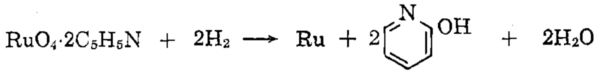
tion colors cotton cloth green. Its green color is fairly stable. $RuO_4 \cdot 2C_5H_5N$ is slowly absorbed from aqueous solution by the cation exchanger Dowex-50, but is unaffected by the anion exchanger Dowex-1. The aqueous solution of the compound is fairly stable when acidic. However, basic solutions are unstable. In hot potassium hydroxide solutions, rapid decomposition to pyridine and ruthenium dioxide (RuO_2) occurs.

Heating the solid compound results in its gradual decomposition without melting. Differential thermal analysis revealed that this decomposition is exothermic. Use of a thermogravimetric balance showed that in the range 50–400° the decomposition proceeds through four steps with the weight at the final step corresponding to the compound RuO_2. Vigorous reactions accompanied by marked reductions in weight were observed at about 160 and 220°. Thermal decomposition in a stream of hydrogen takes place in accordance with the equation



A detailed report of this work will be published at a later date.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Computer Analysis of Stability Constants in Three-Component Systems with Polynuclear Complexes[1]

BY R. STUART TOBIAS AND M. YASUDA

Received July 8, 1963

Recently we published some results of studies on the chelation of a cation which was also a rather strong aquo acid.[2] There are several indications that this cation, the dimethyltin(IV) ion, exists in solution as $[(CH_3)_2Sn(OH_2)_2]^{+2}$.[2,3] By using bidentate ligands, the tendency toward the formation of mixed hydroxo complexes was minimized; nevertheless, the analysis of the experimental data was quite complicated because of the hydrolysis of the cation to $[(CH_3)_2Sn(OH)(OH_2)]^+$ and the partial condensation of this species to the dimer. The determination of the complexing constants in such systems has rarely been undertaken, for it is very laborious. An iterative procedure must be employed, and this is not necessarily strongly convergent. In the case cited,[2] the estimated standard errors in the complexing constants were quite large, *ca.* 0.1 to 0.2 log unit.

Since the completion of this work, we have obtained access to a CDC 1604 computer which vastly reduces the labor involved in evaluating such experimental data. This note is concerned with our observations on the use of two types of Fortran 60 programs for the refinement of the constants.

Computation[4]

The first type of program used was based on the usual Gauss method[5–9] while the second type was based on the "pit mapping" procedure recommended by Sillén.[10,11]

The experimental data[12] were the tetrads C_H, the analytical hydrogen ion concentration; B, the total metal concentration; C_L, the total ligand concentration; and $[H^+]$, the equilibrium hydrogen ion concentration. In addition, the errors in each of these quantities were estimated and used for the computation of the variances. The constants to be refined were the acid dissociation (hydrolysis) constants for the aquo metal ion including that for the formation of the dimer of the simple conjugate base, the acid dissociation constants for the ligand conjugate acids, and the complexing constants.

The two types of program were both designed to minimize the sums of the squares of the weighted residuals in the analytical hydrogen ion concentration where this residual is

$$R = C_H - [H^+] + K_w[H^+]^{-1} + \sum_l \sum_m \sum_n n[L]^l[M]^m[H^+]^{-n}\beta_{lmn}$$

where

$$\beta_{lmn} = [M_mL_lH_{-n}][H^+]^n/[L]^l[M]^m$$

and [M] and [L] are the free metal and ligand concentrations, respectively. The only restrictions on the coefficients l, m, and n are the following: $l \geqslant 0$, $m \geqslant 0$, and n may have any positive value for hydrolysis of the metal ion and any negative value for proton dissociation of the ligand conjugate acids.

The initial values of the free metal and ligand concentrations were calculated using the experimental data together with the approximate values of the constants reported earlier.[2] A Newton–Raphson iteration in the mole balance equations for total metal and total ligand was employed. The two equations for the frac-

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[1] This work was supported, in part, by the National Science Foundation under Grants NSF-G14173 and GP-653.

[2] M. Yasuda and R. S. Tobias, *Inorg. Chem.*, **2**, 207 (1963).

[3] R. S. Tobias, I. Orgins, and B. A. Nevett, *ibid.*, **1**, 638 (1962).

[4] Complete deck listings, flow sheets, and duplicate card decks of all programs described in this communication may be obtained by writing to R. S. T.

