[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

Complex Ions. I. The Identification of Complex Ions in Solution by Spectrophotometric Measurements[1]

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A method for the identification of compounds formed in solutions by reaction of two components has been described by Job.[2] The method is applicable to complex ions. The formation of many complex ions can be represented by the equation

$$A + nB \rightleftarrows AB_n \qquad (I)$$

in which A is a metallic ion and B may be either a molecule like ammonia or an anion. To determine n, solutions of A and B of the same molar concentration are mixed in varying proportions, and a suitable property of the resulting solutions is measured. The difference (Y) between each value found and the corresponding value of the property calculated for no reaction is plotted against the composition. The resulting curve (Y against composition) should have a maximum if the property measured has a larger value for the complex ion than for A or B, or a minimum if smaller. Job has shown that the composition at which the difference Y is a maximum bears a simple relation to n of Equation I and is independent of the equilibrium constant. This method has been called the method of continuous variations.

If the molar concentrations of the solutions of A and B are not the same, the position of the maximum in the curve is a function of the equilibrium constant as well as of n. If n is known and the stability of the complex ion not too great, the equilibrium constant can be determined.

The absorption of monochromatic light is a suitable property for this method, because complex ions are often differently colored from their components. Also, the absorption of light is proportional to the concentration of the absorbing species, which is one of the necessary conditions. Spacu and Popper[3] have used the refractive index also.

While Job's results for several complex ions seemed satisfactory, a series of mixtures containing cupric and bromide ions and another containing nickel ion and ammonia gave inconclusive results. Job noted that de Wijs[4] had found it necessary to assume the formation of three different complex ions from nickel ion and ammonia. In a later paper[5] he has shown that cupric and bromide ions form two different compounds and has pointed out that the method of continuous variations is not generally applicable when more than one compound is formed.

It seemed to the present authors that the method of continuous variations would be more useful if it could be readily ascertained in any particular case whether or not more than one compound is formed from a pair of components. It was also of interest to see what use, if any, could be made of the method when more than one complex ion is formed from the same components.

Theoretical

Let us assume, with Job, that substances A and B react according to Equation 1, and that solutions of A and B, both of concentration M moles per liter, are mixed in varying proportions. Let the mixtures be made by the addition of x liter of B to $(1 - x)$ liter of A ($x < 1$), with no appreciable volume change on mixing. Let c_1, c_2 and c_3 be the concentrations of A, B and AB_n, respectively. For any mixture the following equations apply

$$c_1 = M(1 - x) - c_3 \qquad (1)$$

$$c_2 = Mx - nc_3 \qquad (2)$$

$$c_1c_2^n = Kc_3 \qquad (3)$$

Activity coefficients are not needed in Equation 3 if A and AB_n are ions of the same valence type, and B is a non-electrolyte. The condition for a maximum in the curve of c_3 plotted against x is that

$$dc_3/dx = 0 \qquad (4)$$

Differentiation of Equations 1, 2 and 3 and combination of the three resulting differential equations with Equations 1 to 4 gives

$$n = x/(1 - x) \qquad (5)$$

Determination of the value of x for which c_3 is a maximum allows the calculation of n by Equation 5.

It remains to be shown that a maximum (or

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[1] Part of a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Arts and Sciences of Duke University, June, 1939.

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

[3] Spacu and Popper, *Bul. soc. stiinte Cluj* **7**, 400 (1934); **8**, 5 (1934).

[4] De Wijs, *Rec. trav. chim.*, **44**, 669 (1925).

[5] Job, *Ann. chim.*, [11] **6**, 97 (1936).

minimum) in the absorption of monochromatic light when x is varied coincides with the maximum of c_3. If ϵ_1, ϵ_2 and ϵ_3 are the extinction coefficients of A, B and AB_n at a given wave length, the optical density, d, is

$$d = l(\epsilon_1 c_1 + \epsilon_2 c_2 + \epsilon_3 c_3) \qquad (6)$$

where l is the length of path of the light through the solution.

