value due to a loss of the complex by solution into the aqueous phase or by sublimation, the ratio E_{365}/E_{349} remaining constant within the limits of the measurements.

Attempts to produce similar changes in the absorption spectra of the chelates of zirconium, lanthanum and copper were unsuccessful by either the alkali or the sublimation experiments. It would appear, therefore, that the beryllium chelate may have an absorption spectrum that resembles that of the aluminum complex. The beryllium chelate, however, differs from that of aluminum in that it may also have an absorption spectrum characterized by a single maximum.

At present we do not have enough data to fully characterize the structure of these chelates; however, we feel that the observations presented are of sufficient importance to merit publication. Without this knowledge a beryllium sample may be misnamed aluminum should the investigator attempt to classify it on the basis of the absorption spectrum of its thenoyltrifluoroacetonate. This point is emphasized by the fact that once our beryllium sample gave directly the double-banded beryllium chelate. It may be that our solutions were not acid enough or that the temperature of the laboratory was too high.

Summary

Beryllium thenoyltrifluoroacetonate can exhibit two different spectra in solution, one of which resembles the TTA enol and absorbs maximally at about 350 mμ. The other resembles the aluminum chelate and absorbs maximally at about 350 mμ and 365 mμ.

OAK RIDGE, TENN. RECEIVED AUGUST 29, 1949

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

Spectrophotometric Methods of Establishing Empirical Formulas of Colored Complexes in Solution[1]

BY AUBREY E. HARVEY, JR.,[2] AND DELMER L. MANNING[2]

Various methods have been applied to the investigation of the empirical formulas of colored complexes in solution.[3–8] This paper presents an experimental comparison of the present methods of formula proof. A new method for determining formulas and a modification of the molar ratio method[8] are proposed. The applicability of these methods to the three complexes of ferric ions and disodium 1,2-dihydroxybenzene-3,5-disulfonate, trade name Tiron, and to the complex of ferric and thiocyanate ions was studied.

New Methods Proposed

Slope Ratio Method.—In the reaction

$$m\text{A} + n\text{B} \rightleftarrows \text{A}_m\text{B}_n$$

if the concentration of B is constant and in sufficient excess to make dissociation negligible, the equilibrium concentration of the complex A_mB_n will be essentially proportional to the analytical concentration of A added in the reaction; so

$$[\text{A}_m\text{B}_n] = C_\text{A}/m \qquad (1)$$

where the brackets refer to equilibrium concentration and C to the analytical or total concentration.

From Beer's law there is the relation

$$E = \epsilon d[\text{A}_m\text{B}_n] \qquad (2)$$

where E is the measured extinction, ϵ the molecular extinction coefficient and d the thickness of the cell in cm. Substituting the value of $[\text{A}_m\text{B}_n]$ from (1) into (2)

$$E = \epsilon d C_\text{A}/m \qquad (3)$$

E is plotted against different analytical concentrations of A, keeping the concentration of B constant and in excess. Over the straight line portion of the curve, equation (3) is valid and this straight line will have a slope given by

$$\text{Slope}_1 = \epsilon d/m \qquad (4)$$

Similarly if A is the component in constant excess and the concentration of B is varied

$$[\text{A}_m\text{B}_n] = C_\text{B}/n \qquad (5)$$

and if E is plotted against C_B, the slope of the straight line portion of the curve will be

$$\text{Slope}_2 = \epsilon d/n \qquad (6)$$

The ratio of n to m in the complex may be determined by taking the ratio of the two slopes

$$\text{Slope}_1/\text{Slope}_2 = n/m \qquad (7)$$

This method, in common with other spectrophotometric methods, serves only to establish the ratio of color forming radicals to the metal ion.

Modification of Molar Ratio Method.—Yoe and Jones[8] found that for a very stable complex a plot of optical density against molar ratio of component B to component A, with A constant, rose from the origin as a straight line and broke sharply to constant density at the molar ratio of the components in the complex.

However, a complex that undergoes appreciable dissociation in solution gave a continuous curve which became approximately parallel to the molar ratio axis only when an excess of the variable component was added. Results obtained by extrapolation of this curve are uncertain. It was found in the present investigation that in some cases such a curve may be made to break sharply at the correct molar ratio, if the ionic strength of the solutions is adjusted by the addition of an unreacting electrolyte. Thus the application of the molar ratio method may be extended by carefully controlling the ionic strength of the solutions.

