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SIAS, A COMPUTER PROGRAM FOR THE GENERALISED CALCULATION OF SPECIATION IN MIXED METAL-LIGAND AQUEOUS SYSTEMS

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ABSTRACT

A computer program, SIAS, which calculates the concentrations of species in aqueous solutions of any complexity, is described. It is a corrected and augmented version of COMICS, which contains some errors and has an unsatisfactory output.

Full details of the input required for the program and its output are provided and a complete listing is given.

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AQUEOUS SOLUTIONS; LIGANDS; METALS; COMPLEXES; S CODES; C CODES; COMPUTER CODES

CONTENTS

1. INTRODUCTION

Before the availability of fast electronic computers, the determination of the distribution of chemical species in all but the simplest systems was an arduous task and approximate methods had to suffice. Thus, the method of conditional stability constants [Ringbom 1963] allows estimates of free and complexed metal ion concentrations, for example, to be calculated in the presence of a number of competing equilibria.

Increased demands by analytical and environmental chemists have made it necessary to be able to calculate the speciation of systems of unlimited complexity. Some computer programs have been published in recent years with this capability but these vary considerably in efficiency and approach.

The computer program COMICS [Perrin & Sayce 1967] can calculate the equilibrium speciation in solution of very complex systems. Like all such programs, it requires a knowledge of the appropriate equilibrium constants which is the greatest limitation. Indeed, this limitation can only be overcome by the provision of more reliable equilibrium data, particularly data concerning the hydrolysis of metal ions and the formation of mixed complexes.

The published version of COMICS unfortunately contains some errors and other undesirable features. The errors have been found and corrected and the nature of the output extensively revised. The purpose of the present report is to give details of the updated program, referred to as SIAS ('species in aqueous solution'), and to provide an example of its use.

2. NUMERICAL METHOD

Consider the mass balance equations for just one metal and one ligand together with that for protons (ignoring any charges):

$$T_M = [M] + \Sigma p\ \beta_{p,q,r}\ [M]^p\ [L]^q\ [H]^r$$

$$T_L = [L] + \Sigma q\ \beta_{p,q,r}\ [M]^p\ [L]^q\ [H]^r$$

$$T_H = [H] + \Sigma r\ \beta_{p,q,r}\ [M]^p\ [L]^q\ [H]^r \quad .$$

Here, T_M, T_L and T_H are the total analytical concentrations of metal, ligand and protons, and the quantities in square brackets are the free concentrations. The $\beta_{p,q,r}$ values are the *overall* (cumulative) equilibrium constants. Note that since r is negative for hydrolysed species,

the value of T_H can be negative when the total bound hydroxide exceeds the equilibrium hydrogen ion concentration. To calculate the speciation in a given model, values of T_M, T_L, [H] and $\beta_{p,q,r}$ are required. These generate a series of polynomial equations which, for more than one metal or ligand, requires simultaneous solution for [M] and [L].

The application of the standard Newton-Raphson method of solution of such equations is often not satisfactory except in very simple cases. This is a result of the fact that the initial estimate of the root has to be (a) very close to the true value, or (b) smaller than the true value. If neither of these conditions is fulfilled, a false root is often obtained making the numerical results meaningless. Since [M] and [L] can vary over orders of magnitude, condition (a) cannot be easily met. Alternatively, condition (b) can be achieved by using unrealistically small estimates all the time which, however, will make the process of convergence inefficient. It should be noted that Perrin & Sayce [1967] were unsuccessful in their attempt to use the Newton-Raphson method for this type of calculation.

The numerical method in COMICS uses an empirical approach which solves this problem. Initially, metal complexation is assumed to be nil (that is, $[M] = T_M$); [L] is then calculated from T_L, the pH value given and the appropriate $\beta_{p,q,r}$ value (pKa value). A calculated value of T_M is then formed from the calculated [L] value and the mass balance equation for the metal ion. Obviously, T_M (calc.) will be larger than T_M. The current value of [M] is then multiplied by the quantity $[T_M/T_M\text{(calc.)}]^{\frac{1}{2}}$ and is thus reduced in amount. The analogous calculation is done with [L], the current value being updated by multiplication by $[T_L/T_L(\text{calc})]^{\frac{1}{2}}$. The process is repeated for all metals and ligands present until the difference between calculated and given values of T_M and T_L is less than 0.001 per cent. To increase efficiency, results from the $(n-1)^{th}$ pH value after convergence, are used as initial estimates for the n^{th} pH value. The proton mass balance equation is not involved in this iterative process but can be used to calculate T_H from the equilibrium concentration, H, once convergence has been achieved.

3. THE PROGRAM

The program consists of the main program and a subroutine, COGS, which carries out the iterative procedure. The present version is in double precision. There are no limits to the number of pH values that can be used. The limit on the number of metals (10) and ligands (10),

and the total number of complexes produced (200), is dictated solely by the dimension statements which can be altered as necessary. Thus, since the convergence properties of COMICS as indicated by Perrin & Sayce [1967] and as verified by the present authors are excellent, it is possible to consider thousands of competing equilibria simultaneously.

4. THE INPUT AND OUTPUT

The input (Appendix A) consists largely of an array containing numbered species, their stoichiometry and the formation constants. The exact nature of the input is described at the head of the main program (see Appendix C) in a series of comment statements. In the output (Appendix B), each species is written with the accompanying concentration and the totals are provided to check on convergence to the correct roots. The species are each tagged for identification purposes by the metal number as it appears in the order given in the input.