[5] J. C. Sullivan, J. Rydberg, and W. F. Miller, *Acta Chem. Scand.*, **13**, 2023 (1959).

[6] R. H. Moore and R. K. Zeigler, "The Solution of the General Least Squares Problem with Special Reference to High Speed Computers," LA-2367, March 4, 1960.

[7] Z Z. Hugus, Jr., "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961.

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[10] L. G. Sillén, *Acta Chem. Scand.*, **16**, 159 (1962).

[11] L. G. Sillén and N. Ingri, *ibid.*, **16**, 173 (1962).

[12] These data were deposited as Document No. 7350 with the ADI Auxiliary Publication Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document Number and by remitting $1.25 for photoprints or $1.25 for 35-mm. microfilm in advance by check or money order payable to: Chief, Photoduplication Service, Library of Congress.

TABLE I
REFINEMENT OF HYDROLYSIS CONSTANTS

	β_{11}	β_{22}	Weighted variance	Standard error in $\bar{n}$
Input	$10^{-3.2}$	$10^{-4.6}$	9.259×10^2	. . .
Map	$10^{-3.11 \pm 0.03}$	$10^{-4.6 \pm 0.3}$	7.886×10^1	. . .
Gauss	$10^{-3.10 \pm 0.02}$	$10^{-4.6 \pm 0.2}$	7.897×10^1	. . .
Map-$\bar{n}$	$10^{-3.13 \pm 0.02}$	$10^{-5.0 \pm 0.2}$	. . .	0.036
Map-$\bar{n}$	8.03×10^{-4}	6.63×10^{-5}	. . .	0.037

tional shifts in the free ligand and free metal ion concentrations were solved simultaneously.[13] In the case of the refinement of the ligand acid dissociation constants a simple Newton–Raphson iteration was carried out in the mole balance equation for total ligand to determine the free ligand; in the case of hydrolysis only, the iteration to determine the free metal concentration was in the mole balance equation for total metal only. Convergence was assumed to be satisfactory when $|(B - B_{\text{calcd}})/B|$ and $|(C_L - C_{L\text{calcd}})/C_L| \leqslant 10^{-5}$. These three different iterations are written as subroutines and are common to both types of program together with the matrix inversion subroutine and a subroutine which prints the elements of the matrices and vectors involved in obtaining the shifts in the constants as well as the correlation matrix elements.

The Gauss nonlinear least squares program for calculating the shifts in the constants is conventional. The partial derivatives appearing in the normal equations are obtained numerically by incrementing the constants.[9] In general these were incremented by 0.1%, although when it was noted that the residuals were insensitive to changes in a particular constant, larger values were used to minimize round-off errors. In one form of the program, the derivatives were $(\partial C_H/\partial \log \beta_{lmn})$ and the calculated shifts and standard errors are in the logs of the constants, while a variant on this calculated the shifts and errors in the constants themselves from $(\partial C_H/\partial \beta_{lmn})$. The former program was generally used.

When the residual is set up in terms of a mole balance equation, weighting becomes very important, as has been pointed out by Hugus.[7,14] In this case, small errors in the measured pH correspond to much larger residuals in C_H at low values of the pH than at high values. On the other hand, when the residuals are defined in terms of $\bar{n}$, the use of equal weights is a good approximation.[11] The weighting procedure employed here was suggested to us by Professor Hugus[15] and is an extension of the method described earlier[14] to three-component systems. The variance in the residual is calculated from the estimated variances in the experimental quantities and the usual rules for propagation of variance. Weights are set equal to the reciprocal of the variance.

TABLE II
REFINED VALUES OF THE EQUILIBRIUM CONSTANTS

Picolinic Acid

	log K_{HPic}	Weighted variance	log K_{MPic}	Weighted variance
Input	−5.34	1.850×10^2	5.0	1.042×10^0
Map	−5.320 ± 0.010	6.955×10^1	5.326 ± 0.044	5.454×10^{-1}
Gauss	−5.306 ± 0.006	7.664×10^1	5.327 ± 0.048	5.471×10^{-1}

Phenanthroline

	log K_{HPhen}	Weighted variance	log K_{MPhen}	Weighted variance
Input	−4.94	4.984×10^1	4.2	2.267×10^{-1}
Map	−4.974 ± 0.002	7.655×10^0	3.886 ± 0.035	7.258×10^{-2}
Gauss	−4.960 ± 0.002	9.722×10^0	3.874 ± 0.035	7.314×10^{-2}