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(1) Abstracted from the Master's Thesis of Delmer L. Manning, University of Louisville.

(2) Chemistry Department, University of Arkansas, Fayetteville, Ark.

(3) Job, *Ann. chim.*, [10] **9**, 113 (1928).

(4) Vosburgh and Cooper, THIS JOURNAL, **63**, 437 (1941).

(5) Bent and French, *ibid.*, **63**, 568 (1941).

(6) Molland, *ibid.*, **62**, 541 (1940).

(7) Edmonds and Birnbaum, *ibid.*, **63**, 1471 (1941).

(8) Yoe and Jones, *Ind. Eng. Chem., Anal. Ed.*, **16**, 111 (1944).

Experimental

Instruments.—Spectrophotometric measurements were made with a Beckman Quartz Spectrophotometer, Model DU, using 1-cm. Corex glass transmission cells, and operating at the maximum sensitivity of the instrument. A Beckman glass electrode *p*H meter, model F, was used for all *p*H measurements.

Reagent Solutions.—Stock solutions of Tiron, iron(III) and potassium thiocyanate were prepared in a concentration of 0.02 *M*. Solutions of other concentrations were obtained from these by dilution with distilled water. The potassium thiocyanate solution was standardized against silver nitrate. The Tiron solution was prepared by dissolving the commercial product in distilled water. The standard iron solution was prepared by directions already published.[9]

Buffer Solutions.—Buffers of *p*H from 4 to 6 were prepared by adding the proper amount of concd. HCl to a 0.5 *M* solution of sodium acetate. Buffers of *p*H 8.8 to 9.6 were prepared by mixing 0.2 *M* sodium hydroxide with a solution of 0.2 *M* boric acid in 0.2 *M* potassium chloride.

Electrolyte Solutions.—Solutions of potassium sulfate, 1 *M*, and of ammonium nitrate, 3 *M*, were used to control the ionic strengths of solutions.

Spectrophotometric Studies of the Complexes of Iron and Tiron.—The reagent produces three colors with ferric ions depending upon the *p*H of the solution; blue below 5.6, purple from 5.7 to 6.9 and red above 7.0. Yoe and Jones[8] have shown that the red complex is formed by three molecules of the Tiron coördinating with one ferric ion. However, their data on the blue complex were inconclusive and the formula of the purple complex was not investigated at all.

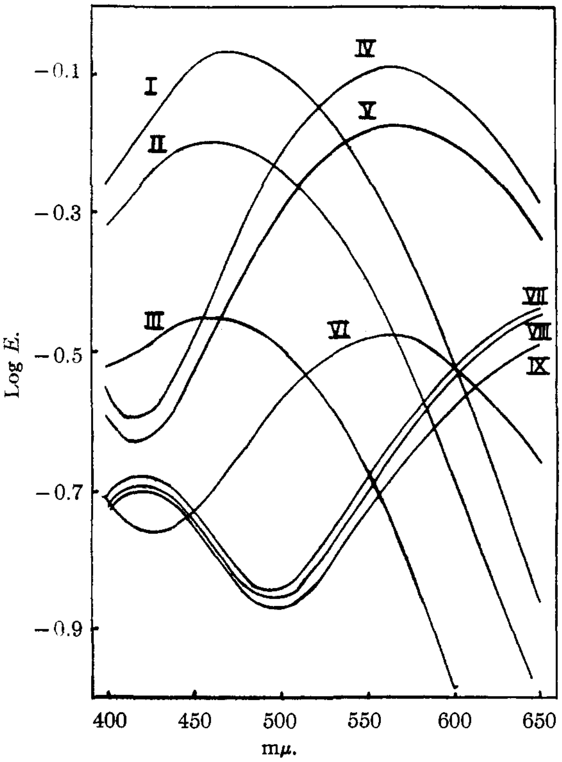
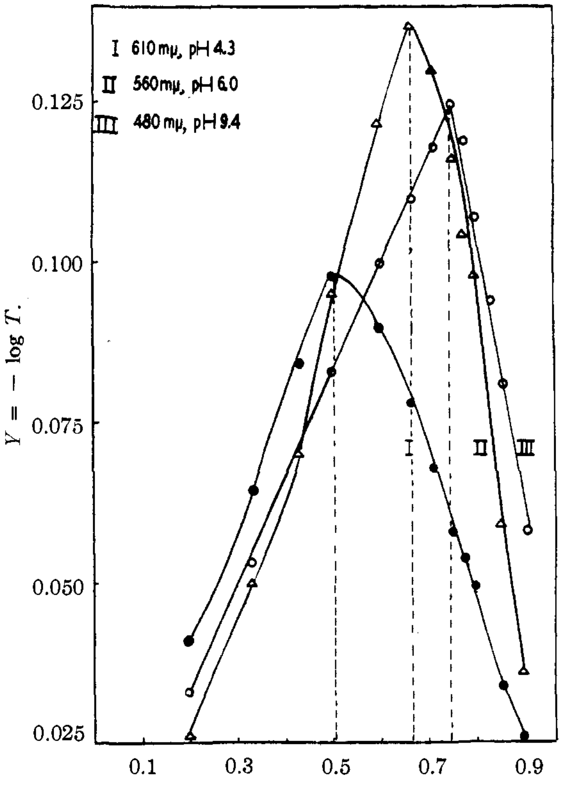