5. AN EXAMPLE OF USAGE

Consider an aqueous system containing the ligands, lactic acid and diethylenetriamminepentaacetic acid (DTPA), and the actinide and lanthanide metal ions shown in Table 1. Table 2 lists reactions for which equilibrium data are available. Most of the constants in Table 2 are for unit ionic strength and 25°C or as close as possible to these conditions. Various pH values of 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5 and 4.0 were chosen for this example.

The input and output for this example are given below. The output only contains the initial results since the rest are repetitive. This calculation took 22 seconds on an IBM360/65 computer. A full compiled listing of the program is provided in Appendix C.

6. REFERENCES

Perrin, D.D. & Sayce, I.G. [1967] - *Talanta*, 14 : 833-842.

Ringbom, A. [1963] - Complexation in Analytical Chemistry. Interscience, New York.

TABLE 1

LIGAND AND METAL ION CONCENTRATIONS

Ligand or Metal *	Program Coding	Concentration mol ℓ^{-1}
Lactate	L1	1.0
DTPA	L2	5.0×10^{-2}
Pu^{3+}	M1	5.0×10^{-5}
Pu^{4+}	M2	5.0×10^{-5}
Am^{3+}	M3	1.0×10^{-6}
Cm^{3+}	M4	1.0×10^{-6}
La^{3+}	M5	1.0×10^{-6}
Ce^{3+}	M6	1.0×10^{-6}
Pr^{3+}	M7	1.0×10^{-6}
Nd^{3+}	M8	1.0×10^{-6}
Sm^{3+}	M9	1.0×10^{-6}
Eu^{3+}	M10	1.0×10^{-6}

TABLE 2

REACTIONS AND EQUILIBRIUM CONSTANTS

No.	Reaction	Log β
1	$H^+ + LACT^- \rightleftharpoons H\ LACT$	3.64
2	$Pu^{3+} + LACT^- \rightleftharpoons Pu\ LACT^{2+}$	2.90
3	$Pu^{3+} + 2LACT^- \rightleftharpoons Pu(LACT)_2^+$	5.10
4	$Pu^{4+} + LACT^- \rightleftharpoons Pu(LACT)^{3+}$	5.67
5	$Pu^{4+} + 2LACT^- \rightleftharpoons Pu(LACT)_2^{2+}$	9.28
6	$Am^{3+} + LACT^- \rightleftharpoons Am\ LACT^{2+}$	2.77
7	$Am^{3+} + 2LACT^- \rightleftharpoons Am(LACT)_2^+$	4.64
8	$Cm^{3+} + LACT^- \rightleftharpoons Cm\ LACT^{2+}$	2.79
9	$Cm^{3+} + 2LACT^- \rightleftharpoons Cm(LACT)_2^+$	4.55
10	$La^{3+} + LACT^- \rightleftharpoons La(LACT)^{2+}$	2.60
11	$La^{3+} + 2LACT^- \rightleftharpoons La(LACT)_2^+$	4.34
12	$La^{3+} + 3LACT^- \rightleftharpoons La(LACT)_3$	5.60
13	$Ce^{3+} + LACT^- \rightleftharpoons Ce(LACT)^{2+}$	2.43
14	$Ce^{3+} + 2LACT^- \rightleftharpoons Ce(LACT)_2^+$	4.11
15	$Ce^{3+} + 3LACT^- \rightleftharpoons Ce(LACT)_3$	5.30
16	$Pr^{3+} + LACT^- \rightleftharpoons Pr(LACT)^{2+}$	2.85
17	$Pr^{3+} + 2LACT^- \rightleftharpoons Pr(LACT)_2^+$	4.90
18	$Pr^{3+} + 3LACT^- \rightleftharpoons Pr(LACT)_3$	6.10
19	$Nd^{3+} + LACT^- \rightleftharpoons Nd\ LACT^{2+}$	2.87
20	$Nd^{3+} + 2LACT^- \rightleftharpoons Nd(LACT)_2^+$	4.97
21	$Nd^{3+} + 3LACT^- \rightleftharpoons Nd(LACT)_3$	6.40
22	$Sm^{3+} + LACT^- \rightleftharpoons Sm(LACT)^{2+}$	2.88
23	$Sm^{3+} + 2LACT^- \rightleftharpoons Sm(LACT)_2^+$	5.09
24	$Sm^{3+} + 3LACT^- \rightleftharpoons Sm(LACT)_3$	6.35

TABLE 2 (Continued)