Acetylacetone

	log K_{HAcac}	Weighted variance	log K_{MAcac}	Weighted variance
Input	−8.75	1.126×10^1	6.5	2.431×10^{-4}
Map	−8.763 ± 0.001	3.002×10^{-1}	5.946 ± 0.059	1.804×10^{-4}
Gauss	−8.763 ± 0.001	2.980×10^{-1}	5.980 ± 0.042	1.802×10^{-4}

The "pit mapping" programs are very similar to the Gauss method programs except that the response surface for the sum of the squares of the weighted residuals $\sum_i w_i R_i^2$ as a function of the equilibrium constants is determined directly by incrementing the constants. In this case, the increments are much larger than with the Gauss program, being in the order of 0.05 to 0.1 log unit when log β_{lmn} was incremented or *ca.* 10 to 25% of the constant when β_{lmn} was incremented. After the first cycle with the pit mapping programs, the estimated standard errors were generally used as the increments. By assuming parabolic cross sections for the response surface,[10,11] the shifts to the minimum may be computed.

Both programs did a satisfactory job in refining the constants, although there are sometimes cases where one or the other or both fail to converge. This is usually found with pronounced correlations among the constants. The Gauss method was slightly easier to program and had somewhat shorter running times, although these differences were not important. In general, when the trial constants were quite uncertain as they were in these examples, the Gauss method is the more rapid. With the pit mapping program, it is necessary to limit the shifts to the edge of the segment of the response surface which has been calculated in order to prevent large overshifts, so the procedure is slow if the trial values are much in error. Also, in certain cases when the starting value of a constant was appreciably in error, the surface cross section along an axis corresponded to an inverted parabola, and the calculated shifts were in the wrong direction.

In general, least squares refinement procedures such as these are best applied to systems where quite accurate measurements have been made, where the errors are strictly random, and where very good trial values of the constants have been obtained by numerical or graphical procedures. On the other hand, from the chemist's point of view, the programs are probably most useful in analyzing quite complicated systems where the constants are known only approximately or in cases where it is desirable to try different sets of postulated

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(13) L. Lapidus, "Digital Computation for Chemical Engineers," McGraw Hill Book Co., New York, N. Y., 1962, p. 309.

(14) Z Z. Hugus, Jr., Proceedings of the 7th International Conference on Coordination Chemistry, Stockholm, June, 1962, p. 204.

(15) Z Z. Hugus, Jr., to be published.

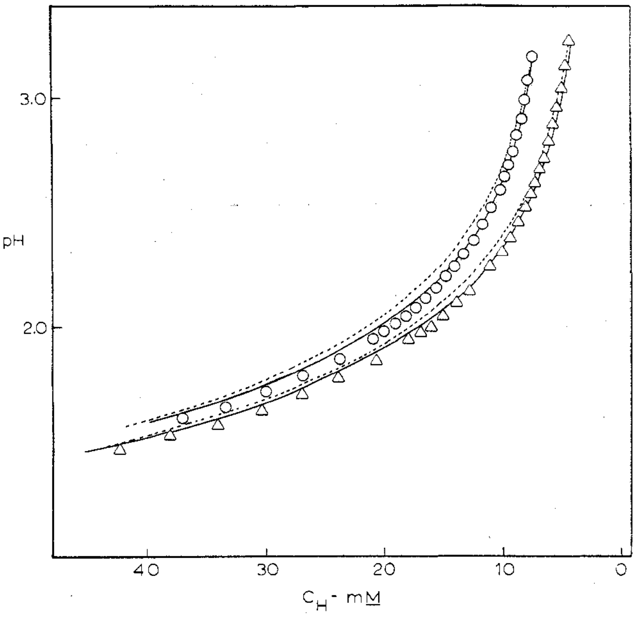

Fig. 1.—The analytical hydrogen ion concentration as a function of the pH; picolinate system: Δ, total metal = 4.00 mM, total ligand = 7.04 mM; O, total metal = 4.00 mM, total ligand = 10.05 mM. Solid curve calculated with refined constants and broken curve calculated with input constants.

species. Systematic errors are frequently present in a given run, although these can, in effect, be randomized by replication of the experiments. A few examples of the application of these programs to such systems are given below.