Fig. 1.—Iron complexes with 1,2-dihydroxybenzene-3,5-disulfonate: red form, *p*H 8.8, moles R:Fe, I 3:1, II 2:1, III 1:1; purple form, *p*H 6.0, moles R:Fe, IV 3:1, V 2:1, VI 1:1; blue form, *p*H 4.5, moles R:Fe, VII 3:1, VIII 2:1, IX 1:1.

Method of Continuous Variations.[10]—It was necessary to determine first whether, in a given *p*H range, iron and Tiron form more than one complex. Plots of log *E versus* wave length are shown in Fig. 1 for each of the color forms at different molar ratios. The curves obtained at different *p*H values show quite different characteristics, but the curves at a given *p*H may be superimposed on each other. This indicates that at each *p*H a different complex of distinctive color is formed with neither of the other complexes present in appreciable concentration.

The curves in Fig. 2 result from the application of the method of continuous variations to the determination of the formulas of the three complexes. The function *Y* which Vosburgh and Cooper[4] defined becomes in this case equal to the observed extinction since the ferric ions showed no absorption in the concentrations used and Tiron is colorless.[9] These curves indicate that the formulas of the blue, purple and red complexes are FeR, FeR_2 and FeR_3, respectively. The latter result is in agreement with the findings of Yoe and Jones.[8]



X, liters reagent added to (1 − *x*) liters equimolar Fe^{+++}.

Fig. 2.—Iron complexes with 1,2-dihydroxybenzene-3,5-disulfonate.

Slope Ratio Method.—For the study of each complex, two series of solutions were prepared. In one series the concentration of iron was varied in the presence of a constant excess of Tiron; in the other, Tiron was the variable and iron the constant component. The *p*H of the solutions was adjusted to the desired value by using 5 ml. of the proper buffer per 25 ml. of solution.

Color formation is immediate. In solutions with excess iron the blue complex, *p*H 4.0, showed marked fading after twenty-five minutes; fading of the purple complex, *p*H 6.0, was less pronounced. In solutions of the red complex, *p*H 9.6, hydrated ferric oxide precipitated if the excess iron

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[9] Yoe and Harvey, THIS JOURNAL, **70**, 648 (1948).

[10] The authors wish to express appreciation to Dr. John H. Yoe for allowing the reproduction of the data in this section from a thesis written under his direction at the University of Virginia.

exceeded a concentration of 20 × 10^{-5} *M;* no color formed if the Tiron concentration was less than 2 × 10^{-5} *M.*

Extinction measurements at the wave length of maximum absorption for each complex were made within twenty minutes after preparing the solutions. Slope ratios obtained from Figs. 3 and 4 are 1:1.02, 1.96:1 and 3.05:1 for the blue, purple and red complexes, respectively. In the case of the purple complex, a slope ratio of 2.05:1 was obtained when the ionic strength of the solutions was adjusted to 0.60 with potassium sulfate. These ratios of Tiron to iron agree with the formulas obtained by the method of continuous variations.

