eisen,[7] with the assumption of the "rigid" model for the activated complex. The resulting calculated ratio $k_H/k_D = 1.54$ does not agree well with the observed value of 1.22. The discrepancy has not been resolved.

The proposed mechanism indicates that $E_H = (E_1 + E_2 + E_4 - E_3)/2 = 37.2$ kcal./mole. Taking $E_2 = 8$ kcal./mole,[8] and estimating $E_3 = 6$ kcal./mole (approximately the activation energy for recombination of CCl_3 radicals),[9] then[10] $E_1 = 72 - E_4$; thus the upper limit for the C–Cl bond dissociation energy in chloroform is 72 kcal./mole. It is of interest to note that Sullivan and Davidson[11] give a value for the C–Cl bond dissociation energy in CCl_4 in the range 68–75 kcal./mole.

A number of other mechanisms were considered; these included primary fission of the C–H bond,[12] intramolecular elimination of HCl, etc., but none yielded the observed rate expression or a calculated isotope effect of a reasonable order of magnitude. The proposed mechanism appears to be the simplest one which explains the main features of the kinetics; unfortunately, even in the initial stages of the decomposition it is inadequate in some details.[13] The over-all reaction is evidently very complex and a complete quantitative treatment appears unlikely.

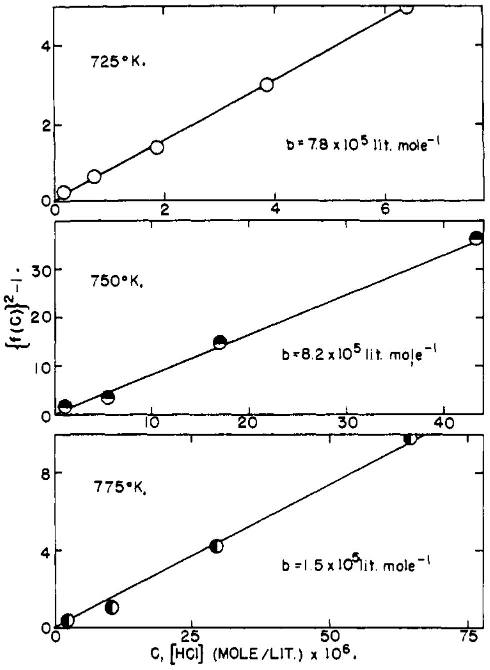

Fig. 5.—Inhibition function *vs.* [HCl].

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(7) J. Bigeleisen, *J. Chem. Phys.*, **17**, 675 (1949).

(8) H. J. Schumacher, *Angew. Chem.*, **53**, 501 (1940).

(9) See the review article by Burnett and Melville, *Chem. Rev.*, **54**, 283 (1954).

(10) From the inhibition plots in Fig. 5, $b = k_{-2}/k_4 \cong 10^6$ l. mole^{-1} at 750°K. ΔH_2 is estimated to be about 12 kcal./mole (from thermochemical data), so $E_{-2} \cong 20$ kcal./mole. Thus $k_2/k_4 >> 10^6$ and it is probable that $E_4 \geq E_2$.

(11) J. H. Sullivan and N. Davidson, *J. Chem. Phys.*, **19**, 143 (1951).

(12) The C–H bond dissociation energy CCl_3H is estimated[10] to lie in the range 89–96 kcal./mole, which is appreciably greater than the highest reasonable value for the C–Cl energy. For a mechanism involving primary C–H bond fission, assuming the "rigid" model for the activated complex, a calculated value of $k_{1H}/k_{1D} = 2.12$ at 750°K. was obtained.

