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CRITICAL EVALUATION OF EQUILIBRIUM
CONSTANTS IN SOLUTION
STABILITY CONSTANTS OF METAL
COMPLEXES

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INTRODUCTORY CHAPTER TO SERIES A OF THE
CRITICAL EVALUATIONS OF EQUILIBRIUM CONSTANTS IN SOLUTION

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CRITICAL EVALUATION OF EQUILIBRIUM CONSTANTS IN SOLUTION*
STABILITY CONSTANTS OF METAL COMPLEXES

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Stability constants of metal complexes are extremely important. In theoretical chemistry, relationships must often be found between such quantities and certain properties of the metal ion or the ligand. Stability constants are widely used in analytical chemistry in devising new methods or estimating interfering effects. They must also be considered in such areas as the kinetics of reaction in solution involving metal complexes; the biological effects of metal ions; etc.

The first and second editions of "Stability Constants" offer excellent sources of equilibrium data for metal complexes [64S]; in the second edition, data referring to 1029 organic and 80 inorganic ligands are listed. A supplement of approximately the same size has recently been published [71S]. As the aim was to give complete collections of published equilibrium data, the reliability of the tabulated data was not considered, although sometimes the compilers did express reservations. In comparing data obtained by different authors for the same system under approximately the same conditions, one frequently finds appreciable differences. As an example, a few "constants" referring to the stability of the tetracyanonickelate(II) complex are collected in Table 1.

TABLE 1

Stability constants of the tetracyanonickelate(II) complex

| <u>Method</u> | <u>log β_4</u> | <u>Ref.</u> |
|---------------------------------|---------------------------------|-------------|
| Electrode potential measurement | 12.5 | 31 M |
| Polarography | 15.5 | 36 S |
| Thermodynamic calculation | 22.0 | 52 L |
| Polarography | >24.0 | 50 H |
| Toxicity measurement | 30.0 | 56 D |
| Spectrophotometry | 31.1 | 59 F |
| Spectrophotometry | 31.5 | 61 M |
| Electrode potential measurement | 22.2 | 68 K |

This is an extreme example, but unfortunately there are many others in which there are differences of as much as an order of magnitude in the constants. Because of this, and the difficulty users of the tabulated constants often have in deciding which values to use, the IUPAC Commission on Equilibrium Data is sponsoring a series of critical surveys of stability constants. The present paper serves as the introduction to this series and outlines the criteria used in judging the reliability of published values. The main aim of the critical surveys is to help users of stability data who are not familiar with this fairly large field and who - seeing the widely diverging values-

* This is an introductory chapter to Series A of the Critical Evaluations of Equilibrium Constants in Solution undertaken by Commission V-6 of IUPAC, Analytical Chemistry Division. Professor Beck is the leader of this project. Series B is concerned with "Equilibrium Constants in Liquid-Liquid Distribution Systems" and is under the direction of Professor A. S. Kertes, Hebrew University of Jerusalem.

may mistakenly conclude that stability constants are not reliable in general.

When the stability constants for a given complex system are available two questions arise:

- 1) Do these adequately describe the properties of the given system?
- 2) Are there other sets of stability constants which describe the system equally well?

Although it is relatively easy to answer the first question, the possibility of alternative formation schemes and hence alternative sets of stability constants is sometimes difficult to exclude.

Even in the case of a simple system such as $\text{Pb}^{2+} - \text{Cl}^-$, polarographic measurements could be explained [54P] equally well by either of the following two sets of stability constants:

$$\beta_1 = 10; \quad \beta_2 = 20; \quad \beta_3 = 100; \quad \beta_4 = 10$$

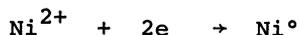
$$\beta_1 = 13; \quad \beta_2 = 0; \quad \beta_3 = 120; \quad \beta_4 = 10$$

The greater the number of complex species, the more difficult it is to find an unambiguous set of equilibrium constants. The different methods are not equally sensitive to the concentrations of different species, and it is possible therefore that different properties of the same system can be quantitatively explained by postulating different numbers of species. Hence it is not a necessary aim of equilibrium studies to find the least number of constants in terms of which one specific property of the system can be described. This statement does not contradict the principle of Occam's razor, because the real set of constants should be consistent with all reliably measured properties of the system. However, it would be even more dangerous if the only criterion for the reliability were "the best fit" of the calculated curve with experimental data. Only very careful consideration can decide which species exist in a given system.