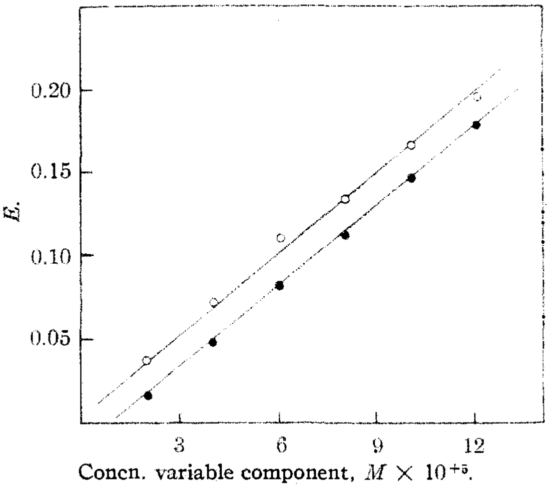

Fig. 3.—Slope ratio, blue complex of Fe and Tiron, *p*H 4.0, 620 mμ: ●, tiron varying; O, Fe varying; constant component 30 × 10^{-5} *M.*

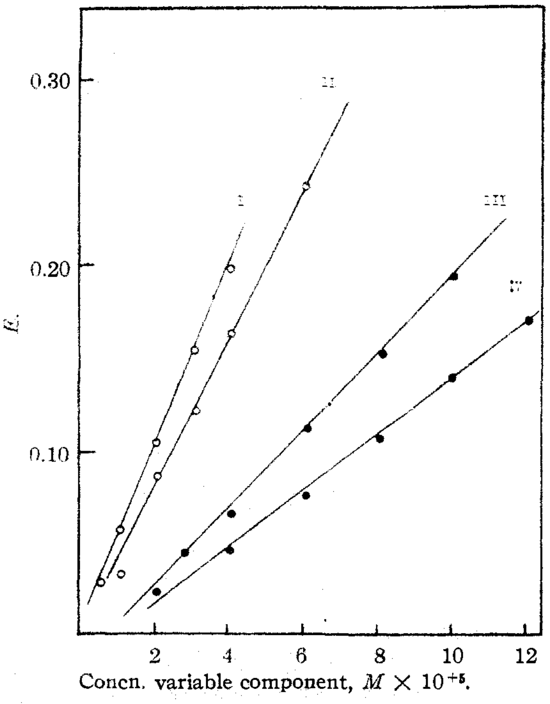

Fig. 4.—Slope ratio: ●, Tiron varying; O, Fe varying; I and IV red complex, *p*H 9.6, 480 mμ, constant component 20 × 10^{-5} *M;* II and III purple complex, *p*H 6.0, 560 mμ, constant component 30 × 10^{-5} *M.*

Modification of Molar Ratio Method.—The formula of the red complex was further investigated by this method. Two series of solutions were prepared with *p*H 9.6 and constant iron concentration of 8 × 10^{-5} and 4 × 10^{-5} *M*, respectively. Curves II and IV in Fig. 5 were obtained by varying the molar ratio of Tiron to iron. The curves show no sharp break at a molar ratio of 3:1, but rather a gradual sloping off to become parallel to the molar ratio axis at a higher ratio. The sloping portion of the curves beyond the 3:1 molar ratio of reagent to iron indicates that at concentrations of iron lower than those used by Yoe and Jones,[8] appreciable dissociation of the complex occurs. No definite formula can be assigned to the complex on the basis of these measurements.