(13) NOTE ADDED IN PROOF: Howlett (private communication) suggests that for decomposition reactions of small molecules in the low pressure range bimolecular steps are more probable. Thus in reactions (1), (3) and (4), another species, "M," would appear. The remitting rate law would be

$$-\frac{d}{dt}[CCl_3H] = \frac{k[M]CCl_3H]}{([M] + b[HCl])^{1/2}}$$

For the flow runs M = He, and the rate law is indistinguishable from that observed; for the static runs M = $CHCl_3$, and the resulting 3/2 order expression for the initial rate would not agree with the approximate 1st order behavior observed (*cf.* Section A).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF TEXAS]

The Mole Ratio Method for Spectrophotometric Determination of Complexes in Solution[1]

BY ALBERT S. MEYER, JR., AND GILBERT H. AYRES

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A mathematical treatment is given of the mole ratio method for deducing the stoichiometry of complexes in solution, for situations in which several complexes exist under a given set of experimental conditions. For the ideal case, the absorbance of the solutions as a function of concentration of variable component is a continuous curve made up of straight line segments. Changes of slope may be observed at any mole ratio of one of the complexes formed, except for very unusual relations between absorptivities, at restricted wave lengths, of adjacent complexes. The stoichiometry of all the complexes in solution can be defined by spectrophotometric measurements of solutions of mole ratios corresponding to each complex, of one solution between successive complexes, and of two solutions above and two solutions below the mole ratio of the terminal complexes, provided measurements are made at sufficient different wave lengths. The absence of a change of slope, in the mole ratio plot, over the entire spectrum is strong evidence that a complex of a given mole ratio does not exist. Consideration of the effects of dissociation of the complexes and the tolerances in the reliability of the spectrophotometric measurements leads to the conclusion that the minimum ratio between successive stepwise dissociation constants must be 600 to permit extrapolation of linear portions of absorbance *versus* mole ratio plots to their intersection point as representing the composition of a complex. The advantages of the mole ratio method over the method of continuous variations are discussed.

The mole ratio method of deducing the composition of complexes in solution from spectrophotometric data was introduced by Yoe and Jones.[2]

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(1) This work was supported jointly by The United States Atomic Energy Commission and The University of Texas, under Contract No. AT-(40-1)-1037.

(2) J. H. Yoe and A. L. Jones, *Ind. Eng. Chem., Anal. Ed.*, **16**, 11 (1944).

The method is based upon considerations of a reaction of the type $S + nR \rightarrow SR_n$. If the product of reaction is very little dissociated, a plot of absorbance against mole ratio of component R to component S, with the concentration of S held constant, rises steeply from the origin as a straight line for mole ratios below that corresponding to the complex formed, then breaks sharply to a constant absorbance at the mole ratio of R/S in the complex. If the concentration of R is held constant and S is varied, the break in the curve indicates the mole ratio S/R in the product. If the complex is much dissociated, the mole ratio plot shows no sharp break, but only a gradual change of slope, approaching asymptotically a constant absorbance at high mole ratios. Breaks in the curves often can be sharpened by working with solutions of high ionic strength.[3]

The mole ratio method has not been considered applicable to systems in which more than one complex is formed under a given set of conditions. However, on the basis of the following considerations the method may be applied to systems containing more than one product, if the complexes are of sufficient stability. For systems involving high-ratio complexes (*e.g.*, R/S = 5/1 or higher) the mole ratio method offers distinct advantages over the method of continuous variations.[4,5]

For the general case in which R reacts with S to form N consecutive complexes, the i-th complex will be designated by SR_{n_i}, and its concentration by $[SR_{n_i}]$. For the reaction $SR_{n_i} \rightleftarrows S + n_iR$ the dissociation constant, k_{n_i}, is

$$k_{n_i} = \frac{[S]\,[R]^{n_i}}{[SR_{n_i}]}$$

It will be assumed that the solutions contain a concentration of electrolyte sufficient to prevent significant change in the activity coefficients of the reaction components, hence the concentration dissociation constant is used, rather than the thermodynamic dissociation constant.

The values $n_0 \ldots n_1 \ldots n_N$ will represent a sequence of increasing integers or rational numbers corresponding to the stoichiometry of the complexes formed. For a given complex of the type S_pR_q, n_i will be equal to q/p and the corresponding absorbance will be determined by the molar concentration of S rather than by the concentration of the complex. For convenience, the first member of a series of complexes will be designated as S, *i.e.*, $S = SR_{n_0}$. The dissociation constant for this hypothetical complex is set equal to one. Applying the mole ratio method, if the absorbances at a given wave length are measured for a series of solutions whose total molar concentration of S is M, and of R is yM, and the absorbance values are plotted against y, the contour of the resulting curve will be determined by the stoichiometry and the dissociation constants of the complexes formed and by the concentration, M, of these solutions.

