Chemistry 301
Computer Lab 5
Roots of Equations: Equilibrium
Lab Work 22 Oct 2001
Report Due 6 Nov 2001 on Web Site
Fall 2001 AV

In this computer lab, algebraic equations will be solved, with an emphasis on equilibrium calculations. Some of the results will be displayed graphically, including logarithmic distribution diagrams. Please work collaboratively in your Lab Group. Use Chemistry computers in GSC 240, 246A, 258, and 261.

1. **Function plotting and Newton-Raphson iteration**
   Equation to be solved for x: f(x) = exp(x) **-** 3x = 0

   a. Obtain a Quattro Pro spreadsheet from the instructor: AVEXP3.w??. Using the spreadsheet, plot f(x) vs x, over the range -5 to +5 for x. Is there more than one root? Estimate the root(s). Capture an image of the spreadsheet, and an image of the graph.

   b. Obtain a Turbo Basic program from the instructor: AVEXP3NR.bas. The program carries out a Newton-Raphson iteration to find a root of the equation. To find (each of) the root(s), run the program, inputting an initial estimate of x for the root, and a termination criterion. Capture a copy of the source code, and of successful run(s) determining the root(s).

   c. Devise a Quattro Pro spreadsheet which also carries out a Newton-Raphson iteration to find a root of the equation. Plot f(x) versus the number of iterations. Print out the spreadsheet. Capture an image of the graph.

2. **Program in BASIC, Fortran, C**, or a spreadsheet

   Next we will write a program (in Basic, Fortran, C, or other language of your choice), or develop a spreadsheet, to solve an algebraic equation. The equation is one used to calculate the pH of an aqueous solution a weak acid.

   Equation to be solved (with X = [H +]):
   $\mathbf{X^3 + Ka*X^2 - (Kw + Ka*C)*X - Ka*Kw = 0}$
   This is based on considerations of equilibrium, mass balance, and charge balance.

   Your program should apply a Newton-Raphson iteration to find X (the [H +] concentration) and pH, for values of pKw, pKa, and log(C) which you read in as data. The Turbo Basic program in Part 1b may be used as a starting point if you wish.

   Carry out several runs, using input data such as the following:

Run:		**a**	**b**	**c**
pKa:		5.0	3.0	9.0
pKw:		14.0	14.0	14.0
log(C):	-3.0	-8.0	-4.0	

   Some of the versions of these languages which are available include Turbo Basic, Power Basic on the PC, and Fortran and C on the IBM RS/6000 computer. Choose the tools (language: Basic, Fortran, or C; or spreadsheet: Quattro Pro or Excel) with which you feel most comfortable, or with which you would like to get further practice. If necessary, ask the instructor or the lab assistant for help in getting started on your program.

3. **Mathcad**

Now use Mathcad software to solve the same problem as in part 2 (but without worrying explicitly about the Newton-Raphson iteration). The root function of Mathcad will be useful.

4. **MINSQ software**

a. Using the MINSQ software, calculate pH for a series of weak acid solutions in water, with characteristics such as: pKa = 4.0, log(C) ranging from -10 to 0, and pKw = 14.0. File LAB5_3a.eqn should be useful. Plot the results: pH (as ordinate) vs log(C). Do a second plot in which you select a somewhat different value of pKa, in the range of 6.0 to 10.0. Print out the equations and the parameters.

b. Using the MINSQ software, plot two titration curves similar to Atkins Fig. 9.11 (p. 233), with different pKa values (selected from pKa = 3, 5, 7, 9, 11). Use 0.10 M HA in the beaker, and 0.10 M NaOH in the buret. To be specific, use 25.0 ml of the acid, and titrate from 0 ml to 50 ml of base. Model LAB5_3B.eqn or TitrWASB.eqn should be useful. Print out the equations and the parameters.

c. In MINSQ, file ERICAWAS.dat contains a set of data for a titration of a known volume of a monoprotic weak acid solution (beaker) with a strong base of known concentration (buret). This data set was collected by Lynda Rasmussen and Erica Umback in Chem 120H lab, during Fall 1990. Assume that Lynda and Erica titrated 25.0 ml of an aqueous solution of a weak acid HA, using 0.100 M NaOH as titrant. Using MINSQ, determine a best fit for the concentration of the weak acid HA, and the pKa of the weak acid HA. Print out the model, the data, the parameters, and the statistics for the MINSQ fit. In the latter, print the results for a 90% confidence interval, and for a 95% confidence interval.