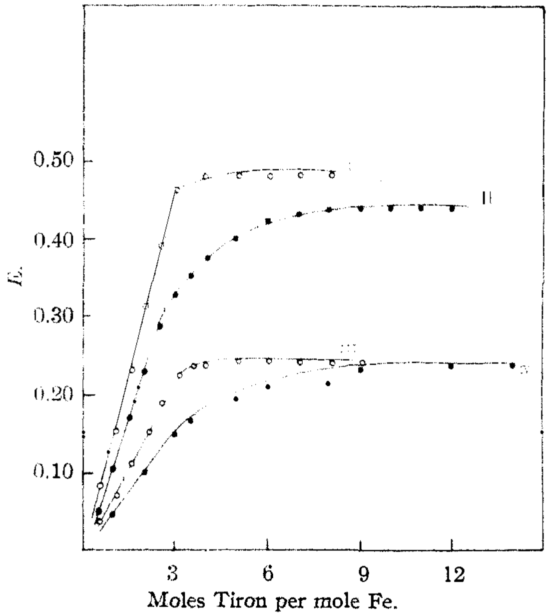

Fig. 5.—Molar ratio, red complex of Fe and Tiron, *p*H 9.6, 480 mμ; ●, μ not adjusted; O, μ 0.60; I and II, C_{Fe} 8 × 10^{-5} *M;* III and IV, C_{Fe} 4 × 10^{-5} *M.*

Solutions were again prepared as stated above, except the ionic strength was adjusted to 0.60 with potassium sulfate. Results are shown in Fig. 5, curves I and III. The curves break sharply from the linear at a ratio of 3 moles of Tiron to 1 mole of iron, becoming parallel immediately to the molar ratio axis. Thus the degree of dissociation of the red complex is considerably decreased by the addition of the electrolyte. Whether or not this result is to be expected on a theoretical basis, it is established experimentally in this case.

A similar study of the purple complex showed that its dissociation also decreased with increasing ionic strength. The molar ratio method with the ionic strength adjusted to 0.60 gave curves breaking sharply at a ratio of 2 moles of Tiron to 1 of iron. In the case of the blue complex, the curve broke sharply at a molar ratio of unity whether or not the ionic strength was adjusted.

Bent and French Method.—The authors are indebted to Dr. Bent[11] for a most helpful discussion of the material in this section. Application of this method to a study of the formulas of the purple and red complexes of iron and Tiron gives curves with limiting slopes of one; previous results having indicated formulas of FeR_2 and FeR_3, respectively. Bent and French stated that their method is only applicable to solutions in which the complex is highly dissociated. The great stability of the complexes in the present study makes it impossible to measure extinction values in one centimeter cells when the solutions are sufficiently dilute

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(11) H. E. Bent, private communications, 1949.

to cause appreciable dissociation in the presence of an excess of one component.

The limiting slope of unity obtained in this investigation may be explained from the following considerations. If the intensity of the color of a solution is a linear function of the concentration, C, of the variable component, a plot of extinction against concentration may be expressed by an equation of the form

$$E = mC \tag{8}$$

and therefore

$$\log E = \log C + \log m \tag{9}$$

Equation (9) indicates that a plot of log E against log C will give a straight line with a slope of unity. Conditions under which this linear relationship of equation (8) is obtained may be deduced. Assume the equilibrium

$$AB_n \rightleftharpoons A + nB\cdot$$

Let C denote total concentration added, brackets the equilibrium concentration and α the degree of dissociation. Assume that C_A is held constant and in large excess so that

$$[A] = C_A = \text{a constant} \tag{10}$$

It follows that

$$[AB_n] = (1 - \alpha)C_B/n \tag{11}$$

Since the extinction is directly proportional to $[AB_n]$, it will be a linear function of the total concentration of B in two cases: (1) When there is no appreciable dissociation, $\alpha = 0$. (2) When there is appreciable dissociation, but α remains constant as the concentration changes.

In the first case equation (11) becomes

$$[AB_n] = C_B/n \tag{12}$$

and a linear plot of E against C_B will result regardless of the value of n. Therefore an attempt to apply the Bent and French method will lead to erroneous results.

Secondly, if dissociation is appreciable, it may be shown that α can be constant only if $n = 1$. At equilibrium

$$[AB_n] = C_A[B]^n/K \tag{13}$$

$$[AB_n] = C_A(\alpha C_B)^n/K \tag{14}$$

and equating (11) and (14) gives

$$C_A(\alpha C_B)^n/K = (1 - \alpha)C_B/n \tag{15}$$

and if α is constant

$$C_B = K'C_B^n \tag{16}$$

Equation (16) can only be correct if n and K' are unity, whence

$$\alpha = K/(K + C_A) \tag{17}$$

If a ratio of unity is obtained experimentally, it is necessary to know the approximate stability of the complex being studied in order to be certain that a high degree of dissociation was obtained at the dilutions used. In this connection it is planned to investigate some of the more stable complexes at extremely high dilutions with greater cell widths.

