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A NUMERICAL METHOD FOR THE COMPUTATION OF STABILITY CONSTANTS

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ABSTRACT

A microcomputer program is presented for the determination of stepwise stability constants for metal complexes. The constants are statistically corrected, and the graphic output includes the distribution diagram. Application of the method is illustrated for the formation of zinc ammine complexes.

INTRODUCTION

The formation of complexes between a metal ion and a series of ligands can be described by the following equations.

$$\begin{array}{lll} M + L & \rightleftharpoons & ML \\ ML + L & \rightleftharpoons & ML_2 \\ " & & " \\ ML_{n-1} + L & \rightleftharpoons & ML_n \end{array} \qquad (1)$$

The equilibrium constants for each successive reaction can be written as

$$K_i = \beta_{i-1} \quad \frac{[ML_i]}{[M][L]^i} \qquad (2)$$

where $\beta_i = \prod_{j=1}^{i-1} K_i$

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The equilibrium constant, K_i, for a particular step is often referred to as a stability constant for the complex formed. The problem in this type of study is to determine the values of the K_i (frequently with $i = 6$) from experimental data (Jones, 1964). This is frequently a laborious and difficult procedure and many approaches have been used (Jones, 1964). A numerical method for the computation of these stability constants using a microcomputer is presented in this work.

METHOD

Bjerrum (1941) derived an equation which described the average number of ligands bound to a metal for a given system. This quantity is more commony referred to as a formation fraction. Bjerrum's equation expressed the formation fraction as a function of ligand concentration and the stability constants. This relationship is

$$\bar{n} = \frac{\sum_{i=1}^{n} i\beta_i [L]^i}{1 + \sum_{i=1}^{n} \beta_i [L]^i} \qquad (3)$$

where n is the formation fraction. Several methods use a form of Eq. (3) to determine the stability constants for a given system (Rossotti and Rossotti, 1961; Beck, 1970). The majority of the methods proposed are graphical methods whose results are approximations to the true solutions. Exact analytical solutions have been derived for systems containing three or fewer steps (Block and McIntyre, 1953). However, most equilibria for the formation of coordination complexes involve more than three steps.

The method presented here can be used for equilibria involving any number of steps. It is based on Eq. (3) which is rearranged to yield

$$\bar{n} + \sum_{i=1}^{n} (n-i)\beta_i [L]^i = 0 \qquad (4)$$

For n stepwise additions, Eq. (4) can be expanded to apply to the matrix system given by Eq. (5).

$$AC=N' \quad \text{or} \quad \begin{bmatrix} a_{11} & \cdots & a_{1n} \\ \vdots & a_{ij} & \vdots \\ a_{n1} & \cdots & a_{nn} \end{bmatrix} \begin{bmatrix} c_1 \\ c \\ c_n \end{bmatrix} = \begin{bmatrix} n'_1 \\ n' \\ n'_n \end{bmatrix} \qquad (5)$$

Where the maxtrix elements are defined by

$$a_{ij} = (\bar{n}_i - j)\ \beta_i [L]_i^{\,j} \tag{6}$$

$$c_i = \beta_i \tag{7}$$

$$n'_i = -\bar{n}_i \tag{8}$$

For an n-step process, n formation fractions at n different ligand concentrations must be determined. This is done experimentally using appropriate techniques such as spectrophotometry, conductance or some other applicable method. The particular method used is dependent upon the system being studied. Once the necessary number of formation fractions and ligand concentrations are known, the A and N matrices may be computed. The solution of Eq. (5) for the C matrix may be carried out by any of the several algorithms. The computer program developed in this work uses a Gauss-Jordan elimination to solve for C. Statistically adjusted stability constants are corrected constants, which reflect the number of sites available for coordination during each step (Jones, 1964). The statistically adjusted stability constants are defined by

$$K'_i = K_i \left(\frac{i}{n+1-i} \right) \tag{9}$$

where i identifies the constant in question and n is the total number of available bonding sites. The program calculates stability constants as well as statistically adjusted stability constants given appropriate formation fractions and ligand concentrations. The program also plots a distribution diagram for the series of complexes. The quantity (identified as ALPHA in the output) used in the distribution plot is defined (Butler, 1964) as

$$\alpha_i = \beta_i [K]^i \alpha_o$$

where $\alpha_o = (1 + \sum_{i=1}^{n} \beta_i [L]^i)^{-1}$ (10)

A complete listing of the program for the Commodore 64 microcomputer with Simon's BASIC extension and the Commodore 1525 graphics printer is given in the Appendix. The program can be easily modified for other computer systems.

