CH_2F_2, CH_3. In CF_4, however, the electron diffraction value for the C–F distance is 1.36 ± 0.02 Å. (Brockway, reference 15).

The C=O distances in H_2CCO and F_2CO (1.16 ± 0.02 Å. and 1.17 ± 0.02 Å.) are shorter than that in H_2CO[22] (1.21 ± 0.01 Å.). The data do not, unfortunately, permit any valid comparison of the C=C distance in C_2F_4 with this distance in other compounds. The rather short C=C distance found in ketene (1.30 ± 0.02 Å.) indicates that this bond distance is appreciably shorter than that in ethylene[23] (1.35 ± 0.01 Å.).

Acknowledgments.—The authors wish to thank Professor Yearian for the use of his electron diffraction apparatus. They are grateful to the Purdue Research Foundation for the fellowship which supported this work. They also acknowledge, with thanks, the samples provided by Dr. C. F. Hammer of the du Pont Company and by the Carbide and Carbon Chemicals Company at Oak Ridge.

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[22] D. P. Stevenson, J. LuValle and V. Shomaker, THIS JOURNAL, **61**, 2508 (1939).

[23] W. S. Galloway and E. F. Barker, *J. Chem. Phys.*, **10**, 88 (1942). (The uncertainty of ±0.01 Å. was assigned by Halnerson, *Rev. Modern Phys.*, **19**, 87 (1947).)

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An Analysis of the General Mathematical Formulations for the Calculation of Association Constants of Complex Ion Systems

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RECEIVED MAY 12, 1952

Three general mathematical methods for the calculation of the association constants of a complex ion system have been examined. The three methods have been shown to yield unique values for the constants of a given system. The transformations in the general case have been developed. Evaluation of the constants of a system by both graphical methods and the solution of simultaneous linear equations have been discussed. The limitations of the methods have been considered. The methods have been applied to the calculation of the constants for the uranium(IV) sulfate complex ion system investigated by Betts. Within the manipulative uncertainties in treating the data, identical values of the constants of the system are obtained by the three methods.

In recent years an increasing amount of interest has been shown in the problems associated with the formation of complex ions in aqueous solution. In a review Bjerrum[1,2] has pointed out that the formation of complexes always appears to occur in stepwise fashion, with the stabilities of the various species MA_j characterized by a series of mass action constants, $k_1, \ldots k_j$. He also shows that if corrections for the statistical effect are made, a certain number of the ligands initially bound to the central atom, M, are attached with about the same affinity and suggests that a mean complexity constant $k = \sqrt[j]{k_1k_2 \ldots k_j}$ can be used as a convenient measure of the tendency to complex formation. From an examination of the relationships of the successive constants he has made deductions about the existence of characteristic coördination numbers, statistical effects, electrostatic effects, as well as certain anomalies—such as might be caused by change in coördination number—that may exist.

In order to correlate the free energy data on various complex systems, particularly if quantitative comparisons are to be made, not only are precise experimental data obtained from demonstrably valid experimental techniques necessary but the data must be treated in as mathematically rigorous and physically significant a manner as possible.

There are available only a limited number of general mathematical methods for the calculation of successive complexity constants although a variety of slight modifications and specific applications of these general formulations have been made by a number of investigators. The three general treatments are those proposed by Leden,[3] Bjerrum[2] and Fronaeus.[4] In the present communication we have undertaken to restate the general mathematical formulation for the calculation of successive complexity constants, examine the foundations in each case, analyze the physical significance of the treatment, apply the various methods to a particular set of data and then critically compare the results obtained, pointing out the aspects of each treatment that might be expected to introduce uncertainties.

I. Calculation of the Successive Constants of Mononuclear Complexes

General equations and definitions:

M = central ion or molecule
[M] = concentration of uncomplexed central ion or molecule
A = ligand
[A] = concentration of unbound ligand
$MA, MA_2 \ldots MA_j$ series of complexes formed
$[MA_j]$ = concentration of *j*th complex

$$M + A = MA, M + 2A = MA_2 \ldots M + jA = MA_j \qquad (1)$$

For the *j*th complex the equilibrium constant

$$\beta_j = \frac{[MA_j]}{[M][A]^j} = \prod_{i=1}^{j} k_i \qquad (2)$$

where the *k*'s are constants for the formation of the individual complexes formed in stepwise manner.

Now the total central ion concentration, C_m, is

$$C_m = [M] + \sum_{i=1}^{j} [MA_i] \qquad (3)$$

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[1] J. Bjerrum, *Chem. Revs.*, **46**, 381 (1950).