Results

Hydrolysis Data.—The results of the refinements of the hydrolysis data with no chelating ligands present are given in Table I. Since these measurements for the 0.1 M NO_3^- medium were made at only three total metal concentrations, the value of β_{22} for the dimer is very poorly defined. More extensive studies over a much wider range of total metal concentrations in 3 M ClO_4^- [3] and 0.1 M Cl^- media have shown that dimer formation is real. Under the conditions of the nitrate measurements, there was a pronounced correlation between the two hydrolysis constants β_{11} and β_{22}, the coefficient of correlation being given by the Gauss program as 0.87.

Another program, map-$\bar{n}$, similar to the one described by Sillén[10,11] which seeks the minimum in the response surface with the residuals set up in $\bar{n}$, was also employed. Here equal weights were used. Refinement was carried out in both the logs of the constants and in the constants themselves. The absence of the estimates of the standard errors in some of the results of the various map programs is a result of negative diagonal elements in the inverse matrix used to obtain the shifts. With the mapping programs, there is nothing to prevent this.

An examination of the value of the weighted variance obtained with the first two programs indicates that the variances in the experimental quantities were considerably underestimated. This is apparently a result of systematic errors being present in a given run with these highly acidic solutions, and this gives a wider scattering of the data than estimated when all of the runs are examined together. Such calculations of the weighted variance or the standard error to the fit are especially useful in determining if the measurements are as accurate as anticipated.

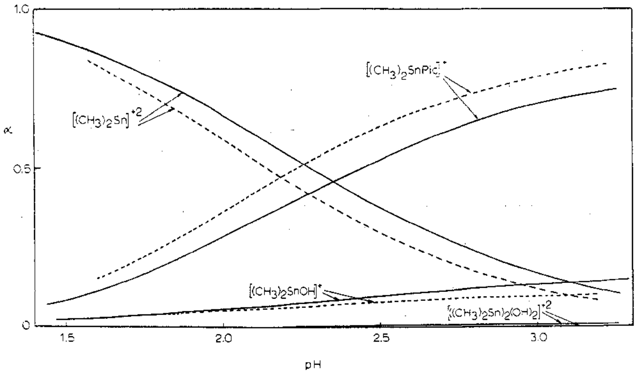

Fig. 2.—The distribution of complexes in the $(CH_3)_2Sn^{+2}$–picolinate system as a function of the pH. The solid curves are calculated for 4.00 mM total metal and 7.04 mM total ligand; the broken curves are calculated for 4.00 mM total metal and 10.05 mM total ligand; $\alpha = m[M_m(\text{Pic})_l(\text{OH})_n/B]$.

Complexing Data.—The following procedure was employed in refining the constants. The hydrolysis data were refined independently as described above. The dissociation constant data for the conjugate acids of the three ligands were then also refined independently. Both types of program worked quite well for the latter refinements. Finally the best values of the hydrolysis and acid dissociation constants were considered as fixed, and the complexing data were refined in terms of the metal–ligand stability constants only. Attempts were also made to refine all of the constants simultaneously; however, there were marked correlations between the aquo metal ion acid dissociation constants and the ligand acid dissociation constants, and this was generally unsuccessful. Because of the correlations, it was often possible to effect correlated shifts in these constants over rather wide limits with little effect on the sum of the squares of the residuals; and in some cases, it was possible to improve the fit slightly by shifting these acid dissociation constants to unrealistic values. Refined values of the complexing and acid dissociation constants together with the starting values are given in Table II.

Of the three ligands studied, picolinate, phenanthroline, and acetylacetonate, the picolinato group was the only ligand which effectively complexed the dimethyltin(IV) ion in aqueous solution. Because of the difficulties in the analysis of the data (7 species were considered: H_2Pic, HPic, Pic, MPic, MOH, $M_2(OH)_2$, and H^+, where M = $(CH_3)_2Sn^{+2}$ and Pic = picolinate) certain systematic deviations in the original calculations made it difficult to evaluate the complexing constants accurately. Figure 1 shows a comparison of the primary experimental data pH(C_H), for the picolinic acid system, the calculated curve for the original constants, and the curve calculated with the refined constants. Figure 2 shows the distribution of complexes in this system. This information, which is printed out by the computer program for each experimental point, is very valuable, for it enables one to determine at a glance the degree of complexing of the metal ion by both the ligand and by hydroxide ion. Considering the intricacy of the calculations used in obtaining these data, it is not feasible to carry out such calculations without using a high-speed computer.