The reliability of a stability constant is determined by the following factors:

- 1) adequacy of the experimental method
- 2) the precision of the experimental work
- 3) consideration of all relevant equilibria
- 4) the proper choice of the medium
- 5) the method of calculation
- 6) the reliability of the auxiliary data used.

The source of the greatest error is often the inadequacy of the experimental method used. In all cases the necessary data are provided by some measurement dependent on concentration. The relationship between the measured quantity and concentration has to be well defined. For example, from a measurement of the electrode potential one can calculate the activity of the solvated metal ion in question, assuming the validity of the Nernst equation. However, this equation is not valid if the electrode reaction is irreversible. The reason for the abnormally small values of β_4 for tetra-cyanonickelate(II) obtained potentiometrically* and polarographically is that the reaction



is not strictly reversible. Hence Hume and Kolthoff [50H] correctly considered their value as the lower limit.

* The value obtained by Kalani [68K] was evaluated from measurements using a nickel amalgam electrode. However, it is well known that nickel does not form amalgam and this example clearly shows that the most recent values are not necessarily the best.

Even the most careful experimental work cannot result in sound data if an inadequate method is used. However, even an ideally suitable experimental method will provide only poor data if the experimental work is not satisfactorily performed. It is necessary to work under well defined conditions: temperature, ionic strength and ionic composition, presence and amounts of organic solvents, etc. Minute amounts of foreign ions may interfere, so that the purity of the materials has to be checked. In the case of autoxidizable organic ligands (e.g. dithizone) it is particularly important to determine whether the compound is contaminated by oxidation products. If the central metal ion is of variable valency, the possibility of redox reactions must always be considered. When buffered solutions are used complex formation may occur between the central metal ion and the components of the buffer. In certain cases a disturbing side interaction may occur between the ligand studied and the buffer. In a study of mixed ligand complex formation in the Fe/III/-EDTA-H₂O₂ system, it was observed [62P] that, if the reaction was performed in solutions containing borax buffer, the absorbance due to the mixed ligand complex was much smaller than if the solution was adjusted to the same pH with ammonia. It was erroneously concluded that ammonia is essential for the development of a violet complex of composition Fe/III/-EDTA-H₂O₂-NH₃. The real explanation is that borate ion reacts with hydrogen peroxide leading to a decrease in peroxide concentration resulting in a smaller conversion of the iron/III/-EDTA complex to the intensely coloured mixed ligand complex, Fe/III/-EDTA-H₂O₂.

In the data provided by good experimental work using adequate methods, all the equilibria contributing substantially to the distribution of different species are reflected. Recently well-founded methods of calculation have been developed for practically all types of simple and complicated complex equilibria. In many cases the consideration of all the equilibria occurring would lead to unsurmountable difficulties, and some simplification is necessary to perform the calculations. The danger here is over-simplification. Mostly in the older papers, but sometimes even nowadays, one encounters the practice of taking into consideration only the stepwise formation of mononuclear binary complexes, while such types of equilibria as protonation of metal complexes, formation of polynuclear species and mixed ligand complexes, and the coordination of ligands in the outer-sphere, are disregarded. This practice may result in erroneous stability constants. For example, the stability constant of the iron/III/-EDTA complex was determined spectrophotometrically by following the effect of increasing acid concentration on the decomposition of the metal chelate [52K]. The value obtained is smaller by nearly two orders of magnitude than that determined by potentiometric measurements at higher pH [51S]. This difference cannot be accounted for by the difference in the ionic strengths. The reason for the discrepancy is twofold [60B]. First, in an acidic medium stepwise protonation of the iron chelate occurs; secondly, at lower pH the formation of positively charged EDTA species has to be taken into account. This example clearly shows that it is necessary to consider the basic character of all the donor groups of a multidentate ligand.

To illustrate the importance of side reactions, the determination of the stability constant of the bismuth/III/-1,2-diaminocyclohexanetetraacetate complex may be mentioned. The constant was determined polarographically, by following the competition between copper/II/ and bismuth/III/ in an acetate buffered medium at pH 4.3. The value obtained [61S] is less by seven orders of magnitude than the correct one [66B] evidently because formation of acetate and hydroxocomplexes of the two metal ions was not considered.