REACTIONS AND EQUILIBRIUM CONSTANTS

No.	Reaction	Log β
25	$Eu^{3+} + LACT^{-} \rightleftharpoons Eu\ LACT^{2+}$	2.95
26	$Eu^{3+} + 2LACT^{-} \rightleftharpoons Eu(LACT)_2^{+}$	5.18
27	$Eu^{3+} + 3LACT^{-} \rightleftharpoons Eu(LACT)_3$	6.43
28	$5H^{+} + DTPA^{5-} \rightleftharpoons H_5\ DTPA$	27.91
29	$Pu^{3+} + DTPA^{5-} \rightleftharpoons Pu\ DTPA^{2-}$	21.20
30	$Pu^{4+} + DTPA^{5-} \rightleftharpoons Pu\ DTPA^{-}$	29.56
31	$Am^{3+} + DTPA^{5-} \rightleftharpoons Am\ DTPA^{2-}$	22.80
32	$Cm^{3+} + DTPA^{5-} \rightleftharpoons Cm\ DTPA^{2-}$	22.90
33	$La^{3+} + DTPA^{5-} \rightleftharpoons La\ DTPA^{2-}$	19.50
34	$Ce^{3+} + DTPA^{5-} \rightleftharpoons Ce\ DTPA^{2-}$	20.40
35	$Pr^{3+} + DTPA^{5-} \rightleftharpoons Pr\ DTPA^{2-}$	21.10
36	$Nd^{3+} + DTPA^{5-} \rightleftharpoons Nd\ DTPA^{2-}$	21.60
37	$Sm^{3+} + DTPA^{5-} \rightleftharpoons Sm\ DTPA^{2-}$	22.30
38	$Eu^{3+} + DTPA^{5-} \rightleftharpoons Eu\ DTPA^{2-}$	22.39
39	$Pu^{3+} + H_2O \rightleftharpoons Pu\ OH^{2+}$	-6.95
40	$Pu^{4+} + H_2O \rightleftharpoons Pu\ OH^{3+}$	-1.60
41	$Am^{3+} + H_2O \rightleftharpoons Am\ OH^{2+}$	-7.00
42	$Cm^{3+} + H_2O \rightleftharpoons Cm\ OH^{2+}$	-7.00
43	$La^{3+} + H_2O \rightleftharpoons La\ OH^{2+}$	-10.12
44	$Ce^{3+} + H_2O \rightleftharpoons Ce\ OH^{2+}$	-9.29
45	$Pr^{3+} + H_2O \rightleftharpoons Pr\ OH^{2+}$	-8.50
46	$Nd^{3+} + H_2O \rightleftharpoons Nd\ OH^{2+}$	-8.50
47	$Sm^{3+} + H_2O \rightleftharpoons Sm\ OH^{2+}$	-8.50
48	$Eu^{3+} + H_2O \rightleftharpoons Eu\ OH^{2+}$	-8.20

APPENDIX A

INPUT

```
 1
        SAMPLE CALCULATION USING SIAS
L1 - LACT, L2 - DTPA
M1 - PU3, M2 - PU4, M3 - AM, M4 - CM, M5 - LA, M6 - CE, M7 - PR, M8 - ND
M9 - SM, M10 - EU


 210 48
1     HLACT            1                                          -1        3.64
2     PU3LACT          1                                                    2.90    1
3     PU3(LACT)2       2                                                    5.10    1
4     PU4LACT          1                                                    5.67    2
5     PU4(LACT)2       2                                                    9.28    2
6     AM(LACT)1        1                                                    2.77    3
7     AM(LACT)2        2                                                    4.64    3
8     CM(LACT)1        1                                                    2.79    4
9     CM(LACT)2        2                                                    4.55    4
10    LA(LACT)1        1                                                    2.60    5
11    LA(LACT)2        2                                                    4.34    5
12    LA(LACT)3        3                                                    5.60    5
14    CE(LACT)2        2                                                    4.11    6
15    CE(LACT)3        3                                                    5.30    6
16    PR(LACT)1        1                                                    2.85    7
17    PR(LACT)2        2                                                    4.90    7
18    PR(LACT)3        3                                                    6.10    7
19    ND(LACT)1        1                                                    2.87    8
20    ND(LACT)2        2                                                    4.97    8
21    ND(LACT)3        3                                                    6.40    8
22    SM(LACT)1        1                                                    2.88    9
23    SM(LACT)2        2                                                    5.09    9
24    SM(LACT)3        3                                                    6.35    9

25    EU(LACT)1        1                                                    2.95   10
26    EU(LACT)2        2                                                    5.18   10
27    EU(LACT)3        3                                                    6.43   10
28    H5DTPA             1                                          -5       27.91
29    PU3DTPA            1                                                   21.2     1
30    PU4DTPA            1                                                   29.5     2
31    AMDTPA             1                                                   22.8     3
32    CMDTPA             1                                                   22.9     4
33    LADTPA             1                                                   19.5     5
34    CEDTPA             1                                                   20.4     6
35    PRDTPA             1                                                   21.1     7
36    NDDTPA             1                                                   21.6     8
37    SMDTPA             1                                                   22.3     9
38    EUDTPA             1                                                   22.39   10
39    PU3OH                                                          1        -6.95    1
40    PU4OH                                                          1        -1.60    2
41    AMOH                                                           1        -7.0     3
42    CMOH                                                           1        -7.0     4
43    LAOH                                                           1       -10.12    5
44    CEOH                                                           1        -9.29    6
45    PROH                                                           1        -8.50    7
46    NDOH                                                           1        -8.50    8
47    SMOH                                                           1        -8.5     9
48    EUOH                                                           1 1      -8.2    10
 0.100E+01 0.500E-01
 0.500E-04 0.500E-04 0.100E-05 0.100E-05 0.100E-05 0.100E-05 0.100E-05 0.100E-05
 0.100E-05 0.100E-05
    0.5000
    1.0000
    1.5000
    2.0000
    2.5000
    3.0000
    3.5000
    4.70001
```