[2] J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

[3] I. Leden, *Z. physik. Chem.*, **A188**, 160 (1941).

[4] S. Fronaeus, Thesis, "Komplexsystem Hos Koppar," Lund, (1948); *Acta. Chem. Scand.*, **4**, 72 (1950).

and the total ligand concentration, C_a, is

$$C_a = [A] + \sum_{i=1}^{j} i[MA_i] \qquad (4)$$

In all cases the fundamental assumption is made that the experimental conditions are controlled so that the activity coefficients of the system do not change and therefore that equations of the type (2) yield significant values for the concentration constants of the system.

The Method of Leden.—Combining (2) and (3) we define the function F([A])

$$\frac{C_m - [M]}{[M][A]} = \sum_{i=1}^{j} \beta_i[A]^{i-1} = \beta_1 + \beta_2[A]^+ \ldots \beta_j[A]^{j-1} = F([A]) \qquad (5)$$

From a plot of $F([A]) = \dfrac{C_m - [M]}{[M]\,[A]}$ against [A] the graphical limit

$$\lim_{[A] \to 0} F([A]) = \beta_1 \qquad (6)$$

is obtained.

In order to place the limiting process on a sounder basis we will demonstrate that the limit of the ratio is actually the desired quantity. This is a matter of some interest since the experimentally determined ratio in (5) is of the indeterminate form 0/0 at [A] = 0 because at that point $C_m - [M] = 0$ and $[M]\,[A] = 0$

$$\lim_{[A] \to 0} \left\{\frac{C_m - [M]}{[M][A]}\right\} = \lim_{[A] \to 0} \left\{\frac{\sum_{i=1}^{j}[MA_i]}{[M][A]}\right\} =$$

$$\lim_{[A] \to 0} \left\{\frac{\frac{\partial}{\partial A}\sum_{i=1}^{j}[MA_i]}{[M]}\right\} = \lim_{[A] \to 0} \{\beta_1 + 2\beta_2[A]\} = \beta_1 \qquad (7)$$

Similarly successive constants may be obtained from successive functions, such as G([A]) where

$$G([A]) = \frac{F([A]) - \beta_1}{[A]} = \beta_1 + \ldots \beta_j[A]^{j-2} \qquad (8)$$

plotted as above since

$$\lim_{[A] \to 0} G([A]) = \beta_2 \qquad (9)$$

In quite an analogous manner we may evaluate the limit of the ratio in (8) as

$$\lim_{[A] \to 0} G([A]) = \lim_{[A] \to 0} \left\{\frac{F([A]) - \beta_1}{[A]}\right\} =$$

$$\lim_{[A] \to 0} \left\{\frac{\frac{\partial^2}{\partial A^2}\sum_{i=2}^{j}[MA_1]}{2[M]}\right\} = \beta_2 \qquad (10)$$

In place of the graphical limiting method it is feasible to solve for the constants directly by forming a system of equations of the form of equation (5) and by treating the equations as linear in the unknowns β_i. For the general case if the determinant $|D|$, where

$$|D| = \begin{vmatrix} 1 & [A_1] & [A_1]^2 \ldots [A^1]^{j-1} \\ 1 & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ 1 & [A_j] & [A_j]^{j-1} \end{vmatrix} \neq 0 \qquad (11)$$

the β's are unique solutions (Cramer's rule). It is obvious that in any experimental investigation this condition would be fulfilled since the $[A_i]$'s would not be zero nor would they be equal.

The evaluation of F([A]) requires that both [M] and [A] be known. In the special case where the central ion is added as a trace concentration of a radioisotope (*e.g.*, in the determination of complexity constants by partition methods such as the extraction of certain metal ions into benzene with the chelating agent, thenoyltrifluoroacetone)[5] and the complexes are weak or only moderately strong, $[A] \approx C_a$. In the case where $[A] \neq C_a$, the value of [A] can be estimated by one of the procedures discussed later.

