JOURNAL OF THE
AMERICAN CHEMICAL SOCIETY

VOLUME 79 SEPTEMBER 11, 1957 NUMBER 17

PHYSICAL AND INORGANIC CHEMISTRY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND LABORATORY FOR NUCLEAR SCIENCE OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Determination of Successive Formation Constants by Spectrophotometry[1]

BY LEONARD NEWMAN AND DAVID N. HUME

RECEIVED JANUARY 2, 1957

General equations have been derived by means of which successive formation constants of mixed and single ligand complexes can be determined from spectrophotometric data. The equations for single ligand systems are shown to be special cases of the more general mixed ligand relations. The two highest constants together with the extinction coefficients describing the absorption characteristics of the species, and also the two lowest formation constants, as well as the corresponding extinction coefficients, can be determined for any system containing one ligand. The first two formation constants for one ligand, Y, replacing another, X, together with the pertinent extinction coefficients, and the corresponding quantities for X replacing Y also can be determined. Under all conditions, the change in ligand ratios can be obtained. The maximum coördination for a particular ligand can be determined unequivocally when the system has three or fewer complexes.

Introduction

In recent years a number of methods have been devised for the determination of formation constants for successive complexation in solution. The interrelationships and utilization of many of the methods have been described in two excellent papers.[2,3] All these methods rely upon the measure of the concentration of either the free ligand, free metal ion or a particular complex ion. When spectrophotometry is utilized, a wave length is usually selected where only one species is absorbing in order to obtain a direct measure of a particular complex ion concentration. Although there are a number of somewhat general methods,[4-10] no single method through which spectrophotometry can be utilized to obtain successive formation constants, extinction coefficients and ligand ratios appears in the literature.

The purpose of this present work is to present one self-consistent derivation by means of which the measure of absorbance can be utilized for the determination of successive formation constants and extinction coefficients for systems containing either single or mixed ligand complexes. The derivation is based upon the fact that the absorbance (optical density) of a mixture is a function of the extinction coefficients, E, stepwise formation constants, k, ligand concentration (X), and central atom concentration (M). A typical example is $A = E(\mathrm{M}) + E_1k_1(\mathrm{M})(\mathrm{X}) + E_2k_1k_2(\mathrm{M})(\mathrm{X})^2 + \ldots\ldots$ Various functions of the extinction coefficients, complex constants, ligand concentrations and experimentally determined absorbances are plotted to evaluate the unknown terms and coefficients. If there are only two components the handling of the equation is a simple matter and has been done by many people. We have found that it is possible to interpret the experimental data for systems as complicated as three components present at once, all contributing to the absorption. Systems containing more than three components at one time have proved to be unmanageable.

The method is limited to the direct determination of four formation constants, and at each wave length, the extinction coefficients of the species involved. As many as two additional formation constants can be determined by difference. It is equally applicable to both single- and mixed-ligand systems and to weak and moderately strong complexes. The most general system to which this

---

(1) Taken in part from the Ph.D. thesis of Leonard Newman, Massachusetts Institute of Technology, June, 1956.

(2) J. C. Sullivan and J. C. Hindman, THIS JOURNAL, **74**, 6091 (1952).

(3) F. J. C. Rossotti and H. S. Rossotti, *Acta Chem. Scand.*, **9**, 1166 (1955).

(4) J. Bjerrum, *Kgl. Dankse Videnskab Selskab., Mat.-Fys. Medd.*, **22**, Nr. 4 (1944).

(5) S. Ahrland, *Acta Chem. Scand.*, **3**, 347 (1949).

(6) W. D. Kingery and D. N. Hume, THIS JOURNAL, **71**, 2393 (1949).

(7) R. Nasanen, *Acta Chem. Scand.*, **3**, 179 (1949); **4**, 140 (1950).

(8) H. McConnell and N. Davidson, THIS JOURNAL, **72**, 3164 (1950).

(9) S. Fronaeus, *Acta Chem. Scand.*, **5**, 139 (1951).

(10) F. Holloway, THIS JOURNAL, **74**, 224 (1952).

method can be applied is one in which two substances with dissimilar coördination properties are forming mononuclear mixed ligand complexes with one central atom. For systems involving three or fewer formation constants, the maximum coördination number with a particular ligand can be obtained unequivocally. In all systems the change in ligand ratio is obtainable.

In other methods of approach, the higher formation constants have been determined by utilization of all the lower ones, thereby introducing the possibility of rather large cumulative errors. In the present system an advantage is obtained by building up from the free metal ion toward the higher complexes and by working down from the highest complex toward the lower ones. We have found that if we start out by deriving the general expressions for the most complicated case that can be handled, the expressions for all other cases can be obtained readily by simplification. The numbering system for the equations uses capital letters to denote major categories (*e.g.*, A indicates mixed dissimilar ligands) one- or two-digit numbers to identify a given set of conditions (*e.g.*. 9 indicates three species, all three absorbing) and lower case letters are used where a subspecification of conditions becomes necessary. The derivation described in this discussion thus can be applied to a wide variety of systems that might be encountered in the spectrophotometric study of complex ions.

