H = n_H/(n_H + n_{HG}) = [H]/[H]_o$ , and  $\alpha_{HG}$  is the mole fraction of the guest-host complex,  $\alpha_{HG} = n_{HG}/(n_H + n_{HG}) = [HG]/[H]_o$ . Given that  $\alpha_H + \alpha_{HG} = 1$ , the observed chemical shift reduces to:

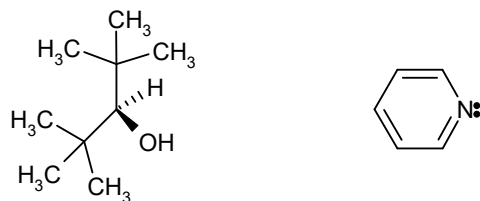
$$\delta_{\text{obs}} = (1 - \alpha_{HG}) \delta_H + \alpha_{HG} \delta_{HG} = (\delta_{HG} - \delta_H) \alpha_{HG} + \delta_H$$

The mole fraction of the bound guest-host complex is calculated by Eq 20.5.22:

$$\delta_{\text{obs}} = (\delta_{\text{HG}} - \delta_{\text{H}}) \left( \frac{(1 + K[\text{H}]_0(1+r)) - \sqrt{(1 + K[\text{H}]_0(1+r))^2 - 4K^2[\text{H}]_0^2 r}}{2K[\text{H}]_0} \right) + \delta_{\text{H}}$$

Although somewhat daunting looking, this equation is easily used in non-linear curve fitting with the “Nonlinear Least Squares Curve Fitting” applet on the text Web site and the companion CD. In particular, the guest and host can be a hydrogen-bonded pair. NMR is an important technique in studies of hydrogen bonding.

The formation of the hydrogen bond between the sterically crowded alcohol, below, and pyridine has been studied:<sup>5</sup>



2,2,4,4-tetramethyl-pentan-3-ol

pyridine

Consider the alcohol as the host and pyridine as the guest. The chemical shift of the alcohol hydrogen is given in the table, below, as a function of the concentration of pyridine in benzene solution. The alcohol concentration is fixed in each solution at 0.100 M. The chemical shift of the free alcohol is  $\delta_{\text{H}} = 1.105$  ppm. The chemical shift difference,  $(\delta_{\text{HG}} - \delta_{\text{H}})$ , and  $K[\text{H}]_0$  are treated as the two variable parameters in the curve fitting. The binding constant is expected to be  $\approx 1$ , since the formation of a single hydrogen bond is a weak interaction.

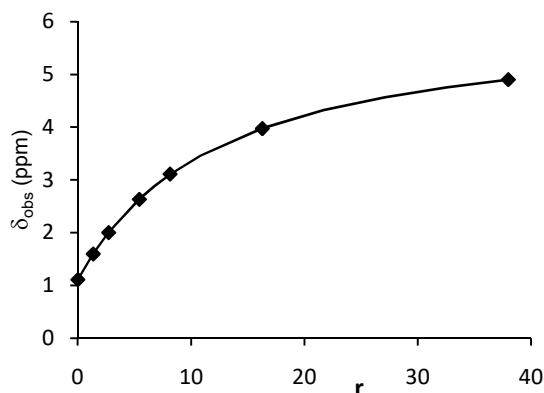
$[\text{G}]_0$ (M)	0	0.136	0.271	0.543	0.814	1.628	3.799
$\delta_{\text{obs}}$ (ppm)	1.105	1.594	2.000	2.630	3.111	3.970	4.901

*Answer:* The guest/host ratios,  $r$ , are calculated using the spreadsheet below and the  $r$  and  $\delta_{\text{obs}}$  values are used in non-linear curve fitting using the “Nonlinear Least Squares Curve Fitting” applet on the text Web site and the companion CD. The fit function is listed in the applet as:

$$a \left\{ \frac{(1+b(1+x)) - \sqrt{(1+b(1+x))^2 - 4(b^2)x}}{2b} \right\} + c$$

where  $a = \delta_{\text{HG}} - \delta_{\text{H}}$ ,  $b = K[\text{H}]_0$ , and  $c = \delta_{\text{H}}$ . The  $c$  value is treated as a fixed constant,  $c = 1.105$  ppm. If initial guesses of  $a = 8$  and  $b = 0.1$  are used, the fit doesn't converge. After this first attempt, the non-converged fit values are listed by the applet as  $a = 4.96$  and  $b = 0.8754$ , which are used as guesses for a second attempt that does converge. The results are listed and plotted below.

[G] <sub>o</sub> (M)	r	δ <sub>obs</sub> (ppm)
0	0.000	1.105
0.136	1.357	1.594
0.271	2.713	2.000
0.543	5.427	2.630
0.814	8.140	3.111
1.628	16.281	3.970
3.799	37.989	4.901



```

===== Results =====
a= 4.9609 +- 0.043
b= 0.087502 +- 0.000062
-----
Output Data
-----
  x          y          y (fit)  residual
-----
-0.0        1.105        1.102        0.003
 1.357       1.594       1.59388      0.00012
 2.713       2.0          2.00167     -0.00167
 5.427       2.63        2.63642     -0.00642
 8.14        3.111       3.10462      0.00638
16.281      3.97        3.97322     -0.00322
37.989      4.901       4.89762      0.00338
-----
sum of squared residuals= 0.0001156
stand. dev. y values= 0.004808
correlation between a & b= -0.9949

```

The value for the binding constant is  $K = b/[H]_o = 0.08750/0.100 = 0.875$ .

The between fit parameters correlation is very large, at  $-0.9949$ . Large between fit parameters correlations are a typical problem in guest-host chemistry for weak interactions. Authors support their results by independent measurements of the chemical shift of the completely complexed species, and by independent repetitions of the experiment.<sup>5</sup> Even so, there are often large inconsistencies between laboratories for the values of binding constants. The uncertainty obtained from the least squares fitting procedure underestimates the true uncertainty of the binding constant (you can prove this to yourself by changing the first chemical shift at  $[G]_o = 0$  to 1.102 ppm and noting the difference in  $K$ , for example). Titration calorimetry is often used as an independent and, in most cases, more accurate method for determining binding constants. However, titration calorimetry is not applicable for all reactions.

32. Derive Eq. 20.5.23.

*Answer:* The plan is to recast the equilibrium expression in terms of  $[H]_o$ ,  $[G]_o$ , and free guest,  $[G]$  using the mass balance. Then the equilibrium expression is used to solve for  $[G]$ .

The mass balance equations are given by Eqs. 20.5.3 and 20.5.15:

$$[H]_o = [H] + [HG] \quad (20.5.3)$$



$$[G]_o = [G] + [HG] \quad (20.5.15)$$

Solving Eq. 20.5.15 for the complex concentration, [HG]:

$$[HG] = [G]_o - [G] \quad 1$$

Solving Eq. 20.5.3 for the free host concentration and then using Eq. 1 for [HG] gives:

$$[H] = [H]_o - [HG] = [H]_o - [G]_o + [G] \quad 2$$

Substitution of the mass balances into the equilibrium expression, Eq. 20.5.1, results in:

$$K = \frac{[G]_o - [G]}{([H]_o - [G]_o + [G])[G]} = \frac{[G]_o - [G]}{([H]_o - [G]_o)[G] + [G]^2} \quad 3$$

Cross-multiplying and rearranging gives a quadratic expression:

$$K[G]^2 + (1 + K([H]_o - [G]_o)) [G] - [G]_o = 0 \quad 4$$

Substitution of the coefficients into the quadratic formula gives:

$$[G] = \frac{-(1+K([H]_o-[G]_o)) \pm \sqrt{(1+K([H]_o-[G]_o))^2 + 4K[G]_o}}{2K} \quad 5$$

Only the positive root gives meaningful concentrations. To express [G] as a function of the mole ratio of the guest and host, multiply and divide the equilibrium constant by [H]<sub>o</sub> to give:

$$[G] = \frac{-(1+K[H]_o(1-[G]_o/[H]_o)) + \sqrt{(1+K[H]_o(1-[G]_o/[H]_o))^2 + 4K[H]_o[G]_o/[H]_o}}{2K[H]_o/[H]_o} \quad 6$$

The mole ratio of the guest to host is  $r \equiv [G]_o/[H]_o$  giving:

$$[G] = [H]_o \left( \frac{-(1+K[H]_o(1-r)) + \sqrt{(1+K[H]_o(1-r))^2 + 4K[H]_o r}}{2K[H]_o} \right) \quad (20.5.23)$$

33. Derive Eq. 20.5.24.

*Answer:* The plan is to recast the equilibrium expression in terms of [H]<sub>o</sub>, [G]<sub>o</sub>, and free host, [H] using the mass balance. Then the equilibrium expression is used to solve for [H].