5. **Logarithmic distribution diagrams**

Obtain another Quattro Pro spreadsheet from the instructor, with a name of the type AVH2A.w??. This spreadsheet generates a logarithmic distribution diagram for a dibasic acid H2A. In this diagram, log[X] vs pH is plotted for the various species present, including H^+ and OH^-. Reference: Thomas R. Blackburn, *Equilibrium: A Chemistry of Solutions*, Holt, Rinehart and Winston, Inc., New York, NY, 1969, Fig. 2-6 and 2-9 (p. 39 and 45).

a. Display the logarithmic distribution diagram in the Quattro Pro spreadsheet. It is for oxalic acid, with pK1 = 1.25 and pK2 = 4.285.

b. Modify a copy of the Quattro Pro spreadsheet so that it represents phosphorous acid, with pK1=1.8 and pK2=6.2. Display the logarithmic distribution diagram.

6. **Report**

Reports for computer exercises, just as other lab reports, go on your web site. We encourage creativity in how you choose to present your results. You may want to consider questions such as the following.

For Part 1b, identify the lines in the source program which are most central to the Newton-Raphson iteration.

For Part 1c, explain the logic of your spreadsheet. Identify the cell formulas which are of greatest importance in the Newton-Raphson iteration.

In part 2, derive the cubic equation which is being solved for the hydrogen ion concentration in theaqueous solution of a weak acid. Take into account equilibrium, mass balance, and charge balance.

The very simplest approximation for calculating the pH of a weak acid is shown in the Atkins Illustration on p. 231. Compare this approximation with the computer output for parts 2 and 3. For which runs (cases) is the approximation fairly good (pH within 0.1 unit)? What assumptions are made in the method of the Atkins Illustration on p. 231? For any run in which the approximation fails the 0.1 pH unit test, try to identify which assumption is not being met.

Compare your results from Part 2 (Newton-Raphson program) and Part 3 (Mathcad) for the same problem.

Compare your graphs in part 4a with Thomas R. Blackburn, *Equilibrium: A Chemistry of Solutions*, Holt, Rinehart and Winston, Inc., New York, NY, 1969, Fig. 2-10 (p. 51). In certain regions of Blackburn Fig. 2-10 (and perhaps in one of your own graphs), three different limiting or asymptotic slopes (dpH/dlog(C)) may be identified. What are the three slopes? (Give numerical values). To what limiting types of chemical behavior are these three slopes related? Show how the approach of the Atkins Illustration on p. 231 is related to one of these limiting slopes.

In Parts 4a and 4b, discuss the equations and parameters, in relation to pertinent equilibrium, charge balance, and/or material balance considerations.

In Part 4c, report the concentration of the weak acid, its pKa, their standard deviations, their 90% confidence intervals, and their 90% confidence intervals. Suppose that the weak acid is acetic acid. Discuss the the pKa from MINSQ in relation to a literature value for acetic acid. How might the comparison be affected by activity coefficients, or by pH meter calibration with buffers?

In part 5, label the various curves (lines) in each logarithmic distribution diagram with respect to which chemical species is being represented (H_2A, HA^- , etc.).

In part 5, find cells in the spreadsheet which calculate $[HA^-]$. Examine the formula in the cell, and explain briefly.

In part 5b, consider a solution of 0.10 M NaH_2PO_3 in water. Logarithmic distribution diagrams are discussed in Thomas R. Blackburn, *Equilibrium: A Chemistry of Solutions*, Holt, Rinehart and Winston, Inc., New York, NY, 1969, Chapter 2. The proton balance from the reference level NaH_2PO_3 plus H_2O is given by

$$[H^+] + [H_3PO_3] = [OH^-] + [HPO_3^{2-}]$$

To obtain an excellent approximation to the solution of this equation, look for the highest intersection of one of the curves on the left with one of the curves on the right of the equal sign. Within the accuracy of reading the graph, what is the pH of 0.10 M NaH_2PO_3?