APPENDIX B

OUTPUT

SAMPLE CALCULATION USING SIAS

		L1	L2	L3	L4	L5	L6	L7	L8	L9	L10	M1	M2	M3	M4	M5	M6	M7	M8	M9	M10	OH	LOG BETA
1	HLACT	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-1	3.6400
2	PU3LACT	1	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	2.9000
3	PU3(LACT)2	2	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	5.1000
4	PU4LACT	1	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	5.6700
5	PU4(LACT)2	2	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	9.2800
6	AM(LACT)1	1	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	2.7700
7	AM(LACT)2	2	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	4.6400
8	CM(LACT)1	1	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	2.7900
9	CM(LACT)2	2	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	4.5500
10	LA(LACT)1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	2.6000
11	LA(LACT)2	2	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	4.3400
12	LA(LACT)3	3	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	5.6000
13	CE(LACT)1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	2.4300
14	CE(LACT)2	2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	4.1100
15	CE(LACT)3	3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	5.3000
16	PR(LACT)1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	2.8500
17	PR(LACT)2	2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	4.9000
18	PR(LACT)3	3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	6.1000
19	ND(LACT)1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	2.8700
20	ND(LACT)2	2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	4.9700
21	ND(LACT)3	3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	6.4000
22	SM(LACT)1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	2.8800
23	SM(LACT)2	2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	5.0924
24	SM(LACT)3	3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	6.3500
25	EU(LACT)1	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	2.9500
26	EU(LACT)2	2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	5.1300
27	EU(LACT)3	3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	6.4300
28	H5DTPA	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-5	27.9100
29	PU3DTPA	0	1	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	21.2000
30	PU4DTPA	0	1	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	29.5000
31	AMDTPA	0	1	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	22.8000
32	CMDTPA	0	1	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	22.9000
33	LADTPA	0	1	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	19.5000
34	CEDTPA	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	20.4000
35	PRDTPA	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	21.1000
36	NDDTPA	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	21.6000
37	SMDTPA	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	22.3000
38	EUDTPA	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	22.3900
39	PU3OH	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	1	-6.9500
40	PU4OH	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	1	-1.6000
41	AMOH	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	1	-7.0000
42	CMOH	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	1	-7.0000
43	LAOH	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	1	-10.1200
44	CEOH	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	1	-9.2900
45	PROH	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	1	-8.5000
46	NDOH	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	1	-8.5000
47	SMOH	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	1	-8.5000
48	EUOH	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	1	-8.2000

L1 - LACT, L2 - DTPA

M1 - PU3, M2 - PU4, M3 - AM, M4 - CM, M5 - LA, M6 - CE, M7 - PR, M8 - ND

M9 - SM, M10 - EU

(continued)

TOTAL CONCN. OF LIGAND (1) = 3.1000+01
TOTAL CONCN. OF LIGAND (2) = 3.5000-01
TOTAL CONCN. OF METAL (1) = 3.5000-04
TOTAL CONCN. OF METAL (2) = 0.5000-04
TOTAL CONCN. OF METAL (3) = 0.1000-05
TOTAL CONCN. OF METAL (4) = 0.1000-05
TOTAL CONCN. OF METAL (5) = 0.1000-05
TOTAL CONCN. OF METAL (6) = 0.1000-05
TOTAL CONCN. OF METAL (7) = 0.1000-05
TOTAL CONCN. OF METAL (8) = 0.1000-05
TOTAL CONCN. OF METAL (9) = 0.1000-05
TOTAL CONCN. OF METAL (10) = 0.1000-05

PH = 3.500

NUMBER OF ITERATIONS = 22

	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10
FREE METALS	3.3470-05	2.5600-08	6.9000-07	6.8260-07	7.6940-07	8.3220-07	6.4330-07	6.3030-07	6.1930-07	5.7950-07
FREE LIGANDS	7.2390-04	1.9450-27								
% FREE METALS	6.0940+01	5.1200-02	6.9000+01	6.8260+01	7.6940+01	8.3220+01	6.4330+01	6.3030+01	6.1930+01	5.7950+01

DISTRIBUTION OF METAL 1

		%	CONCN
2	PU3LACT 2	3.5040+01	1.7520-05
3	PU3(LACT)2 3	4.0200+00	2.0100-06
29	PU3DTPA 29	1.8780-04	9.3910-11
39	PU3OH 39	2.1620-05	1.0810-11
	FREE M	6.0940+01	3.0470-05
		---------	---------
	TOTAL	1.0000+02	5.0000-05

DISTRIBUTION OF METAL 2

		%	CONCN
4	PU4LACT 4	1.7340+01	8.6680-06
5	PU4(LACT)2 5	5.1120+01	2.5560-05
30	PU4DTPA 30	3.1490+01	1.5740-05
40	PU4OH 40	4.0670-03	2.0340-09
	FREE M	5.1200-02	2.5600-08
		---------	---------
	TOTAL	1.0000+02	5.0000-05

(continued)

DISTRIBUTION OF METAL 3			%	CONCN
6	AM(LACT)1	6	2.941D+01	2.941D-07
7	AM(LACT)2	7	1.578D+00	1.578D-08
31	AMDTPA	31	8.466D-03	8.466D-11
41	AMOH	41	2.182D-05	2.182D-13
	FREE M		6.900D+01	6.900D-07
			---------	---------
		TOTAL	1.000D+02	1.000D-06