The mass balance equations are given by Eqs. 20.5.3 and 20.5.15:

$$[H]_o = [H] + [HG] \quad (20.5.3)$$

$$[G]_o = [G] + [HG] \quad (20.5.15)$$

Solving Eq. 20.5.3 for the complex concentration, [HG]:

$$[HG] = [H]_o - [H] \quad 1$$

Solving Eq. 20.5.15 for the free guest concentration and then using Eq. 1 for [HG] gives:

$$[G] = [G]_o - [HG] = [G]_o - [H]_o + [H] \quad 2$$

Substitution of the mass balances into the equilibrium expression, Eq. 20.5.1, results in:

$$K = \frac{[H]_o - [H]}{[H] ([G]_o - [H]_o + [H])} = \frac{[H]_o - [H]}{([G]_o - [H]_o)[H] + [H]^2} \quad 3$$

Cross-multiplying and rearranging gives a quadratic expression:

$$K[H]^2 + (1 + K([G]_o - [H]_o)) [H] - [H]_o = 0 \quad 4$$

Substitution of the coefficients into the quadratic formula gives:

$$[H] = \frac{-(1+K([G]_o-[H]_o)) \pm \sqrt{(1+K([G]_o-[H]_o))^2 + 4K[H]_o}}{2K} \quad 5$$

Only the positive root gives meaningful concentrations. To express  $[G]$  as a function of the mole ratio of the guest and host, multiply and divide the equilibrium constant by  $[H]_o$  to give:

$$[H] = \frac{-(1+K[H]_o ([G]_o/[H]_o - 1)) + \sqrt{(1+K[H]_o ([G]_o/[H]_o - 1))^2 + 4K[H]_o}}{2K[H]_o/[H]_o} \quad 6$$

The mole ratio of the guest to host is  $r \equiv [G]_o/[H]_o$  giving:

$$[H] = [H]_o \left( \frac{-(1+K[H]_o (r-1)) + \sqrt{(1+K[H]_o (r-1))^2 + 4K[H]_o}}{2K[H]_o} \right) \quad (20.5.24)$$

34. An alternative form for the concentration of the guest-host complex often encountered in biochemical studies is based on the dissociation equilibria:



where  $K_D$  is the dissociation constant. The relationship to the association constant and Eq. 20.5.1 is  $K_D = 1/K$ . (a). Show that the guest-host concentration is given by:

$$[HG] = \frac{([H]_o + [G]_o + K_D) - \sqrt{([H]_o + [G]_o + K_D)^2 - 4 [H]_o [G]_o}}{2}$$

(b). Find the relationship in terms of the guest-host ratio,  $r = [G]_o/[H]_o$ .

*Answer:* The plan is to recast the equilibrium expression in terms of  $[H]_o$ ,  $[G]_o$ , and the guest-host complex,  $[HG]$ , using the mass balance. Then the equilibrium expression is used to solve for  $[HG]$ .

The mass balance equations are given by Eqs. 20.5.3 and 20.5.15:

$$[H]_o = [H] + [HG] \quad (20.5.3)$$

$$[G]_o = [G] + [HG] \quad (20.5.15)$$

Solving Eqs. 20.5.3 and 20.5.15 for the free host and free guest concentrations:

$$[H] = [H]_o - [HG]$$

$$[G] = [G]_o - [HG]$$

Substitution of the mass balances into the dissociation equilibrium expression results in:

$$K_D = \frac{[H][G]}{[HG]} = \frac{([H]_o - [HG])([G]_o - [HG])}{[HG]} = \frac{[H]_o[G]_o - ([H]_o + [G]_o)[HG] + [HG]^2}{[HG]}$$

Cross-multiplying and rearranging gives a quadratic expression:

$$[HG]^2 - ([H]_o + [G]_o + K_D)[HG] + [H]_o[G]_o = 0$$

Substitution of the coefficients into the quadratic formula gives:

$$[HG] = \frac{([H]_o + [G]_o + K_D) - \sqrt{([H]_o + [G]_o + K_D)^2 - 4[H]_o[G]_o}}{2}$$

Only the negative root gives meaningful concentrations. To express  $[HG]$  as a function of the mole ratio of the guest and host, factor out  $[H]_o$  to give:

$$[HG] = [H]_o \frac{(1 + [G]_o/[H]_o + K_D/[H]_o) - \sqrt{(1 + [G]_o/[H]_o + K_D/[H]_o)^2 - 4[G]_o/[H]_o}}{2}$$

The mole ratio of the guest to host is  $r \equiv [G]_o/[H]_o$  giving:

$$[H] = [H]_o \left( \frac{(1 + r + K_D/[H]_o) - \sqrt{(1 + r + K_D/[H]_o)^2 - 4r}}{2} \right)$$

The fit parameters for non-linear least-square curve fitting are  $a = [H]_o$  and  $b = K_D/[H]_o$ .

35. Determine if the following statements are true or false. If the statement is false, describe the changes that are necessary to make the statement true, if possible. If the statement is true, but too restrictive, give the more general statement.

- The relationship  $\Delta_r G^\circ = -RT \ln K_p$  shows that  $\Delta_r G^\circ$  is the reaction Gibbs energy at equilibrium.
- The position of equilibrium for a constant volume process is determined by the extent of the reaction,  $\xi$ .
- The position of equilibrium is unaffected by addition of an inert gas, such as helium, since the inert gas will not participate in the reaction.
- The position of equilibrium for the reaction types  $2A \rightleftharpoons B + C$  and  $A + B \rightleftharpoons C + D$  will be the same if the equilibrium constants are the same.
- The rate of the reaction  $2A \rightarrow B + C$  increases with temperature so the equilibrium position of the reaction shifts to the right with an increase in temperature.
- The rate of the reaction  $2A \rightarrow B + C$  is fast so the equilibrium constant for the reaction is large.

*Answer:* (a). False: The reaction Gibbs energy at equilibrium is zero. The standard state reaction Gibbs energy corresponds to each pure reactant and product under standard state conditions,  $P^\circ = 1$  bar. It is highly unlikely that the reaction will be at equilibrium with pure reactants and products for each substance at  $P_i = 1$  bar, which is required to give  $\Delta_r G^\circ = 0$ .

(b). True but too restrictive: The statement is true for constant  $V$ ,  $P$ , and  $T$ . The statement should be: The position of equilibrium is determined by the extent of the reaction,  $\xi$ .

(c). The effect of an inert gas depends on the conditions. The statement is true for a constant volume reaction and false for a constant pressure problem if  $\Delta_r n_g \neq 0$ . At constant pressure the addition of an inert gas changes the volume of the system, lowering the partial pressure for each gaseous reactant and product. The statement also neglects changes in activity coefficients and the changes in chemical potentials of solids, liquids, and solutions for large changes in total pressure. The statement should be: The position of equilibrium for a reaction at constant volume is unaffected by addition of an inert gas, for moderate changes in total pressure.

(d). False: The reactant for  $2A \rightleftharpoons B + C$  has no entropy of mixing while the reactants in  $A + B \rightleftharpoons C + D$  do have an entropy of mixing. The favorable entropy of mixing for the reactants for  $A + B \rightleftharpoons C + D$  will lower the Gibbs energy of the reactants compared to the pure constituents and shift the position of equilibrium to the left compared to  $2A \rightleftharpoons B + C$ . The statement should be: The position of equilibrium for the reaction  $2A \rightleftharpoons B + C$  will be to the right of the position of equilibrium for  $A + B \rightleftharpoons C + D$ , assuming comparable equilibrium constants.

(e). False: don't confuse kinetic and equilibrium considerations. The equilibrium constant is the ratio of the forward and reverse overall reaction rates,  $K_p = k_f/k_r$ . Both forward and reverse reaction rates change with temperature. The equilibrium position can shift left or right with an increase in forward reaction rate. The correct statement is: The shift in equilibrium position with temperature is determined by the standard state reaction enthalpy.

(f). False: don't confuse kinetic and equilibrium considerations. The equilibrium constant is the ratio of the forward and reverse overall reaction rates,  $K_p = k_f/k_r$ . The reverse reaction rate can be faster than the forward reaction rate, which would make the equilibrium constant small.

36. The ITC titration of the enzyme ribonuclease A with the ligand 2'CMP is given in the table below. Consider ribonuclease A as the host and 2'CMP as the guest. The host concentration in the titration cell was  $6.272 \times 10^{-5}$  M, the guest concentration in the automated buret was  $2.19 \times 10^{-3}$  M, the titration cell volume was 1.4389 mL, and the titrant was added in 9.00  $\mu$ L increments. The association constant was determined to be  $6.99 \times 10^5$  and the reaction enthalpy was  $-70.6 \text{ kJ mol}^{-1}$  using non-linear curve fitting. (a). Calculate  $\Delta_r G^\circ$  and  $\Delta_r S^\circ$ . (b). Use the fit values to reproduce the titration curve. Neglect any corrections for exclusion of material from the constant volume titration cell (as discussed in the addendum). [Hint: construct a spreadsheet using Eq. 20.5.22. Show the titration curve with the calculated and experimental values, for comparison.]