Since these data indicated that the picolinate group did complex the dimethyltin ion quite effectively and that $\bar{n}$ values approaching 1 had been attained, a refinement assuming the formation of two complexes, $[(CH_3)_2SnPic]^+$ and $[(CH_3)_2Sn(Pic)_2]$, was also tried for the case with $C_L > B$, even though it seemed unlikely that the bis-(picolinato) complex would be appreciably soluble. No precipitation had been observed at any point during the experimental study. A trial value of the cumulative constant for the addition of two ligands was obtained assuming the second stepwise constant, K_2, had the same value as the first, K_1. With both the map and Gauss programs, the log of the cumulative constant for the bis complex ($= \log K_1 + \log K_2$) was reduced to about the value of the first stepwise constant, and the estimated standard error in this constant was very large, indicating that it should be set equal to zero. Its inclusion did not reduce the weighted variance. As has been indicated by the earlier studies, there appears to be little tendency for the tin in these dialkyltin compounds to attain a coordination number greater than four. Similar procedures as outlined here could prove quite useful in testing various hypotheses for other systems and could perhaps be used to obtain values for mixed complexing constants.

Calculations of the distribution of the total dimethyltin among the various species for the phenanthroline and acetylacetone systems immediately verified the conclusion that these ligands did not compete favorably with the hydroxide ion. The maximum fraction in the form of the phenanthroline complex was *ca.* 20% while the corresponding value for acetylacetone was but 15%, both at pH values where almost 50% of the dimethyltin was in the form of the monohydroxo complex.

Acknowledgments.—The authors wish to express their appreciation to Professor Z Z. Hugus, Jr., for many helpful discussions and for a matrix inversion subroutine, to Professor L. G. Sillén and Dr. Å. Olin for information on "pit mapping," to Dr. R. M. Rush for copies of ORNL programs, and to Professor M. L. Stein and the Numerical Analysis Laboratory of the University of Minnesota for free computer time.

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The Nature of R_2Sn Compounds[1a]

By D. H. Olson and R. E. Rundle[1b]

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From the information available on inorganic compounds of divalent tin, one would expect to find organic divalent tin compounds of the type R_2Sn. Unless hindered by steric factors,[2] monomeric R_2Sn compounds tend to polymerize rapidly. With the exception of dicyclohexyltin,[3] no monomeric R_2Sn alkyl species have been reported. A few aryl R_2Sn compounds have been reported to be monomeric, but only when freshly prepared.[2,4–6] Recent chemical work on dimethyltin, diethyltin, and diphenyltin has indicated that polymerization results in the formation of tin–tin bonds and of tetravalent tin. Our X-ray work, reported here, on a diphenyltin polymer has verified this type of polymerization.

Brown and Morgan have reported that $(CH_3)_2Sn$, prepared by reaction of $(CH_3)_2SnCl_2$ with Na in liquid NH_3, has two molecular forms, linear chains of 10–100 catenated tin atoms and a six-membered ring of tin atoms, *i.e.*, dodecamethylcyclohexastannane.[7] Recently, Neumann and Neumann and Konig reported the preparation of several R_2Sn compounds containing five to eight tin–tin bonds in a ring or chain. By decomposing $(C_2H_5)_2SnH_2$ with amines, Neumann[8] prepared $((C_2H_5)_2Sn)_n$, where n is in the range 6–9 and $n = 7$ is the main product. From degradation results and analysis of the n.m.r. spectrum, he has concluded that the structure of $((C_2H_5)_2Sn)_7$ is a seven-membered ring containing tin–tin bonds. In a similar manner Neumann and Konig[9] have prepared $H-((C_6H_5)_2Sn)_6-H$, $((C_6H_5)_2Sn)_6$, and $((C_6H_5)_2Sn)_5$. Based upon the above diethyltin studies and molecular weight and degradation results, they propose an open chained structure for $H-((C_6H_5)_2Sn)_6-H$ and five- and six-membered ring structures for $((C_6H_5)_2Sn)_5$ and $((C_6H_5)_2Sn)_6$, respectively. The X-ray work to be described verifies this six-membered ring structure.

Experimental

The following procedure, which was developed by Kuivila, *et al.*,[10] was used in preparing single crystals of diphenyltin for

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(1) (a) Contribution No. 1345. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. (b) Deceased, October 9, 1963.

(2) G. Baker and R. Gelius, *Ber.*, **91**, 829 (1958).

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