DISTRIBUTION OF METAL 4			%	CONCN
8	CM(LACT)1	8	3.046D+01	3.046D-07
9	CM(LACT)2	9	1.269D+00	1.269D-08
32	CMDTPA	32	1.054D-02	1.054D-10
42	CMOH	42	2.158D-05	2.158D-13
	FREE M		6.826D+01	6.826D-07
			---------	---------
		TOTAL	1.000D+02	1.000D-06

DISTRIBUTION OF METAL 5			%	CONCN
10	LA(LACT)1	10	2.217D+01	2.217D-07
11	LA(LACT)2	11	8.819D-01	8.819D-09
12	LA(LACT)3	12	1.162D-02	1.162D-10
33	LADTPA	33	4.731D-06	4.731D-14
43	LAOH	43	1.846D-08	1.846D-16
	FREE M		7.694D+01	7.694D-07
			---------	---------
		TOTAL	1.000D+02	1.000D-06

DISTRIBUTION OF METAL 6			%	CONCN
13	CE(LACT)1	13	1.621D+01	1.621D-07
14	CE(LACT)2	14	5.617D-01	5.617D-09
15	CE(LACT)3	15	6.297D-03	6.297D-11
34	CEDTPA	34	4.065D-05	4.065D-13
44	CEOH	44	1.350C-07	1.350D-15
	FREE M		8.322D+01	8.322D-07
			---------	---------
		TOTAL	1.000D+02	1.000D-06

DISTRIBUTION OF METAL 7			%	CONCN
16	PR(LACT)1	16	3.296D+01	3.296D-07
17	PR(LACT)2	17	2.677D+00	2.677D-08
18	PR(LACT)3	18	3.071D-02	3.071D-10
35	PRODTPA	35	1.575D-04	1.575D-12
45	PROH	45	6.433D-07	6.433D-15
	FREE M		6.433D+01	6.433D-07
			---------	---------
		TOTAL	1.000D+02	1.000D-06

DISTRIBUTION OF METAL 8			%	CONCN
19	ND(LACT)1	19	3.382D+01	3.382D-07
20	ND(LACT)2	20	3.082D+00	3.082D-08
21	ND(LACT)3	21	6.005D-02	6.005D-10
36	NDDTPA	36	4.880D-04	4.880D-12
46	NDOH	46	6.303D-07	6.303D-15
	FREE M		6.303D+01	6.303D-07
			---------	---------
		TOTAL	1.000D+02	1.000D-06

DISTRIBUTION OF METAL 9			%	CONCN
22	SM(LACT)1	22	3.400D+01	3.400D-07
23	SM(LACT)2	23	4.014D+00	4.014D-08
24	SM(LACT)3	24	5.258D-02	5.258D-10
37	SMDTPA	37	2.403D-03	2.403D-11
47	SMOH	47	6.193D-07	6.193D-15
	FREE M		6.193D+01	6.193D-07
			---------	---------
		TOTAL	1.000D+02	1.000D-06

DISTRIBUTION OF METAL 10			%	CONCN
25	EU(LACT)1	25	3.739D+01	3.739D-07
26	EU(LACT)2	26	4.596D+00	4.596D-08
27	EU(LACT)3	27	5.916D-02	5.916D-10
38	EUDTPA	38	2.766D-03	2.766D-11
48	EUOH	48	1.156D-06	1.156D-14
	FREE M		5.795D+01	5.795D-07
			---------	---------
		TOTAL	1.000D+02	1.000D-06

APPENDIX C

A LISTING OF PROGRAM SIAS

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LEVEL  20.1 (AUG 71)                          OS/360  FORTRAN H