$i V_{inj} (\mu\text{L})$	9	18	27	36	45	54	63	72	81	90	99
$q/n_{inj} (\text{kJ mol}^{-1})$	-68.3	-67.3	-64.2	-56.3	-35.6	-14.6	-6.41	-3.61	-2.33	-1.64	-1.3

*Answer:* (a).  $\Delta_r G^\circ = -RT \ln K = -33.4 \text{ kJ mol}^{-1}$  and:

$$\Delta_r S^\circ = \frac{\Delta_r H^\circ - \Delta_r G^\circ}{T} = \frac{(-70.6 \text{ kJ mol}^{-1} - (-33.4 \text{ kJ mol}^{-1}))(1000 \text{ J/1 kJ})}{298.15 \text{ K}} = -125. \text{ J K}^{-1} \text{ mol}^{-1}$$

which completes the thermodynamic characterization of the reaction.

(b). The plan is to use Eqs. 20.6.3 and 20.6.4 to find  $[G]_o$  and  $r = [G]_o/[H]_o$ . Eq. 20.5.22 is then used to find  $[HG]$ . Eqs. 20.6.5-20.6.7 are then used to calculate the enthalpy change per mole of added titrant at each step of the titration, which is compared to the experimental values.

The spreadsheet is:

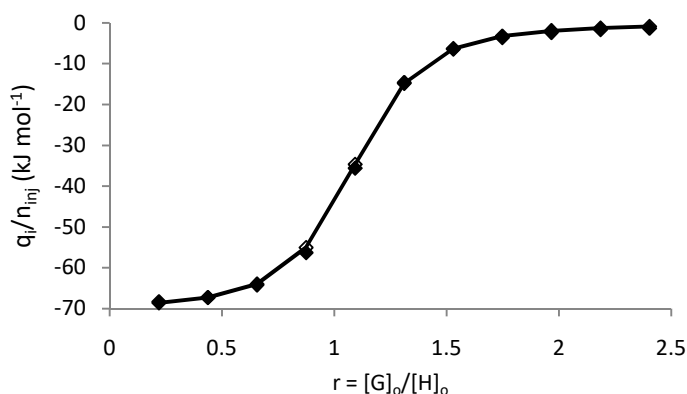
A1	B	C	D	E	F	G	H	I	J
2									
3	host	[H] <sub>o</sub> =	6.272E-05	M	K=	6.99E+05			
4	titrant	[G] <sub>o</sub> =	2.190E-03	M	Δ <sub>r</sub> H=	-70600	J/mol		
5	cell	V <sub>cell</sub> =	1.4389	mL					
6	titrant add	V <sub>inj</sub> =	9	uL					
7									
8	volume titrant:								
9	i V <sub>inj</sub> (μL)	[G] <sub>o</sub>	r=[G] <sub>o</sub> /[H] <sub>o</sub>	1+K[H] <sub>o</sub> (1+r)	factor	[HG] (M)	Δn <sub>HG,i</sub> (mol)	q <sub>i</sub> (mJ)	q <sub>i</sub> /n <sub>inj</sub> (kJ mol <sup>-1</sup> )
10	9	1.37E-05	0.218	54.416	35.805	1.33E-05	1.92E-08	-1.352	-68.613
11	18	2.74E-05	0.437	63.991	27.141	2.64E-05	1.88E-08	-1.325	-67.242
12	27	4.11E-05	0.655	73.566	19.356	3.88E-05	1.79E-08	-1.262	-64.003
13	36	5.48E-05	0.874	83.141	14.000	4.95E-05	1.54E-08	-1.085	-55.046
14	45	6.85E-05	1.092	92.716	14.167	5.62E-05	9.68E-09	-0.684	-34.684
15	54	8.22E-05	1.310	102.291	19.717	5.91E-05	4.14E-09	-0.292	-14.838
16	63	9.59E-05	1.529	111.865	27.571	6.03E-05	1.77E-09	-0.125	-6.343
17	72	1.10E-04	1.747	121.440	36.262	6.09E-05	9.10E-10	-0.064	-3.259
18	81	1.23E-04	1.966	131.015	45.311	6.13E-05	5.42E-10	-0.038	-1.940
19	90	1.37E-04	2.184	140.590	54.540	6.16E-05	3.56E-10	-0.025	-1.276
20	99	1.51E-04	2.402	150.165	63.870	6.17E-05	2.51E-10	-0.018	-0.900

The terms in Eq. 20.5.22 were separated to make the calculations easier and to provide the opportunity to check for mistakes. The factor term is:  $\text{factor} = \sqrt{(1+K[H]_o(1+r))^2 - 4K^2[H]_o^2 r}$ .

The formulas are:

C10: =B10/1000000\*\$D\$4/\$D\$5\*1000  
D10: =C10/\$D\$3  
E10: =1+\$G\$3\*\$D\$3\*(1+D10)  
F10: =SQRT(E10^2-4\*\$G\$3^2\*\$D\$3^2\*D10)  
G10: =\$D\$3\*((E10-F10)/2/\$G\$3/\$D\$3)  
H10: =G10\*\$D\$5/1000  
H11: =(G11-G10)\*\$D\$5/1000  
I10: =H10\*\$G\$4\*1000  
J10: =(I10/1000000)/(\$D\$6/1000000\*\$D\$4)

A plot of the modeled q<sub>i</sub>/n<sub>inj</sub> and experimental values is:



The modeled values are shown with outlined symbols and the experimental values are shown with solid symbols. The discrepancies are in part caused by neglecting the volume exclusion corrections.

37. Eq. 20.5.22 can be used directly in non-linear curve fitting for finding association constants from ITC titration curves. The results for each step in an ITC experiment are given by Eqs. 20.6.5-20.6.7. Consider the first two steps in the titration. The sum of the  $q_{i,m}$  values for the first two steps gives, using Eqs. 20.6.6 and 20.6.7:

$$q_{\text{tot}} = q_{1,m} + q_{2,m} = q_2/n_{\text{inj}} + q_1/n_{\text{inj}} = (\Delta n_{\text{HG},2} + \Delta n_{\text{HG},1}) \Delta_r H^\circ / n_{\text{inj}}$$

Then using Eq. 20.6.5 the total calorimetric enthalpy is given in terms of [HG] as:

$$q_{\text{tot}} = q_{1,m} + q_{2,m} = q_2/n_{\text{inj}} + q_1/n_{\text{inj}} = ([\text{HG}]_2 - [\text{HG}]_1 + [\text{HG}]_1 - [\text{HG}]_0) \Delta_r H^\circ V_{\text{cell}}/n_{\text{inj}}$$

$$q_{\text{tot}} = q_{1,m} + q_{2,m} = q_2/n_{\text{inj}} + q_1/n_{\text{inj}} = [\text{HG}]_2 \Delta_r H^\circ V_{\text{cell}}/n_{\text{inj}}$$

since  $[\text{HG}]_0 = 0$ . Solving for  $[\text{HG}]_2 \Delta_r H^\circ$  gives:

$$q_{\text{tot}} n_{\text{inj}}/V_{\text{cell}} = \Delta_r H^\circ [\text{HG}]_2$$

In a similar fashion, if we add the calorimetric enthalpies for the first  $n$  steps:

$$q_{\text{tot}} n_{\text{inj}}/V_{\text{cell}} = (q_{1,m} + q_{2,m} + \dots + q_{2,n}) n_{\text{inj}}/V_{\text{cell}} = \Delta_r H^\circ [\text{HG}]_n$$

Eq. 20.5.22 can then be used to calculate the concentration of the host-guest complex:

$$q_{\text{tot}} \left( \frac{n_{\text{inj}}}{V_{\text{cell}} [\text{H}]_0} \right) = \Delta_r H^\circ \left( \frac{(1+K[\text{H}]_0(1+r)) - \sqrt{(1+K[\text{H}]_0(1+r))^2 - 4K^2[\text{H}]_0^2 r}}{2K[\text{H}]_0} \right)$$

where  $r$  is the guest-host ratio at the  $n^{\text{th}}$  step of the titration. The two adjustable parameters for curve fitting are  $a = \Delta_r H^\circ$  and  $b = K[\text{H}]_0$ .

Use the data in the last problem to find the association constant and reaction enthalpy for the binding of ribonuclease A with 2'CMP.