Mixed Ligand Complexes

Mixed Dissimilar Ligands.—The most general system to which this method can be applied is one in which two ligands, X and Y, are attached to one central atom, M, where the ligands have dissimilar coördination properties (*e.g.*, mono- and bidentate anions). The maximum coördination, n, for ligand X, is not necessarily the same as that of X and Y together, or that of Y by itself. The following equations are obtained under the assumption that the central atom is maintained in its highest coördination state by a sufficiently high total ligand concentration. Under these conditions either the highest single complex or the highest mixed ligand complexes are present at all times.

The first two formation constants are defined as

$$k_n = \frac{[\mathrm{MX}_n][\mathrm{Y}]^s}{[\mathrm{MX}_{n-m}\mathrm{Y}_s][\mathrm{X}]^m} \qquad \text{(A1)}$$

$$k_{n-m} = \frac{[\mathrm{MX}_{n-m}\mathrm{Y}_s][\mathrm{Y}]^w}{[\mathrm{MX}_{n-m-p}\mathrm{Y}_{s+w}][\mathrm{X}]^p} \qquad \text{(A2)}$$

The most complicated case is for all three species to be absorbing

$$A = E_n[\mathrm{MX}_n] + E_{n-m}[\mathrm{MX}_{n-m}\mathrm{Y}_s] + E_{n-m-p}[\mathrm{MX}_{n-m-p}\mathrm{Y}_{s+w}] \qquad \text{(A3)}$$

where A is the absorbance for the mixture of three species and E is the extinction coefficient for a particular species. If the path length is other than 1.000 cm., the appropriate factor must be introduced in this and succeeding equations. If only one ligand, X, is added and in great excess compared to the concentration of the central atom we obtain

$$A_0 = E_nM_0 \qquad \text{(A4)}$$

where M_0 is the concentration of the central atom added, all of which is assumed to be in the form of the highest complex, MX_n. In a given experiment the total concentration of central atom added is

$$M_\mathrm{t} = [\mathrm{MX}_n] + [\mathrm{MX}_{n-m}\mathrm{Y}_s] + [\mathrm{MX}_{n-m-p}\mathrm{Y}_{s+w}] \qquad \text{(A 5)}$$

If $X_\mathrm{t} + Y_\mathrm{t}$, the total ligand concentration added, is large compared to M_t, then substituting equations A1, A3, and A4 into A5 and solving for $\mathrm{MX}_{n-m}\mathrm{Y}_s$ and $\mathrm{MX}_{n-m-p}\mathrm{Y}_{s+w}$ we obtain

$$\mathrm{MX}_{n-m}\mathrm{Y}_s = \frac{A - E_{n-m-p}M_\mathrm{t}}{E_{n-m} + \frac{A_0}{M_0}k_n\frac{X_\mathrm{t}^m}{Y_\mathrm{t}^s} - E_{n-m-p}\left(1 + k_n\frac{X_\mathrm{t}^m}{Y_\mathrm{t}^s}\right)} \qquad \text{(A6)}$$

$$\mathrm{MX}_{n-m-p}\mathrm{Y}_{s+w} = \frac{M_\mathrm{t}\left(E_{n-m} + \frac{A_0}{M_0}k_n\frac{X_\mathrm{t}^m}{Y_\mathrm{t}^s}\right) - \mathrm{A}\left(1 + k_n\frac{X_\mathrm{t}^m}{Y_\mathrm{t}^s}\right)}{E_{n-m} + \frac{A_0}{M_0}k_n\frac{X_\mathrm{t}^m}{Y_\mathrm{t}^s} - E_{n-m-p}\left(1 + k_n\frac{X_\mathrm{t}^m}{Y_\mathrm{t}^s}\right)} \qquad \text{(A7)}$$