First, consider the curve obtained for an ideal system in which the relationship between the dissociation constants and the concentration is such that the influence of dissociation is less than the experimental error of a measurement. For this ideal system, when the value of y corresponds to the mole ratio for the formation of one of the complexes, SR_{n_j}, (where n_j is less than n_N), the concentration of this complex will be equal to M, and the absorbance A will be given by $A = Mba_{n_j}$, where b is the optical path length and a_{n_j} is the absorptivity of the complex. Similarly, at $y = n_{j+1}$, $A = Mb \cdot a_{n_{j+1}}$. For intermediate values of y, the absorbance is represented by the equation

$$A(y)_{n_j \leq y \leq n_{j+1}} = Mb\left(a_{n_j} + (y - n_j)\frac{a_{n_{j+1}} - a_{n_j}}{n_{j+1} - n_j}\right)_{n_j \leq y \leq n_{j+1}} \quad (1)$$

For the complex of highest mole ratio, SR_{n_N}, the absorbance will be given by

$$A(y)_{y \geq n_N} = Mb\,(a_{n_N} + a_R(y - n_N))_{y \geq n_N}$$

The entire curve may be represented by summing over j to yield

$$A(y) = \sum_{j=0}^{N} Mb\left[a_{n_j} + (y - n_j)\frac{a_{n_{j+1}} - a_{n_j}}{n_{j+1} - n_j}\right]_{n_j \leq y \leq n_{j+1}} + Mb[a_{n_N} + a_R(y - n_N)]_{y \geq n_N} \quad (2)$$

Therefore, for the ideal case, $A(y)$ is a continuous curve made up of straight line segments. Changes of slope may be observed at any mole ratio of one of the complexes formed. A change of slope will be found at $y = n_j$, unless

$$\text{Slope 1} = \frac{a_{n_j} - a_{n_{j-1}}}{n_j - n_{j-1}} = \frac{a_{n_{j+1}} - a_{n_j}}{n_{j+1} - n_j} = \text{Slope 2} \quad (3)$$

While this relationship may be found at some wave lengths, it is unlikely to hold over a wide wave length region. The absence of change of slope over a given wave length region indicates that the existence of the complex cannot be established directly by spectrophotometric measurement in this region, and the absence of change of slope over the entire measurable spectrum is strong evidence that a complex of such ratio does not exist.

For the ideal case, the stoichiometry of the complexes involved and the spectral curves of the complexes may be defined by the spectrophotometric measurements of solutions of mole ratios corresponding to each complex, and of one solution between successive complexes, plus at least two solutions above and two solutions below the mole ratios of the terminal complexes.

Where systems show a significant dissociation effect, it may be possible to decrease the dissociation by increasing the concentration. If the values of the dissociation constants and concentration limits are such that dissociation is still appreciable at mole ratios corresponding to complexes formed, the technique may be modified by making measurements on several solutions whose mole ratios lie between that of the complex under consideration and the preceding and following complexes. The dissociation will be lowered in these concentration ranges by buffer action. If an appropriate rela-

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(3) A. E. Harvey and D. L. Manning, THIS JOURNAL, **72**, 4488 (1950).

(4) P. Job, *Ann. chim.*, (*Paris*), [10] **9**, 113 (1928).

(5) W. C. Vosburgh and G. R. Cooper, THIS JOURNAL, **63**, 437 (1941).

tionship is obtained between the concentration and the dissociation constants, the system will approach ideality in these regions, and the absorptivity and the stoichiometry of the complex may be obtained by extending the straight-line portions of the absorptivity–composition curve until they intersect.