      COMPILER OPTIONS - NAME=  MAIN,OPT=00,LINECNT=55,SIZE=0000K,
                         SOURCE,EBCDIC,NOLIST,NODECK,LOAD,NOMAP,NOEDIT,NOID,NOXREF
            C             ************************************
            C             *                                  *
            C             *          PROGRAM SIAS            *
            C             *                                  *
            C             *    UPDATED VERSION OF RSPECIES   *
            C             *                                  *
            C             *      BASED ON COMICS PROGRAM     *
            C             *      TALANTA,VOL14,833,(1967)    *
            C             *                                  *
            C             ************************************
            C
            C                          INPUT DATA
            C     1  NUMBER OF SETS OF EXPERIMENTAL CONDITIONS TO BE RUN (I2)
            C        SEE NOTE BELOW
            C
            C     2  TITLE OF FIRST (SECOND, THIRD ...ETC.) EXPERIMENTAL CONDITION
            C        ANY CHARACTERS IN COLUMNS 1-80
            C
            C     3  A SERIES OF FIVE CARDS COMPRISING THE ARRAY TEXT
            C        WHEREIN THE USER PROVIDES A DESCRIPTION OF THE METALS AND LIGANDS
            C        FOR RECORDING IN THE OUTPUT.
            C        ANY CHARACTERS IN COLUMNS 1-80
            C
            C     4  NUMBER OF LIGANDS, OF METALS, AND OF SPECIES FORMED
            C        (INCLUDING PROTONATED LIGANDS AND HYDROLYSED METAL IONS) (2I2,I3)
            C
            C     5  SPECIES NUMBER AND SPECIES DESCRIPTION IN COLUMNS 1-15 (SUPPLIED
            C        BY THE USER), THE NUMBER OF MOLECULES OF LIGAND (1), (2), (3)
            C        ...UP TO 10, THE NUMBER OF METAL IONS (1), (2), (3)...UP TO 10,
            C        THE NUMBER OF HYDROXO-GROUPS (A POSITIVE INTEGER, IF ANY),
            C        OR OF PROTONS (A NEGATIVE INTEGER, IF ANY), THE LOGARITHM OF
            C        THE CUMULATIVE FORMATION CONSTANT OF THE SPECIES,
            C        AND SPECIES IDENTIFIER DESCRIBED BY THE METAL PRESENT WHICH IS
            C        GIVEN BY THE ORDER OF THE METAL (1,2,3...) IN ITEM 4 ABOVE
            C        (FOR LIGANDS ONLY, A BLANK) (15A1,5X,21I2,6X,F8.4,I2)
            C
            C     6  THE TOTAL CONCENTRATION OF EACH LIGAND (EACH E10.3)
            C
            C     7  THE TOTAL CONCENTRATION OF EACH METAL ION (EACH E10.3)
            C
            C     8  A SERIES OF CARDS BEARING THE PH VALUE AND INDEX.
            C        INDEX IS BLANK OR ZERO FOR ALL PH CARDS EXCEPT THE LAST
            C        WHEN INDEX IS 1(F10.4,I1)
            C
            C     9  RETURN TO ITEM 2 ABOVE UNTIL THE TOTAL NUMBER OF EXPERIMENTAL
            C        CONDITIONS (GIVEN BY ITEM 1 ABOVE) HAS BEEN REACHED
            C        ************************************************************
            C
            C        NOTE:
            C        THE CHANGE IN PH VALUES IS SHOWN ON THE PH CARDS (ITEM 8 ABOVE)
            C        AND IS HANDLED WITHIN A SINGLE RUN
```

(continued)

```
C
C       A CHANGE IN A LIGAND OR METAL CONCENTRATION REQUIRES A NEW RUN
C       AND HENCE A COMPLETE DATA DECK
C
C       THE PROGRAM AUTOMATICALLY CONSIDERS HYDROXIDE AS A LIGAND
ISN 0002        IMPLICIT REAL*8 (A-H,O-Z)
ISN 0003        REAL*4 TITLE,TEXT
ISN 0004        DIMENSION E(200),DM(10),DMY(10),TITLE(20),TEXT(20,5), PFM(10),PCS(
               1200),IML(200),IP(200),SNAME(200,15)
ISN 0005        COMMON C(200),Y1(10),Y2(10),Y3(10),Y4(10),BTOT(10),CLTOT(10),TX(10
               1),VX(10),ML(10,200),MM(10,200),MN(200),AL(10,200),AM(10,200),AN(20
               10),B(200)
ISN 0006        COMMON NL,NM,N,IPT,UX
C
ISN 0007       1 FORMAT(I2)
ISN 0008       2 FORMAT (15A1,5X,21I2,6X,F8.4,I2)
ISN 0009       6 FORMAT (1X,15A1,2X,20(2X,I2),3X,I2,2X,F8.4)
ISN 0010       8 FORMAT( 8E10.3)
ISN 0011       9 FORMAT(24H TOTAL CONCN. OF METAL (,I2,4H)  =,E10.3)
ISN 0012      10 FORMAT(25H TOTAL CONCN. OF LIGAND (,I2,4H)  =,E10.3)
ISN 0013      11 FORMAT(23X,'C1          C2          C3          C4          C5
                1 C6          C7          C8          C9          C10')
ISN 0014      12 FORMAT (2I2,I3)
ISN 0015      17 FORMAT (F10.4,I1)
ISN 0016      30 FORMAT(1H0,'PH = ',F6.3)
ISN 0017      33 FORMAT(1X,20X,'L1  L2  L3  L4  L5  L6  L7  L8  L9  L10 M1  M2  M3
                1 M4  M5  M6  M7  M8  M9  M10 OH  LOG BETA')
ISN 0018      34 FORMAT(1H0,'FREE METALS',6X,10(1X,1PE10.3))
ISN 0019      36 FORMAT(1H0,'FREE LIGANDS',5X,10(1X,1PE10.3))
ISN 0020      63 FORMAT (1H0,13X,'  DISTRIBUTION OF METAL',I3,28X,'%',12X,'CONCN')
ISN 0021      73 FORMAT (40X,15A1,I3,2(5X,1PE10.3))
ISN 0022      83 FORMAT (1H0,57X,'TOTAL',1PE10.3,5X,1PE10.3)
ISN 0023      93 FORMAT (52X,'FREE M',5X,1PE10.3,5X,1PE10.3)
ISN 0024      90 FORMAT (64X,'---------',6X,'---------')
ISN 0025     122 FORMAT (/1H0)
ISN 0026     123 FORMAT(20A4)
ISN 0027     124 FORMAT(1X,20A4/)
ISN 0028     125 FORMAT(1H0,'% FREE METALS',4X,10(1X,1PE10.3))
ISN 0029     130 FORMAT (20A4)
ISN 0030     131 FORMAT (1X,20A4//)
ISN 0031     234 FORMAT(1H0)
ISN 0032     800 FORMAT(1H0,'**********************************************************
               1**********************************************************
               2*********')
ISN 0033     900 FORMAT(1H1)
C
ISN 0034         READ(1,1)NJ
ISN 0035         NJ0=0
ISN 0036     106 WRITE(3,900)
ISN 0037         READ(1,130) TITLE
ISN 0038         WRITE(3,131)(TITLE(I),I=1,20)
ISN 0039         WRITE(3,33)
ISN 0040         READ(1,123)TEXT
```

(continued)