*Answer:* The plan is to use Eqs. 20.6.3 and 20.6.4 to find  $[\text{G}]_0$  and  $r = [\text{G}]_0/[\text{H}]_0$ . The value for  $q_{\text{tot}} n_{\text{inj}}/(V_{\text{cell}} [\text{H}]_0)$  is then calculated as discussed in the problem introduction. The spreadsheet is:

A1	B	C	D	E	F	G
2						
3	host	$[\text{H}]_0 =$	6.272E-05	M		
4	titrant	$[\text{G}]_0 =$	2.190E-03	M		
5	cell	$V_{\text{cell}} =$	1.4389	mL		
6	titrant add	$V_{\text{inj}} =$	9	uL		
7						
8	volume titrant:					
9	$i V_{\text{inj}} (\mu\text{L})$	$[\text{G}]_0$	exp (kJ mol <sup>-1</sup> )	$\Sigma q_i/n_{\text{inj}}$ (kJ mol <sup>-1</sup> )	$r=[\text{G}]_0/[\text{H}]_0$	$\Sigma q_i$ (J mol <sup>-1</sup> )
10	9	1.37E-05	-68.3	-68.3	0.218	-1.492E+04
11	18	2.74E-05	-67.3	-135.6	0.437	-2.961E+04
12	27	4.11E-05	-64.2	-199.8	0.655	-4.364E+04
13	36	5.48E-05	-56.3	-256.1	0.874	-5.593E+04
14	45	6.85E-05	-35.6	-291.7	1.092	-6.371E+04
15	54	8.22E-05	-14.6	-306.3	1.310	-6.690E+04
16	63	9.59E-05	-6.41	-312.71	1.529	-6.830E+04
17	72	1.10E-04	-3.61	-316.32	1.747	-6.908E+04
18	81	1.23E-04	-2.33	-318.65	1.966	-6.959E+04
19	90	1.37E-04	-1.64	-320.29	2.184	-6.995E+04
20	99	1.51E-04	-1.3	-321.59	2.402	-7.023E+04

The column labeled "exp" gives the experimental  $q_i/n_{\text{inj}}$  values from the calorimeter. The first  $\Sigma q_i/n_{\text{inj}}$  column is the successive sum of the experimental enthalpies,  $q_{\text{tot}} = \Sigma(q_i/n_{\text{inj}})$ . The guest-

host ratio is calculated using Eq. 20.6.4. The last column is the value for  $q_{\text{tot}} n_{\text{inj}} / (V_{\text{cell}} [H]_o)$  in units of joules per mol for the reaction. Cell G10 is:

$$\text{“=D10*1000*SD$4*SD$6*0.000001/SD$5/0.001/SD$3”}.$$

The final two columns are used as input in non-linear curve fitting using the “Nonlinear Least Squares Curve Fitting” applet on the text Web site and the companion CD. The fit function is:

$$a\{(1+b(1+x)) - \sqrt{[(1+b(1+x))^2 - 4(b^2)x]}\}/2b + c$$

with fixed  $c = 0$ . The results are shown below.

```

===== Results =====
a= -71422 +- 188
b= 39 +- 1.4
Output Data
-----
  x      y      y (fit)  residual
0.218  -14920.0  -15079.9659  159.9659
0.437  -29610.0  -29893.45311 283.45311
0.655  -43640.0  -43866.56378 226.56378
0.874  -55930.0  -55853.66829 -76.33171
1.092  -63710.0  -63439.95773 -270.04227
1.31   -66900.0  -66841.80936 -58.19064
1.529  -68300.0  -68357.87206 57.87206
1.747  -69080.0  -69146.2291 66.2291
1.966  -69590.0  -69621.5504 31.5504
2.184  -69950.0  -69934.19432 -15.80568
2.402  -70230.0  -70155.46303 -74.53697
-----
sum of squared residuals= 253900
stand. dev. y values= 168
correlation between a & b= 0.9463

```

The final results are  $\Delta_r H^\circ = -71.42 \pm 0.19 \text{ kJ mol}^{-1}$  and

$$K = [H]_o b = 6.272 \times 10^{-5} (39.) = 6.22 \times 10^{-5} \pm 0.22 \times 10^{-5}$$

Notice that the between fit parameter correlation is high, but acceptable, at 0.9463. The results deviate from the values listed in the last problem,  $K = 6.99 \times 10^{-5}$  and  $\Delta_r H^\circ = -70.6 \text{ kJ mol}^{-1}$ , because we didn't correct for exclusion of material from the constant volume titration cell (as discussed in the addendum).

38. Comparison of Eqs. 20.1.17 and 20.1.5 might at first seem conflicting:

$$G = n_A \mu_A + n_B \mu_B + n_C \mu_C + n_D \mu_D \quad (20.1.17)$$

$$\Delta_r G = c \mu_C + d \mu_D - a \mu_A - b \mu_B \quad (20.1.5)$$

Derive Eq. 20.1.5 from Eq. 20.1.17, thus showing that the two equations are consistent. [Hint: remember that the reaction Gibbs energy is the Gibbs energy for the products minus the Gibbs energy for the reactants.]

*Answer:* Write the reaction as:  $a A + b B \rightleftharpoons c C + d D$ . We note using Eq. 3.1.4,  $dn_i = v_i d\xi$ , that as the reaction proceeds from reactants to products, for a given extent,  $n_i$  changes from:

$$n_i: n_{i,0} \rightarrow n_{i,0} + v_i \xi$$

where  $n_{i,0}$  is the initial amount of constituent  $i$ . For the reaction run to completion:



Finally:  $\Delta_r G = G_{\text{products}}(\xi=1) - G_{\text{reactants}}(\xi=0)$ . Substituting Eqs. 2 into Eq. 20.1.17 at  $\xi = 1$  and  $\xi = 0$  gives:

$$\begin{aligned} \Delta_r G &= G_{\text{products}} - G_{\text{reactants}} \\ &= [(n_{A,0} - a)\mu_A + (n_{B,0} - b)\mu_B + (n_{C,0} + c)\mu_C + (n_{D,0} + d)\mu_D] - [n_{A,0}\mu_A + n_{B,0}\mu_B + n_{C,0}\mu_C + n_{D,0}\mu_D] \end{aligned}$$

$$\Delta_r G = G_{\text{products}} - G_{\text{reactants}} = [c\mu_C + d\mu_D] - [a\mu_A + b\mu_B]$$

which is Eq. 20.1.5.

The alternative path is to note that both 20.1.17 and 20.1.5 result from integration of the total differential of the Gibbs energy, Eq. 20.1.2. Correspondingly, Eq. 20.1.17 is the Gibbs energy for the reaction mixture at some point during the reaction and  $\Delta_r G$  is the change in Gibbs energy for the reaction of  $a$ -moles of  $A$  and  $b$ -moles of  $B$  to give  $c$ -moles of  $C$  and  $d$ -moles of  $D$ . Eq. 20.1.17 is valid at any point during the reaction, while Eq. 20.1.5 corresponds to the change for the reaction run to completion.

39. Calculate the equilibrium constant for the *anti*- to *gauche*-conformers for dichloroethane from  $\Delta_r G^\circ$  and also the statistical approach. Use molecular mechanics to estimate of the difference in steric energy. Assume no significant change in vibrations between the two conformers.

*Answer:* The MMFF94x gas phase steric energy difference for *anti*- and *gauche*-dichloroethane is  $-5.143 \text{ kJ mol}^{-1}$ . Using MM3, the difference is  $-4.325 \text{ kJ mol}^{-1}$ . Just as for butane, Example 20.4.1, there are two equivalent *gauche*-conformers and one *anti*-conformer. The reaction entropy for the conformational change is, assuming no significant change in vibrations (or rotational constants):

$$\Delta_r S^\circ = S_{\text{anti}} - S_{\text{gauche}} = R \ln(1/2) = -5.763 \text{ J K}^{-1} \text{ mol}^{-1}$$

Then  $\Delta_r G^\circ = G_{\text{anti}} - G_{\text{gauche}} = \Delta_r H^\circ - T\Delta_r S^\circ$  using the MMFF values gives:

$$\Delta_r G^\circ = -5.143 \text{ kJ mol}^{-1} - (298.2 \text{ K})(-5.763 \text{ J K}^{-1} \text{ mol}^{-1})(1 \text{ kJ}/1000 \text{ J})$$

$$\Delta_r G^\circ = -3.425 \text{ kJ mol}^{-1} \text{ (MMFF) or } -2.607 \text{ kJ mol}^{-1} \text{ (MM3)}$$

$$\text{giving: } K = e^{-\Delta_r G^\circ/RT} = \frac{[\textit{anti}]}{[\textit{gauche}]} = 3.981 \text{ (MMFF) or } 2.862 \text{ (MM3)}$$

The *anti*-conformer has the lowest energy, which we assign as  $\epsilon_{\text{anti}} = 0$ . Then the *gauche*-conformer has an energy  $\epsilon_{\text{gauche}} = 5.143 \text{ kJ mol}^{-1}$  above the *anti*-state using MMFF or  $\epsilon_{\text{gauche}} = 4.325 \text{ kJ mol}^{-1}$  using MM3. The table, below, gives the calculation for the probabilities using Eq. 20.4.1 and the MMFF steric energy difference at 298.15 K.