Let Y be the difference between d of Equation 6 and the optical density that the solution would have had if there had been no reaction on mixing the solutions of A and B.

$$Y = l\,[\epsilon_1 c_1 + \epsilon_2 c_2 + \epsilon_3 c_3 - \epsilon_1 M(1 - x) - \epsilon_2 Mx] \qquad (7)$$

By differentiation of Equation 7 with respect to x it can be shown that Y is a maximum when c_3 is a maximum if $\epsilon_3 > \epsilon_1$, or a minimum when c_3 is a maximum if $\epsilon_3 < \epsilon_1$.

It has been assumed so far that only one complex ion is formed. Let us now suppose that a second complex ion is formed according to the equation

$$AB_n + qB \rightleftarrows AB_{(n+q)} \qquad (II)$$

Let the concentration of the second complex ion be c_4. A c_4 term must be added to Equation 1, another to Equation 2, and another equation added, namely

$$c_3 c_2^q = K' c_4 \qquad (8)$$

The condition for a maximum in c_3 can be shown to be

$$n = \frac{x}{1 - x} + \frac{q(q + n)c_4}{M(1 - x)} \qquad (9)$$

If the stability of the two complex ions is such that when c_3 is a maximum c_4 is small, n can be determined, provided that the maximum in c_3 can be found experimentally. Similarly, it can be shown that $(n + q)$ can be determined from the composition corresponding to a maximum in c_4, provided that at the maximum c_3 is small.

If three complex ions can be formed from the same two components, and if they are rather stable, the situation should not be much different than when only two are formed. When an appreciable amount of the third ion is present, the amount of the first should be small, and it is necessary to consider only two complex ions at a time.

The use of the optical density for the determination of the composition values corresponding to the concentration maxima is not as simple when two or more compounds are possible as when only a single compound is formed. If the extinction coefficient of compound B is assumed to be zero, which is often true in complex ion formation, the optical density of any of the solutions is given by

$$d = l(\epsilon_1 c_1 + \epsilon_3 c_3 + \epsilon_4 c_4) \qquad (10)$$

The difference Y, defined as for Equation 7, is

$$Y = l[\epsilon_1 c_1 + \epsilon_3 c_3 + \epsilon_4 c_4 - \epsilon_1 M(1 - x)] \qquad (11)$$

Differentiation of Equation 11 and combination with

$$\frac{dc_1}{dx} = -M - \frac{dc_3}{dx} - \frac{dc_4}{dx} \qquad (12)$$

(see Equation 1) gives

$$\frac{dY}{dx} = l\left[(\epsilon_3 - \epsilon_1)\frac{dc_3}{dx} + (\epsilon_4 - \epsilon_1)\frac{dc_4}{dx}\right] \qquad (13)$$

In general, the maximum (or minimum) value of Y will not coincide with the maximum in either c_3 or c_4, since it is not necessary for either dc_3/dx or dc_4/dx to be zero when dY/dx is zero. Furthermore, the value of x at which dY/dx is zero should vary with the values of the extinction coefficients and so with the wave length used.

However, there are some useful special cases in the application of Equation 13. If the wave length can be chosen so that $\epsilon_4 = \epsilon_1$ and $\epsilon_3 \neq \epsilon_1$, the maximum in Y corresponds to the maximum in c_3. Also, if the wave length is such that $\epsilon_3 = \epsilon_4$ the same is approximately true, provided that the complex ions are highly stable. The condition for maximum Y is then

$$\frac{dc_3}{dx} + \frac{dc_4}{dx} = 0 \qquad (14)$$

When c_4 and dc_4/dx are small, as they must be when c_3 is a maximum (if compound AB_n is highly stable), the maximum in Y corresponds approximately to the maximum in c_3.

It can be shown similarly that a slightly different Y-function is a maximum when c_4 is a maximum, provided that ϵ_4 is considerably larger than ϵ_3. Beyond the point of maximum AB_n concentration, as more B is added, $AB_{(n+q)}$ is formed from AB_n. If $\epsilon_4 = \epsilon_3$, this reaction causes no change in light absorption, but if ϵ_4 is enough larger than ϵ_3, the optical density of the solution will continue to increase after c_3 is a maximum in spite of the continuous dilution of the solution as B is added. Let us define Y' as the difference between the actual optical density and the density calculated on the assumption that all of the A has been converted to AB_n, but that the latter does not react further with B. Let us assume further that the complex ions are so stable that when considerable $AB_{(n+q)}$ is present, there is no appreciable A left uncombined. The condition for maximum Y' can then be shown to be

$$(\epsilon_4 - \epsilon_3)\frac{dc_4}{dx} = 0$$

and since $\epsilon_4 - \epsilon_3$ is finite, dc_4/dx must be zero and c_4 is either a maximum or a minimum.