```
ISN 0041            READ(1,12)NL,NM,N
ISN 0042            DO 7 J=1,N
ISN 0043          3 READ (1,2)(SNAME(J,I),I=1,15),(ML(I,J),I=1,10),(MM(I,J),I=1,10),MN
                   1(J),E(J),IML(J)
ISN 0044          7 WRITE (3,6)(SNAME(J,I),I=1,15),(ML(I,J),I=1,10),(MM(I,J),I=1,10),M
                   IN(J),E(J)
ISN 0045            WRITE (3,122)
ISN 0046            WRITE(3,124)TEXT
ISN 0047            READ(1,8)(CLTOT(I),I=1,NL)
ISN 0048            READ(1,8)(BTOT(I),I=1,NM)
ISN 0049            WRITE(3,10)(I,CLTOT(I),I=1,NL)
ISN 0050            WRITE(3,9)(I,BTOT(I),I=1,NM)
ISN 0051            WRITE(3,900)
ISN 0052            HX=DLOG(10.DO)
ISN 0053            IPT=1
ISN 0054            DO 4 J=1,N
ISN 0055            AN(J)=MN(J)
ISN 0056            DO 4I=1,10
ISN 0057            AL(I,J)=ML(I,J)
ISN 0058          4 AM(I,J)=MM(I,J)
ISN 0059            DO 13 I=1,N
ISN 0060         13 B(I)=DEXP(HX*E(I))
ISN 0061            DO 14I=1,NM
ISN 0062         14 Y1(I)=BTOT(I)*1.D-5
ISN 0063            DO 15 I=1,NL
ISN 0064         15 Y3(I)=CLTOT(I)*1.D-5
ISN 0065         16 READ(1,17)PH,INDEX
ISN 0066            WRITE(3,30)PH
ISN 0067            WRITE(3,234)
ISN 0068            UX=DEXP(HX*PH)
ISN 0069            IF(IPT-1)18,18,27
ISN 0070         18 DO 19I=1,NM
ISN 0071         19 VX(I)=BTOT(I)
ISN 0072            DO 20 I=1,NL
ISN 0073            DMY(I)=1.DO
ISN 0074            DO 22 J=1,N
ISN 0075            IF(ML(I,J))22,22,200
ISN 0076        200 DO 21 K=1,NM
ISN 0077            IF (MM(K,J))22,21,22
ISN 0078         21 CONTINUE
ISN 0079            DM(I)=(DEXP(HX*E(J)))*UX**MN(J)
ISN 0080            DMY(I)=DMY(I)+DM(I)
ISN 0081         22 CONTINUE
ISN 0082         20 CONTINUE
ISN 0083            DO 23 I=1,NL
ISN 0084         23 TX(I)=CLTOT(I)/DMY(I)
                 C
ISN 0085            27 CALL COGS
                 C
ISN 0086            WRITE(3,11)
ISN 0087            WRITE(3,34) (VX(I),I=1,NM)
ISN 0088            WRITE(3,36) (TX(I),I=1,NL)
ISN 0089            DO 500 I=1,NM
```

(continued)

```
ISN 0090        500 PFM(I)=100.D0*VX(I)/BTOT(I)
ISN 0091            DO 550 J = 1,N
ISN 0092            IF(IML(J).EQ.0) GO TO 550
ISN 0094            MC = IML(J)
ISN 0095            AM(MC,J) = MM(MC,J)
ISN 0096            PCS(J) = 100.D0*C(J)*AM(MC,J)/BTOT(MC)
ISN 0097        550 CONTINUE
ISN 0098            WRITE(3,125)(PFM(I),I=1,NM)
ISN 0099            DO 350 I = 1,NM
ISN 0100            WRITE (3,63) I
ISN 0101            TC = 0.0
ISN 0102            TP = 0.0
ISN 0103            DO 300 J = 1,N
ISN 0104            MC = IML(J)
ISN 0105            IF (MC .NE. I) GO TO 300
ISN 0107            WRITE (3,73)   (SNAME(J,NB),NB=1,15),J,PCS(J),C(J)
ISN 0108            TP = TP + PCS(J)
ISN 0109            TC = TC + C(J)
ISN 0110        300 CONTINUE
ISN 0111            TTP = TP + PFM(I)
ISN 0112            TTC = TC + VX(I)
ISN 0113            WRITE (3,93) PFM(I),VX(I)
ISN 0114            WRITE (3,90)
ISN 0115            WRITE (3,83) TTP,TTC
ISN 0116        350 CONTINUE
ISN 0117            WRITE(3,234)
ISN 0118            WRITE(3,800)
ISN 0119            IF(INDEX)31,16,31
ISN 0120         31 NJD=NJD+1
ISN 0121            IF(NJD-NJ)106,32,32
ISN 0122         32 STOP
ISN 0123            END