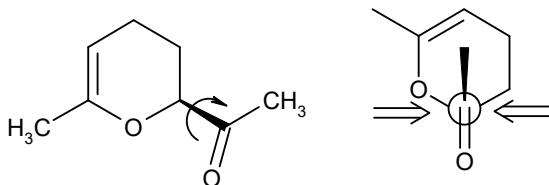
Conformation	$\epsilon_i$ (kJ mol <sup>-1</sup> )	$\epsilon_i/RT$	$e^{-\epsilon_i/RT}$	$e^{-\epsilon_i/RT}/q$	$\epsilon_i$ (kJ mol <sup>-1</sup> )	$p_i = e^{-\epsilon_i/RT}/q$
<i>gauche</i>	5.143	2.075	0.1256	0.1004	5	0.1004
<i>gauche</i>	5.143	2.075	0.1256	0.1004		
<i>anti</i>	0	0	1	0.7992	0	0.7992
				$q=1.2512$		

To calculate  $q$  we sum the weighting factors in column 4. Then we use  $q$  to calculate the probabilities in the last column. The ratio the *anti*- to *gauche*-probabilities is:

$$K = \frac{\sum \text{probabilities for } anti}{\sum \text{probabilities for } gauche} = \frac{0.7992}{0.1004 + 0.1004} = 3.981 \text{ (MMFF)} \quad \text{or} \quad 2.862 \text{ (MM3)}$$

There are roughly four molecules in the *anti*-conformation for every molecule in a *gauche*-conformation at 25°C, using the MMFF results.

40. The dimer of methylvinylketone is shown below, at left. The bond with free rotation is marked. Consider only the axial conformer for the  $-\text{CO}-\text{CH}_3$  side chain. Calculate the equilibrium constant for the two low energy conformers. (b). Which face of the carbonyl is more susceptible to nucleophilic attack? Nucleophilic attack will be perpendicular to the trigonal plane of the  $\text{sp}^2$  hybridized carbon, as shown by the arrows for one possible conformation at right. According to Cram's rule, the less hindered side is most susceptible to attack by nucleophiles. You may use molecular mechanics, semi-empirical AM1, *ab initio* HF/6-31G\*, or B3LYP/6-31G\* density functional methods to determine the energies.



*Answer:* The plan is to first determine the low energy conformers about the side-chain C-C bond to the ring. A conformational search around this bond can be done or several possible starting conformations can be minimized. The less sterically hindered side of the low energy conformer is noted. Space filling models are helpful in looking at steric influences.

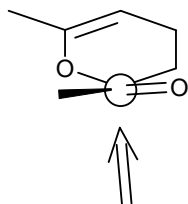
For this problem we will study just the axial conformer for the  $-\text{CO}-\text{CH}_3$  side chain. The energy differences and Boltzmann weighting factors are given below using gas phase MMFF94x, MM3, AM1, HF/6-31G(d), and B3LYP/6-31G(d). The starting structures for the molecular orbital calculations were the MMFF minimized conformers. The equilibrium constant is given for the reaction written as: *anti*  $\rightleftharpoons$  *syn*, where the *anti* conformer is the low energy conformer:

$$K = [\textit{syn}]/[\textit{anti}]$$

The *anti*-conformer has the O-C-C=O dihedral near  $-144^\circ$  and the *syn*- near  $-4^\circ$  using MMFF.

	high $\epsilon$ (kJ mol <sup>-1</sup> )	low $\epsilon$ (kJ mol <sup>-1</sup> )	$\Delta\epsilon$ (kJ mol <sup>-1</sup> )	$e^{-\Delta\epsilon/RT}$	q	$p_0$	$p_1$	K
MMFF	81.7867	64.19009	17.5966	0.000826	1.000826	0.999175	0.000825	$8.3 \times 10^{-4}$
MM3	61.8918	41.79398	20.0978	0.000301	1.000301	0.999699	0.000301	$3.0 \times 10^{-4}$
AM1	-313.709	-319.661	5.95132	0.090639	1.090639	0.916894	0.083106	0.0906
HF	-1206787.	-1206799.	11.6751	0.009005	1.009005	0.991075	0.008925	$9.0 \times 10^{-3}$
B3LYP	-1214304.	-1214315.	10.4392	0.014826	1.014826	0.985390	0.014610	0.0148

The favored direction of attack changes with conformation of the side chain. There are two low energy conformers; the lowest energy conformer of the axial isomer is shown below. The arrow shows the side of the carbonyl that is preferentially attacked by nucleophiles.



41. The next two problems develop a model for the equilibrium profile of NO in the lower troposphere. In the atmosphere, NO and NO<sub>2</sub> approach equilibrium (see Problem 16 and Ch. 5 Problems 10-12):



In a given initial volume, let the number of moles of NO be “a”, the moles of O<sub>2</sub> be “b”, and the moles of other gases in the atmosphere be “n”. These last contributions include primarily N<sub>2</sub> with small amounts of H<sub>2</sub>O vapor, CO<sub>2</sub>, and Ar. Assume that the initial amount of NO<sub>2</sub> is zero and the reaction runs at constant total pressure, P. To help simplify the relationships for the mole fractions, define  $\alpha \equiv \xi/a$  as the fraction of NO oxidized,  $r \equiv b/a$ , and  $q \equiv n/a$ . Show that the equilibrium expression is:

$$K_p = \frac{\alpha}{1 - \alpha} \left( \frac{1 + r + q - \alpha/2}{r - \alpha/2} \right)^{1/2} (P/P^\circ)^{-1/2} \quad \text{P20.41.2}^\circ$$

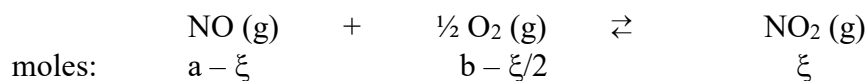
The concentration of NO<sub>x</sub> in the atmosphere is typically in the ppm range. Correspondingly, r and q are much larger than  $\alpha$ . Let  $P_{\text{NO},0}$  be the initial partial pressure of NO, before any oxidation occurs. Show that an excellent approximation is then:

$$K_{\text{eff}} \cong \frac{\alpha}{1 - \alpha} \quad \text{with} \quad K_{\text{eff}} = K_p \left( \frac{r}{r + q} \right)^{1/2} (P/P^\circ)^{1/2} \quad (P_{\text{NO},0} \ll P_{\text{O}_2}, P_{\text{N}_2}) \quad \text{P20.41.3}^\circ$$

*Answer:* Assume that the initial amount of NO<sub>2</sub> is zero. The total moles at equilibrium is then:

$$n_{\text{tot}} = (a - \xi) + (b - \xi/2) + \xi + n = a + b + n - \xi/2 \quad 1$$

The relationship of the mole amounts to the partial pressures is then:



$$\begin{array}{l}
 Y_i: \quad \frac{a - \xi}{a + b + n - \xi/2} \quad \frac{b - \xi/2}{a + b + n - \xi/2} \quad \frac{\xi}{a + b + n - \xi/2} \\
 Y_i: \quad \frac{1 - \alpha}{1 + b/a + n/a - \alpha/2} \quad \frac{b/a - \alpha/2}{1 + b/a + n/a - \alpha/2} \quad \frac{\alpha}{1 + b/a + n/a - \alpha/2} \\
 Y_i: \quad \frac{1 - \alpha}{1 + r + q - \alpha/2} \quad \frac{r - \alpha/2}{1 + r + q - \alpha/2} \quad \frac{\alpha}{1 + r + q - \alpha/2} \quad 2
 \end{array}$$

To obtain the final listed mole fractions, we divided by the moles of a in the numerator and denominator and substituted  $\alpha = \xi/a$  to measure the degree of the reaction.  $\alpha$  is the fraction of NO oxidized or alternatively the fraction of NO<sub>2</sub> formed. We then define  $r \equiv b/a$  and  $q \equiv n/a$ . For the total pressure dependence,  $\Delta_r n_g = -1/2$ . The equilibrium expression is then:

$$\begin{aligned}
 K_p &= \frac{(P_{\text{NO}_2}/P^\circ)}{(P_{\text{NO}}/P^\circ)(P_{\text{O}_2}/P^\circ)^{1/2}} = K_x (P/P^\circ)^{\Delta_r n_g} = \frac{\left(\frac{\alpha}{1 + r + q - \alpha/2}\right)}{\left(\frac{1 - \alpha}{1 + r + q - \alpha/2}\right)\left(\frac{r - \alpha/2}{1 + r + q - \alpha/2}\right)^{1/2}} (P/P^\circ)^{-1/2} \\
 &= \frac{\alpha}{1 - \alpha} \left(\frac{1 + r + q - \alpha/2}{r - \alpha/2}\right)^{1/2} (P/P^\circ)^{-1/2} \quad (\text{P20.41.1}^\circ)
 \end{aligned}$$

The maximum value of  $\alpha$  is 1 for the reaction as written. The concentration of NO in the atmosphere is typically in the ppm range. Then  $r$  and  $q$  are much larger than  $\alpha$ . An excellent approximation is then to neglect the 1 and  $\alpha$  terms to give:

$$K_p \cong \frac{\alpha}{1 - \alpha} \left(\frac{r + q}{r}\right)^{1/2} (P/P^\circ)^{-1/2} \quad (P_{\text{NO},o} \ll P_{\text{O}_2}, P_{\text{N}_2}) \quad 3^\circ$$

where  $P_{\text{NO},o}$  is the initial partial pressure of NO before oxidation. An effective equilibrium constant can then be defined to simplify the calculations:

$$K_{\text{eff}} \cong \frac{\alpha}{1 - \alpha} \quad \text{with} \quad K_{\text{eff}} = K_p \left(\frac{r}{r + q}\right)^{1/2} (P/P^\circ)^{1/2} \quad (\text{P20.41.2}^\circ)$$

The effective equilibrium constant,  $K_{\text{eff}}$ , is a constant at a given altitude.