PROGRAM DESCRIPTION

The program was written to run on a Commodore 64 microcomputer using Simon's Basic. The algorithm used to solve the system of matrices was adapted from that given by Miller (1981). Table 1 contains a brief description of the different parts of the program. The run time required for the Zn(II) ammonia system described earlier, was approximately 20 seconds. Operation of the program is simple. During its operation, the user is prompted for all of the input data, which are then displayed on the screen. The user is given the opportunity to change any or all of the input data. Once satisfied that all of the data are correct, the only other user interaction is to give the computation a descriptive title. A sample output is included with the application.

Table 1. A general description of the different parts of the computer program used to calculate stability constants.

Lines	Description
100-490	Contains all data input routines
500-600	Computes A and N matrices
620-1730	Solves AC = N' for C by Gauss-Jordan elimination
1760-2080	Contains the printer output routines
2100-3000	Contains the graphics routines used to generate the distribution diagram
5000-5050	Contains a scaling routine used to calculate Pixel coordinates on a 320 × 200 Pixel bit mapped screen

APPLICATION OF THE METHOD

In order to illustrate the use of the method, the stepwise formation of complexes between Zn(II) and ammonia will be considered. This has been previously studied and the equilibria can be shown as follows (Bjerrum, 1941; Yatsimirskii and Vasil'ey, 1960).

$$\begin{aligned} &Zn^{2+} + NH_3 \rightleftharpoons ZnNH_3^{2+} \\ &ZnNH_3^{2+} + NH_3 \rightleftharpoons Zn(NH_3)_2^{2+} \\ &Zn(NH_3)_2^{2+} + NH_3 \rightleftharpoons Zn(NH_3)_3^{2+} \\ &Zn(NH_3)_3^{2+} + NH_3 \rightleftharpoons Zn(NH_3)_4^{2+} \end{aligned} \qquad (11)$$

In this case, four formation fractions at four ligand concentrations are necessary for the computation. These input data are given in Table 2.

Table 2. Formation fractions and ligand concentrations used in the calculation of stability constants for the Zn(II) ammonia system.

Formation Fraction	Ligand Concentration
0.330	1.00×10^{-3}
0.857	2.00×10^{-3}
2.366	5.00×10^{-3}
3.250	1.00×10^{-2}

Data from Yatsimirskii and Vasil'ey, 1960.

The calculated stability constants and statistically adjusted stability constants for each step are given in Table 3, and the distribution diagram is shown in Figure 1. The Zn(II) ammonia system provides an excellent example of the importance of using statistically adjusted stability constants. The stability constants in this case predict the four coordinate Zn(II) complex to be the least stable. However, it is well known that the four coordinate complex is the most stable (Yaksimirskii and Vasil'ey, 1960).

Table 3. Comparison of results obtained from the computer program with experimental results. K = stability constants, K' = statistically adjusted stability constants.

Step	K	K'	K[a]	% Difference
1	2.34×10^2	5.84×10^1	2.34×10^2	0.0
2	2.79×10^2	1.86×10^2	2.75×10^2	1.1
3	3.10×10^2	4.65×10^2	3.16×10^2	1.9
4	1.43×10^2	5.73×10^2	1.41×10^2	1.4

[a] From Bjerrum, 1941.

The method described in this article will simplify the computation of stability constants for systems involving complex equilibria. It may also have application to other systems where there are competing reactions. The program can be adapted to other microcomputers which have bit mapped graphics support.