The only time the total ligand concentration cannot be made large compared to the central atom concentration and still permit appreciable ionization of the complex is when the complex formed is very stable. Upon substitution of A6 and A7 into A2

$$k_{n-m} = \frac{(A - M_\mathrm{t}E_{n-m-p})\,Y_\mathrm{t}^w}{\left[M_\mathrm{t}\left(E_{n-m} + \frac{A_0}{M_0}k_n\frac{X_\mathrm{t}^m}{Y_\mathrm{t}^s}\right) - A\left(1 + k_n\frac{X_\mathrm{t}^m}{Y_\mathrm{t}^s}\right)\right]X_\mathrm{t}^p} \qquad \text{(A8)}$$

and rearranging terms we obtain the equation for

3 Species, 3 Absorbing

$$A = k_{n-m}\left\{\left[k_n\left(A_0\frac{M_\mathrm{t}}{M_0} - A\right)\frac{X_\mathrm{t}^m}{Y_\mathrm{t}^s} - A + E_{n-m}M_\mathrm{t}\right]\frac{X_\mathrm{t}^p}{Y_\mathrm{t}^w}\right\} + E_{n-m-p}M_\mathrm{t} \qquad \text{(A9)}$$

where M_t, M_0, X_t and Y_t have known values, A and A_0 are measured quantities, and E_{n-m}, k_n, m and s are obtainable from subsequent equations. Values of p and t have to be assumed and if the correct values are chosen a plot of A *vs.* the brace-enclosed terms of the right-hand side gives a straight line, the slope of which is the second formation constant, k_{n-m}. The extinction coefficient, E_{n-m-p}, can be obtained from the intercept. In this, as in all subsequent equations from which constants are desired, the left-hand side is plotted against the brace-enclosed terms. The desired constants are obtained from the slopes and intercepts of the straight lines.

If a wave length is now selected where only the two higher species are absorbing, E_{n-m-p} becomes zero and, upon rearrangement, eq. A9 gives for

3 Species, 2 Absorbing, $E_{n-m-p} = 0$

$$k_n\left(A_0\frac{M_\mathrm{t}}{M_0} - A\right)\frac{X_\mathrm{t}^m}{Y_\mathrm{t}^s} - A - \frac{1}{k_{n-m}}\left\{A\frac{Y_\mathrm{t}^w}{X_\mathrm{t}^p}\right\} - E_{n-m}M_\mathrm{t} \qquad \text{(A10)}$$

which permits the determination of E_{n-m}, necessary for A9 and also permits a check on the value of k_{n-m}.

If a wave length can be found where only the highest species is absorbing, E_{n-m} becomes zero and equation A10 upon rearrangement and taking logarithms gives for

3 Species, 1 Absorbing, $E_{n-m-p} = 0$, $E_{n-m} = 0$

$$\log\left[\frac{k_n\left(A_0\frac{M_\mathrm{t}}{M_0} - A\right)\frac{X_\mathrm{t}^m}{Y_\mathrm{t}^s} - A}{A}\right] = \left\{\log\frac{Y_\mathrm{t}^w}{X_\mathrm{t}^p}\right\} - \log k_{n-m} \qquad \text{(A11a)}$$

which permits the determination of k_{n-m} at still another wave length. A knowledge of k_n is assumed in the use of equation A11a. A check on this value can be obtained if we rearrange eq. A11a and again obtain for

3 Species, 1 Absorbing, $E_{n-m-p} = 0$, $E_{n-m} = 0$

$$\left(\frac{A_0 \dfrac{M_t}{M_0} - A}{A}\right) \frac{X_t^m}{Y_t^s} = \frac{1}{k_n k_{n-m}} \left\{\frac{Y_t^w}{X_t^p}\right\} + \frac{1}{k_n} \quad \text{(A11b)}$$

Analogous equations may be derived for one and two absorbing species in which it is not necessarily the highest complexes which are absorbing. Such situations, however, are seldom encountered in practice.

For all of the previous equations m and s had to be known and for most, a knowledge of k_n and E_{n-m}. In order to obtain these quantities, experimental conditions are selected such that only two species are present, whereby terms in k_{n-m} become equal to zero.

When both species are absorbing eq. A10 can be rearranged and we have for

2 Species, 2 Absorbing, $\mathrm{MX}_{n-m-p}\mathrm{Y}_{s+w} = 0$, $E_{n-m-p} = 0$

$$A = k_n \left\{\left(A_0 \frac{M_t}{M_0} - A\right) \frac{X_t^m}{Y_t^s}\right\} + E_{n-m}M_t \quad \text{(A12)}$$

If the proper values of m and s are assumed a straight line is obtained from the known quantities M_t, M_0, X_t and Y_t and from the measured quantities A and A_0. The slope is k_n and E_{n-m} is obtained from the intercept.

If finally a wave length is selected where only the highest of the two species is absorbing E_{n-m} becomes zero and eq. A12 upon rearrangement gives for

2 Species, 1 Absorbing, $\mathrm{MX}_{n-m-p}\mathrm{Y}_{s+w} = 0$, $E_{n-m-p} = 0$, $E_{n-m} = 0$

$$\log \left(\frac{A_0 \dfrac{M_t}{M_0} - A}{A}\right) = -\left\{\log \frac{X_t^m}{Y_t^s}\right\} - \log k_n \quad \text{(A13)}$$

Again if the proper values of m and s are assumed, a straight line is obtained with negative unit slope and an intercept equal to $-\log k_n$. For this case where we have mixed dissimilar ligands the change in the combining ratios (s and m, w and p) cannot be obtained directly; however, the correct values are assured if the plots are straight lines and the same values of the constants are obtained in going from wave length to wave length and in changing the total number of species present.