The Method of Bjerrum.[2]—Bjerrum points out that if one defines a quantity, $\bar{n}$, the average number of ligands attached to the central group M

$$\bar{n} = \frac{\sum_{i=1}^{j} i[MA_i]}{[M] + \sum_{i=1}^{j}[MA_i]} = \frac{C_a - [A]}{C_m} \qquad (12)$$

knowing $\bar{n}$ as a function of the concentration of the free ligand it is possible to determine the concentration constants of the system. Combination of equations (12) and (2) with the elimination of [M] gives

$$\bar{n} = \frac{\beta_1[A] + 2\beta_2[A]^2 + \ldots j\beta_j[A]^j}{1 + \beta_1[A] + \ldots \beta_j[A]^j} \qquad (13)$$

which may be rearranged into the form

$$\bar{n} + (\bar{n} - 1)\beta_1[A] + (\bar{n} - 2)\beta_2[A]^2 + \ldots (\bar{n} - j)\beta_j[A]^j = 0 \qquad (14)$$

Bjerrum gives a number of approximation methods for the solution of what is essentially (14).

The solution for the $\beta_{i's}$ where j experiments have been performed thus giving j equations of the type of (14), by determinants using Cramer's rule is straightforward. The criterion for uniqueness of the solution is again fulfilled if we examine the determinant of the coefficients $|D_1|$ which is

$$|D_1| = \begin{vmatrix} (\bar{n}_1 - 1)[A_1] \ldots (\bar{n}_j - j)[A_1]^j \\ \cdot \\ \cdot \\ \cdot \\ (\bar{n}_1 - 1)[A_j] \ldots (\bar{n}_j - j)[A_j]^j \end{vmatrix} \neq 0 \qquad (15)$$

since the values of the columns would not be zero or equal in any experiment. Although by Cramer's rule the same unique values for the constants are obtained by each method no simple transformation exists between the two formulations. This can be shown from equations (5) and (12) which give on combination

$$F([A]) = \frac{\left[\sum_{i=1}^{j} i[MA_i]\right] - \bar{n}[M]}{\bar{n}[M][A]} \qquad (16)$$

The simultaneous equations of the form of equation (14) may be expediently solved by taking [A] values at half integral values of $\bar{n}$. Such a selection simplifies the coefficients of the determinant, the values are sufficiently spaced so that a good representation of the curve is obtained and under spec-

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(5) R. E. Connick and W. McVey, THIS JOURNAL, **71**, 3182 (1949).

ial conditions (where the successive k's are sufficiently spaced so that the formation curve is wavelike) these values of $\bar{n}$ correspond to the condition that approximately equal amounts of the $[\mathrm{MA}_{i-1}]$ and $[\mathrm{MA}_i]$ complexes are present in the solution. In this case an approximation to k_i can be made by the equation

$$k_i \cong \left(\frac{1}{[\mathrm{A}]}\right)_{\bar{n}=i-{}^1/_2} \tag{17}$$

$\bar{n}$ is not readily obtained from equation (12) if $C_a \cong [\mathrm{A}]$. In this case the concept of the degree of formation of the separate complexes, a_j, is introduced.

$$a_j = \frac{[\mathrm{MA}_j]}{C_m} = \frac{\beta_j[\mathrm{A}]^j}{1 + \sum\limits_{i=1}^{j}\beta_i[\mathrm{A}]^i} \tag{18}$$

Transformation and differentiation of equation (18) leads to

$$\frac{\partial a_j}{\partial[\mathrm{A}]}\left(1 + \sum_{i=1}^{j}\beta_i[\mathrm{A}]^i\right) + a_j\sum_{i=1} i\beta_i[\mathrm{A}]^{i-1} - j\beta_j[\mathrm{A}]^{j-1} = 0 \tag{19}$$

combining

$$\frac{\partial \log a_j}{-\partial \log [\mathrm{A}]} = \frac{-[\mathrm{A}]\partial a_j}{a_j\partial[\mathrm{A}]} \tag{20}$$

with equations (12) and (19) we obtain

$$\bar{n} = j - \frac{\partial \ln a_j}{\partial \ln [\mathrm{A}]} \tag{21}$$

It is therefore possible if the concentration of the central ion or of any one of the complexes is known as a function of the free ligand concentration to obtain $\bar{n}$ by graphical differentiation of the curve one obtains by plotting log [A] against log a_j. Then a plot of $\bar{n}$ against log [A] gives the formation curve of the system. Where [M] is the measured quantity, $j = 0$, and equation (21) reduces to the form

$$\bar{n} = \frac{\partial \log [\mathrm{M}]}{-\partial \log [\mathrm{A}]} \tag{21A}$$

In this case as well as in other cases where the experimentally determined quantity is not [A] and where the approximation $[\mathrm{A}] \cong C_a$ is not valid, successive approximation must be made to establish $\bar{n}$ and [A] as described in the following section.