*OPTIONS IN EFFECT*      NAME=  MAIN,OPT=00,LINECNT=55,SIZE=0000K,

*OPTIONS IN EFFECT*      SOURCE,EBCDIC,NOLIST,NODECK,LOAD,NOMAP,NOEDIT,NOID,NOXREF

*STATISTICS*     SOURCE STATEMENTS =     122 ,PROGRAM SIZE =    33944

*STATISTICS*  NO  DIAGNOSTICS GENERATED

***** END OF COMPILATION *****                                   83K BYTES OF CORE NOT USED
```

(continued)

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LEVEL 20.1 (AUG 71)                          OS/360  FORTRAN H

          COMPILER OPTIONS - NAME=  MAIN,OPT=00,LINECNT=55,SIZE=0000K,
                             SOURCE,EBCDIC,NOLIST,NODECK,LOAD,NOMAP,NOEDIT,NOID,NOXREF
  ISN 0002            SUBROUTINE COGS
                    C
  ISN 0003            IMPLICIT REAL*8 (A-H,O-Z)
  ISN 0004            DIMENSION TERM(200),TERN(200),ALO(10),BO(10),TY(10),VY(10)
  ISN 0005            COMMON C(200),Y1(10),Y2(10),Y3(10),Y4(10),BTOT(10),CLTOT(10),TX(10
                     1),VX(10),ML(10,200),MM(10,200),MN(200),AL(10,200),AM(10,200),AN(20
                     10),B(200)
  ISN 0006            COMMON NL,NM,N,IPT,UX
                    C
  ISN 0007          99 FORMAT(1HO,'NUMBER OF ITERATIONS = ',I4)
  ISN 0008         234 FORMAT(1HO)
  ISN 0009         998 FORMAT(1HO,'ITERATION DID NOT CONVERGE')
                    C
  ISN 0010            NIT=0
  ISN 0011            DO 1 K=1,N
  ISN 0012           1 TERM(K)=B(K)*UX**MN(K)
  ISN 0013           2 DO 3 K=1,N
  ISN 0014           3 TERN(K)=TERM(K)
  ISN 0015             DO 4 K=1,N
  ISN 0016             DO 4 J=1,NM
  ISN 0017           4 TERN(K)=TERN(K)*VX(J)**MM(J,K)
  ISN 0018             DO 5 K=1,N
  ISN 0019             DO 15 J=1,NL
  ISN 0020          15 TERN(K)=TERN(K)*TX(J)**ML(J,K)
  ISN 0021           5 C(K)=TERN(K)
  ISN 0022             NIT=NIT+1
  ISN 0023             DO 7I=1,NM
  ISN 0024             BO(I)=VX(I)
  ISN 0025             DO 8 K=1,N
  ISN 0026           8 BO(I)=BO(I)+AM(I,K)*C(K)
  ISN 0027             RATIO=BO(I)/BTOT(I)
  ISN 0028             VY(I)=VX(I)/DSQRT(RATIO)
  ISN 0029           7 Y2(I)=DABS(BO(I)-BTOT(I))
  ISN 0030             DO 9I=1,NL
  ISN 0031             ALO(I)=TX(I)
  ISN 0032             DO 10 K=1,N
  ISN 0033          10 ALO(I)=ALO(I)+AL(I,K)*C(K)
  ISN 0034             RATIO=ALO(I)/CLTOT(I)
  ISN 0035             TY(I)=TX(I)/DSQRT(RATIO)
  ISN 0036           9 Y4(I)=DABS(ALO(I)-CLTOT(I))
  ISN 0037             IF(NIT-999)11,11,999
  ISN 0038          11 DO 12I=1,NM
  ISN 0039             IF(Y1(I)-Y2(I))14,12,12
  ISN 0040          12 CONTINUE
  ISN 0041             DO 13I=1,NL
  ISN 0042             IF(Y3(I)-Y4(I))14,13,13
  ISN 0043          13 CONTINUE
  ISN 0044             IPT=IPT+1
  ISN 0045             WRITE(3,99)NIT
  ISN 0046             WRITE(3,234)
  ISN 0047             RETURN
```

(continued)

```
   ISN 0048          14 DO 16I=1,NL
   ISN 0049          16 TX(I)=TY(I)
   ISN 0050             DO 17I=1,NM
   ISN 0051          17 VX(I)=VY(I)
   ISN 0052             GO TO 2
   ISN 0053         999 WRITE(3,998)
   ISN 0054             IPT=1
   ISN 0055             RETURN
   ISN 0056             END

*OPTIONS IN EFFECT*       NAME=  MAIN,OPT=00,LINECNT=55,SIZE=0000K,

*OPTIONS IN EFFECT*       SOURCE,EBCDIC,NOLIST,NODECK,LOAD,NOMAP,NOEDIT,NOID,NOXREF

*STATISTICS*      SOURCE STATEMENTS =       55 ,PROGRAM SIZE =      5782

*STATISTICS*  NO  DIAGNOSTICS GENERATED

*****  END OF COMPILATION *****                                    103K BYTES OF CORE NOT USED

*STATISTICS*  NO  DIAGNOSTICS THIS STEP
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