In the corresponding case where

$$k_n = \frac{[\mathrm{MX}_n][\mathrm{X}]^s}{[\mathrm{MY}_{n-m}\mathrm{X}_s][\mathrm{Y}]^m}$$

$$k_{n-m} = \frac{[\mathrm{MY}_{n-m}\mathrm{X}_s][\mathrm{X}]^w}{[\mathrm{MY}_{n-m-p}\mathrm{X}_{s+t}][\mathrm{Y}]^p}$$

all the previous equations hold if X and Y replace each other. Since the coördination properties of X and Y were assumed to be different it is possible that any or all of the ligand ratios n, m, p, s and w might take on different values. There is, of course, no reason to assume that the formation constants are the same. Using this corresponding case, two more constants and three more extinction coefficients can be obtained.

Method of Application

The absorbance of a solution containing $X_t >> M_0$ is measured and eq. A4 is used to determine E_n.

The absorbance of solutions containing varying amounts of X_t plus Y_t and a constant or varying amount of M_t is determined at all wave lengths of interest. The sum of X_t plus Y_t must always be maintained greater than M_t. When the ratio X_t/Y_t is large, eq. A13 is applicable at all wave lengths and A12 at those wave lengths where only the highest species is absorbing. If the proper values of m and w are assumed a plot of eq. A13 should give a straight line the slope of which is -1. If the proper slope is observed k_n is obtained from the intercept. Using these values of m and t one obtains k_n and E_{n-m} from eq. A12. In the utilization of A12 it is assumed that only one of the two species present is absorbing. This is true only if the same value of k_n is obtained from A12 as that obtained from A13. At a particular wave length the accuracy with which all constants can be obtained is dependent on the magnitude of the absorbance. If the most precise values are desired, M_t is adjusted to maintain the absorbance at approximately 0.2 to 0.8 absorbance unit.

The presence of three species is indicated when deviations from straight lines are observed in the plots of eq. A13 and A12. When these deviations are observed. eq. A11b, A11a, A10 and A9 become applicable. This occurs at lower ratios of X_t/Y_t. The magnitude at which this transition takes place is dependent on the values of the formation constants.

If a wave length is selected where only one of the three species is absorbing, equations A11b and A11a are applicable. In the utilization of A11a, a knowledge of k_n is assumed; however, if the proper values of w and p are chosen, k_{n-m} can be obtained from the intercept. Here the proper choice of w and p is indicated by obtaining a straight line with a slope of unity. If a check on k_n is desired, equation A11b can be utilized from which both k_n and k_{n-m} can be determined.

If wave lengths are now selected where two of the three species are absorbing, eq. A10 permits the determination of E_{n-m} and k_{n-m}. If only one species was actually absorbing at the wave lengths where A11b and A11a were employed and if the proper values of m and w were selected, then the same value of k_{n-m} should be obtained.

Finally, wave lengths are selected where all three species present are absorbing. Equation A9 becomes applicable and k_n and E_{n-m} can be determined. Since the same value of k_{n-m} should be obtained we have a check as to whether A10 was used in the proper wave length range.

The choice of wave length at which a particular number of species is absorbing is not an arbitrary one. There is usually some regularity to the shift of the absorption spectrum as the absorbance becomes dependent on different species. A preliminary study of the system should be made to determine this shift. If the absorption curves are compared at various X_t/Y_t ratios, this regularity usually can be determined. One fairly good rule is that, for a given ligand, the absorption shifts to longer wave lengths as the combining ratio increases.

Mixed Similar Ligands.—If the central atom, M, is complexed by two ligands, X and Y, with the same coördination characteristics, then s equals m and w equals p. The formation constants become

$$k_n = \frac{[\mathrm{MX}_n]}{[\mathrm{MX}_{n-m}\mathrm{Y}_m]}\left[\frac{\mathrm{Y}}{\mathrm{X}}\right]^m \qquad \text{(B1)}$$

$$k_{n-m} = \frac{[\mathrm{MX}_{n-m}\mathrm{Y}_m]}{[\mathrm{MX}_{n-m-p}\mathrm{Y}_{m+p}]}\left[\frac{\mathrm{Y}}{\mathrm{X}}\right]^p \qquad \text{(B2)}$$

and it follows directly that A9, A10, A11a, A12 and A13 become eq. B9, B10, B11a, B12 and B13 by replacing w with p and s with m.