Experimental

Formation of Dichromate Ion.—The above theory indicates that if two or more compounds can be formed from components A and B, the value of x at which Y is a maximum should vary with the wave length of the light used for the measurement. If only a single compound is formed, Y should be a maximum at a fixed value of x regardless of the wave length, provided that the extinction coefficient of the compound differs from that of the colored reactant. It should then be possible to determine whether or not more than one compound is formed, by use of several different wave lengths.

Before testing this conclusion with a pair of components that may be presumed to form more than one compound, it seemed desirable to try a pair that form only one. For this purpose potassium chromate and hydrochloric acid were chosen. The acid chromate ion $HCrO_4^-$ is a weak acid, but the first ionization constant of chromic acid is so large that a negligible amount of undissociated chromic acid would be present in a solution of acid chromate (and dichromate) containing only a small excess of hydrochloric acid.[6] It can be considered that practically the only reactions are

$$CrO_4^{=} + H_3O^+ \rightleftarrows HCrO_4^-$$
$$2HCrO_4^- \rightleftarrows Cr_2O_7^{=} + H_2O$$

The formation of the dichromate ion will not interfere with the method; the maximum concentration of dichromate ion must come at the same value of x as the maximum concentration of acid chromate ion. The maximum in both ions should come at the point at which equal volumes of the equimolar solutions of acid and chromate have been mixed. The maximum in Y should coincide with the composition maximum. These conclusions are strictly correct only if the ionic strength remains constant as the composition is changed, since activity coefficients should be included in the equilibrium equations. The activity coefficients, if constant, have no more effect on the position of the maximum than the equilibrium constant. However, constant ionic strength was not considered necessary in the present case, because the object was to test the effect of varying wave length.

A 0.1 M potassium chromate solution was prepared by weighing the required quantity of the recrystallized salt. Mixtures of this solution with 0.1 M hydrochloric acid solution were made in the proportions shown in Fig. 1, x ml. of acid solution being added to $(1 - x)$ ml. of chromate solution. The optical densities were measured at wave lengths 555, 545, 535, 525 and 505 mμ by means of a Bausch and Lomb spectrophotometer. Some additional measurements were made using 0.001 M solutions at wave lengths 470 and 410 mμ by the use of a Coleman Double Monochromator spectrophotometer with a 30 mμ slit.[7] Figure 1 shows the values of the difference, Y, between the measured density and that calculated from the density at the same wave length of the pure chromate solution assuming no reaction on mixing the two solutions. For most of the curves the Y-values have been multiplied by a factor (constant for a particular curve) to save space. All wave lengths gave a definite maximum or minimum at $x = 0.5$. This is what would be expected on the basis of the above theory for a pair of substances that react (appreciably) only in the molar ratio of one to one. The curve for 410 mμ has a minimum instead of a maximum because the extinction coefficient for the chromate ion is larger than that for the dichromate ion at this wave length

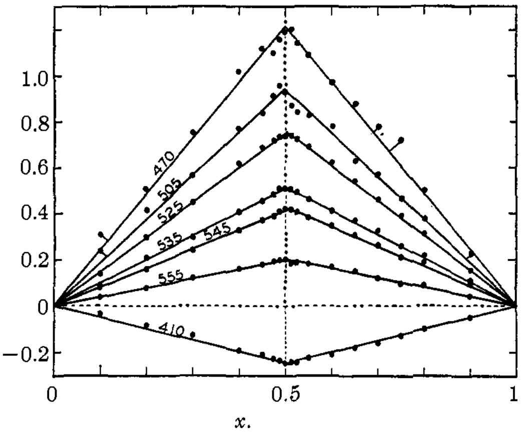

Fig. 1.—Difference Y for mixtures of equimolar solutions of potassium chromate and hydrochloric acid. The ordinates of most of the curves have been either increased or decreased for economy of space.