42. Use Eq. P20.41.2<sup>o</sup> to determine the equilibrium partial pressure of NO up to an altitude of 2000 m in the troposphere. Use the barometric formula, Eqs. 1.3.16<sup>o</sup> and 1.3.17, to estimate the total pressure as a function of altitude. Assume that  $r$  and  $q$  are constant with altitude (that is, the atmosphere is well-mixed before any oxidation occurs). Assume also that the temperature in the troposphere decreases 6.0 K per 1000 m: the environmental lapse rate is  $\gamma = -0.006 \text{ K m}^{-1}$ . For the oxidation, Eq. P20.41.1,  $\Delta_r G^\circ = -35.24 \text{ kJ mol}^{-1}$  and  $\Delta_r H^\circ = -57.07 \text{ kJ mol}^{-1}$ . Assume  $\Delta_r H^\circ$  is constant over the temperature range. Assume the temperature is 298.15 K and the total pressure is 1.00 bar at sea level. The initial partial pressure at sea level for O<sub>2</sub> is 0.200 bar and for NO is  $1.00 \times 10^{-5}$  bar (10 ppm) before any oxidation.

The barometric formula is derived assuming the temperature is constant at each altitude. However, for a realistic model, we also need to take into account the decrease in temperature with altitude. An easy way to take both pressure and temperature effects into account is to use an average temperature of 282.7 K with the barometric formula to calculate the pressure profile in the atmosphere. Separately, the variation of temperature is then determined using  $\gamma = -0.006 \text{ K m}^{-1}$  starting at 298.2 K at sea level,  $h = 0$ .

*Answer:* The spreadsheet and the plot of the partial pressure of NO as a function of altitude are given below. The barometric formula, Eq. 1.3.16°, is used with the average molar mass of air of  $28.8 \text{ g mol}^{-1}$  and the average effective temperature in the lower troposphere of 282.7 K to calculate the pressure as a function of altitude in column D. The temperature profile in column E starts at 298.2 K and decreases  $-0.006 \text{ K m}^{-1}$  as the altitude increases. The initial  $K_p$  at 298.2 K is calculated using  $K_p = e^{-\Delta_r G^\circ/RT} = 1.492 \times 10^6$ . The  $K_p$  at decreasing temperature (increasing altitude) is calculated using Eq. 20.1.29 and listed in column F:

$$K_{p,T_2} = K_{p,T_1} e^{\frac{-\Delta_r H^\circ}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)} = 1.492 \times 10^6 e^{\frac{-(-5.707 \times 10^4 \text{ J mol}^{-1})}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \left( \frac{1}{T_2} - \frac{1}{298.2 \text{ K}} \right)}$$

The molar ratio of  $\text{O}_2$  to NO is given by the initial conditions at sea level:

$$\begin{aligned} r &= b/a = n_{\text{O}_2,0}/n_{\text{NO},0} = (n_{\text{O}_2,0} RT/V)/(n_{\text{NO},0} RT/V) = P_{\text{O}_2,0}/P_{\text{NO},0} \\ &= 0.200/1.00 \times 10^{-5} = 2.00 \times 10^4 \end{aligned}$$

where  $n_{\text{NO},0}$  is the initial amount of NO at sea level before any oxidation. The change in partial pressure of  $\text{O}_2$  during the reaction is negligible. The partial pressure of  $\text{N}_2$  and other minor constituents in air at sea level is given by Dalton's law of partial pressures:  $P_{\text{N}_2} = P_{\text{tot}} - P_{\text{O}_2} - P_{\text{NO}} = (1.00 - 0.200 - 1.00 \times 10^{-5}) \text{ bar}$ . The molar ratio of  $\text{N}_2$  to NO from the initial conditions at sea level is  $q = n/a = P_{\text{N}_2}/P_{\text{NO}} = 8.00 \times 10^4$ . The effective equilibrium constant at a given altitude is calculated using Eq. P20.41.2° assuming  $r$  and  $q$  are constant with altitude. The degree of reaction  $\alpha = \alpha_{\text{NO}}$  is then calculated using Eq. P20.41.2° in column H. The partial pressure of NO is then given in column I using Problem 41 Eq. 2 for the mole fraction of NO:

$$P_{\text{NO}}(h) = \left( \frac{1 - \alpha}{1 + r + q - \alpha/2} \right) P(h)$$

where  $P(h)$  is the total pressure at the given altitude. Finally the accuracy of the calculation is checked by using the partial pressures to calculate  $Q$  at equilibrium, which should be equal to the equilibrium constant:

$$Q = \frac{(P_{\text{NO}_2}(h)/P^\circ)}{(P_{\text{NO}}(h)/P^\circ)(P_{\text{O}_2}(h)/P^\circ)^{1/2}}$$

A1	B	C	D	E	F	G	H	I	J
2	$\Delta_r G^\circ$	28.8	$\text{g mol}^{-1}$	$\Delta_r G^\circ$	-35.24	$\text{kJ mol}^{-1}$			
3	T	282.7	K	$\Delta_r H$	-57.07	$\text{kJ mol}^{-1}$			
4	R	8.3145	$\text{J K}^{-1} \text{mol}^{-1}$	$K_p (298 \text{ K})$	1.492E+06				
5	g	9.8067	$\text{m s}^{-1}$	$P_o(\text{NO})$	1.00E-05	bar			
6	$P_o$	1	bar	$P_o(\text{O}_2)$	0.2	bar			
7	$\gamma$	-0.006	$\text{K m}^{-1}$	$r = b/a =$	2.00E+04				
8				$q = n/a =$	8.00E+04	$(q+r/r)^{1/2} =$	2.2361		
9									check $K_p$
10	h	P	T (K)	$K_p$	$K_p * (Pr/q+r)^{1/2}$	$\alpha_{\text{NO}}$	P(NO)	Q	
11	0	1	298	1.492E+06	6.672E+05	0.999998501	1.50E-11	1.492E+06	
12	200	0.976	296.8	1.638E+06	7.236E+05	0.999998618	1.35E-11	1.638E+06	
13	400	0.953	295.6	1.799E+06	7.853E+05	0.999998727	1.21E-11	1.799E+06	
14	600	0.930	294.4	1.977E+06	8.530E+05	0.999998828	1.09E-11	1.977E+06	
15	800	0.908	293.2	2.175E+06	9.272E+05	0.999998921	9.80E-12	2.175E+06	
16	1000	0.887	292	2.395E+06	1.009E+06	0.999999009	8.79E-12	2.395E+06	
17	1200	0.866	290.8	2.639E+06	1.098E+06	0.999999089	7.88E-12	2.639E+06	
18	1400	0.845	289.6	2.910E+06	1.196E+06	0.999999164	7.06E-12	2.910E+06	
19	1600	0.825	288.4	3.212E+06	1.305E+06	0.999999234	6.32E-12	3.212E+06	
20	1800	0.806	287.2	3.547E+06	1.424E+06	0.999999298	5.66E-12	3.547E+06	
21	2000	0.786	286	3.922E+06	1.555E+06	0.999999357	5.06E-12	3.922E+06	

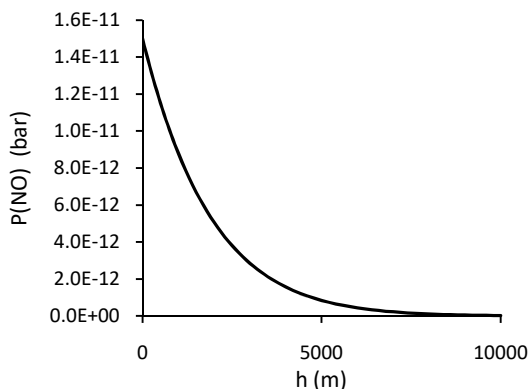


Figure P20.42.1: Equilibrium Partial Pressure of NO as a function of Altitude in the Troposphere.

