DECUS
PROGRAM LIBRARY

DECUS NO.	FOCAL8-113
TITLE	ACID-BASE TITRATION CURVES
AUTHOR	Edgar H. Nagel
COMPANY	Valparaiso University Valparaiso, Indiana
DATE	July 9, 1970
SOURCE LANGUAGE	FOCAL 1969

ACID-BASE TITRATION CURVES

DECUS Program Library Write-up

DECUS No. FOCAL8-113

The program is initiated by reading in the program tape under FOCAL control and typing GO followed by a carrage return. After a heading is typed, the program requests the number of replaceable hydrogens. [The program was tested with up to five replaceable hydrogens.] The successive pK_a values are entered when requested by the program. The plot is generated after entery of the last pK_a.

The exact equations describing a general titration curve are derived from relationships given in Laitinen [1]. A charge balance on the system, assuming NaOH is the titrant is

$$[Na^+] + [H^+] = [OH^-] + \sum_{i=1}^{N} i[H_{[N-i]}A^{-i}] \qquad [1]$$

where N is the number of replaceable hydrogens. The concentration of Na is

$$[Na^+] = CV/[V + V_o] \qquad [2]$$

C and V are the concentration of NaOH and the volume of NaOH added. V_o is the initial volume of acid. The $[OH^-]$ in Equation [1] can be replaced by

$$[OH^-] = K_w/[H^+] \qquad [3]$$

where K_w is the autoprotolysis constant for water.

From Laitinen [1]

$$[H_{[N-i]}A^{-i}] = \alpha_i C_{H_NA} \qquad [4]$$

where

$$\alpha_i = \frac{[H^+]^{[N-i]} \prod_{j=0}^{i} K_j}{\sum_{k=0}^{N} [H^+]^{[N-k]} \prod_{j=0}^{k} K_i} \qquad [4a]$$

$K_o = 1.00$ and K_i are the successive stepwise dissociation constants for the acid.

$C_{H_NA} = C_oV_o/[V + V_o]$ = the total analytical concentration of acid. C_o is the initial concentration of acid.

Substitution of Equations [2], [3] and [4] in Equation [1] yields

$$0 = \frac{V + V_o}{C_oV_o}[K_w/[H^+] - [H^+]] - CV/[C_oV_o] + \sum_{i=1}^{N} i\alpha_i \qquad [5]$$

Defining $CV/[C_oV_o] = \phi$ = fraction titrated and substituting in Equation [5] for both $CV/[C_oV_o]$ and V one obtains

$$0 = \frac{C + \phi C_o}{CC_o}[K_w/[H^+] - [H^+]] - \phi + \sum_{i=1}^{N} i\alpha_i \qquad [6]$$

If one intends to plot pH as a function of Ø, Equation [6] must be solved for H^+ for various values of Ø. This is a rather formitable task since even for one replaceable hydrogen on a weak acid, Equation [6] yields a cubic in H^+ [c.f. Fleck [2]]. However, an accurate solution of the equation is not required. All that is required is to determine if the solution for a particular value of Ø is between two scale values of pH. That is for a plot to the nearest 0.25 pH units, is the pH between pH_1 and $pH_1 + 0.25$?

Equations [4a] and [6] are used in the calculations. The program starts with Ø = pH = 0 and calculates the value of the expression on the right hand side of Equation [6]. The pH is then incremented by 0.25 and the right hand side is evaluated again. This process is continued until there is a change in sign. The pH is then plotted and the value of Ø is incremented by 0.05. A new point is calculated and plotted and the process continues until the value of Ø is greater than N + 0.1.

References:

1. Laitinen, H. A., "Chemical Analysis" Chapter 3, 1960. McGraw-Hill, New York.

2. Fleck, George M., "Equilibria in Solution" Chapter 4, 1966. Holt Rinehart and Winston, New York.

Variable Table

A[I]	Dummy Variable
B[I]	Dummy Variable
C[I]	$i\alpha_i$
H	H^+
J	pH
N	number of replaceable hydrogens
P	fraction titrated

```
C-FOCAL,1969

01.10 T !"TITRATION WITH 0.1M REAGENTS. PH VERSUS FRAC. TITR."
01.20 A !"NUMBER OF REPLACEABLE HYDROGENS ="N
01.40 S A(1)=1;F I=2,N+1;D 8
01.41 T !"          0    1    2    3    4    5    6    7    8"
01.42 T "    9   10   11   12   13",!
01.60 S J=0;S Q=-.01
01.80 F P=0,.05,N+.1;D 3

03.10 I (P-Q)3.3,3.2,3.2
03.20 T %4.02,"  "P,"*",#;S Q=Q+.5;D 5
03.30 S H=FEXP(-J*2.303);S J=J+.25
03.40 S S=0;F I=1,N+1;S B(I)=A(1)*H↑(N+1-I);S S=S+B(I)
03.50 F I=2,N+1;S C(I-1)=(I-1)*B(I)/S
03.60 S S=0;F I=1,N;S S=S+C(I)
03.70 S Y=S-P+(.1+P*.1)*(1.E-14/H-H)/.01
03.80 I (.26-J)3.9;S T=FSGN(Y);G 3.3
03.90 I (T+FSGN(Y))3.3,3.91,3.3
03.91 S J=J-.5;F I=0,.25,J+2;T " "
03.92 T "O",!;T "          *",#

04.10 Q

05.10 T "          *...*...*...*...*...*...*...*...*...*"
05.20 T "...*...*...*...*",#

08.10 A !"PKA"K;S K=FEXP(-K*2.303);T !
08.20 S A(I)=A(I-1)*K
*
```

```
TITRATION WITH 0.1M REAGENTS. PH VERSUS FRAC. TITR.
NUMBER OF REPLACEABLE HYDROGENS =:2
PKA:3.5

PKA:7.5

          0    1    2    3    4    5    6    7    8    9   10   11   12   13
  =   0.00*...*...*0..*...*...*...*...*...*...*...*...*...*...*...*...*...*
          *          0
          *           0
          *            0
          *            0
          *             0
          *             0
          *             0
          *              0
          *              0
  =   0.50*...*...*...*.0.*...*...*...*...*...*...*...*...*...*...*...*...*
          *                0
          *                0
          *                 0
          *                 0
          *                 0
          *                  0
          *                   0
          *                   0
          *                     0
  =   1.00*...*...*...*...*...*.0.*...*...*...*...*...*...*...*...*...*...*
          *                           0
          *                            0
          *                            0
          *                             0
          *                              0
          *                              0
          *                              0
          *                               0
          *                               0
  =   1.50*...*...*...*...*...*...*...*...*.0.*...*...*...*...*...*...*...*
          *                                  0
          *                                  0
          *                                   0
          *                                   0
          *                                   0
          *                                    0
          *                                     0
          *                                     0
          *                                       0
  =   2.00*...*...*...*...*...*...*...*...*...*...*0...*...*...*...*...*...*
          *                                                  0
          *                                                   0
          *                                                   0
*         *
```