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Demonstrating Job's Method with Colorimeter or Spectrophotometer

It is common practice in courses in instrumental methods of analysis to illustrate the use of any given instrument as a research tool rather than merely as a means of analysis. In recent years the determination of the formulas of complexes by Job's method of continuous variations employs the spectrophotometer as a valuable research tool. It appears to the author that an experiment designed to illustrate this application of the spectrophotometer would be a significant addition to the repertory of the teacher of a course in instrumental methods.

The method of continuous variations was worked out by Denison (*1*) in connection with his studies of compound formation in liquid mixtures. Later it was applied by Job (*2*) to the spectrophotometric determination of the formulas of complexes that are products of incomplete equilibrium reactions. The equation for such an equilibrium reaction may be written:

$$A + nB \rightleftharpoons AB_n$$

According to the principle of the method of continuous variations, when different amounts of A and B are brought together in solution with the imposed restriction that the sum of their *original* concentrations is in all cases a fixed, constant value, then the concentration of the complex produced *at equilibrium* will approach a maximum value as the ratio of the original concentrations $[B_0/A_0]$ approaches n.

In practice, equimolar solutions of the two reactants are mixed in varying ratios and the absorbance of each mixture is determined at the selected wave length. By the principle described above, the ratio that corresponds to the mole ratio of the components in the complex will have the maximum absorbance. (If either reactant is colored, the absorbance of each mixture must be corrected for the contribution made by this component). A plot of the (corrected) measured absorbance against the volume of either solution added, yields a curve with a maximum. From the position of the maximum on the graph one may easily determine the value of n and the formula of the complex.

Phillips (*3*) suggested the reaction between hydrogen ion and chromate ion,

$$2H^+ + 2CrO_4^{=} \rightleftharpoons Cr_2O_7^{=} + H_2O$$

which had previously been studied by Vosburg and Cooper (*4*), as suitable for the experimental demonstration of Job's method. Rossotti and Rossotti (*5*) have included this same reaction as one of two examples of the application of the method. The equilibrium constant of this reaction is of the order of magnitude of 4×10^{14}, and the reaction is quite complete even at the low concentrations specified. Reilley and Sawyer (*6*) describe a similar experiment involving the reaction between copper(II) ion and iminodiacetic acid, which also produced a complex of great stability. Land (*7*) uses the reaction between copper(II) ion and cupferron (phenylnitrosohydroxylamine) in an experiment designed to illustrate both Job's method and the use of the nephelometer as a research tool. In this case also, the reaction is quite complete since the product is only very slightly soluble in water.

Such determinations of the formula of a complex of high stability constant, like dichromate ion and copper-iminodiacetic acid do not require the employment of Job's method. Rather, the formulas may be determined just as easily by the application of analytical methods (volumetric, gravimetric, or colorimetric) based on exact stoichiometric relationships. However, in the case of complexes with low stability constants, reactions are incomplete. Accordingly, the concentration of the product in any mixture at equilibrium is a function not only of the original concentrations of both reactants, but also of the equilibrium constant. As a result, the application of methods based on exact stoichiometric relationships is precluded.

The method of continuous variations developed by Denison and applied by Job was designed, and has been used successfully, to determine the formula of the products of incomplete equilibrium reactions in solution. The importance of Job's method lies in its successful application to *equilibrium* systems and not in its application to systems which, because of the completeness of the reaction, can easily be resolved by the application of the common methods of analysis. It is true that there is nothing in the derivation of Job's method that precludes its application to a system in which the reaction is practically complete. However, the selection of such a reaction to demonstrate the use of Job's method is unfortunate in that it would tend to give a student a faulty notion of the basis for selecting the method in any given case.

The writer selected the equilibrium reaction between iron(III) ion and thiocyanate ion,

$$Fe^{+++} + CNS^- \rightleftharpoons FeCNS^{++}$$

as an example of the application of Job's method, principally because it is a well-known reaction and one that can be followed by the colorimeter as well as the more sophisticated (and more costly) spectrophotometer. Also, it serves to illustrate the utility and simplicity of the method as compared to other possible methods. Gould and Vosburg (*8*) employed the method to check the formula of this particular complex ion, which had been determined by Bent and French (*9*) and by Edmonds and Birnbaum (*10*) using much more complicated and time-consuming methods.

Procedure

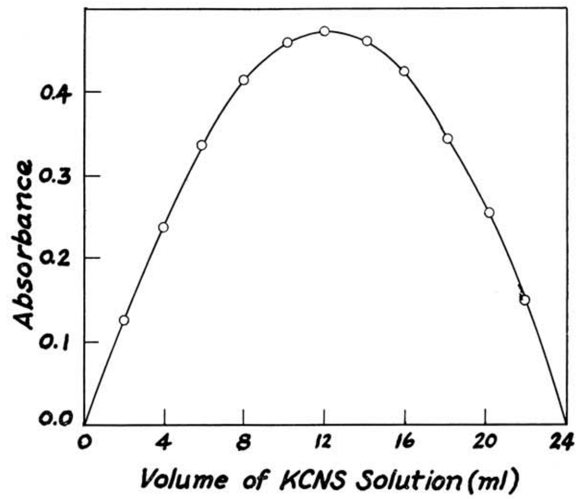
The experiment requires the preparation of two solutions:[1]

Solution (A): $Fe(NO_3)_3$, 0.00100 *M*
HNO_3, 0.010 *M*

Solution (B): KCNS, 0.00100 *M*
HCl, 0.015 *M*

The concentration of HNO_3 in solution (A) is sufficient to suppress most of the hydrolysis of the iron(III) ion. At the same time, it is not so great as to cause significant oxidation of the thiocyanate ion when the solutions (A) and (B) are mixed. The HCl is added to solution (B) to bring the ionic strength of this solution up to that of solution (A); viz; 0.016. The original ionic strengths of all mixtures of the two solutions would, accordingly, be the same. This is substantially true also for the equilibrium mixtures, since, under the conditions of the experiment, only a small fraction of the iron(III) ion is complexed in any one of them.

Nine 24-ml mixtures of solutions (A) and (B) are prepared with volume ratios varying from 2:22 to 22:2. The absorbances of the mixtures are measured and the values plotted against the volume of either solution in the mixtures. A plot of data obtained by one of our students is shown in the figure. The smooth curve in the region of the maximum is characteristic of an equilibrium reaction. This is in sharp contrast to that obtained when a reaction is complete, in which case the maximum occurs at the junction of two practically straight lines.



Absorbance of mixtures of equimolar solutions of KCNS and $Fe(NO_3)$ (total volume, 24 ml).

[1] The concentrations of the solutions of the reactants specified are those suitable for a colorimeter with an absorption path of approximately 1 in. For colorimeters with shorter absorption paths, correspondingly higher concentrations may be selected.

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