

HANDBOOK OF CHEMICAL EQUILIBRIA IN ANALYTICAL CHEMISTRY

Stanislav Kotrlý
and
Ladislav Šúcha

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Foreword

It is a pleasure and a privilege to write an introduction to this book. The authors are both well known for their care and thoroughness in teaching the theory of analytical chemistry to students and applying it in research. They are also noteworthy for their ability to write a clear and accurate account of the ways in which stability constants and other physicochemical data can be used to elucidate the nature of the equilibria existing in solutions that are of interest to analysts and to research workers in inorganic and co-ordination chemistry. In this book they show the reader how to steer a safe course between the Scylla of inadequate chemical insight and the Charybdis of mathematical complexity. The various tables given cover most of the systems likely to be found in ordinary chemical practice, and will save the reader many excursions to the library and the reference books. The data given have been extracted from many sources and conscientiously checked against the original literature, and some of them have been recalculated *ab initio*; in this search for the 'best' values, Martell and Smith's invaluable compilation *Critical Stability Constants* (Plenum Press) was, of course, the yardstick used, and it was found that their selection of values could not be faulted. Professors Martell and Smith (and Plenum Press) have very generously given permission to use the values given in that collection.

The compilation of the tables was practically all done by Ladislav Šúcha, and Stanislav Kotrlý felt that Šúcha's name should be the first on the title page, but Šúcha would not agree to this. Šúcha's sad death during the final stages of preparation of the book precluded further argument, and his wishes have been respected, but Stanislav Kotrlý will join with me in saying that this book is a fitting and lasting monument to a very good friend and a fine and talented researcher and teacher.

R. A. CHALMERS
Aberdeen

CHAPTER 1

Chemical reactions and equilibria in analytical chemistry

Development of instrumentation, which has so profoundly changed science and technology over the past 30 years, has resulted in the introduction of numerous new instrumental methods and techniques for chemical analysis. Some of these methods of analytical determination are based on interaction between energy and the matter of the component to be determined in the sample; the need for a chemical reaction with an analytical reagent is thus eliminated from the finish of the analysis. Automated spectrometry (quantometry), which is widely used in metallurgy, is a typical example of such an instrumental method. However, most analytical methods and procedures currently used are still based on chemical reactions.

Reaction chemistry is important, especially for the following stages of chemical analysis. (1) Treatment of the sample in order to obtain a form suitable for further analysis; for many sample materials, dissolution in acids or fusion is necessary in order to convert the components into compounds soluble in water or another solvent. (2) Separation of individual components of the sample material. (3) The determination itself.

As can be seen, chemical reactions will remain indispensable for chemical analysis for the foreseeable future, and new inspiring applications that help to achieve higher selectivity or lower the limit of determination, often in combination with instrumental techniques, will be found.

Analytical chemistry is thus concerned with many aspects of the kinetics and thermodynamics of chemical reactions. From the view-point of chemical kinetics all chemical reactions applicable in analytical chemistry should proceed rapidly (best within the mixing time of reactants) and without formation of side-products, which implies a one-way reaction mechanism. Kinetic methods of chemical analysis represent an exception in this respect: determination of the concentration of a component is in this case based on a measurement influenced by the rate of the reaction.