

REACTIONS OF ACIDS AND BASES IN ANALYTICAL CHEMISTRY

ADAM HULANICKI

*Professor of Chemistry,
University of Warsaw*

Translation Editor:
MARY R. MASSON

*Department of Chemistry,
University of Aberdeen*



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**REACTIONS OF ACIDS AND BASES
IN ANALYTICAL CHEMISTRY**



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Table of Contents

Preface to the first Polish edition	9
Preface to the second Polish edition	11
Chapter 1—Introduction	
1.1 General remarks	13
1.2 Law of mass action	14
1.3 The concept of activity.	17
1.3.1 The Debye–Hückel theory	20
1.4 Equilibrium constants and other thermodynamic quantities	25
1.5 Methods of presenting the equilibrium constant	28
1.5.1 Conditional constants	30
1.5.2 Protonation constants	32
1.5.3 Compilations of data	32
Problems	33
Chapter 2—Properties of acids and bases in solution	
2.1 Dissociation of water	36
2.2 The ion-product of water	37
2.3 Dissociation of other solvents	38
2.4 The development of concepts of acids and bases	39
2.5 Brønsted–Lowry theory	40
2.6 Dissociation constants of conjugate acids and bases	43
2.7 Strong and weak acids and bases	47
2.8 Protolytic reactions	51
2.9 Polyprotic acids and bases	55
2.10 Amphoteric substances	59
2.11 Acids and bases in non-aqueous solvents	66
2.12 A scale of acidity and basicity—pH	69

2.13 pH and the activity of hydrogen ions	71
2.14 Acid-base indicators	74
2.15 Methods for measurement of pH in solutions	79
2.16 Acidity scales in other solvents	85
Problems	96
Chapter 3—Calculation of the pH in solutions of acids and bases	
3.1 Solutions of strong acids and strong bases	97
3.2 Calculation of the pH of strong acids and strong bases: general case	98
3.3 Solutions of weak acids	101
3.4 Solutions of weak bases	107
3.5 General cases of pH calculations for solutions of weak electrolytes	110
3.6 Buffer solutions	118
3.7 Buffer capacity	125
3.8 Preparation of buffer solutions	131
3.9 Solutions of polyprotic acids and bases	135
3.10 Acid-base equilibria involving metal ions	149
3.11 Mixtures of acids and mixtures of bases	160
3.12 Mixtures of acids and bases	164
3.13 Solutions of amphiprotic substances	170
3.14 Graphical methods for illustrating acid-base systems	173
3.15 Hammett's acidity function	187
Problems	192
Chapter 4—Theory of acid-base titrations	
4.1 General remarks	199
4.2 Titration of a strong acid with a strong base	200
4.3 General equation for the titration of a strong acid with a strong base	204
4.4 Titration of a weak acid with a strong base	207
4.5 Titration of a weak base with a strong acid	212
4.6 General equation for the titration of a weak acid or a weak base	214
4.7 Titration curves for polyprotic acids and mixtures of acids	219
4.8 Titration error	231
4.9 Precision of titrations	244
4.10 Location of titration end-points by use of indicators	250
Problems	255

Chapter 5—Acids and bases and the structure of molecules

5.1 Evaluation of acid–base properties from thermodynamic data	258
5.2 Dependence of acid–base properties on molecular structure	261
5.3 Some trends in the changes of acid strength in solutions . .	267

Chapter 6—Other theories of acids and bases

6.1 Solvent theory of acids and bases	270
6.2 The Lewis electronic theory	273
6.3 Pearson's principle of hard and soft acids and bases . . .	282
6.4 Usanovich's theory	286
6.5 Some reactions occurring in molten salts	287

Appendix	292
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Solutions of problems	298
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Bibliography	302
-------------------------------	------------

Subject index	305
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Preface to the first Polish edition

The aim of this book is to present acid-base reactions primarily in the context of the Brønsted-Lowry theory. The general foundations of that theory can be found in many Polish textbooks of analytical chemistry. However, one constantly comes across remnants of the Arrhenius theory in those textbooks, particularly in the treatment of the reaction traditionally called hydrolysis, and in some other, more complicated, cases. The present author's guiding idea was to avoid this duality, which, incidentally, is also common in the foreign literature.

The study and applications of acid-base reactions in analytical chemistry require knowledge of the states of thermodynamic equilibrium of the systems under consideration. The calculation of ionic equilibria, often elementary, presents difficulties in more complicated cases. Success can only be ensured by a systematic approach to problem solving, and a precise statement of those simplifying assumptions which make it possible to obtain the final result. Textbooks usually cover only the simplest cases of ionic equilibrium calculations. The next stage should be a full understanding of the equilibria, permitting results which give a better representation of the real state. The present book should be an introduction to such an approach, which is helpful in solving analytical problems.

The book was primarily written for junior students of chemistry. This can be seen most clearly in the initial chapters. Owing to their elementary character those chapters are a good introduction to the subject. The book also discusses some topics which might be considered either superfluous or too complicated for beginners. In order to be easily identified, the appropriate sections are marked with an asterisk in the table of contents and in the text. They are included in the book to provide a more detailed description of the basic problems concerning acid-base reactions.