The method of application is exactly the same as for the previous case. This system has the added advantage that no values have to be assumed. The constants, s and w, do not appear in the equations and m and p are determined directly from the slopes of eq. B13 and B11. The same checks on the values of the constants are, of course, applicable.

In the corresponding case where X and Y replace each other, it still holds that s equals m and w equals p; however, there is no reason to assume the m of $\mathrm{MX}_{n-m}\mathrm{Y}_m$ to equal that of $\mathrm{MY}_{n-m}\mathrm{X}_m$ or for the p of $\mathrm{MX}_{n-m-p}\mathrm{Y}_{m+p}$ to equal that of $\mathrm{MY}_{n-m-p}\mathrm{X}_{m+p}$. Since the coördination characteristics are the same, the values of n in both cases are equal.

Single Ligand Complexes

Highest Constants.—The similarity between the single and the mixed ligand case is best realized if one remembers that water, by coördinating with the central atom, in general maintains it in its maximum coördination state. In essence we are always dealing with mixed ligands. It is actually seldom necessary to take the coördination of water into consideration[11] and if we assume that the activity of the water is constant, its value can be included in the formation constants. As is the usual custom, the complexes are written without the attached water molecules. Therefore, if we let Y represent the water molecule the two highest formation constants for the one ligand, X, become

$$k_n = \frac{[\mathrm{MX}_n]}{[\mathrm{MX}_{n-m}][\mathrm{X}]^m} \qquad \text{(C1)}$$

$$k_{n-m} = \frac{[\mathrm{MX}_{n-m}]}{[\mathrm{MX}_{n-m-p}][\mathrm{X}]^p} \qquad \text{(C2)}$$

Each of the equations for the mixed similar ligand case is directly applicable, except that Y drops out of all equations. The method of application is slightly different. Instead of varying the X_t/Y_t ratio, the ratio of X_t/M_t is gradually decreased, however, always maintaining $X_t >> M_t$. As sufficient ionization of the highest and next highest complexes takes place it is possible to obtain a measure of the two highest formation constants, the change in ligand ratios, and the three extinction coefficients.

Lowest Constants.—When the two lowest constants are desired for a one-ligand system, three considerations have to be taken into account. The situation most similar to the ones already discussed is that in which the formation constants are weak. Then in order to obtain appreciable complexation, X_t has to be maintained sufficiently greater than M_t that its change in concentration, due to complexation, can be neglected. However, for larger values of k, in order to obtain the lowest constant it is necessary to maintain M_t in the same order of magnitude as that of X_t. Therefore, the concentration of both the central atom and the complexing ligand change due to the formation of complexes. If the first formation constant is small in relation to the second, it is necessary to maintain M_t sufficiently greater than X_t to prevent the formation of the second complex. In this case it is the concentration of M_t that remains unchanged as complexation takes place.

In each of the three methods to be described there are three ways of obtaining the formation constants and the extinction coefficients. One is to maintain M_t constant and to vary X_t; another, to vary both; and finally, to keep X_t constant and to vary M_t. The nature of the constants and the experimental limitations will determine which is the most suitable method.

X_t Greater Than M_t.—The two lowest constants are defined as

$$k_q = \frac{[\mathrm{MX}_q]}{[\mathrm{M}][\mathrm{X}]^q} \qquad \text{(D1)}$$

$$k_{q+r} = \frac{[\mathrm{MX}_{q+r}]}{[\mathrm{MX}_q][\mathrm{X}]^r} \qquad \text{(D2)}$$

and the absorbance is

$$A = E[\mathrm{M}] + E_q[\mathrm{MX}_q] + E_{q+r}[\mathrm{MX}_{q+r}] \qquad \text{(D3)}$$

If the central atom shows absorption

$$A_0' = EM_0 \qquad \text{(D4a)}$$

when the absorbance is measured with only M present. However, it is often advantageous to obtain

$$A_0'' = E_qX_0 \qquad \text{(D4b)}$$

which is the absorbance of the first complex when M is added in large excess to X. The total concentration of M in any given experiment is

$$M_t = [\mathrm{M}] + [\mathrm{MX}_q] + [\mathrm{MX}_{q+r}] \qquad \text{(D5)}$$

If M absorbs, then both D4a and D4b can usually be obtained. Depending upon whether or not E and/or E_q are determinable the analogous equations to A9, A10, A11a, A12 and A13 become

3 Species, 3 Absorbing, E and E_q known

$$A = \frac{1}{k_{q+r}}\left\{\left[\frac{1}{k_q}(EM_t - A)\frac{1}{X_t^q} - A + E_qM_t\right]\frac{1}{X_t^r}\right\} + E_{q+r}M_t \qquad \text{(D9)}$$

