ON THE PROBLEM OF STEPWISE COMPLEX FORMATION*

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In a published paper [1] L. P. Adamovich and M. S. Novakovsky come out with a criticism of the method proposed by us for calculating the constants of unstable complexes in stepwise complex formation. Their objection reduces to the statement that "it is known from experiment that in the process of stepwise dissociation there can simultaneously cleave not 1, but several, for example, 2 ions". In such case the method proposed by us for calculating the instability constants is inapplicable. In connection with the above it is first of all necessary to mention that the remarks of the authors refer not only to the method proposed by us, but also to all of the other currently existing methods for calculating the instability constants in stepwise complex formation. Such methods are, for example, the methods of Bjerrum [2], Leden [3] Fronaeus [4] and others. Recently these methods have been subjected to thorough analysis and have been expanded further [5-7].

The possibility of forming all of the intermediate forms in the dissociation of a complex follows directly from the theory of stepwise complex formation, proposed by Bjerrum [2] and receiving expansion and support in the numerous studies of A. K. Babko. For some reason the authors of the mentioned paper were completely silent on this important point. Consequently, the discussion deals not only with the method proposed by us, but with all of the methods that currently exist for calculating the instability constants in stepwise complex formation, and even with the theory of stepwise complex formation itself. Finally, the authors indicate that contradictions exist in our published paper [8].

The statement made by us of the possible absence of certain intermediate forms in stepwise complex formation was highly conjectural and in part was based on our proposed attempt to interpret the data on the thermochemistry of the nickel ammine complexes [9]. Incidentally, we will mention here that a more thorough analysis of the experimental data convinced us that it is possible to interpret them by another method, without disturbing one of the basic tenets of the theory of stepwise complex formation.

To refute the basic tenets of the theory of stepwise complex formation some experimental facts should be presented (if the authors have such at their disposal), and not limit the discussion to the phrase that we cited above. However, the questions raised by the authors serve as evidence that actually some new methods should be found to verify experimentally the formation of all of the intermediate complex forms in stepwise complex formation.

It is possible that the formation and existence of intermediate complex forms can be verified by the method studying the absorption spectra in the infrared region and the Raman spectra. This method was recently used by Jones and Penneman to study the cyanide complexes of silver [10]. In this case the authors were able to conclusively show the existence of intermediate forms.

L. P. Adamovich and M. S. Novakovsky also state that "analysis of the $E\frac{1}{2}$ - log C relationship can lead to a demonstration of the existence of complex compounds with a definite coordination number only when considerable linear portions (corresponding, for example, to a change of 2 units in log C) are observed on the curve". Such should be encountered only in the absence of stepwise complex formation or with an enormous difference in the stepwise instability constants of the individual complexes (by several orders) [11]. In the vast majority of actual cases the stepwise instability constants differ by one to two orders, and in the systems there coexist two, three, or a greater number of complexes with different coordination numbers.

* In connection with the paper by L. P. Adamovich and M. S. Novakovsky "Problem of Determination of the Composition of Complexes by Stepwise Complex Formation," published in J. Gen. Chem. 25, 1308 (1955) (C. B. Translation p. 1253).

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