As is known, the formation curve is necessarily symmetrical if $N = 1$ or 2 . If $N > 2$, the formation curve is generally unsymmetrical; some symmetry of the formation curve indicates a particular relationship in the ratio of successive constants. However, Nagypál, Gergely and Jékel pointed out [69N] that from the formation curve certain other functions can be derived which exhibit symmetry if the assumption that only mononuclear binary complexes are formed is correct. As appears from Figs. 1 and 2, this approach is a very valuable tool for deciding the reliability of the constants. (One inherent difficulty of this method is that it cannot distinguish between the formation of inner-sphere and outer-sphere complexes having the same molar ratio of ligand: central ion.)

In applying stability constants to explain any property of a complex system, it is important to realize that the total concentrations of the

metal ion(s), ligand(s) and hydrogen ion should be within the relevant range in the equilibrium study. In other words, beyond certain concentration ranges, additional equilibria should be taken into consideration.

As was stated earlier, the stability constants are strongly dependent on the medium. It is fairly rare for complexes to be studied at an ionic strength low enough for the Debye-Hückel equation or its extended forms to be applied to calculate activity coefficients. If these equations are used to calculate the activity coefficients outside their valid ranges of ionic strength, the stability constants are not reliable and indeed stability constants of non-existent species may even be obtained. For example Kivaló [56K] found a very clean-cut set of constants for the species PbCl^+ , PbCl_2 and PbCl_3^- in a constant ionic environment. While working in a variable medium and supposedly making refined activity corrections, Papoff [55P, 56P] was obliged to postulate the presence of the species PbCl_6^{4-} in the series. The same experimental and computation techniques were applied by both authors. All chemical evidence suggests that under the experimental conditions used higher species ($n > 4$) are not present in appreciable concentration.

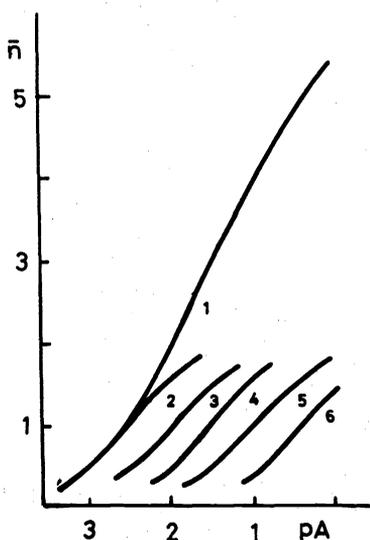


Fig. 1

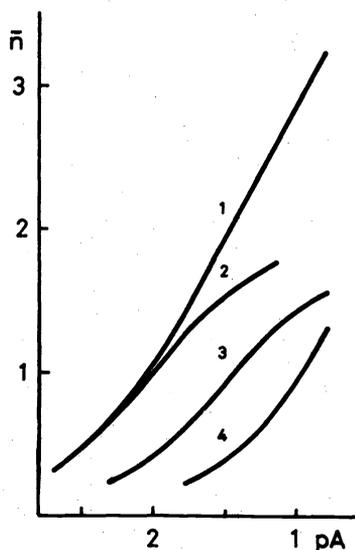


Fig. 2

Fig. 1 Experimental and partial formation curves of the Ni/II/-ammonia system.

1. Experimental formation curve;
2., 3., 4., 5., 6., Partial formation curves.

Note the symmetry of all the five partial formation curves which indicates that in this system only the stepwise formation of Ni/II/-ammine complexes need be considered.

Fig. 2 Experimental and partial formation curves of the Ce/III/-glycollate system.

1. Experimental formation curve;
2., 3., 4., Partial formation curves.

Note the full symmetry of the first and the almost full symmetry of the second partial formation curve. The asymmetry of the third partial formation curve indicates that at higher pH's hydrolysis takes place concurrently with the formation of the tris-/glycollato-/Ce/III/ complex.