Molland Method.—This method, applied to the study of the three complexes of iron and Tiron, was found to be valid only within the limits of concentration in which the extinction is a linear function of the concentration of the component not in excess. Molland[6] bases his method on the assumption that, with one component in excess, the maximum amount of complex will be determined by the other component. This assumption will be correct only when dissociation may be ignored. A series of measurements, as in the slope ratio method, is needed to show that, at the concentrations used, the extinction is proportional to the concentration of the variable component.

Edmonds and Birnbaum Method.—Because of the great stability of the complexes of iron and Tiron, the method of Edmonds and Birnbaum[7] cannot be used to investigate the formulas if extinction values are measured in 1-cm. cells. In this method the concentration of one component is held constant and the other component is added in such large excess that the amount used in complex formation is negligible. Extinction values obtained by varying the concentration of the excess component may be used in calculating the dissociation constant if the proper value of n in the complex AB_n is chosen.

In the case of stable complexes, when one component is in such large excess that its concentration is practically unchanged by the reaction, the extinction will remain constant as the concentration of this excess component is varied. Assume the reaction

$$AB_n \rightleftharpoons A + nB$$

the concentrations at equilibrium are

$$[A] = C_A - [AB_n],\ C_A = \text{constant} \tag{18}$$

$$[B] = C_B - n[AB_n] \cong C_B \tag{19}$$

the equilibrium constant is

$$(C_A - [AB_n])C_B^n/[AB_n] = K \tag{20}$$

$$[AB_n] = C_AC_B^n/(K + C_B^n) \tag{21}$$

When K is much smaller than C_B^n, equation (21) reduces to

$$[AB_n] = C_A = \text{a constant} \tag{22}$$

In applying the Edmonds and Birnbaum method, C_B^n must be of the same order of magnitude as the dissociation constant or smaller. This will require extremely high dilutions with the more stable complexes.

An examination of Fig. 5 will show that with Tiron in only a twofold excess of the stoichiometric concentration, the extinction has reached a constant maximum. This was also found to be the case for smaller concentrations of iron down to the limit which could be measured in 1-cm. cells. It is possible that working with wider cells at higher dilutions will extend the applicability of this method to more stable complexes.

Methods Applied to the Complex of Iron and Thiocyanate

Slope Ratio Method.—In deriving the slope ratio method, the assumption was made that the equilibrium concentration of the colored complex is essentially proportional to the analytical concentration of the component not in excess. When applying this method to a highly dissociated complex such as $FeCNS^{++}$, this assumption should be examined with care.

If the degree of dissociation of the complex be taken as α, equations (1) and (5) must be rewritten

$$[A_mB_n] = (1 - \alpha)C_A/m \qquad (23)$$

$$[A_mB_n] = (1 - \alpha')C_B/n \qquad (24)$$

When there is no appreciable dissociation, alpha may be neglected and equations (23) and (24) become identical with equations (1) and (5). When alpha cannot be neglected, it must still be constant over any range in which the extinction is a linear function of the concentration of either component. If α and α' are equal, they will cancel, giving the ratio of the slopes by equation (7).

Equation (16) shows that α and α' will be constant only when m and n, respectively, are unity, in which case α and α' are equal if the constant concentration is the same when either A or B are in excess (equation 17). The slope ratio method is reliable as long as linearity of the curves shows that the extinction is directly proportional to the concentration, provided that the concentration of the excess component is identical in the two series of measurements.

In applying the slope ratio method to ferric thiocyanate, the concentration of the excess component was 40×10^{-4} M; the molarity of the other component varying from 1×10^{-4} to 6×10^{-4} M. The solutions were 0.009 M in hydrogen ion with the ionic strength adjusted to 0.60. Extinction measurements were made at 460 mμ within twenty minutes after the formation of the color, which shows pronounced fading after about thirty minutes. These data gave linear curves with a slope ratio of 1.09:1, in agreement with the findings of other workers.