Nickel Ion and *o*-Phenanthroline.—Nickel ion may be expected to form more than one complex ion with *o*-phenanthroline in solution, since solid complex salts containing two and three molecules of the base to one atom of nickel have been prepared.[8] Also, copper complex salts containing one and two molecules of *o*-phenanthroline to one atom of copper have been prepared by Blau[8b] (page 683). It seemed possible that nickel ion might form complex ions with *o*-phenanthroline having coördination numbers (neglecting hydration) of two, four and six, as it does with ammonia according to de Wijs.[4]

Since *o*-phenanthroline is little soluble in water, it was not possible to prepare a solution of suitable concentration. To make a series of mixtures, $40(1 - x)$ ml. of 0.1 M nickel sulfate solution was diluted with $40x$ ml. of water and the amount of solid *o*-phenanthroline required for $40x$ ml. of 0.1 M solution was dissolved in the solution. The nickel sulfate had been treated for the removal of cobalt[9] and recrystallized. The *o*-phenanthroline was recrystallized.

The optical density of the solutions was measured at wave lengths 500, 525, 540, 550, 585, 611, 635 and 650 mμ by means of the Bausch and Lomb spectrophotometer

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(6) Neuss and Rieman, THIS JOURNAL, **56**, 2242 (1934).

(7) For these measurements the authors are indebted to Mr. Robert K. Gould.

(8) (a) Pfeiffer and Tapperman, *Z. anorg. allgem. chem.*, **215**, 273 (1933); (b) Blau, *Monatsh.*, **19**, 679 (1898).

(9) Deakin, Scott and Steele, *Z. physik. Chem.*, **69**, 126 (1909).

and a curve was drawn for each solution in order that interpolations could be made.

It will be apparent later, in agreement with theory, that a random selection of a single wave length for the determination of a curve similar to one of the curves of Fig. 1 would lead to unsatisfactory conclusions. In order to be able to select wave lengths in accordance with the theory, the absorption spectra were determined of solutions containing nickel ion and *o*-phenanthroline in the molar ratios 1:1, 1:2 and 1:3. They are shown in Fig. 2. If it is tentatively assumed that relatively stable compounds are formed in these ratios, wave lengths may be selected that should be suitable for testing the assumption. For the first compound, the wave length 620 mμ should be suitable, since at this wave length the 1:1 and 1:2 mixtures have the same extinction coefficient, and it may be presumed that the corresponding compounds have nearly the same extinction coefficient. The small absorption of the third compound at 620 mμ is favorable, also. Similarly for the second compound, the wave length 580 mμ should be suitable and for the third 528 mμ, since for the third it is only necessary that the extinction coefficient exceed that of the second as much as possible.[10]

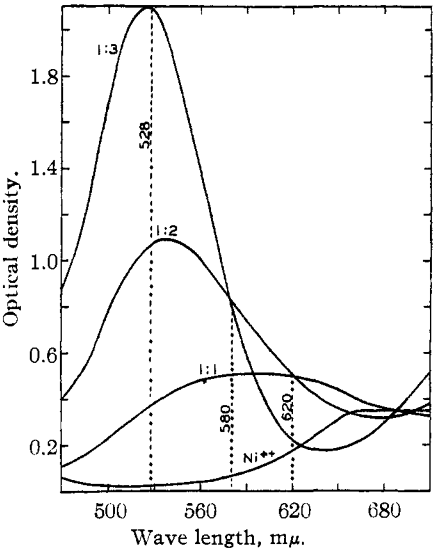

Fig. 2.—Absorption spectra of solutions containing 0.02 mole of nickel sulfate per liter and 0.02, 0.04 and 0.06 mole, respectively, of *o*-phenanthroline. The tube length was 4 cm.

At the appropriate wave lengths, density values were read from the above-mentioned curves for the mixtures of the 0.1 *M* nickel sulfate solution with water and phenanthroline. These densities were plotted against the composition *x*, giving the three curves of Fig. 3 that are labelled with wave lengths. The straight line in the lowest part of Fig. 3 represents the calculated densities for no reaction. The differences in ordinates between the density curve and the straight line were plotted against *x* giving the curve labelled *Y*. The difference *Y* has its maximum value when $x = 0.475$ which is as close to 0.50 as could be expected. This indicates the existence of an ion of the composition $Ni(phen)^{++}$.