In the case of weak complexes the only possibility of obtaining thermodynamically meaningful equilibrium constants is by application of the principle of constant ionic medium [52B]. According to this, the formation of complexes by gradual exchange of a small fraction of the inert swamping salt by the ligand involves a negligible change in the medium. Thus, a well selected salt solution may serve as the standard state. The most frequently applied constant ionic medium is 3 molar NaClO_4 . One must bear in mind, however, that both sodium and perchlorate ions can form complexes and for certain complexes other swamping salts must be used. The constants obtained from measurements in different well-defined ionic media as standard states cannot be directly compared with one another.

When a constant is determined by liquid-liquid distribution, one must take into account the fact that the standard state is not pure water or a given ionic medium but water/or the applied salt solution/ saturated by the organic solvent in question. Even if the organic solvent is not very soluble in water, fairly big differences may occur among the stability constants obtained by use of different solvents. For example, for the mono- and diperchlorato outer-sphere complexes of tris(1, 10-phenanthroline) ruthenate/II/ the following constants were obtained [74T] by applying chloroform as extractant: $K_1 = 240$ and $K_2 = 54 \text{ l mole}^{-1}$; while when acetophenone was used as extractant the widely different values $K_1 = 2,7 \cdot 10^5$ and $K_2 = 310 \text{ l mole}^{-1}$ were calculated. Preferential solvation is responsible for this behavior. On the other hand the good agreement between equilibrium constants which are obtained independently of the solvents used for liquid-liquid distribution experiments is a strong indication of the non-participation of the organic solvent in the solvation of the solute in the aqueous phase.

The most frequent error in the evaluation of experimental data is the abuse of Bjerrum's "half value" method. Although Bjerrum himself stressed the limitations of this approximation [41B], it is so rapid and simple that many authors cannot resist the temptation to apply it even when the system does not meet the necessary requirement that $K_1 \gg K_2$. If the K_1/K_2 ratio is less than 10^4 , the use of the half value method is associated with some error; if this ratio is less than 10^2 , the method cannot be applied. Unfortunately there are cases where this method is applied even when $K_1 < K_2$. The K_1/K_2 ratio can be simply obtained [66S] in the case of $N = 2$ from the values of the free ligand concentration relating to $\bar{n} = 0.5$ and 1.5 :

$$\frac{K_1}{K_2} = \frac{([\text{L}]_{1.5} - 3 [\text{L}]_{0.5})^2}{[\text{L}]_{1.5} \cdot [\text{L}]_{0.5}}$$

If $K_1/K_2 > 10^4$, the ratio

$$\frac{[\text{L}]_{1.5}}{[\text{L}]_{0.5}} = \frac{K_1}{K_2}$$

As the ratio of the constants gradually decreases, the ratio of the free ligand concentrations at the half-value points also decreases, but it must always be greater than or equal to 3. However, when $N > 2$, the ratio $[\text{L}]_{1.5}/[\text{L}]_{0.5}$ may be less than 3. If an experimentally found $[\text{L}]_{1.5}/[\text{L}]_{0.5}$ ratio is less than 3, this can be considered as an indication of an extreme relation of the successive constants. In such a case the "half value" method obviously cannot be applied.

Although the importance of the reliability of all the auxiliary constants used in the evaluation of stability constants need not be stressed again, it is particularly important to ensure that their reference states are in harmony with the experimental conditions used.

In judging the reliability of a stability constant, the different relationships found between such constants and the different properties of the metal ions and/or ligands, the comparison of a series of similar metal ions

and ligand analogues is extremely helpful. For example, the comparison of a large number of metal complexes of ethylenediaminetetraacetate and 1, 2-diaminecyclohexanetetraacetate indicates that the stability constant of the complex of a given metal ion with the latter ligand is greater by two or three orders of magnitude than that with the former ligand. This suggests that the stability constant of the bismuth/III/-1,2-diaminecyclohexanetetraacetate complex determined polarographically is probably not reliable. As a matter of course, very careful consideration is necessary before stating, as a result of comparison with other stability constants, that a particular constant is not reliable, because in some cases specific effects do occur. The aforementioned relationship between the metal complexes of aminopolycarboxylic acids is not valid for oxyanions. Molybdenum/V/ forms a well defined and fairly stable complex with EDTA but no complex formation could be detected with DCTA [67H].

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