

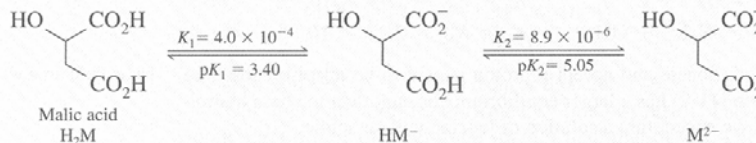
Analytical Chemistry
Problem Set 7
Due Monday, April 6, 2009 (at 4:00 p.m.)
Total Number of Points = 58

- Consult Appendix G in your text for any K_a values you need for calculations.
 - Assume that all activity coefficients are 1 in your calculations.
 - You do not need to justify on paper how you have solved a quadratic equation.
1. (4 points) Harris 9-18
 2. (13 points) Harris 9-21. Please note the following:
 - You must use a systematic treatment of equilibrium for this problem. That is, start by writing equilibrium constant expressions, a charge balance, and (at least one) mass balance. Then derive an equation that lets you solve the problem. State any assumptions you make to simplify the algebra, and justify them at the end of the problem.
 - Remember that for any conjugate acid/base pair, $K_a K_b = K_w$
 - The 0.050 “M” NaCN in the problem statement actually refers to the formal (that is, initial) concentration of NaCN.
 3. (4 points) Harris 9-32. You must justify your answer.
 4. (4 points) Harris-9.33.
 5. (18 points) Harris 10-5. In your calculations for part (b), you do not need to perform more than one iteration.
 6. (12 points) Harris 10-9. Unlike Harris 10-5(b), the point of this problem is precisely to perform multiple iterations. Also note:
 - Use Excel to solve this problem. Be sure to turn in a printout of your spreadsheet.
 - For both parts (a) and (b), you should iterate until two successive calculations of $[HA^-]$ agree to two significant figures and two successive calculations of pH agree to three significant figures (that is, three decimal places).
 - I have included on the back of the problem set a copy of Harris’ 6th edition explanation of solving by successive approximations. You will find it more helpful than the explanation in your edition of the textbook. (Yes, I am a very nice guy.)
 7. (3 points) Explain briefly why in Problem 6 (Harris 10-9), it was necessary to perform several more iterations to converge the answers to part (b) than to converge the answers to part (a).

Box 11-1 Successive Approximations

The method of *successive approximations* is a good way to deal with difficult equations that do not have simple solutions. For example, Equation 11-11 is not a good approximation when the concentration of the intermediate

(amphiprotic) species of a diprotic acid is not close to F , the formal concentration. This situation arises when K_1 and K_2 are nearly equal and F is small. Consider a solution of 1.00×10^{-3} M HM^- , the intermediate form of malic acid.



As a first approximation, we assume that $[\text{HM}^-] \approx 1.00 \times 10^{-3}$ M. Plugging this value into Equation 11-10, we calculate first approximations for $[\text{H}^+]$, $[\text{H}_2\text{M}]$, and $[\text{M}^{2-}]$.

$$\begin{aligned}
 [\text{H}^+]_1 &= \sqrt{\frac{K_1 K_2 (0.00100) + K_1 K_w}{K_1 + (0.00100)}} = 5.04 \times 10^{-5} \text{ M} \\
 \Rightarrow [\text{H}_2\text{M}]_1 &= 1.26 \times 10^{-4} \text{ M} \\
 [\text{M}^{2-}]_1 &= 1.77 \times 10^{-4} \text{ M}
 \end{aligned}$$

Clearly, $[\text{H}_2\text{M}]$ and $[\text{M}^{2-}]$ are not negligible relative to $F = 1.00 \times 10^{-3}$ M, so we need to revise our estimate of $[\text{HM}^-]$. The mass balance gives us a second approximation:

$$\begin{aligned}
 [\text{HM}^-]_2 &= F - [\text{H}_2\text{M}]_1 - [\text{M}^{2-}]_1 \\
 &= 0.00100 - 0.000126 - 0.000177 = 0.000697 \text{ M}
 \end{aligned}$$

Using the value $[\text{HM}^-]_2 = 0.000697$ in Equation 11-10 gives

$$[\text{H}^+]_2 = \sqrt{\frac{K_1 K_2 (0.000697) + K_1 K_w}{K_1 + (0.000697)}} = 4.76 \times 10^{-5} \text{ M}$$

$$\begin{aligned}
 \Rightarrow [\text{H}_2\text{M}]_2 &= 8.29 \times 10^{-5} \text{ M} \\
 [\text{M}^{2-}]_2 &= 1.30 \times 10^{-4} \text{ M}
 \end{aligned}$$

The values of $[\text{H}_2\text{M}]_2$ and $[\text{M}^{2-}]_2$ can be used to calculate a third approximation for $[\text{HM}^-]$:

$$[\text{HM}^-]_3 = F - [\text{H}_2\text{M}]_2 - [\text{M}^{2-}]_2 = 0.000787 \text{ M}$$

Plugging $[\text{HM}^-]_3$ into Equation 11-10 gives

$$[\text{H}^+]_3 = 4.86 \times 10^{-5}$$

and the procedure can be repeated to get

$$[\text{H}^+]_4 = 4.83 \times 10^{-5}$$

We are homing in on an estimate of $[\text{H}^+]$ in which the uncertainty is already less than 1%. This is more accuracy than is justified by the accuracy of the equilibrium constants. The fourth approximation gives $\text{pH} = 4.32$, compared with $\text{pH} = 4.30$ from the first approximation and $\text{pH} = 4.23$ from the formula $\text{pH} \approx \frac{1}{2}(\text{p}K_1 + \text{p}K_2)$. Considering the uncertainty in pH measurements, all this calculation was

hardly worth the effort. However, the concentration $[\text{HM}^-]_5$ is 0.000768 M, which is 23% less than the original estimate of 0.00100 M.

Successive approximations can be carried out by hand, but the process is more easily and reliably performed with a

spreadsheet. Column B uses the same formulas as column C, except that $[\text{HM}^-]$ in column B is equated to the formal concentration, F , in cell $\$A\8 . Once column C has been set up, it can be copied into further columns for each approximation.

	A	B	C	D	E
1	Successive approximations for the intermediate form of a diprotic acid				
2					
3	K1 =	1st approx.	2nd approx.	3rd approx.	4th approx.
4	4.00E-04	[HM-]	[HM-]	[HM-]	[HM-]
5	K2 =	1.000E-03	6.974E-04	7.866E-04	7.604E-04
6	8.90E-06	[H+]	[H+]	[H+]	[H+]
7	F =	5.043E-05	4.757E-05	4.858E-05	4.830E-05
8	1.00E-03	[H2M]	[H2M]	[H2M]	[H2M]
9	Kw =	1.261E-04	8.293E-05	9.553E-05	9.181E-05
10	1.00E-14	[M2-]	[M2-]	[M2-]	[M2-]
11		1.765E-04	1.305E-04	1.441E-04	1.401E-04
12		pH	pH	pH	pH
13		4.297	4.323	4.314	4.316
14					
15	B5 = \$A\$8				
16	B7 = SQRT((\$A\$4*\$A\$6*B5+\$A\$4*\$A\$10)/(\$A\$4+B5))				
17	B9 = B7*B5/\$A\$4				
18	B11 = \$A\$6*B5/B7				
19	B13 = -LOG10(B7)				
20	C5 = \$A\$8-B9-B11				
21	C7 = SQRT((\$A\$4*\$A\$6*C5+\$A\$4*\$A\$10)/(\$A\$4+C5))				