3 Species, 2 Absorbing, $E_{q+r} = 0$, E known

$$\log\left[\frac{1}{k_q}\left(A'_0\frac{M_t}{M_0} - A\right)\frac{1}{X_t^q} - A + A_0''\frac{M_t}{X_0}\right] = r\,\{\log \mathrm{X}_t\} + \log k_{q+r} \qquad \text{(D10a)}$$

3 Species, 2 Absorbing, $E_{q+r} = 0$, E_q known

$$k_q\left(A_0''\frac{M_t}{X_0} - A\right)X_t^q - A = k_qk_{q+r}\,\{AX_t^{q+r}\} - EM_t \qquad \text{(D10b)}$$

3 Species, 2 Absorbing, $E = 0$, E_q known

$$A = \frac{1}{k_{q+r}}\left\{\left(A_0''\frac{M_t}{X_0} - A - \frac{A}{k_qX_t^q}\right)\frac{1}{X_t^r}\right\} + E_{q+r}M_t \qquad \text{(D10c)}$$

---

[11] G. C. B. Cave and D. N. Hume, THIS JOURNAL, **75**, 2893 (1953).

3 Species, 2 Absorbing, $E_{q+r} = 0$, E known

$$\frac{1}{k_q}\left(A_0' \frac{M_t}{M_0} - A\right)\frac{1}{X_t^q} - A = k_{q+r}\,\{AX_t^r\} - E_qM_t \tag{D10d}$$

3 Species, 2 Absorbing, $E_q = 0$, E known

$$A = \frac{1}{k_{q+r}}\left\{\left[\frac{1}{k_q}\left(A_0' \frac{M_t}{M_0} - A\right)\frac{1}{X_t^q} - A\right]\frac{1}{X_t^r}\right\} + E_{q+r}M_t \tag{D10e}$$

3 Species, 1 Absorbing, $E_{q+r} = 0$, $E = 0$, E_q known

$$\log\left[\left(\frac{A_0'' \frac{M_t}{X_0} - A}{A}\right)X_t^q - \frac{1}{k_q}\right] = (q + r)\,\{\log X_t\} + \log k_{q+r} \tag{D11a}$$

3 Species, 1 Absorbing, $E_{q+r} = 0$, $E_q = 0$, E known

$$\log\left[\frac{1}{k_q}\left(\frac{A_0' \frac{M_t}{M_0} - A}{A}\right)\frac{1}{X_t^q} - 1\right] = r\,\{\log X_t\} + \log k_{q+r} \tag{D11b}$$

3 Species, 1 Absorbing, $E_q = 0$, $E = 0$

$$A = -\left\{\frac{1}{k_{q+r}}\left(1 + \frac{1}{k_qX_t^q}\right)\frac{A}{X_t^r}\right\} + E_{q+r} \tag{D11c}$$

2 Species, 2 Absorbing, $\mathrm{MX}_{q+r} = 0$, $E_{q+r} = 0$, E and E_q known

$$\log\left(\frac{A_0' \frac{M_t}{M_0} - A}{A - A_0'' \frac{M_t}{X_0}}\right) = q\,\{\log X_t\} + \log k_q \tag{D12a}$$

2 Species, 2 Absorbing, $\mathrm{MX}_{q+r} = 0$, $E_{q+r} = 0$, E_q known

$$A = k_q\left\{\left(A_0'' \frac{M_t}{X_0} - A\right)X_t^q\right\} + EM_t \tag{D12b}$$

2 Species, 2 Absorbing, $\mathrm{MX}_{q+r} = 0$, $E_{q+r} = 0$, E known

$$A = \frac{1}{k_q}\left\{\left(A_0' \frac{M_t}{M_0} - A\right)\frac{1}{X_t^q}\right\} + E_qM_t \tag{D12c}$$

2 Species, 1 Absorbing, $\mathrm{MX}_{q+r} = 0$, $E_{q+r} = 0$, $E = 0$, E_q known

$$\log\left(\frac{A}{A_0'' \frac{M_t}{X_0} - A}\right) = q\,\{\log X_t\} + \log k_q \tag{D13a}$$

2 Species, 1 Absorbing, $E_{q+r} = 0$, $\mathrm{MX}_{q+r} = 0$, $E_q = 0$, E known

$$\log\left(\frac{A_0' \frac{M_t}{M_0}}{A}\right) = q\,\{\log X_t\} + \log k_q \tag{D13b}$$

When the conditions for each of the above equations is met, the related information can be obtained. Several of these relations have been derived and used by prior workers as special cases applied to their particular problems, but this appears to be the first attempt to include all possibilities in a general method of approach. If D4a and/or D4b is known, the three extinction coefficients and the two formation constants can be obtained for the first three species in a series, providing the formation constants are small enough to permit X_t to remain substantially greater than M_t. When Y is the complexing ligand the system is exactly analogous to the above case. It is obvious that the same sort of checks are available here in order to ascertain whether the proper number of species were absorbing at a particular wave length and as to whether the proper number of species were present over the range of X_t/M_t selected.