The formulas are:

D12: “=SC\$6\*EXP(-SC\$2/1000\*SC\$5\*C12/SC\$4/SC\$3)”

E12: “=E11+SC\$7\*(C12-C11)”

F12: “=F\$4\*EXP(-F\$3\*1000/SC\$4\*(1/E12-1/SE\$11))”

G12: “=F12\*SQRT(D12)/SH\$8”

H12: “=G12/(1+G12)”

I12: “=(1-H12)/(1+F\$7+F\$8-H12/2)\*D12”

J12: “=(F\$5\*D12-I12)/I12/SQRT(0.2\*D12)”

You can change the acceleration of gravity to zero to see the effect of temperature alone. The equilibrium shifts in the exothermic direction with increasing height, which favors  $\text{NO}_2$  at altitude. You can change  $\gamma$  to zero to see the effect of pressure alone. The equilibrium shifts to the left with increasing height, which favors NO at altitude, although  $\Delta_r G^\circ$  is so negative that  $\text{NO}_2$  remains the predominant species.

43. Consider the reaction  $A + B \rightleftharpoons C + D$  in solution from a thermodynamic perspective and from a kinetic perspective. The equilibrium constant is a function of the solution activities, but the rate law is conventionally written in terms of the concentrations:

$$K_a = \frac{a_C a_D}{a_A a_B} \qquad v = \frac{1}{V} \frac{d\xi}{dt} = k_f [A][B] - k_r [C][D]$$

(a). Use detailed balance to prove that the rate law is also expressible in terms of the solution activities:

$$v = \frac{1}{V} \frac{d\xi}{dt} = k_f' a_A a_B - k_r' a_C a_D$$

(b). Relate the two sets of rate constants,  $k_f$  and  $k_r$  with  $k_f'$  and  $k_r'$ , given the activity coefficients for each species.

*Answer:* Detailed balance requires that the forward and reverse rates are equal for a reaction at equilibrium and that the ratio of the forward and reverse rate constants gives the equilibrium constant. Since the true thermodynamic equilibrium constant must be specified in terms of activities, the equilibrium constant that results from the kinetic rate law must also be written in terms of activities:

$$v = \frac{1}{V} \frac{d\xi}{dt} = k_f' a_A a_B - k_r' a_C a_D = 0 \qquad K_a = \frac{k_f'}{k_r'} = \frac{a_C a_D}{a_A a_B}$$

with  $a_A = \gamma_A [A]$ ,  $a_B = \gamma_B [B]$ , etc.

(b). The rate constants for the reaction rate written in terms of concentration and in terms of activities are then related through the activity coefficients using:

$$v = \frac{1}{V} \frac{d\xi}{dt} = k_f' \gamma_A \gamma_B [A][B] - k_r' \gamma_C \gamma_D [C][D]$$

Comparing with the rate law in terms of concentrations gives:

$$v = \frac{1}{V} \frac{d\xi}{dt} = k_f' \gamma_A \gamma_B [A][B] - k_r' \gamma_C \gamma_D [C][D]$$

$$v = \frac{1}{V} \frac{d\xi}{dt} = \underset{\uparrow}{k_f} [A][B] - \underset{\uparrow}{k_r} [C][D]$$

to give:  $k_f = k_f' \gamma_A \gamma_B$  and  $k_r = k_r' \gamma_C \gamma_D$ .

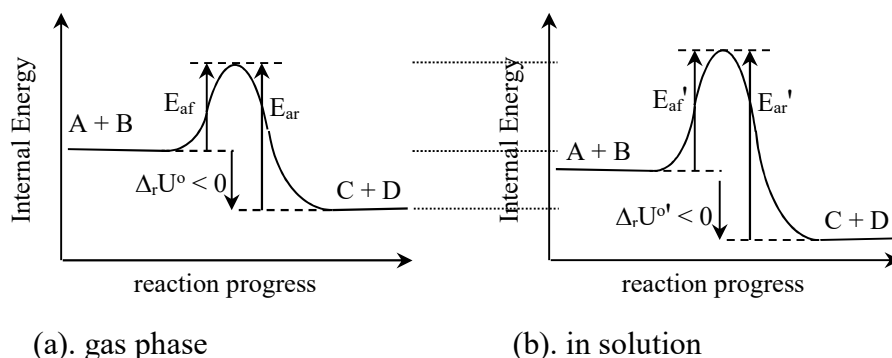
In other words, by convention for concentration based kinetic expressions, the activity coefficients of the reactants and products are incorporated into the rate constants. The corresponding true thermodynamic equilibrium constant is given by:

$$K_a = \frac{k_f'}{k_r'} = \left( \frac{\gamma_C \gamma_D}{\gamma_A \gamma_B} \right) \frac{k_f}{k_r}$$

As a case in point, we will use Debye-Hückel electrostatic theory to understand the kinetic salt effect in the chapter on molecular reaction dynamics. The energetic relationships are explored further in the next problem.

**44. Challenge Problem:** In the previous problem, we showed that the rate law for a reaction is best expressed in terms of activities, rather than concentrations, for consistency with detailed balance. However, by convention in concentration based kinetic expressions, the activity coefficients of the reactants and products are incorporated into the rate constants. The activity of a species deviates from the analytical concentration because of solute-solvent interactions. Rationalize the fact that solute-solvent interactions of the reactants and products have an effect on chemical reactions rates. However, be careful to separate thermodynamic and kinetic concerns. Assume that the kinetics follow Arrhenius behavior, and reason through the reaction profile, Figure 4.5.2.

*Answer:* We first must avoid using thermodynamic arguments to make a kinetic point. Consider a gas phase reaction and the same reaction in solution. For a particular example, assume an exothermic reaction and that the reactants and products are stabilized by solute-solvent forces while the transition state is destabilized by solute-solvent forces, as shown in the following figure.



We assume a constant volume process, so that the internal energy or Helmholtz energies are the appropriate thermodynamic variables. The parameters of the solution reaction are listed with primes, e.g.  $\Delta_r U^{o'}$ . First take the thermodynamic perspective.  $\Delta_r U^o$  and  $\Delta_r U^{o'}$  are independent of the transition state energy, and clearly have an effect on the equilibrium constant through  $\Delta_r A^{o'} = \Delta_r U^{o'} - T \Delta_r S^o$ . The standard states are typically chosen as Henry's Law standard states for the reactants and products, and therefore include solute-solvent interactions.  $\Delta_r U^{o'}$  is changed, compared to the gas phase, if the reactants and products are stabilized by solute-solvent interactions to a different extent. Now take the kinetic perspective.

Detailed balance requires that  $E_{af} - E_{ar} = \Delta_r U^o$  for the gas phase reaction and  $E_{af}' - E_{ar}' = \Delta_r U^{o'}$  for the solution phase reaction. The rates of the reaction, forward and reverse are strong functions of the activation energies. There are four possibilities:

1. For the particular example in the figure, if the reactants and products are stabilized by solute-solvent interactions and the transition state is destabilized, then the activation energies are increased and the reaction rates decrease.

2. However, if the reactants and products are stabilized by solute-solvent interactions and the transition state is also stabilized to a similar degree, then the activation energies are little changed.

3. Alternately, if the reactants and products are destabilized by solute-solvent interactions and the transition state is destabilized, then the activation energies are little changed.

4. Or, the final possibility is if the reactants and products are destabilized by solute-solvent interactions and the transition state is stabilized, then the activation energies are decreased and the reaction rates increase.

In any event, the effect of solute-solvent forces is to change the energies of the reactants and products, which in turn changes the activation energy:  $E_{af} = E_{\text{transition-state}} - E_{\text{reactants}}$  and  $E_{ar} = E_{\text{transition-state}} - E_{\text{products}}$ . At thermodynamic equilibrium the transition-state energy cancels out:

$$\Delta_r U^\circ = E_{af} - E_{ar} = (E_{\text{transition-state}} - E_{\text{reactants}}) - (E_{\text{transition-state}} - E_{\text{products}}) = E_{\text{products}} - E_{\text{reactants}}$$

The activity coefficients then have an effect on both the thermodynamic equilibrium and the reaction rates through changes in energy or chemical potential of each reactant and product:

$$\mu_i = \mu_i^\circ + RT \ln \gamma_i c_i$$

In summary, it matters little in the final effect if the rate law is written in terms of concentrations or activities; energetic interactions of the solutes with the solvent have an effect on the rates and equilibria of chemical reactions.

$$v = \frac{1}{V} \frac{d\xi}{dt} = k_f [A][B] - k_r [C][D] \quad \text{or} \quad v = \frac{1}{V} \frac{d\xi}{dt} = k_f' a_A a_B - k_r' a_C a_D$$

The kinetic changes are difficult to predict, however, because the effect of the solvent on the transition state must also be determined. Even if the transition state is traversed in a non-equilibrium, purely dynamical way, the effective activation energy still depends on the energies of the reactants and products. The energies of the reactants and products are altered by interactions with the solvent.