Obviously, the book does not contain everything that might be relevant to its title. It deals with selected topics of a more fundamental character,

and intentionally leaves out the practical side, the methodology of analytical determination based on acid-base titrations, and a vast range of theoretical and practical problems relating to the influence of acid-base reactions on redox reactions, complexation, precipitation, and also catalytic, kinetic and other effects. To discuss these problems, even superficially, the book would have to grow into several volumes. However, it seemed useful to devote one chapter to other acid and base theories, which are extensions of the Brønsted and Lowry theory.

The general plan of the book is not based on any particular textbook, although many of the books listed in the auxiliary bibliography have influenced the presentation of the problems, suggesting ways for their formulation or exemplification. The final opinion as to whether the design of the book is appropriate is left to the readers, and especially to those who will be able to test its usefulness for teaching purposes. The author will appreciate any critical remarks in this matter. A considerable role in the preparation of the book has been played by Professor Wiktor Kemula, who was my teacher in the field of research and teaching over many years. I wish to thank him for numerous stimulating discussions and words of encouragement. I also thank Professor Jerzy Minczewski and Professor Antoni Swinarski for their valuable and kind remarks, which beneficially influenced the content of the book.

ADAM HULANICKI

Warsaw, April 1971

Preface to the second Polish edition

The warm reception of my book by the readers of the first edition has stimulated the preparation of a subsequent edition, which does not differ in general outline from the original version. The additions introduced in the present edition include a slightly more extensive treatment of acid-base ionic equilibria involving metal ions and also of problems arising from the increasing interest in reactions in non-aqueous solvents. However, since I regard usefulness in teaching during the initial years of chemical studies as the main aim of the book, I have abstained from expanding those problems too much, for fear of losing the proportions which—I believe—were just right in the first edition. For the same reasons I have only slightly expanded the final chapters, e.g. by briefly discussing the hard and soft acid-base theory.

In eliminating errors and obscurities I was greatly helped by the kind remarks of my colleagues and friends, mainly from the Institute of Fundamental Problems in Chemistry, Warsaw University. I wish to express my thanks to all of them. I am particularly indebted to Dr Marek T. Krygowski for his remarks concerning non-aqueous solvents. I also thank Professor Zygmunt Marczenko for his numerous constructive remarks. I am very grateful to Dr B. J. Kapłań of the Institute of Analytical Chemistry and Geochemistry in Moscow, who pointed out several defects in the work while preparing its Russian translation, and who helped in eliminating them. I wish to thank Mrs Zofia Boglewska-Bareja for her assistance in preparing the present edition.

ADAM HULANICKI

Warsaw, September 1977

Introduction

1.1 GENERAL REMARKS

The reactions of acids and bases, which we encounter in many chemical problems, particularly in analytical chemistry, are most familiar when they occur in aqueous solutions, although they can also take place in solution in other solvents, in molten salts and even in solids. The rules that govern these reactions are general rules for chemical processes. This introductory chapter reviews the elementary reactions and definitions, since they are necessary for a proper understanding of the subsequent chapters.

Reactions of acids and bases in solutions are fundamentally ionic reactions. Ions in a solution occur as a result of either dissociation of ionic compounds or ionization and dissociation of molecules with polarized covalent bonds. The crystal structure of an ionic compound (present in the solid state as an ionic crystal lattice) under the influence of molecules of water—a polar solvent—is broken down with formation of hydrated ions (aquo-ions). In an aquo-ion, the ion, which in a crystal lattice was surrounded by other ions, becomes surrounded instead by molecules of water. Such a process is observed for instance during dissolution of sodium chloride or sodium hydroxide.

Compounds with polarized bonds behave in a slightly different way, since under the influence of the dipoles of the solvent, their molecules become ionized as a result of a total displacement of an electron pair in the direction of a more electronegative atom, after which each ion becomes hydrated. In a dissociation process these ions become separated and exist in solution independently of one another. Such behaviour is typical of those covalent molecules which in solutions form strong acids, e.g. HCl. In many cases, despite the polarized character of the bond, many molecules are not completely ionized, and we do not observe complete dissociation in the solution. We then have solutions of weak, incompletely dissociated electrolytes. An example of such an electrolyte is hydrogen

sulphide. Complete dissociation of this acid requires agents stronger than molecules of water, e.g. hydroxide ions.

Reactions of acids and bases are in most cases reversible—they can be made to proceed in either direction by changing the concentration. This applies also to dissociation reactions of acids and bases in cases where the solution contains undissociated molecules. On the other hand, dissociation of strong electrolytes, for which undissociated molecules do not exist in solutions, e.g. NaOH or HCl, cannot be reversed. This holds for processes occurring in dilute solutions. It is formally expressed by using equations with a single arrow to denote the process of dissolving strong electrolytes. A double arrow \rightleftharpoons is used only when the reaction is reversible and when the molecules appearing in the equation are actually present in the solution.