In order to establish the limitations of the method, the following relationships are formulated. From the previous definition of M and of k_{n_i}

$$M = \sum_{i=0}^{N} [\mathrm{SR}_{n_i}] = [\mathrm{S}] \sum_{i=0}^{N} \frac{[\mathrm{R}]^{n_i}}{k_{n_i}} \tag{4}$$

By eliminating [S] between the mass law expressions for $[\mathrm{SR}_{n_i}]$ and $[\mathrm{SR}_{n_j}]$, we get

$$[\mathrm{SR}_{n_i}] = \frac{k_{n_j}}{k_{n_i}} [\mathrm{SR}_{n_j}] [\mathrm{R}]^{(n_i - n_j)} \tag{5}$$

Since dissociation of a mole of the j-th component according to the reaction $\mathrm{SR}_{n_j} \rightleftarrows \mathrm{SR}_{n_i} + (n_j - n_i)\mathrm{R}$ yields $(n_j - n_i)$ moles of R, for a solution in which the concentration $y = n_j$, we have

$$[\mathrm{R}] = \sum_{i=0}^{N} (n_j - n_i)[\mathrm{SR}_{n_i}] = [\mathrm{S}] \sum_{i=0}^{N} (n_j - n_i) \frac{[\mathrm{R}]^{n_i}}{k_{n_i}} \tag{6}$$

From the additive property of absorbances

$$A = b \sum_{i=0}^{N} [\mathrm{SR}_{n_i}]\, a_{n_i} \tag{7}$$

We will define the fraction of M in the form of the i-th complex by $f_{n_i} = [\mathrm{SR}_{n_i}]/M$, and the fraction of M dissociated by $F = (f_{n_{j(\text{ideal})}} - f_{n_j})/f_{n_{j(\text{ideal})}}$, where SR_{n_j} is the principal component if the system is considered as ideal. The absolute value of the relative error introduced will be equal to $(A_{\text{ideal}} - A_{\text{dissociated}})/A_{\text{ideal}}$. When the value of y equals n_j, then

$$\frac{\Delta A}{A} = \frac{Mba_{n_j} - \sum\limits_{i=0}^{N} [\mathrm{SR}_{n_i}]a_{n_i}}{Mba_{n_j}} = 1 - \frac{\sum\limits_{i=0}^{N} fSR_{n_i}a_{n_i}}{ba_{n_j}} \tag{8}$$

If we assume that the dissociation is small and make the approximation that only the principal component and adjacent complexes contribute to the summations, we may write

$$\begin{aligned}\frac{\Delta A}{A} &= (1 - f_{n_j}) - f_{n_{j-1}} \frac{a_{n_{j-1}}}{a_{n_j}} - f_{n_{j+1}} \frac{a_{n_{j+1}}}{a_{n_j}} \\ &= F - f_{n_{j-1}} \frac{a_{n_{j-1}}}{a_{n_j}} - f_{n_{j+1}} \frac{a_{n_{j+1}}}{a_{n_j}}\end{aligned} \tag{9}$$

Since $y = n_j$, $f_{n_j}(\text{ideal}) = 1$, and from the definition of F, $(1 - f_{n_j})/1 = F$.

Equation 9 indicates that no absolute value for the fraction dissociated may be assigned. When the value of the absorptivity of SR_{n_j} is greater than that of either of the adjacent complexes, the error of measurement cannot exceed the fraction dissociated. Equation 9 may be expressed in terms of the slopes involved, by introduction of the definition of the slopes given in eq. 3

$$\frac{\Delta A}{A} = \frac{f_{n_{j-1}}(n_j - n_{j-1}) \text{ Slope 1} - f_{n_{j+1}}(n_{j+1} - n_j) \text{ Slope 2}}{a_{n_j}} \tag{10}$$

This equation may be further simplified by assuming that the concentration of R is negligible with respect to that of complexes $\mathrm{SR}_{n_{j-1}}$ and $\mathrm{SR}_{n_{j+1}}$. By considering only $\mathrm{SR}_{n_{j-1}}$, SR_{n_j} and $\mathrm{SR}_{n_{j+1}}$, and setting [R] equal to zero in eq. 6, rearrangement of terms gives

$$\frac{[\mathrm{SR}_{n_{j-1}}]}{[\mathrm{SR}_{n_{j+1}}]} = \frac{f_{n_{j-1}}}{f_{n_{j+1}}} = \frac{n_{j+1} - n_j}{n_j - n_{j-1}} \tag{11}$$