The Evaluation of [A].—The evaluation of [A] where the approximation $[\mathrm{A}] \cong C_a$ is not valid can be made as follows: The average number of ligands per complexed metal ion, N, defined by Leden

$$N = \frac{\sum\limits_{i=1}^{j} i[\mathrm{MAi}]}{\sum\limits_{i=1}^{j}[\mathrm{MAi}]} = \frac{\sum\limits_{i=1}^{j} i[\mathrm{MAi}]}{C_m - [\mathrm{M}]} = \frac{\sum\limits_{i=1}^{j} i\beta i[\mathrm{A}]^{i-1}}{\sum\limits_{i=1}^{j}\beta i[\mathrm{A}]^{i-1}} \tag{22}$$

is used in combination with the relation

$$[\mathrm{A}] = C_a - N(C_m - [\mathrm{M}]) \tag{23}$$

obtained by combining equations (3), (4) and (22) to determine [A].

The procedure used by Leden to make the first approximation was to select a measured quantity whose value was proportional to N and from a plot of the logarithm of this quantity *versus* the logarithm of [A], taken as equal to C_a, evaluate N. [A] values were then computed from equation (23) and a set of preliminary constants calculated by means of equations (5), (8), etc. These preliminary constants can then be substituted in equation (22) to give a second approximation to N, which substituted in equation (23) allows an estimate of [A]. These new values of [A] may then be used to establish a second set of constants and the procedure repeated until convergence of the calculated β's to the desired degree of constancy is obtained. From the Nernst equation and equation (21) it can be readily shown that for the case where the cell potential is determined by [M], as in the case of the cadmium cells investigated by Leden, the slope of the dV/d ln A plot rigorously defines $\bar{n}$ according to the equation

$$\frac{\mathrm{d}V}{\mathrm{d} \ln [\mathrm{A}]} = -\bar{n}\,[RT/nF] \tag{21B}$$

so that N can only be approximated in the case where $C_m >> [\mathrm{M}]$ since

$$\bar{n} = N\left(\frac{C_m - [\mathrm{M}]}{C_m}\right) \tag{24}$$

Alternatively, therefore, it is possible to make use of the $\bar{n}$ concept in conjunction with Leden's method and calculate the [A] values by equation (25).

$$[\mathrm{A}] = C_a - \bar{n}C_m \tag{25}$$

Further approximations to [A] may be made either by the procedure outlined above or by making successive approximations to $\bar{n}$ by graphical differentiation of d log [M] plots *versus* d log [A] plots where the successive values of [A] are computed from equation (25). The latter procedure is also used in the methods of Bjerrum and Fronaeus for the case where [M] is the experimentally determined quantity.

The Method of Fronaeus.[4]—This method incorporates the concept of average number of ligands, n, attached to the central atom along with a limiting process of evaluating constants similar to that proposed by Leden. The method was originally formulated for use in systems of mixed complexes, *i.e.*, those in which two dissimilar ligands are attached to the central atom. For a system in which only one type of ligand is present this method may be derived as follows.

A function X([A]) is defined by the equation

$$\mathrm{X}([\mathrm{A}]) = 1 + \beta_1[\mathrm{A}] + \beta_2[\mathrm{A}]^2 + \ldots . + \beta_j[\mathrm{A}]^j \tag{26}$$

Differentiation of (26)

$$\frac{\partial \mathrm{X}([\mathrm{A}])}{\partial[\mathrm{A}]} = \sum_{i=1}^{j} i\beta_i[\mathrm{A}]^{i-1} = \beta_1 + 2\beta_2[\mathrm{A}] + \ldots . j\beta_j[\mathrm{A}]^{j-1} \tag{27}$$

A function $\bar{n}/[\mathrm{A}]$ is formed from (13) and (27)

$$\frac{\bar{n}}{[\mathrm{A}]} = \frac{\partial \mathrm{X}([\mathrm{A}])}{\partial[\mathrm{A}]}\Big/ \mathrm{X}([\mathrm{A}]) = \frac{\partial}{\partial[\mathrm{A}]}\{\log(1 + [\mathrm{A}]\mathrm{F}([\mathrm{A}])\} \tag{28}$$

that is

$$\frac{\partial \log \mathrm{X}([\mathrm{A}])}{\partial \log [\mathrm{A}]} = \bar{n} \tag{29}$$

X([A]) is evaluated numerically by graphical integration of the right-hand side of equation (30).

$$\ln \mathrm{X}([\mathrm{A}]) = \int_0^A \frac{\bar{n}}{[\mathrm{A}]}\,\partial[\mathrm{A}'] \tag{30}$$

β_1 is determined from the function

$$Y([A]) = \frac{X([A]) - 1}{[A]} = \beta_1 + \beta_2[A] + \ldots + \beta_j[A]^{j-1} \quad (31)$$

$$\lim_{[A] \to 0} Y([A]) = \beta_1$$

using the values of X([A]) obtained from (30).