X_t Comparable to M_t.—The first constant has often to be determined when the concentration of M_t and X_t are in the same order of magnitude. If this is the case eq. A3 and A5 become for a one-ligand system

$$A = E[\mathrm{M}] + E_q[\mathrm{MX}_q] \tag{E3}$$

$$M_t = [\mathrm{M}] + [\mathrm{MX}_q] \tag{E5a}$$

$$X_t = [\mathrm{X}] + q[\mathrm{MX}_q] \tag{E5b}$$

By combination of E3, E5a and E5b with D1 we obtain the first formation constant as

$$k_q = \frac{A - EM_t}{\left[\frac{A(E_q - E) - E_q(A - EM_t)}{E}\right]\left[X_t - q\,\frac{A - EM_t}{E_q - E}\right]^q} \tag{E8}$$

Substituting D4a and D4b into E8, taking the logarithms and rearranging we have for

2 Species, 2 Absorbing, $\mathrm{MX}_{q+r} = 0$, $E_{q+r} = 0$

$$\log\left(\frac{A - A_0' \frac{M_t}{M_0}}{A_0'' \frac{M_t}{X_0} - A}\right) = q\left\{\log\left[X_t - q\left(\frac{A - A_0' \frac{M_t}{M_0}}{\frac{A_0''}{X_0} - \frac{A_0'}{M_0}}\right)\right]\right\} + \log k_q \tag{E12}$$

2 Species, 1 Absorbing, $\mathrm{MX}_{q+r} = 0$, $E_{q+r} = 0$, $E_q = 0$

$$\log\left(\frac{A_0' \frac{M_t}{M_0} - A}{A}\right) = q\left\{\log\left[X_t - q\left(M_t - \frac{A}{A_0'}\,M_0\right)\right]\right\} + \log k_q \tag{E13a}$$

2 Species, 1 Absorbing, $\mathrm{MX}_{q+r} = 0$, $E_{q+r} = 0$, $E = 0$

$$\log\left(\frac{A}{A_0'' \frac{M_t}{X_0} - A}\right) = q\left\{\log\left(X_t - q\,\frac{A}{A_0''}\,X_0\right)\right\} + \log k_q \tag{E13b}$$

From E12, E13b or E13a, q and k_q can be obtained. For the three equations the value of q has first to be assumed. This value is most often equal to unity; however, it is checked by the attainment of a straight line, the slope of which should equal the assumed value of q. Another check is to obtain the same value of k_q at more than one wave length.

M_t Greater than X_t.—If the ratio k_{q+r}/k_q is sufficiently large it might be necessary to determine k_q when M_t is in great excess to X_t. Equation E5a becomes

$$M_t = [\mathrm{M}] \tag{F5}$$

and E12 and E13b become for

2 Species, 2 Absorbing, $\mathrm{MX}_{q+r} = 0$, $E_{q+r} = 0$

$$\log\left(\frac{A - A_0' \frac{M_t}{M_0}}{\frac{A_0''}{X_0}}\right) = q\left\{\log\left[X_t - q\left(\frac{A - A_0' \frac{M_t}{M_0}}{\frac{A_0''}{X_0}}\right)\right]\right\} + \log k_q \tag{F12}$$

2 Species, 1 Absorbing, $\mathrm{MX}_{q+r} = 0$, $E = 0$

$$\log\left(\frac{A}{A_0''}\,X_0\right) = q\left\{\log\left(X_t - q\,\frac{A}{A_0''}\,X_0\right)\right\} + \log k_q \tag{F13}$$

From both F12 and F13 q and k_q are determined when the proper value of q is assumed.

Possibility of Determining Additional Constants

Under highly favorable conditions, two more constants can be determined. It is believed that the data will never be sufficiently accurate to determine more than six extinction coefficients.

Starting from the central atom we can determine the first two formation constants in the manner already indicated. Under highly favorable conditions the approach of Kingery and Hume[6] permits the determination of the next formation constant. The method employs the utilization of the calculated constants and extinction coefficients to determine the absorbance of a solution for a particular ligand and central atom concentration. The difference between the calculated and the observed absorbance is attributed to the formation of a fourth species which has to be assumed not to absorb at the wave length selected. A log plot similar to that of eq. D13b is made for the equilibrium between the third and fourth species. The change in ligand ratio and another constant can be determined.

It has also been seen that starting with the central atom in its highest complexed state, the two highest formation constants can be determined. Once again, the method of Kingery and Hume can be employed whereby the third highest formation constant can be calculated. Therefore, under highly favorable conditions, as many as six formation constants can be determined.