LITERATURE CITED

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APPENDIX

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10 REM ********************************
15 REM * STABILITY CONSTANT            *
20 REM *                 CALCULATOR    *
25 REM *                               *
30 REM * BY: E. A. SCHMITT             *
32 REM *       J. E. HOUSE JR.         *
35 REM ********************************
40 REM * IMPORTANT VARIABLES           *
45 REM * F()  FORMATION FRACTIONS      *
50 REM * L()  LIGAND CONCENTRATIONS    *
55 REM * N(,) CONSTANT MATRIX          *
60 REM * A(,) MAIN MATRIX              *
65 REM * C(,) SOLUTION MATRIX          *
70 REM * K()  EQUILIBRIUM CONSTANTS    *
75 REM * N1   # OF COMPLEXES           *
80 REM ********************************
85 REM :
90 REM ***** INPUT ROUTINES **********
100 DIML(8),F(8),K(8),A(6,6),N(6,6),C(6,6),N(6,6),CK(6,6)
110 PRINT"{SC}    COMPLEX EQUILIBRIUM CALCULATOR"
120 INPUT"{CD}{CD}{CD}ENTER NUMBER OF COMPLEXES TO BE            CONSIDERED";N1
130 N2=N1:N3=1:Z=1
140 PRINT"{SC}FOR";N1;"COMPLEXES THE FOLLOWING DATA MUST BE ENTERED"
150 PRINT"{CD}";N1;"  FORMATION FRACTIONS"
160 PRINTN1;"  LIGAND  CONCENTRATIONS"
170 PRINT"{RV}                                        {RO}"
180 PRINT"{CD}{CD}{CD}{RV}                                                 {RO}"
190 PRINT"TRIAL     FRMTN FRAC          [L]"
200 PRINT"@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@"
210 FORI=1TON1
220 PRINT I
230 NEXTI
240 PRINT"{CD}{RV}                                          {RO}"
250 FORI=1TON1
260 PRINT"{HM}{CD}{CD}{CD}{CD}{CD}{CD}{CD}TRIAL";I
270 INPUT"FORMATION FRACTION";F(I)
280 PRINT"{CU}                                     "
290 INPUT"{CU}LIGAND CONCENTRATION";L(I)
300 PRINT"{CU}                                     "
310 PRINT AT(8,I+14)""+STR$(F(I))AT(24,I+14)""+STR$(L(I))
320 NEXTI
330 PROC CORRECTION
340 PRINT"{HM}{CD}{CD}{CD}{CD}{CD}{CD}{CD}DO YOU WISH TO MAKE ANY CORRECTIONS"
350 INPUT"(Y/N) ";Q$
360 IFQ$="N"THENCALL SETUP
370 PRINT"{CU}{CU}                                            "
380 PRINT"                              "
390 INPUT"{CU}{CU}TRIAL #";I
400 PRINT"{CU}                            "
410 PRINT AT(7,I+14)"******************************"
420 PRINT"{HM}{CD}{CD}{CD}{CD}{CD}{CD}{CD}TRIAL";I
430 INPUT"FORMATION FRACTION";F(I)
440 PRINT"{CU}                                  "
450 INPUT"{CU}LIGAND CONCENTRATION";L(I)
460 PRINT"{CU}                                  "
470 PRINT AT(7,I+14)"                                      "
480 PRINT AT(8,I+14)""+STR$(F(I))AT(24,I+14)""+STR$(L(I))
490 CALL CORRECTION
500 :
510 REM**** SET UP MATRICES ********
520 PROC SETUP
530 FORI=1TON1
540 FORJ=1TON1
550 A(I,J)=(F(I)-J)*L(I)^J
560 NEXTJ
570 NEXTI
580 FORI=1TON1
590 N(I,1)=-F(I)
600 NEXTI
610 :
```