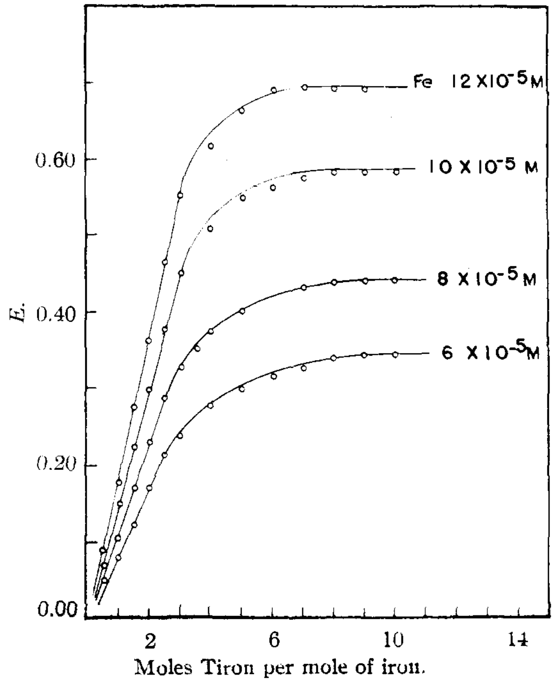

Fig. 6.—Effect of concn. on dissociation, red complex of Fe and Tiron: pH 9.6, 480 mμ.

Evaluation of the Equilibrium Constants

Complexes of Iron and Tiron.—Consider the dissociation to be expressed as

$$\begin{array}{llll} FeR_n \rightleftarrows & Fe + & nR & \\ C & 0 & 0 & \text{initial concentration} \\ C(1 - \alpha) & \alpha C & n\alpha C & \text{equilibrium concentrations} \end{array}$$

C is the total concentration of the complex in moles per liter assuming no dissociation, and α is the degree of dissociation. The equilibrium constant may be written as

$$K = (\alpha C)(n\alpha C)^n/C(1 - \alpha) \qquad (25)$$

The value n for each complex having been established, values of α and C for the red complex may be obtained from the curves in Fig. 6 by the following relationship

$$\alpha = (E_m - E_s)/E_m \qquad (26)$$

E_m is the maximum extinction obtained from the horizontal portion of the curve, indicating that all the iron is present in the form of the complex. E_s is the extinction at the stoichiometric molar ratio of Tiron to iron in the complex, the total concentration of the complex being equal to the concentration of the iron. Similar measurements were made for the purple complex. An average K of $(7.6 \pm 0.9) \times 10^{-14}$ and $(1.4 \pm 0.2) \times 10^{-9}$ was obtained for the red and purple complexes, respectively. The α values obtained for the blue complex are not reliable since the curves break sharply.

In determining the equilibrium constants given above, the fact that ferric ions also form complexes with hydroxyl or buffer anions was not taken into account. The values, however, serve to show the relative stability of the complexes.

Complex of Iron and Thiocyanate.—The Edmonds and Birnbaum[7] equation was used to calculate the dissociation constant for this complex, using only those extinction values obtained with the thiocyanate concentration in large excess. An average value for K of 0.017 ± 0.001 was obtained. This compares favorably with the value of 0.033 given by Bent and French.[5]

Summary

1. A new spectrophotometric method and a modification of the molar ratio method are proposed for establishing the formulas of colored complexes in solution.

2. The formulas FeR, FeR_2 and FeR_3 for the blue, purple and red complexes, respectively, of iron and Tiron have been determined by these methods. These findings have been verified by the method of continuous variations.

3. The new slope ratio method shows the formula $FeCNS^{++}$ for the ferric thiocyanate complex, which agrees with results reported by others.

4. The applicability to these complexes of other spectrophotometric methods for determining formulas has been investigated.. Certain limitations of these methods are discussed.

5. The dissociation constants for the complexes have been determined by spectrophotometric methods.

RECEIVED JANUARY 15, 1950

[CONTRIBUTION FROM THE PHYSICS DEPARTMENT, UNIVERSITY OF CHICAGO]

Overlap Integrals and Chemical Binding[1]

BY ROBERT S. MULLIKEN

I. Introduction

In their classical papers on the theory of valence, Slater and Pauling proposed the "criterion of maximum overlapping" of the bonding AO's (atomic orbitals) of two atoms for deciding what kinds of AO's should give the strongest bonds.[1a] Pauling[2] concluded that "the energy of a bond is about proportional to the product of the [strengths] of the bond orbitals of the two atoms," with "strength" defined as "the magnitude of the bond orbital in its angular dependence," that is, a number proportional to the value of the angular part of the bond orbital in the direction of the bond.[3,4] This index of bond-forming power has the value 1 for *s–s* bonds, $\sqrt{3}$ for $p\sigma$–$p\sigma$ bonds, and between 1 and 2 for $hy\sigma$–$hy\sigma$ bonds, where *hy* denotes any $s,p\sigma$ hybrid AO, with a maximum value 2 for *te–te* bonds (te = tetrahedral hybrid AO). The index is not defined for π–π bonds.