Similarly, β_2, is obtained from

$$Z([A]) = \frac{Y([A]) - \beta_1}{[A]} = \beta_2 + \beta_3[A] + \ldots + \beta_j[A]^{j-2} \quad (32)$$

$$\lim_{[A] \to 0} Z([A]) = \beta_2$$

Alternatively equation 31 may be graphically differentiated in the neighborhood of the origin to obtain a value for β_2. A third procedure is to compute the constants from a system of simultaneous linear equations derived from (31).

The condition that the values for the constants be unique solutions is given by

$$|D_2| = \begin{vmatrix} 1 & [A_1] \ldots & [A_1]^{j-1} \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ 1 & [A_j] & [A_j]^{j-1} \end{vmatrix} \neq 0 \qquad (33)$$

Again for any experiment in which the $[A_i]$'s are not zero, equal or multiples the condition is obviously fulfilled. Since, as before, the equations for the determinant are linear in the unknowns, β_i, the same unique values of the constants are given by this method as by those of Leden or Bjerrum.

The transformation from the system of Leden to that of Fronaeus is quite simple.

$$X([A]) = [A]F([A]) + 1 \qquad (34)$$

while again no simple transform from the equations of Bjerrum to those of Froneaus can be made in terms of [A] and X([A]) as seen by equation (28).

Physical Significance of the Calculated Constants.—The constants calculated by any of these methods have physical significance insofar as it can be demonstrated that they represent the minimum number of parameters required to represent the experimental material. This is most readily established by a measurement of $\bar{n}$ as the following will show. Assume we have a system MA, MA_2, MA_3, MA_4 and have measured a maximum $n = 3.9$. Equation (14) becomes

$$3.9 + 2.9\beta_1[A] + 1.9\beta_2[A]^2 + 0.9\beta_3[A]^3 - 0.1\beta_4[A]^4 = 0 \qquad (35)$$

and $\beta_4[A]^4$ becomes

$$\beta_4[A]^4 = 39 + 29\beta_1[A] + 19\beta_2[A]^2 + 9\beta_3[A]^3 \qquad (36)$$

Since all quantities on both sides of (36) are positive the expression is physically meaningful. Now we can clearly see that an attempt to satisfy the measured value of n in terms of only 3 parameters leads to a physically meaningless expression since in this case equation (14) becomes

$$3.9 + 2.9\beta_1[A] + 1.9\beta_2[A]^2 + 0.9\beta_3[A]^3 = 0 \qquad (37)$$

Since all the [A]'s are positive and negative values for the constants are not meaningful less than four constants will not describe the system.

Comparison of the Methods.—The following general remarks can be made about these procedures for calculating complexity constants. First, it should be emphasized that since all three methods yield unique values for the constants in the general case any discrepancies in calculations for a given system must be merely a reflection of the inherent uncertainties involved in manipulation of the data.

Leden's method as outlined has two limitations: (1) It is applicable only to systems in which the concentration of [M] is the experimentally measured quantity. (2) The physical significance of the calculation is not readily apparent. For the condition that $[A] \cong C_a$, it has the great advantage that graphical manipulation of the data can be avoided. Even in the case where the concentration of [A] must be determined by successive approximations none of the suggested approximation procedures require more than a single graphical differentiation except the one employing the $\bar{n}$ method of computing [A].

The method of Bjerrum has two advantages: (1) It is applicable in all cases whether the measured quantity be the concentration of [M], [A] or one of the $[MA_i]$ complexes. (2) The $\bar{n}$ *versus* [A] plot immediately indicates the number of complexes one has to deal with. However, where the free ligand concentration, [A], is approximately equal to C_a, as in the case of a weak complex or where the central ion is added as a trace concentration of a radioisotope, and where the measured quantity is the concentration of [M] or one of the $[MA_i]$ complexes equation (12) cannot be used directly to calculate $\bar{n}$. There are a number of obvious errors inherent in the graphical differentiation of the smoothed experimental curve according to equation (21) and such errors in the determination of $\bar{n}$ will be reflected in the values of the constants finally obtained. It is equally obvious that these errors will be magnified in those cases where $\bar{n}$ and [A] must be determined by successive graphical approximations.

