Multiple Equilibria, Approximation, and Iteration

A Graphing Calculator Approach

Background

Any diprotic acid dissociates according to the following general equation.

$$XH_2 \; <-> \; X^{2-} + 2H^+$$

This equation can be further expressed as the following two equilibia.

Equilibrium One

pKa1 $\quad XH_2 \; <-> \; XH^- + H^+$

Equilibrium Two

pKa2 $\quad XH^- \; <-> \; X^{2-} + H^+$

The following table outlines the concentrations of all species at equilibrium.

	XH_2	XH^-	X^{2-}	H^+
Initial	C	0	0	0
Equilibrium 1	-x	x	0	x
Equilibrium 2	0	-y	y	y
Final	C-x	x-y	y	x+y

At equilibrium, the following conditions exist:

Equilibrium 1	*Equilibrium 2*
$K_1 = \frac{[XH^-][H^+]}{[XH_2]}$	$K_2 = \frac{[X^{-2}][H^+]}{[XH^-]}$
$K_1 = \frac{[x-y][x+y]}{[C-x]}$	$K_2 = \frac{[y][x+y]}{[x-y]}$
$K_1 = \frac{[x^2-y^2]}{[C-x]}$	

Under equilibrium conditions, the following approximations are appropriate:

Equilibrium 1	*Equilibrium 2*
$x << C$ $y << x$	$y << x$
–so –	–so –
$K_1 = \frac{[x^2]}{[C]}$	$K_2 = \frac{[y][x+y]}{[x-y]}$
$x_1 = \sqrt{K_1 \cdot C}$	$y_1 = K_2$

With three approximations, the concentration of any species can be determined. However, the value of x and y must be verified by iteration to determine if the approximations are valid

In this iteration, a value for x and y will be determined and substituted back into the original equation. From this substitution, new x and y values can be compared to their previous values. This process is repeated until the values of x and y converge on constant values. The original approximations are validated if x and y converge to constant values.

Below are the formulas for the first three iterations:

$$x_1 = \sqrt{K_1 \cdot 0.01}$$
$$y_1 = K_2$$

$$x_2 = \sqrt{K_1 \cdot [0.01 - x_1] + y_1^2}$$
$$y_2 = \frac{K_2 \cdot [x_1 - y_1]}{[x_1 + y_1]}$$

$$x_3 = \sqrt{K_1 \cdot [0.01 - x_2] + y_2^2}$$
$$y_3 = \frac{K_2 \cdot [x_2 - y_2]}{[x_2 + y_2]}$$

The process of making the iterations and determining the final concentrations can be a tedious algebraic process. The process can be greatly simplified with a program running on a graphing calculator.

Creating a Calculator Program for Approximation and Iteration

Note: *The following directions are provided for the TI-83 graphing calculator, but the general principals could be adapted for any programmable calculator or computer. The program code can be entered on the calculator or typed on the compute r and transferred with the TI -Graph Link cable.*

Create the following program and attempt the practice problems.

Instructions	Program Text
Create a new program.	PRGM Create New
Name the program.	APPROX
Set the calculator mode to six decimal places by selecting MODE and FLOAT 6. Prompt the user for the important variables. A is K1, B is K2 and C is the initial concentration of XH_2. Define the mathematical operations just as you would on the calculator home screen. Note the arrow is the store key (STO). The variable 'I' defines the iteration number. The label command (LBL) marks a point in the program to refer to in the future. LBL A point is our reference point for a repeating loop. The I+1 -> 1 command identifies the iteration number with each pass through the loop. Commands like 'Clrhome' and 'Output (' can be found under the program menu (PRGM). The menu command creates a menu for the user and then redirects the program flow to a label command based on the user's selection. The calculator program variables: A = K_1 B = X_2 C = $[XH_2]$ initial D = Y2 and $[X^{-2}]$ final F = $[XH_2]$ final G = $[XH^-]$ final H = $[H^+]$ final I = Iteration number J = pH X = Y = Z = K_2	**Fix 6 ClrHome Disp "ENTER K1.." Prompt A Disp "ENTER K2.." Prompt Z Disp "ENTER [XH2].." Prompt C Lbl Z √(A*C)X ZY 0I Lbl A I+1I √(A*(C-X)+Y^2)B Z*(X-Y)/(X+Y)D ClrHome Disp X,B,Y,D,I Output(1,1,"X1") Output(2,1,"X2") Output(3,1,"Y1") Output(4,1,"Y2") Output(5,1,"ITT") Output(8,5,"[ENTER]") Pause ClrHome Menu("SELECT","REPEAT",B,"STOP",C) Lbl B BX DY Goto A Lbl C ClrHome C-BF B-DG B+DH -log(H)J Fix 6 Disp F,G,D,H,J Output(1,1,"[XH2]") Output(2,1,"[XH-]") Output(3,1,"[X-2]") Output(4,1,"[H+] Output(5,1,"PH") Stop**

Practice Problems

1. Fumerate ($HO_2CCH{=}CHCO_2H$ *trans*) is a polyprotic acid with, pKa1=3.1 and pKa2=4.6. Determine the pH of 0.01M solution.

2. Succinic acid ($HO_2CCH_2CH_2CO_2H$) has two pKa values, 4.19 and 5.57. Calculate the concentrations of all species and the pH of a 0.02M succinic acid solution, correct to three significant figures.

3. Oxalic acid (HO_2CCO_2H) is a polyprotic acid with, pKa1=1.27 and pKa2=4.28. Determine the pH of 0.15M solution.

4. Maleic acid ($HO_2CCH{=}CHCO_2H$ *cis*) has two pKa values, 1.83 and 6.07. Calculate the concentrations of all species and the pH of a 0.02M maleic acid solution, correct to three significant figures.

Findings

1. Explain how the program could be modified to account for a substance like phosphoric acid (H_3PO_4) which has three acidic protons.

Answers to Practice Problems 1-2

1. pH = 2.6

2. After 3 iterations:

XH_2 = 0.0189 M
XH^- = 0.00110 M
X^{-2} = 2.68 x 10^{-6} M
H^+ = 0.00111 M
pH = 2.96