The utilization of many of the equations for the mixed similar ligands and for one-ligand systems will be demonstrated in subsequent papers.

Acknowledgments.—This work was supported, in part, by the United States Atomic Energy Commission. One of us (D.N.H.) wishes to express thanks to the John Simon Guggenheim Memorial Foundation for a Fellowship during a portion of the period of the investigation.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND LABORATORY FOR NUCLEAR SCIENCE OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

A Spectrophotometric Study of the Bismuth–Chloride Complexes[1]

BY LEONARD NEWMAN AND DAVID N. HUME

RECEIVED JANUARY 2, 1957

By application of spectrophotometric methods developed in a previous paper, the following constants were determined for the bismuth–chloride system: $270 \pm 5 = [BiCl^{++}]/[Bi^{+++}][Cl^-]$, $900 \pm 100 = [BiCl_2^+]/[BiCl^{++}][Cl^-]$, $20 \pm 10 = [BiCl_3]/[BiCl_2^+][Cl^-]$, $60 \pm 5.0 = [BiCl_4^-]/[BiCl_2^+][Cl^-]^2$, $2.7 \pm 1.0 = [BiCl_4^-]/[BiCl_3][Cl^-]$, and $3.0 \pm 0.5 = [BiCl_5^{--}]/[BiCl_4^-][Cl^-]$. All were determined in 1 M perchloric acid and the last three in a salt concentration of 4.0 M. The absorption spectra for all the species except $BiCl_2^+$ were resolved.

Introduction

Although the existence of complex formation between bismuth(III) and chloride ions is well known, comparatively little information is available concerning the nature or stability of the species formed. None of the earlier workers[2,3] undertook extensive studies on the system and the more recent work[4,5] has not taken fully into consideration the effects of variable ionic strength. The observation by Merritt, Hershenson and Rogers[6] that the ultraviolet absorption of bismuth in acid solution was influenced profoundly by chloride concentration has prompted us to investigate the system spectrophotometrically using the methods developed and described in a previous paper.[7]

Exerimental

Materials and Apparatus.—Solutions of bismuth perchlorate were prepared by dissolving Baker and Adamson reagent bismuth oxide in a stoichiometric concentration of warm Mallinckrodt 60% perchloric acid analytical reagent and then diluting to the proper concentration. A 5 M stock solution of sodium perchlorate was prepared by dissolving and then filtering Fisher Scientific Company purified sodium perchlorate. Stock solutions of 5 M sodium chloride were prepared by dissolving and filtering Mallinckrodt analytical reagent material.

Two spectrophotometers were used: A Beckman model DU quartz spectrophotometer equipped with a photomultiplier attachment, and a Cary recording spectrophotomer model 11 MS. Unless otherwise specified, 1.000 cm. cells were used and cell corrections applied if necessary. For each experiment the spectrophotometer used is specified.

General Characteristics of the Absorption Curves.—The absorption spectra of solutions containing 15 p.p.m. bismuth, 1 M perchloric acid, and varying ratios of sodium chloride to sodium perchlorate to maintain a salt concentration of 4.0 M were measured against a blank containing 1 M perchloric acid on the Cary. It can be seen in Fig. 1 that at 4 M sodium chloride, there is an absorption peak at 327 mμ for a bismuth complex of the form $BiCl_n^{3-n}$. There is a gradual shift of the peak as the chloride concentration is decreased, indicating that chloride complexes lower than n must also be formed. Since the blank contained only 1 M perchloric acid the curves include the absorption due to sodium perchlorate and sodium chloride. The absorption due to sodium perchlorate can be neglected throughout the wave length covered. Although the absorbance of 4 M sodium chloride becomes significant at wave lengths less than 260 mμ, it does not affect the spectra around the absorption peaks for the high chloride concentrations. When the peaks are shifted to the region of 260 mμ (*e.g.*, expt. 15, Fig. 1) the chloride concentration is so low that its contribution to the spectra is negligible.

---

[1] Taken in part from the Doctoral Thesis of Leonard Newman, Massachusetts Institute of Technology, May, 1956.

[2] A. A. Noyes, F. W. Hall and J. A. Beattie, THIS JOURNAL, **39**, 2526 (1917).

[3] T. DeVries and E. M. Mattox, *Proc. Indiana Acad. Sci.*, **44**, 138 (1934).

[4] A. K. Babko and A. M. Golub, *Sbornik Statei Obschchei Khim., Akad. Nauk, S.S.S.R.*, **1**, 64 (1953).

[5] K. B. Yatsimirskii, *ibid.*, **1**, 97 (1953).

[6] C. Merritt, H. M. Hershenson and L. B. Rogers, *Anal. Chem.*, **25**, 572 (1953).

[7] L. Newman and D. N. Hume, THIS JOURNAL, **79**, 4571 (1957).