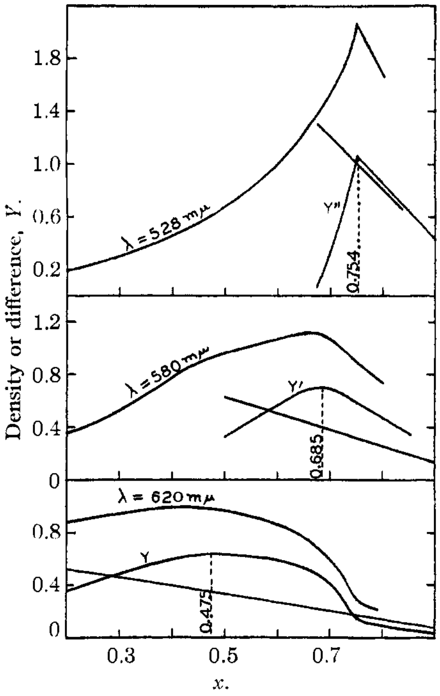

Fig. 3.—Absorption of mixtures of $(1 - x)$ liter of 0.1 *M* nickel sulfate solution with *x* liter of water and 0.1 *x* mole of *o*-phenanthroline for wave lengths 528, 580 and 620 mμ. The straight lines are calculated density curves for no reaction, and the curves *Y*, *Y'* and *Y''* show the differences between the density curves and the straight lines. The measurements were made in 10-cm. tubes and the measured densities were multiplied by 0.75 in plotting.

In the middle part of Fig. 3 the straight line gives densities calculated on the assumption that the ion $Ni(phen)^{++}$ is formed, but does not react with excess phenanthroline. The density of the hypothetical pure $Ni(phen)^{++}$ solution at $x = 0.5$ was calculated from the point on the density curve for wave length 580 mμ at which $x = 0.25$, together with the data for nickel ion from Fig. 2. Errors in this calculated density would have only a small effect on the conclusions. The difference curve for 580 mμ, labelled *Y'*, gives the difference between the other two curves as a function of *x*. The maximum comes at 0.685 as compared with the expected 0.667 for the ion $Ni(phen)_2^{++}$.

The upper part of Fig. 3 is enough like the middle part to need no special description. The maximum in the curve Y'' comes at $x = 0.754$ indicating the ion $Ni(phen)_3^{++}$. Curves similar to the *Y''* curve were constructed directly from the experimental densities for wave lengths of 500, 540 and 550 mμ and they were very similar to the *Y''* curve and had maximum values close to $x = 0.75$.

Nickel Ion and Ethylenediamine.—A similar series of experiments was carried out with nickel sulfate and ethylenediamine solutions. Three different ions may be ex-

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[10] This is true if no compound exists with a higher ratio of *o*-phenanthroline to nickel ion than one to three. Some more recent experiments have shown that a solution containing nickel ion and *o*-phenanthroline in one-to-four ratio gives a curve little different from the one-to-three curve of Fig. 2.

pected here also. Grossman and Schück[11] prepared thiocyanates with one, two and three moles of ethylenediamine per mole of nickel thiocyanate and Inoue[12] found evidence from absorption spectra of the existence of the three corresponding ions in solution.

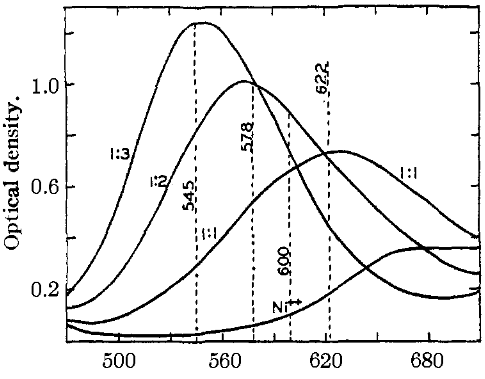

Fig. 4.—Absorption spectra of solutions containing 0.02 mole of nickel sulfate and 0.02, 0.04 and 0.06 mole of ethylenediamine per liter; tube length 4 cm.