Since the complex SR_{n_j} is assumed to dissociate only into the adjacent complex species, then $F = f_{n_{j+1}} + f_{n_{j-1}}$. By use of the relationship shown in eq. 11, $f_{n_{j+1}}$ and $f_{n_{j-1}}$ can be eliminated individually from eq. 10 and thus an explicit expression can be obtained for the prevalence of each of the species. Summation of these expressions and rearrangement of terms gives the simplified expression

$$\frac{\Delta A}{A} = \frac{F(n_{j+1} - n_j)(n_j - n_{j-1})}{(n_{j+1} - n_{j-1})} \frac{\text{Slope 1} - \text{Slope 2}}{a_{n_j}} \tag{12}$$

This equation indicates that, for cases where the change of slope is small, extensive dissociation may be tolerated. Such cases represent measurements at wave lengths for which slight evidence for the existence of the complex will be observed, and therefore will be of little interest. When one or both of the adjacent complexes absorbs much more than the intermediate complex, it may be necessary to limit the effect of dissociation to values much smaller than the experimental error in order to obtain absorbances which do not deviate from those of the ideal curve. It is not possible, therefore, to set an absolute limit to the dissociation for this case. In order to establish some limitation for the applicability of the method, it is necessary to select some practical value for this relationship; we will assume the same value for the effect of dissociation as for the limiting value obtained when the complex absorbs more strongly than those adjacent, namely, F equals the experimental error.

It has been shown by Ayres[6] that the relative error of measurements made with the Beckman Model DU spectrophotometer may be limited to approximately 1% over a reasonable working range of concentration; the following calculations will be based on a maximum dissociation of 1%.

When the value of y corresponds to the mole ratio of the j-th complex, elimination of [S] between eq. 4 and 6 yields

$$M = \sum_{i=0}^{N} \frac{[\mathrm{R}]^{1+n_i}}{k_{n_i}} \Bigg/ \sum_{i=0}^{N} (n_j - n_i) \frac{[\mathrm{R}]^{n_i}}{k_{n_i}} \tag{13}$$

This equation represents an implicit function of [R] in terms of M and the dissociation constants in-

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(6) G. H. Ayres, *Anal. Chem.*, **21**, 652 (1949).

volved. For specific values of n_i and small dissociation, the equation may be solved for [R], and the limiting relationship between the constants and M can be determined. The explicit equation for [R] may not be determined for the general case, however, and since the final limitation on the dissociation constants is determined by the extrapolation method, specific solutions will not be considered for the concentration of R.

The minimum range of y from which extrapolation of the linear portion of the mole ratio curve may be made will vary with the slopes of these lines and with the intervals separating values of n. For this evaluation we will consider this minimum range as one-half of the interval separating adjacent complexes. On this basis for the j-th complex, the absorbance should conform to the ideal values at mole ratios indicated by

$$n_j - (n_j - n_{j-1})/4;\ n_j + (n_{j+1} - n_j)/4$$

At these mole ratios the value of [R] is determined by the ratio of the two principal components. For no dissociation at $y = n_j + (n_{j+1} - n_j)/4$, [R] obtained from eq. 5 is given by

$$[\mathrm{R}] = \left[\frac{[\mathrm{SR}_{n_j}]k_{n_j}}{[\mathrm{SR}_{n_{j+1}}]\,k_{n_{j+1}}}\right]^{\frac{1}{n_j - n_{j+1}}} = \left[\frac{3k_{n_j}}{k_{n_{j+1}}}\right]^{\frac{1}{n_j - n_{j+1}}} \quad (14)$$

If the dissociation, F, is limited to 1%, the resulting change in [R] may be neglected. The effect of the unassociated reactant R may be minimized if M is increased until $[\mathrm{R}]/n_jM$ is negligible with respect to $[\mathrm{SR}_{n_j}]$; but because of the buffering action, the contribution of reactant S and the remaining complexes may not be decreased below a limiting value determined by the separation of the dissociation constants.