In general those comments applicable to Bjerrum's method apply to the method of Fronaeus. In addition, where it is feasible to measure $\bar{n}$ according to equation (12) it is still necessary to perform a graphical integration. There are a number of uncertainties always connected with such a procedure.

II. Application of the Equations to the Calculation of the Successive Constants of the Uranium(IV) Sulfate Complex System

The general methods of treatment outlined in the previous section lend themselves for use in conjunction with almost any well designed experiment, spectrophotometric, potentiometric, polarimetric, etc., whose purpose it is to determine the successive complexity constants for a given system. The specialized forms of the equations used depend on the quantities measured. Additional examples of the application of the general equations to the evaluation of complexity constants from different kinds of experimental data may be found in reference (6). To illustrate the methods and check their empirical agreement, the data on a particular system will be examined.

The number of systems in which adequate data are available for calculations of this kind are relatively few and in large part confined to investigations by authors who have used one or the other of the general methods described and whose results should therefore be comparable. One of the exceptions is the uranium(IV) sulfate system investigated by Betts and Leigh.[7] These authors used the experimental method first described by Connick and McVey[5] in which the variation in distribution of uranium(IV) between an aqueous and a benzene phase containing thenoyltrifluoroacetone (tta) is studied as a function of the bisulfate concentration in the aqueous phase. Crucial points such as the hydrogen ion and thenoyltrifluoroacetone dependence of the extraction were carefully investigated. Constant ionic strength and constant acidity were maintained. No test for polynuclear species was made. However, the experimental conditions are such (C_m small) that polynuclear complex formation would be minimized. This, together with the fact that the data can be adequately represented by the mononuclear complex constants suggests that ignoring possible polynuclear complex formation is probably justified in this case.

These data are of particular interest since the constants calculated by the authors give much lower values of k_2 than would have been expected on statistical grounds or by comparison with the values reported for the similar zirconium(IV)[5] or thorium(IV) sulfate complexes.[8]

The Experimental Data

In Table I are presented the pertinent data in the form of the experimental extraction coefficient, E_c, and normalized extraction coefficient, E, as a function of the bisulfate concentration, $[HSO_4^-]$.

TABLE I

THE EXTRACTION COEFFICIENT AS A FUNCTION OF THE BISULFATE CONCENTRATION, $[HSO_4^-]$

E_c = concn. M in organic phase/concn. M in aqueous phase

$[HSO_4^-]$ mole/liter	E_c	(for $a_{tta}^E = 1$)
0	0.712	1.23 × ′ E_0)^4
1.83 × 10^{-3}	.601	1.02 × $10^4$01
4.59 × 10^{-3}	.495	8.20 × 10^3
9.18 × 10^{-3}	.366	5.87 × 10^3
1.835 × 10^{-2}	.228	3.49 × 10^3
4.59 × 10^{-2}	.089	1.30 × 10^3
4.59 × 10^{-2}	1.24	1.34 × 10^3
9.25 × 10^{-2}	0.434	5.28 × 10^2

The Method of Leden.—Using the data in Table I, we may calculate the functions defined by equations (5) and (8) in the form given by equation (5A).

$$\left(\frac{E_0}{E} - 1\right) \Big/ [A] = \frac{C_m - [M]}{[M][A]} \qquad (5A)$$

In these experiments the total metal concentration was sufficiently high so that $[A] \neq C_a$ and successive approximations to [A] must be made. The F([A]) and G([A]) values given in Table II were obtained using [A] values computed using Leden's N method of approximation (equations (22) and (23)). Graphical extrapolation gives β_1 = 131 and β_2 = 1380. The value of β_2 may be obtained in yet another way. From equation (5) it is obvious that the slope of the function in the neighborhood of the intercept will be a measure of this constant. Performing the graphical differentiation one obtained a value of 1320. Using the $\bar{n}$ method of approximating [A], and graphical extrapolation β_1 = 128 and β_2 = 1370. Using simultaneous equations β_1 = 130 and β_2 = 1330. In these calculations it must be remembered that the C_m to be used in the estimation of [A] is the total *aqueous* metal concentration which is readily computed from the original U(IV) concentration (3.25 × 10^{-3} M) and the E_c values given in Table I.