However, the *overlap integral S*, computed *at the experimental bond distance R* for the two AO's which overlap when a bond is formed, might reasonably be expected to form the basis of an even more satisfactory index of bond energy. This integral takes account of *both the radial and the angular properties* of the two AO's concerned, and *is a direct measure* of the extent of overlap of these AO's. It is defined by

$$S = \int \chi_a \chi_b \, dv \qquad (1)$$

where χ_a and χ_b stand for suitable normalized AO's of the two atoms *a* and *b* concerned. The integral is computed in terms of the coördinates of a single electron, and extends over all space. Its value is a function of the interatomic distance *R* as well as of the nature of the two AO's.

All overlap integrals have values between -1 and $+1$. The value of any overlap integral is zero for $R = \infty$, but increases as *R* decreases, provided the signs of χ_a and χ_b are suitably chosen. If χ_a and χ_b are *s* valence orbitals of two like atoms, then *S* steadily increases toward a limiting value $+1$ at $R = 0$ (*cf.* Fig. 1). For the hydrogen molecule at its actual bond distance, $S = 0.75$.

For $p\sigma$–$p\sigma$ bonds, if we choose the signs of χ_a and χ_b to be the same for the overlapping lobes of the two $p\sigma$ orbitals, then as *R* decreases, *S* first rises to a maximum, then falls again as the positive lobe of each orbital more and more overlaps the negative as well as the positive lobe of the other. For two identical atoms, $S = -1$ at $R = 0$, since χ_b then becomes identical with $-\chi_a$.

For the overlap of two like σ orbitals of *s,p hybrid* type, *S* behaves in a manner intermediate between that for *s* and that for $p\sigma$ overlap (*cf.* Fig. 1). For the overlap of π orbitals, *S* is always between 0 and $+1$, just as for *s* orbitals.

Partly because *S* might prove to be a useful index of bond energy, partly because *S* values are needed in quantum-mechanical computations on molecular electronic structures and spectra, Mrs. C. A. Rieke and the writer some time ago computed *S* values for several cases involving *s* and *p* AO's, supplementing previously existing calculations.[5] Later it was noted that the value of *S* for $p\pi$–$p\pi$ boron–boron bonds is remarkably large, and it was suggested that this might help in explaining the stability of certain boron hydrides.[6] It also seemed possible that a comparative study of overlap integrals in the first and higher rows of the periodic system might throw light on the relative weakness of multiple bonds in the latter.

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(1) This work was assisted by the ONR under Task Order IX of Contract N6ori-20 with the University of Chicago.

(1a) All AO's which have cylindrical symmetry about the bond axis are called σ AO's. This includes $s\sigma$ AO's (*i. e.*, *s* AO's), $p\sigma$AO's (often called *p* orbitals), and the various *s*, *p* hybrid AO's. Single bonds involve a pair of electrons in σ AO's. Double or triple bonds involve the use in addition to a σ pair of, respectively, one or two pairs of electrons in π AO's.

(2) *Cf.* L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939. For Pauling's index of bond strength see p. 78 and L. Pauling and J. Sherman, THIS JOURNAL, **54**, 1450 (1937).

(3) Pauling's index of bond strength involves the explicit assumption that Slater orbitals (including Slater's use of equal *Z* values for *ns* and *np* AO's) are adequate approximations for the AO's.[4]

(4) The effects of using more accurate AO's are discussed in Section III and in ref. 7.

(5) The results for C–C bonds in Table I were presented at a symposium some time ago, but only a descriptive abstract has hither to been published: R. S. Mulliken and C. A. Rieke, *Rev. Mod. Phys.*, **14**, 259 (1942).

(6) R. S. Mulliken, *Chem. Revs.*, **41**, 207 (1947).