The problem of selecting a permissible value for the fraction of SR_{n_j} dissociated is now more complex than when the mole ratio equals that of one of the complexes; at least four complexes must be considered as contributing to the absorbance. A value of 0.01 will be selected as a reasonable value for the permissible change in the fraction of the ideal quantity of S which is lost by SR_{n_j} to the other complex species, subject to further limitations for unusual relationships between the absorptivities. Assuming that only four complexes are present in significant concentrations, the following expression can be obtained from the definition of F

$$0.75MF = [\mathrm{SR}_{n_{j-1}}] + [\mathrm{SR}_{n_{j+2}}] + ([\mathrm{SR}_{n_{j+1}}] - 0.25M) \quad (15)$$

From a material balance for the concentration of R the value for the last term, $([\mathrm{SR}_{n_{j+1}} - 0.25M)$, is found to be

$$\frac{(n_j - n_{j-1})[\mathrm{SR}_{n_{j-1}}] - (n_{j+2} - n_j)[\mathrm{SR}_{n_{j+2}}] - ([\mathrm{R}'] - [\mathrm{R}])}{n_{j+1}} \quad (16)$$

where [R′] is defined as the concentration of R when the ratio is 3:1. The last term in eq. 15 can be neglected when M is large enough to make the concentration of R negligible.

By substituting the value of [R] from eq. 14 into eq. 5, the concentration of $\mathrm{SR}_{n_{j-1}}$ and of $\mathrm{SR}_{n_{j+2}}$ can be calculated

$$[\mathrm{SR}_{n_{j-1}}] = \frac{0.75Mk_{n_j}}{k_{n_{j-1}}}\left[\frac{3k_{n_j}}{k_{n_{j-1}}}\right]^{\frac{n_j - n_{j+1}}{n_{j+1} - n_j}} \quad (17)$$

$$[\mathrm{SR}_{n_{j+2}}] = \frac{0.75Mk_{n_j}}{k_{n_{j+2}}}\left[\frac{3k_{n_j}}{k_{n_{j+1}}}\right]^{\frac{n_j - n_{j+2}}{n_{j+1} - n_j}} \quad (18)$$

Bjerrum[7] has pointed out that from statistical considerations each successive molecule of complexing agent added will be less strongly bound than the preceding ones. On this basis, there should be expected a greater concentration of the n_{j-1} complex than of the higher complexes. The relative amounts of these complexes cannot be obtained unless the successive values of n are given, but it would appear conservative to assign one-half of the products of dissociation to the n_{j-1} complex. On this basis, eq. 15 becomes $0.75MF = 2[\mathrm{SR}_{n_{j-1}}]$. By introducing the resulting value for $[\mathrm{SR}_{n_{j-1}}]$ into eq. 17 and limiting the dissociation to 1%, it is found that the system will conform to the ideal case at the upper limit for extrapolation to $[\mathrm{SR}_{n_j}]$ so long as

$$\frac{k_{n_{j-1}}}{k_{n_j}}\left(\frac{k_{n_{j+2}}}{k_{n_j}}\right)^{\frac{n_j - n_{j-1}}{n_{j+1} - n_j}} \geq 200(3)^{\frac{n_j - n_{j-1}}{n_{j+1} - n_j}} \quad (19)$$

Similar calculations for the minimum value of the extrapolation range $y = n_j - (n_j - n_{j-1})/4$ yield the similar relationship for the ratio of the constants

$$\frac{k_{n_{j+1}}}{k_{n_j}}\left(\frac{k_{n_{j-1}}}{k_{n_j}}\right)^{\frac{n_j - n_{j-1}}{n_{j+1} - n_j}} \geq 200(3)^{\frac{n_{j-1} - n_j}{n_j - n_{j-1}}} \quad (20)$$

When $n_j - n_{j-1} = n_{j+1} - n_j$, the above relationship reduces to

$$\frac{k_{n_{j-1}}}{k_{n_j}} \geq 600\,\frac{k_{n_j}}{k_{n_{j+1}}} \quad (21)$$

The above value represents the minimum ratio between the successive stepwise dissociation constants which will allow the extrapolation method to be applied. Rather rigid limitations have been placed in the assignment of tolerances for a given measurement, and the method could undoubtedly be used to determine the stoichiometry of some systems which do not conform to the above criteria. It is doubtful whether accurate values for the absorptivities of the individual complexes may be obtained unless the system meets these requirements.