The Method of Bjerrum.—The experimental conditions are such that equation (12) cannot be applied directly. In the present case the data show that a single species is formed in the benzene layer. $\bar{n}$ can therefore be determined directly by graphical differentiation of a plot of the smoothed extraction coefficient, E, against log [A] (equation 21c). The

$$\bar{n} = -\frac{\partial \log E}{\partial \log [A]} \qquad (21c)$$

$\bar{n}$ values obtained by successive approximations are given in Table II. Solving equation (14) by determinants the constants obtained are β_1 = 128 and β_2 = 1480.

TABLE II

CALCULATION OF THE FUNCTIONS F([A]), G([A]) AND $\bar{n}$

Original $[HSO_4^-]$, mole/liter	F([A])	G([A])	$\bar{n}$
1.83 × 10^{-3}	140		0.134
4.59 × 10^{-3}	131		.367
9.18 × 10^{-3}	140	1036	.600
1.835 × 10^{-2}	157	1540	.795
4.59 × 10^{-2}	200	1614	1.17
4.59 × 10^{-2}	186	1235	1.17
9.25 × 10^{-2}	250	1320	1.29

The Method of Fronaeus.—Using the $\bar{n}$ values given in Table II, the function defined by equation (28) can be calculated. By graphical integration the values of the function ln X ([A]) are obtained (equation 30). The functions Y([A]) and Z([A]) are then calculated according to equations (31) and (32). The results are given in Table III. Taking the appropriate limits graphically the value of β_1 = 126 and β_2 = 1210. From differentiation of Y($[HSO_4^-]$) in the region of the origin β_2 = 1160.

TABLE III

THE FUNCTIONS X([A]), Y([A]) AND Z([A]) FOR THE URANIUM(IV) SULFATE SYSTEM

[A], mole/liter	$-\frac{\bar{n}}{[A]}$	X([A])	Y([A])	Z([A])
0.005	85.0	1.610	122	
.015	53.3	3.120	151	
.030	31.66	5.817	161	1170
.050	24.2	10.03	181	1300
.075	17.13	17.33	218	1230
.100	13.00	24.94	239	1130

Comparison of the Results.—As examination of the tabulation of the values of the constants in Table IV shows the three methods give constants in very good agreement. The agreement is better than expected since the values of the constants should be expressed with a 10% uncertainty for β_1 and a 25% uncertainty for β_2. These uncertainties are a reflection of the maximum random errors as estimated from the spreading of the points over the various plots made. There is an average deviation of ±2% between the experimental extraction coefficients and those calculated on the basis of the constants tabulated in Table IV.

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(6) (a) A. F. Holloway, THIS JOURNAL, **74**, 224 (1952), spectrophotometric; (b) S. Fronaeus, *Acta. Chem. Scand.*, **5**, 139 (1951), spectrophotometric and potentiometric; (c) S. Ahrland, *ibid.*, **3**, 374 (1949), spectrophotometric and potentiometric; (d) E. L. King, THIS JOURNAL, **71**, 319 (1949), solubility; (e) D. DeFord and D. N. Hume, *ibid.*, **73**, 5321 (1951), polarographic; (f) S. Fronaeus, *Acta Chem. Scand.*, **5**, 859 (1951), ion-exchange; (g) J. Rydberg, *ibid.*, **4**, 1503 (1950), partition.

(7) R. H. Betts and R. Leigh, *Can. J. Research*, **B28**, 514 (1950).

(8) E. L. Zebroski, H. W. Alter and F. K. Heumann, THIS JOURNAL, **73**, 5646 (1951).

TABLE IV

VALUES OF THE CONSECUTIVE COMPLEXITY CONSTANTS, β_1 AND β_2 FOR THE URANIUM(IV) SULFATE SYSTEM

$\beta_1 = (k_1/[H^+])$	$\beta_2 = \left(\frac{k_1k_2}{[H^+]^2}\right)$	$k_2/[H^+]$	k_1/k_2	Method
131	1380 1320	10.5	12.5	Leden
128	1370	10.7	12.0	
130	1330	10.2	12.7	
128	1480	11.6	11.0	Bjerrum
126	1210 1160	9.6	13.1	Fronaeus
168	62.2	0.37	454	Betts and Leigh

For the $[H^+]$ dependent reactions the constants calculated refer to the expressions given below

$$\beta_1 = \frac{k_1}{[H^+]} = \frac{[USO_4^{++}]}{[U^{+4}][HSO_4^-]} \qquad (38)$$

$$\frac{k_2}{[H^+]} = \frac{[U(SO_4)_2]}{[USO_4^{++}][HSO_4^-]} \qquad (39)$$

The discrepancy between the constants calculated by the methods described in the present paper and those reported by Betts and Leigh arise in large part from the weighting of the data by these authors. Their values for the constants are based primarily on the extraction coefficients for the two highest bisulfate concentrations. If a log E' *versus* log $[HSO_4^-]$ plot is made it is found that the curve using their constants passes through only these two experimental points and deviates from all their other points in such manner that at a given bisulfate concentration the calculated E' is less than that experimentally determined. It is obvious that the inherent uncertainty introduced in any attempt to describe the whole of a smoothed curve using parameters derived from one small region is greater than the probable error that can *a priori* be assigned to any given experimental point.