One deficiency in our argument is that we have considered energetic issues and have ignored entropic considerations. Certainly, solvation effects can have large entropic contributions. Entropic contributions to reaction rate constants are expressed primarily through the pre-exponential factor,  $A$ , in the Arrhenius expression  $k_2 = A e^{-E_a/RT}$ . Similar arguments can be framed through changes in the pre-exponential factors with entropic changes caused by solvation. The pre-exponential factor is referenced to the entropy of the reactants or products, for the forward and reverse reactions, respectively.

45. The temperature dependence of isomerization is conveniently followed by experimental techniques that have additive response of the two forms in equilibrium. The equilibrium constant of the two forms is given by:

$$A \rightleftharpoons B \quad \text{with} \quad K = [B]/[A] \quad \text{P20.45.1}$$



One example of an experimental technique with additive response is infrared spectroscopy. The wave number of an IR band is the mole fraction weighted average of the two forms:

$$\tilde{\nu}_{\text{obs}} = \tilde{\nu}_A x_A + \tilde{\nu}_B x_B \quad (\text{additive response}) \quad \text{P20.45.2}$$

where  $x_A$  and  $x_B$  are the mole fractions of A and B, respectively. The absorption wave numbers of the pure components are  $\tilde{\nu}_A$  and  $\tilde{\nu}_B$ , respectively.

(a). Let the total analytical moles be  $a$ , with  $n_A + n_B = a$ , where  $n_A$  and  $n_B$  are the number of moles of A and B. The total volume of the solution is  $V$ . Show that the corresponding concentrations are related by  $[A] + [B] = [a]$ , with concentrations in moles per liter.

(b). Show that the observed wave number is given in terms of the concentrations as:

$$\tilde{\nu}_{\text{obs}} = \tilde{\nu}_A \frac{[A]}{[a]} + \tilde{\nu}_B \frac{[B]}{[a]} \quad (\text{additive response}) \quad \text{P20.45.3}$$

(c). Using P20.43.1 show that the equilibrium concentrations are given by:

$$[A] = \frac{1}{1+K} [a] \quad [B] = \frac{K}{1+K} [a] \quad \text{P20.45.4}$$

(d). Using Eqs. P20.43.2-P20.43-4, show that the equilibrium constant is determined by:

$$K = \frac{\tilde{\nu}_{\text{obs}} - \tilde{\nu}_A}{\tilde{\nu}_B - \tilde{\nu}_{\text{obs}}} \quad (\text{additive response}) \quad \text{P20.45.5}$$

*Answer:* (a). The mole fractions and concentrations of the two forms are given by the numbers of moles of the two forms,  $n_A$  and  $n_B$ , and the total analytical moles,  $a$ :

$$x_A = n_A/a \quad x_B = n_B/a \quad n_A + n_B = a \quad \text{and} \quad x_A + x_B = 1 \quad 1$$

$$[A] = n_A/V \quad [B] = n_B/V \quad [a] = a/V \quad 2$$

Substituting the concentrations into the mass balance,  $n_A + n_B = a$ , gives:

$$[A] + [B] = [a] \quad 3$$

(b). The observed frequency can be written in terms of the concentrations of the two forms and the total analytical concentrations,  $[A]$ ,  $[B]$ ,  $[a]$ , respectively using Eq. 20.45.2:

$$\tilde{\nu}_{\text{obs}} = \tilde{\nu}_A x_A + \tilde{\nu}_B x_B = \tilde{\nu}_A n_A/a + \tilde{\nu}_B n_B/a = \tilde{\nu}_A \frac{n_A/V}{a/V} + \tilde{\nu}_B \frac{n_B/V}{a/V} \quad 4$$

$$\tilde{\nu}_{\text{obs}} = \tilde{\nu}_A \frac{[A]}{[a]} + \tilde{\nu}_B \frac{[B]}{[a]} \quad (\text{P20.45.3}) \quad 5$$

(c). From the mass balance, Eq. 3,  $[A] = [a] - [B]$  giving the equilibrium constant as:

$$K = \frac{[B]}{[a] - [B]} \quad \text{solving for } [B] \text{ gives: } [B] = \frac{K}{1+K} [a] \quad (\text{P20.45.4}) \quad 6$$

Solving for  $[A]$  using the mass balance gives:

$$[A] = [a] - [B] = \left(1 - \frac{K}{1+K}\right) [a] = \frac{1}{1+K} [a] \quad (\text{P20.45.4}) \quad 7$$

(d). The observed frequency from Eqs. 5, 6, and 7 is then:

$$\tilde{\nu}_{\text{obs}} = \tilde{\nu}_A \frac{1}{1+K} + \tilde{\nu}_B \frac{K}{1+K} = \frac{\tilde{\nu}_A + \tilde{\nu}_B K}{1+K} \quad 8$$

Cross multiplying by  $1+K$  gives:

$$\tilde{\nu}_{\text{obs}} + \tilde{\nu}_{\text{obs}}K = \tilde{\nu}_A + \tilde{\nu}_B K \quad \text{or} \quad K = \frac{\tilde{\nu}_{\text{obs}} - \tilde{\nu}_A}{\tilde{\nu}_B - \tilde{\nu}_{\text{obs}}} \quad (\text{P20.45.5}) \quad 9$$

The last equation allows the equilibrium constants to be determined completely from the shift in the band frequency.

46. The infrared absorption of an intramolecular hydrogen-bonded amine (see Problem Ch. 10.13: N-[2-(dimethylamino)ethyl]-N-methylguanidium ion) as a function of temperature is at:

T (°C)	25.0	30.0	35.0	40.0	45.0
$\tilde{\nu}_{\text{obs}}$ (cm <sup>-1</sup> )	1520	1540	1548	1570	1573

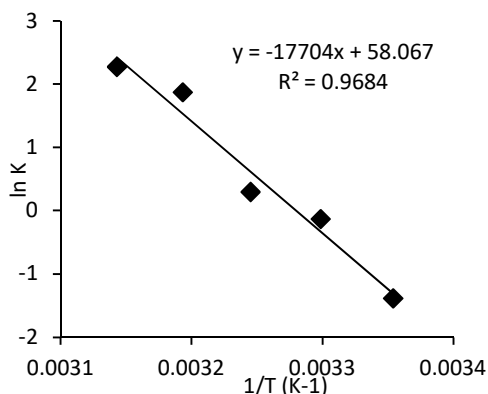
Equilibrium is established between the closed and open forms; the closed form is hydrogen-bonded and the open form is not hydrogen-bonded:  $C \rightleftharpoons O$ . The wave number of the closed form is:  $\tilde{\nu}_C = 1505 \text{ cm}^{-1}$  and the open form is  $\tilde{\nu}_O = 1580 \text{ cm}^{-1}$ . Using Eq. P20.45.5, determine the equilibrium constant and reaction Gibbs energy as a function of temperature.

*Answer:* The plan is to note that the equilibrium constant for an isomerization is determined completely from the observed band shifts using Eq. P20.45.5, while the linearized form of the temperature dependence is:  $\ln K = -\Delta_r H^\circ / RT + \ln c$ .

A spreadsheet was set up using Eq. P20.45.5 using the association of  $C \rightleftharpoons O$  with  $A \rightleftharpoons B$ :

T (K)	$\nu_{\text{obs}}$ (cm <sup>-1</sup> )	K	1/T (K <sup>-1</sup> )	ln K	$\Delta_r G^\circ$ (kJ mol <sup>-1</sup> )
298.15	1520	0.2500	0.003354	-1.38629	3.437
303.15	1540	0.8750	0.003299	-0.13353	0.337
308.15	1548	1.3438	0.003245	0.295464	-0.757
313.15	1570	6.5000	0.003193	1.871802	-4.874
318.15	1573	9.7143	0.003143	2.273598	-6.014

slope	-17704	58.0673	intercept
$\pm$	1846.3	5.99645	$\pm$
$r^2$	0.9684	0.30777	s(y)
F	91.943	3	df
SS <sub>reg</sub>	8.7092	0.28417	SS <sub>resid</sub>



The reaction enthalpy is then determined from the slope of  $\ln K$  vs.  $1/T$  giving  $\Delta_r H^\circ = -\text{slope}(R) = 147. \pm 15. \text{ kJ mol}^{-1}$ . The reaction Gibbs energies are then given by  $\Delta_r G^\circ = -RT \ln K$ . Assuming an uncertainty of  $\pm 2 \text{ cm}^{-1}$  in the observed wave numbers, the uncertainty in the Gibbs energy is  $\pm 0.005 \text{ kJ mol}^{-1}$ . The reaction enthalpy is much larger than the hydrogen bond strength since proton transfer reactions accompany the formation of the hydrogen bond and shifts in pH occur with the changes in temperature.

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