The ethylenediamine was purified by fractional distillation. A solution was prepared and standardized by titration with standard acid, with methyl orange as the indicator. Solutions were prepared 0.02 *M* in nickel sulfate and in addition 0.02, 0.04 and 0.06 *M* in ethylenediamine, respectively. Figure 4 shows the absorption spectra of these solutions. Mixtures were then prepared of 0.1 *M* nickel sulfate and 0.1 *M* ethylenediamine solutions and the optical densities measured at several wave lengths. The Y-curves are given in Fig. 5. These were constructed in the same manner as the corresponding curves of Fig. 3, except that the density values were directly determined instead of being found by interpolation. The Y-curve for 622 mμ has a maximum at $x = 0.483$ indicating the ion $Ni(en)^{++}$. The Y' curve for 578 mμ has a maximum at $x = 0.67$ indicating $Ni(en)_2^{++}$, and two Y''-curves, for 545 and 530 mμ, have maxima a little beyond $x = 0.75$, indicating $Ni(en)_3^{++}$.

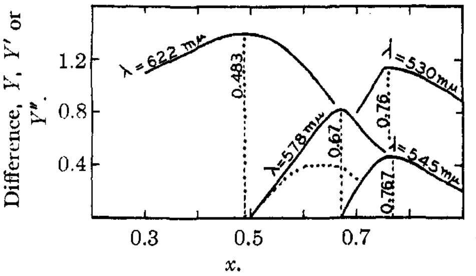

Fig. 5.—Differences Y, Y' and Y'' for mixtures of $(1 - x)$ liter of 0.1 *M* nickel sulfate and x liter of 0.1 *M* ethylenediamine. The dotted curve is for 600 mμ. The ordinates of the curve for 530 mμ have been increased by 0.60.

The dotted curve starting at $x = 0.5$ is the Y'-curve for wave length 600 mμ. Reference to Fig. 4 shows that this is an incorrect choice, since the one-to-three mixture has an appreciably smaller density at this wave length than the one-to-two mixture. The resulting Y-curve has a broad maximum between $x = 0.60$ and $x = 0.65$, and this does not correspond to any simple ratio of ethylenediamine to nickel ion.

The curve for 530 *mμ* was determined with 0.199 *M* solutions. Its ordinates were increased by 0.60 in plotting to avoid confusion. That the curves for both 545 and 530 mμ have maxima near $x = 0.75$ emphasizes again the fact that for the identification of the compound of highest B content any wave length that is absorbed considerably more strongly by this compound than by the others will be satisfactory.

Copper Ion and Ammonia.—Job[2] (p. 186) measured the absorption of a series of mixtures of a copper nitrate solution and an ammonia solution. His Y-curve had a maximum at $x = 0.8$ indicating the ion $Cu(NH_3)_4^{++}$. Since his measurements were made at only one wave length, 615 mμ, there was no evidence that this ion is the only one formed.

In addition to the ion $Cu(NH_3)_4^{++}$ there is reason to look for the ion $Cu(NH_3)_2^{++}$ because of the existence of complex salts containing one mole of dipyridyl or *o*-phenanthroline per gram-atom of copper[8b] and because of the evidence for the analogous nickel compound.[4]

The absorption spectra of a series of solutions containing 0.02 mole of copper sulfate, about 2.5 moles of ammonium sulfate, and from 0.02 to 0.12 mole per liter of ammonia are given in Fig. 6. The absorption spectra do not suggest the existence of more than two compounds, although more definite conclusions might be possible if the region of wave lengths longer than 710 mμ were available.

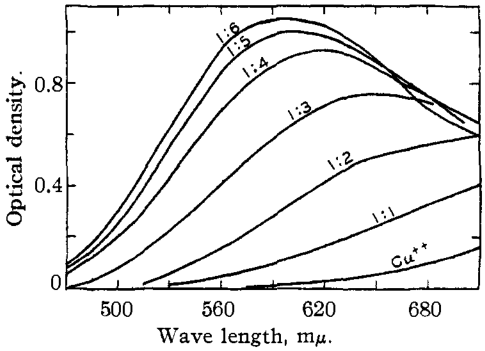

Fig. 6.—Absorption spectra of solutions containing 0.02 mole of copper sulfate, 0.02 to 0.12 mole of ammonia and 2.5 moles of ammonium sulfate per liter. The tube length was 1 cm.