Acknowledgment.—The authors wish to express their appreciation to Dr. George W. Evans II, whose advice and criticism enhanced the rigor of our analysis.

LEMONT, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, SYRACUSE UNIVERSITY]

The Calculation of Vapor Pressure Curves from Data at One Temperature. A Study of the Hildebrand Rule[1]

BY OLIVER L. I. BROWN[2]

RECEIVED JUNE 16, 1952

All liquids obeying the Hildebrand rule will fall on the same curve of log (P_{mm}/T) *versus* log (T/θ). log θ is a constant obtained from any one pair of P and T values. A standard table is presented by means of which the entire vapor pressure curve of any liquid obeying the Hildebrand rule may be calculated from data at a single temperature. Departures from the Hildebrand rule are presented as a function of vapor volume in the case of some hydrocarbons. It is found that for straight chained paraffin hydrocarbons the excess entropy of vaporization at constant vapor volume is a linear function of the number of carbon atoms from 4 to 12 carbon atoms.

Hildebrand's rule[3] that the molal entropy of vaporization is the same for all normal liquids when measured at the temperatures at which their vapors have equal molal volumes was shown by Hildebrand to lead to the conclusion that for all normal liquids the plots of log P *versus* log T could be superimposed by sliding them along a line of unit slope. He also showed that a general vapor pressure equation could be written for all such liquids with a single constant to be determined from a single pair of P and T values. Hildebrand[4] showed the degree of agreement reached by taking slopes of log P *versus* log T plots for a number of substances at a value of log $nR/V = 0.1$ corresponding to a vapor volume of 49.5 liters per mole.

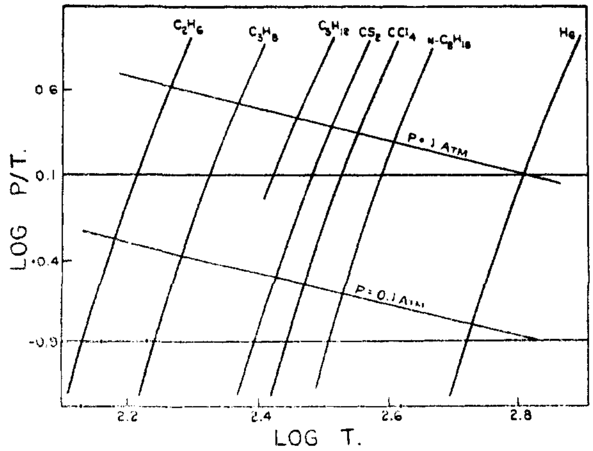

Fig. 1.

The rule can be given a more stringent test by a slight revision in the method of treatment. Since from the perfect gas law $P/T = nR/V$, different liquids at the same value of P/T have the same vapor volume per mole. Also $(d \log P)/(d \log T) = \Delta S_v/R$ for the low pressure region, and so by subtracting $(d \log T)/(d \log T)$ from both sides we obtain $d \log (P/T)/d \log T = \Delta S_v/R - 1$. Thus all liquids which obey Hildebrand's rule will have the same slope for the same value of log (P/T). It will be noted in Fig. 1 that all plots of log (P/T) against log T for the normal liquids shown can be made to coincide by subtracting log θ from each value of log T, where log θ is a constant for each substance to be determined from any one pair of P and T values. It will be observed that all the liquids of Fig. 1 have vapor pressures of one atmosphere or less at the value log $(P/T) = 0.1$ used by Hildebrand.

In order to test the Hildebrand rule and to

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(1) Presented before the Division of Physical and Inorganic Chemistry, 121st Meeting of the American Chemical Society, Buffalo, N. Y., March 26, 1952.

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(3) J. H. Hildebrand, THIS JOURNAL, **37**, 970 (1915); **40**, 45 (1918).

(4) J. H. Hildebrand, *J. Chem. Phys.*, **7**, 233 (1939).