Reactions for which this method would be inapplicable may be divided into three classes: (1) systems for which an appropriate relationship does not exist between successive dissociation con-

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(7) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941, p. 24.

stants; (2) systems which meet the first requirement, but for which the concentrations may not be increased to values sufficient to limit the dissociation without either exceeding the solubility of some of its components or introducing significant changes in the activity coefficients of the components and (3) systems which satisfy the above requirements but whose absorbances limit the increase in concentration to values below those necessary to limit dissociation.

Reactions which fall into the first two categories may be studied by this method only if the properties of the system are modified, *e.g.*, by a change of solvent. For the third case, when the optical paths available are too long to permit measurements on solutions of the requisite concentration, it may be possible to extend the method by a differential technique. Following this approach, solutions of ratio $y + \Delta y$ would be measured against a reference sample containing a solution of ratio y, thus allowing an increase in the measurable concentration limit. By such a procedure, the curve obtained by plotting absorbance against y would approach constant absorbance values at y values intermediate between the mole ratios of any pair of complexes, and would undergo rapid transition in the immediate neighborhood of the complexes.

Use of the differential technique should prove satisfactory for the determination of the stoichiometry, but would be subject to serious limitations for the estimation of absorptivities of complexes. Hiskey and Young[8] have pointed out that when differential methods are used, deviations from Beer's law are accentuated both by the increased slit width necessary to balance the reference solution, and by the alteration in the energy distribution of the light transmitted by the reference solution. Values for absorptivities estimated from such measurements would generally be lower than the true values.

Deviations from Beer's law may sometimes give rise to spurious indication of complexes when the measurements are made in spectral regions where the absorptivities change rapidly with wave length. Since the absorbance is measured for radiation covering a finite band width, the measured values of low absorbances will be determined predominantly by the more strongly absorbed components of the radiation, while the measurements at high absorbances will approach the value corresponding to the component of least absorption. The resulting changes of slope might, in extreme cases, be interpreted to indicate the existence of a weak complex. Breaks arising in this manner will seldom be sharp and will always be concave downward. When the optical path is decreased, these deviations from Beer's law will lead to an increase in the slope of the mole ratio plot. Accordingly, a change in optical path length may lead to relatively sharp breaks in the curve. Such breaks will always be concave upward. The shape of the spectral curves and the spectral band width of the radiation should be considered, therefore, when the evidence obtained by the mole ratio method is evaluated.

For cases in which the mole ratio method may be used, it offers several advantages over the method of continuous variations. In the mole ratio method the amount of one of the reactants is held constant; this simplifies the preparation of solutions and facilitates the use of small volumes when one of the reagents is available in limited supply. In the ideal case, fewer than three solutions may be required for each complex present in the system, and some of these solutions correspond to those normally measured to select wave lengths for application of the continuous variations method.

The mole ratio method is especially suitable for determining the composition of high ratio complexes. For complexes of mole ratios of 4:1, 5:1 and 6:1, the abscissa values in the plot for the method of continuous variations are 0.800, 0.833 and 0.857, respectively. As a result, an error of 2% in the preparation of the solutions or in the estimation of the position of the maximum is sufficient to produce a unit change in the observed mole ratio. For the corresponding complexes, an error of from 6 to 10% is necessary to produce unit change by the mole ratio method. In the continuous variations method, the relative concentration of a particular complex is decreased with increasing divergence of the mole ratio from 1:1. This leads to more pronounced dissociation effects which produce definite translations of the maxima of the terminal complexes.[9]

In a study of the platinum(II)–tin(II) chloride system[10] the mole ratio method established the existence of a series of reaction products corresponding to seven different mole ratios of platinum to tin.

The mole ratio method as outlined is applied for a series of closely spaced wave lengths over as much of the absorption spectrum as possible. The Vosburgh and Cooper[5] modification of the method of continuous variations usually is confined to a limited number of wave lengths, the selection of which may be based on an assumed limitation to the number of complexes in the system. Thus, the mole ratio method provides more positive indication for the absence of any spectrophotometrically distinguishable complexes other than those proven to be present.

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(8) C. F. Hiskey and I. G. Young, *Anal. Chem.*, **23**, 1196 (1951).

(9) L. I. Katzin and E. Gebert, THIS JOURNAL, **72**, 5455 (1950).

(10) A. S. Meyer, Jr., and G. H. Ayres, *ibid.*, **77**, 2671 (1955).