If only the ions $Cu(NH_3)_2^{++}$ and $Cu(NH_3)_4^{++}$ exist, a variety of wave lengths should be available for confirmation of the tetrammine ion by the method of continuous variations, among them the 615 mμ used by Job. The diammine ion could only be found with a wave length in the vicinity of 710 mμ, where the absorption is nearly the same for several of the mixtures, particularly the one-to-two and one-to-six mixtures. Figure 7 shows the Y

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[11] Grossman and Schück, *Z. anorg. Chem.*, **50**, 4 (1906).

[12] Inoue, *J. Chem. Soc. Japan*, **54**, 65 (1933); *Chem. Abstracts*, **27**, 2382 (1933).

and Y' curves resulting from measurements of a series of mixtures of 0.104 *M* copper sulfate solution and 0.103 *M* ammonia solutions, with enough ammonium sulfate to prevent precipitation. Wave lengths 710 and 720 mμ led to maxima at x-values of 0.65 and 0.68, respectively, indicating the ion $Cu(NH_3)_2^{++}$. The curve for wave length 575 mμ has a maximum at 0.795, indicating the ion $Cu(NH_3)_4^{++}$. Wave length 545 mμ gave practically the same results as 575.

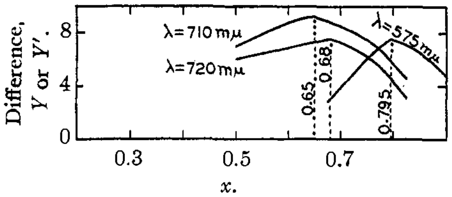

Fig. 7.—Differences Y and Y' for mixtures of $(1 - x)$ liter of 0.104 *M* copper sulfate and x liter of 0.103 *M* ammonia, and enough ammonium sulfate in both solutions to prevent precipitation. The ordinates of the curve for 720 mμ have been decreased by 0.10 in plotting.

Some measurements were made on solutions containing nickel ion and ammonia, but the results were less satisfactory than for copper. The complicated nature of the equilibria, combined with too low stability of the ions formed, was probably the reason. The results, as far as they went, were in agreement with the conclusions of de Wijs[4] concerning this system.

Discussion

As Job has pointed out,[5] the method of continuous variations is a simple and rapid method for determining the formula and also the stability of a compound provided there is assurance that only a single compound is formed from the components in question. The above observations give a method of determining whether or not more than one compound is formed, provided that the absorption of light is the property employed. It is only necessary to make measurements with a variety of wave lengths, covering the region of the spectrum absorbed. If all wave lengths lead to the same result, as in Fig. 1, it may be concluded that only a single compound is formed. One exception to this should be mentioned; a colorless compound might be overlooked if formed in addition to a colored one.

If more than one compound is formed, the method of continuous variations can still help in gaining information as to the formulas for the compounds, if the compounds are sufficiently stable. Caution is necessary in such cases, and the conclusions might well be held as provisional until checked by a quantitative method.

Indications are sometimes given by the shape of the curves in the method of continuous variations as to the existence of more than one compound. For example, Fig. 1 may be compared with the topmost curve in Fig. 3. The latter is convex toward the x-axis because the first compound formed when *o*-phenanthroline is added to nickel ion does not absorb much light of wave length 528 mμ. As x increases more and more of the strongly absorbing compound is formed at the expense of the first. Job's curve for copper sulfate and ammonia is similar in shape, as were also the corresponding copper–ammonia curves for wave lengths 575 and 545 mμ of this investigation. This is additional evidence for a compound of copper ion and ammonia with less than four moles of ammonia per gram-atom of copper.

Summary

The theory of the method of continuous variations as given by Job is reviewed and extended to cases in which more than one compound is formed from a given pair of components.

The method has been applied to the formation of acid chromate and dichromate ions as an example of the case where the components react in only a single ratio. It has been applied to the complex ions formed by nickel ion with *o*-phenanthroline and with ethylenediamine, and also to the complex ions of copper ion and ammonia, as examples of cases in which the components react in more than a single ratio. The absorption of monochromatic light was the property measured in each case. When only a single compound is formed, the results are independent of the wave length of the light used. When more than one compound is formed, the results obtained depend on the wave length of the light, and for useful conclusions the wave lengths used must be carefully selected.

Both *o*-phenanthroline and ethylenediamine unite with nickel ion in the proportions of one, two and three moles to one mole of nickel ion. Copper ion and ammonia form a complex ion with two moles of ammonia per gram atom of copper as well as the one with four.

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