```
620 REM **** SOLVE MATRICES *********
630 GOSUB670
640 GOSUB1670
650 STOP
670 F3=0
680 REM: I5=1
690 REM:N3=1
700 FORI=1  TO  N2
710 FORJ=1TON2
720 A2(I,J)=A(I,J)
730 NEXTJ
740 FORJ=1TON3
750 C(I,J)=N(I,J)
760 NEXTJ
770 CK(I,3)=0
780 NEXTI
790 F2=1
800 FORI=1TON2
840 F1=0
850 FORJ=1TON2
860 IF(CK(J,3)=1)THEN950
870 FORK=1TON2
880 IF(CK(K,3)>1)THEN1630
890 IF(CK(K,3)=1)THEN940
900 IF(F1>=ABS(A2(J,K)))THEN940
910 F4=J
920 F5=K
930 F1=ABS(A2(J,K))
940 NEXTK
950 NEXTJ
960 CK(F5,3)=CK(F5,3)+1
970 CK(I,1)=F4
980 CK(I,2)=F5
1000 IF(F4=F5)THEN1140
1010 F2=-F2
1020 FORL=1TON2
1030 TP=A2(F4,L)
1040 A2(F4,L)=A2(F5,L)
1050 A2(F5,L)=TP
1060 NEXTL
1070 IF(N3<1)THEN1140
1080 FORL=1TON3
1090 TP=C(F4,L)
1100 C(F4,L)=C(F5,L)
1110 C(F5,L)=TP
1120 NEXTL
1140 F7=A2(F5,F5)
1150 F2=F2*F7
1160 A2(F5,F5)=1
1170 FORL=1TON2
1180 A2(F5,L)=A2(F5,L)/F7
1190 NEXTL
1200 IF(N3<1)THEN1260
1210 FORL=1TON3
1220 C(F5,L)=C(F5,L)/F7
1230 NEXTL
1260 FORL1=1TON2
1270 IF(L1=F5)THEN1370
1280 T=A2(L1,F5)
1290 A2(L1,F5)=0
1300 FORL=1TON2
1310 A2(L1,L)=A2(L1,L)-A2(F5,L)*T
1320 NEXTL
1330 IF(N3<1)THEN1370
1340 FORL=1TON3
1350 C(L1,L)=C(L1,L)-C(F5,L)*T
1360 NEXTL
1370 NEXTL1
1380 NEXTI
1390 FORI=1TON2
1400 L=N2-I+1
1410 IF(CK(L,1)=CK(L,2))THEN1490
1420 F4=CK(L,1)
1430 F5=CK(L,2)
```

```
1440 FORK=1TON2
1450 TP=A2(K,F4)
1460 A2(K,F4)=A2(K,F5)
1470 A2(K,F5)=TP
1480 NEXTK
1490 NEXTI
1500 FORK=1TON2
1510 IF(CK(K,3)<>1)THEN1630
1520 NEXTK
1530 F3=0
1540 IF(F6=1)THEN1650
1550 FORI=1TON2
1560 FORJ=1TON2
1570 PRINTA2(I,J);
1580 NEXTJ
1590 PRINT
1600 NEXTI
1620 RETURN
1630 F3=1
1650 RETURN
1660 END
1670 K(1)=C(1,1)
1675 PRINT"(SC)"
1680 FORI=2TON1
1690 K(I)=C(I,1)/C(I-1,1)
1700 NEXTI
1710 FORI=1TON1
1720 K2(I)=K(I)*(I/(N1+1-I))
1730 NEXTI
1750 :
1760 REM **** OUTPUT ROUTINE ****
1770 PROC OUT
1780 INPUT"(SC)TITLE";T$
1790 POKE53265,PEEK(53265)AND239
1800 OPEN1,4
1810 L=LEN(T$)
1820 SP=INT((80-L*2)/2)-1
1830 FORI=1TOSP
1840 PRINT#1,"*";
1850 NEXTI
1860 PRINT#1," ";
1870 PRINT#1,CHR$(14)T$;
1880 PRINT#1,CHR$(15)"  ";
1890 FORI=1TOSP:PRINT#1,"*";
1895 NEXTI
1900 PRINT#1,CHR$(10)
1901 PRINT#1,CHR$(10)
1902 PRINT#1,CHR$(14)"STABILITY CONSTANTS"
1903 FORI=1TO50
1904 PRINT#1,CHR$(15)"@";
1905 NEXTI
1910 PRINT#1
1930 PRINT#1,CHR$(16)"01STEP";
1940 PRINT#1,CHR$(16)"20K";
1950 PRINT#1,CHR$(16)"40K'"
1960 FORI=1TO50
1970 PRINT#1,"@";
1980 NEXTI
1990 PRINT#1
2000 FORI=1TON1
2010 PRINT#1,CHR$(16)"01";I;
2020 PRINT#1,CHR$(16)"15";K(I);
2030 PRINT#1,CHR$(16)"35";K2(I)
2040 NEXTI
2050 FORI=1TO50
2060 PRINT#1,"@";
2070 NEXTI
2075 PRINT#1,CHR$(10)
2080 PRINT#1,CHR$(10)
```