It is characteristic of reversible reactions that a certain state of chemical equilibrium, which is a dynamic equilibrium, is reached. In a stage of dynamic equilibrium the rate of reaction from left to right is the same as that from right to left. As a result, the total concentrations of substrates and products do not change in this state, they characterize the state of equilibrium.

1.2 LAW OF MASS ACTION

The *rate of a chemical reaction* depends on the probability of collisions between the molecules present at a given instant in the space where the reaction takes place. Consider the reaction $A + B \rightleftharpoons C + D$; the rate of the reaction occurring between the molecules of A and B is proportional to their actual molar concentrations. If these concentrations, expressed in moles per litre, are denoted by the symbols in square brackets, then the rate of the reaction is given by

$$v_{A,B} = k_1[A][B] \quad (1.1)$$

where k_1 is the proportionality factor, called the reaction-rate constant. As the reaction progresses, the concentrations of reactants decrease, and this causes the reaction to slow down until it reaches the equilibrium state.

At the beginning of course of the reaction between A and B, the concentrations of the products C and D are negligible, but as more and more molecules of A and B react, the concentrations of the products increase. There is then, of course, a possibility of collisions between molecules C and D, and such collisions will result in formation of molecules of A and B, if the reaction is a reversible one. The rate of this reverse reaction de-

depends on the probability of collisions between molecules C and D, which is proportional to the concentrations of these molecules. Consequently, the rate of the reaction between C and D is given by

$$v_{C,D} = k_2[C][D] \quad (1.2)$$

and is small at first, but gradually attains higher and higher values. Finally, the rate of the reverse reaction becomes equal to the rate of the reaction between A and B, for the given composition of the mixture. The number of molecules A and B reacting in unit time is then equal to the number of molecules of A and B formed as a result of the reaction between molecules C and D. This final rate determines the final composition of the reaction. It can be measured directly from measurements of changes in the concentrations of products (or reactants) in unit time.

The rates of the two reactions become equal at chemical equilibrium, which, as previously stated, is a state of dynamic equilibrium. At equilibrium, $v_{A,B} = v_{C,D}$, and hence

$$k_1[A][B] = k_2[C][D] \quad (1.3)$$

or

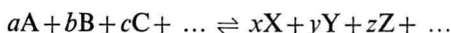
$$K = \frac{k_1}{k_2} = \frac{[C][D]}{[A][B]} \quad (1.4)$$

The statement that the rate of a chemical reaction is proportional to the actual concentrations of reactants is the essence of the law of mass action, formulated by Guldberg and Waage in 1863. This law implies that for the state of equilibrium the ratio of the product of the concentrations of species formed to the product of concentrations of reactants is a constant quantity, characterizing a given reaction at a given temperature. This quantity is called the *equilibrium constant*.

An analogous argument applies to the reaction $2A \rightleftharpoons C + D$. The equilibrium constant will then be expressed by

$$K = \frac{[C][D]}{[A][A]} = \frac{[C][D]}{[A]^2} \quad (1.5)$$

In the most general case,



the equilibrium constant is expressed as:

$$K = \frac{[X]^x [Y]^y [Z]^z \dots}{[A]^a [B]^b [C]^c \dots} \quad (1.6)$$

The equilibrium constant derived on the assumption of a certain reac-

tion mechanism remains valid whatever the mechanism of the reaction, provided that all the steps are reversible reactions. If, for instance, the product ABC_2 were formed from reactants A, B and C, then one of many possible mechanisms could be assumed, e.g.:



The equilibrium constant of each of these reactions would reflect the situation at the general equilibrium state. Hence the product of the equilibrium constants at each stage

$$K_1 = \frac{[AC]}{[A][C]}, \quad K_2 = \frac{[BC]}{[B][C]}, \quad K_3 = \frac{[ABC_2]}{[AC][BC]}$$

would be equal to the general equilibrium constant:

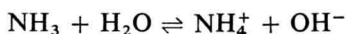
$$K = \frac{[ABC_2]}{[A][B][C]^2} \quad (1.7)$$

The law of mass action and the concept of the chemical equilibrium constant are applicable to all reactions which can be considered reversible, in particular to ionic reactions, e.g. to dissociation reactions. Consequently, if a molecule AB in an aqueous solution dissociates into ions A^+ and B^- , then the equilibrium constant for the reaction is equal to

$$K = \frac{[A^+][B^-]}{[AB]} \quad (1.8)$$

where the symbols of ions in square brackets denote the actual concentrations of ions at the state of equilibrium.

Equilibrium constants can characterize a variety of kinds of chemical reactions occurring between substances in various states of aggregation. Under certain conditions, the concentrations of some substances may be effectively constant; then they do not have to be taken into account in the equation of the equilibrium constant. For instance, for a reaction taking place in aqueous solution in which molecules of water are reactants



we can write the equilibrium constant as

$$K = \frac{[NH_4^+][OH^-]}{[NH_3]} \quad (1.9)$$

by omitting the concentration of H_2O , which is practically constant in an aqueous solution, and so can be included in the value of the constant.