```
2085 PRINT#1,CHR$(14)"DISTRIBUTION DIAGRAM"
2086 CLOSE1
2090 :
2100 REM *** DISTRIBUTION DIAGRAM ***
2110 POKE53265,PEEK(52365)OR16
2120 HIRES0,1
2130 REC 0,0,319,199,1
2140 XI=-1.5:XA=4:YI=-.15:YA=1
2150 X=-1:Y=0:EXEC SCALE
2160 LINEX,Y,X,0,1
2170 LINEX,Y,319,Y,1
2180 X1=X:Y1=Y
2190 FORI=.1TO1STEP.1
2195 P=48+I*10
2200 Y=I:X=1:EXEC SCALE
2210 LINE(X1-2),Y,(X1+2),Y,1
2215 CHAR(X1-10),Y-4,P,1,1
2216 CHAR(X1-17),(Y-4),46,1,1
2220 NEXTI
2230 FORI=-.5TO4STEP.5
2240 X=I:Y=1:EXEC SCALE
2250 LINEX,(Y1-2),X,(Y1+2),1
2260 IFI=INT(I)THENP=48+I:CHAR(X-3),(Y1+4),P,1,1
2270 NEXTI
2280 TEXT150,190,"{$2}P{$1}[L]",1,1,8
2290 TEXT1,75,"{$1}A",1,1,1
2300 TEXT1,87,"{$1}L",1,1,1
2310 TEXT1,99,"{$1}P",1,1,1
2320 TEXT1,111,"{$1}H",1,1,1
2330 TEXT1,123,"{$1}A",1,1,1
2340 FORI=-1TO4STEP.02
2350 X=I
2360 A=1
2370 FORJ=1TON1
2380 A=A+C(J,1)*(10^-I)^J
2390 NEXTJ
2400 A=1/A
2410 FORJ=1TON1
2420 Y=C(J,1)*(10^-I)^J*A
2430 X=I:EXEC SCALE
2440 PLOTX,Y,1
2450 NEXTJ
2460 NEXTI
2470 COPY
3000 GOTO3000
5000 PROC SCALE
5010 XR=ABS(XA-XI):YR=ABS(YA-YI)
5020 XD=320/XR:YD=200/YR
5030 X=INT(XD*X+320-XA*XD)
5040 Y=INT(YA*YD-Y*YD)
5050 END PROC
```

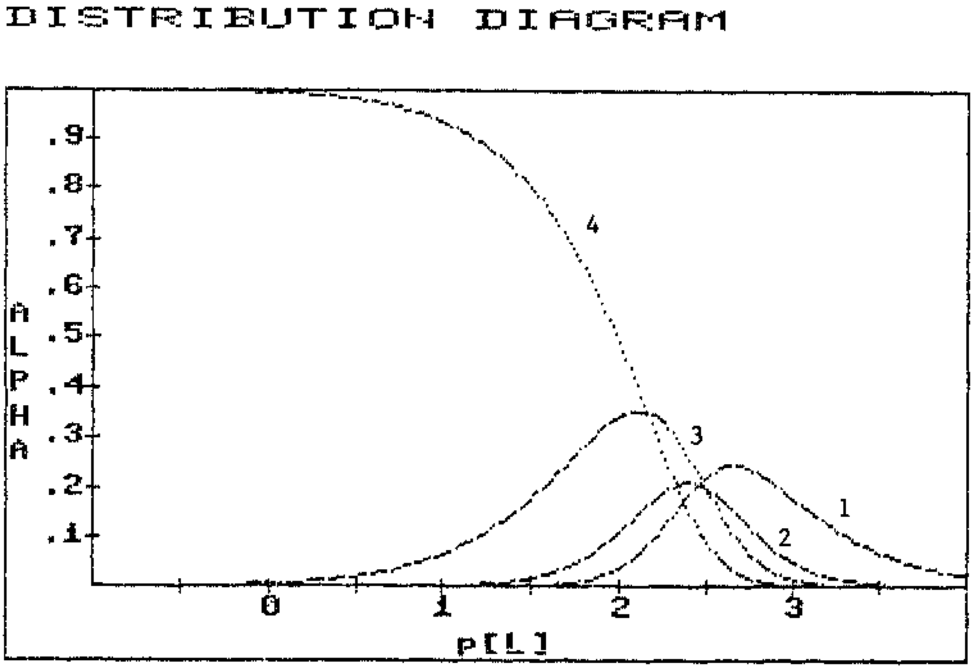

Fig. 1 Distribution diagram for complexes formed by Zn(II) with NH_3.
1 = monoammine; 2 = diammine; 3 = triammine; 4 = tetraammine.