Complex ions in aqueous solutions

Jaques Arthur
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Author: Jaques Arthur

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PREFACE

In compiling this volume the needs—and criticism—of a large class of students versed in physical chemistry have been especially kept in view, and it is considered that the introduction of some elementary matter, such as proofs of formule, which the advanced reader will not require, is by no means out of place.

In giving an account of the methods in Chapters III.—VI., it was found necessary to introduce examples, but these were made as brief as possible in order to avoid confusing these chapters with the later ones which deal with practical investigations, where more than one method is generally used at a time. The tension experiments in Chapter VIII. form a method of investigation in which the examination of different salts shows so little variation that it appeared unnecessary to devote a separate chapter to the method.

The chief aim of the book is to give some account of the more important experimental work in this subject, and no apology is offered for the absence of theories of valency.

Chapter X. contains an account of some results besides the identification of complex compounds, which have been arrived at by similar methods, and which are likely to form the basis of further experiments.

A. J.

Polmont,
Stirlingshire,
May, 1914.
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CHAPTER I

INTRODUCTION

A. Introductory.

The suggestion that the abnormal behaviour of certain electrolytes might be accounted for by assuming the formation of complex ions in them was first put forward by Hittorf, who, in the course of his study of migration, made the classical discovery that the migration ratio for the anion in solutions of many double salts and certain single ones increased rapidly with increase in the concentration of the solution and at high concentrations became greater than unity. Hittorf suggested that this was due to the formation of a "double salt" in the solution, which gradually dissociated on dilution. In this way our knowledge of the mode of ionisation of a number of salts in solution was established.

Later, the subject was investigated by other methods, notably by pure chemical means and by cryoscopic measurements. The latter method, however, yields somewhat uncertain results.

A new method was introduced by Roloff (Zeit. phys. Chem., 13, 341 (1894)), who measured the distribution ratio of a solute between two solvents, and showed that the increase in the solubility of bromine in water observed on adding potassium bromide to the system is due to the formation of the complex ion Br₃⁻. Two years later Jakowkin (Zeit. phys. Chem., 20, 19 (1896)), employing the same method, found that solutions of iodine and potassium iodide show similar behaviour.

In the last fifteen years two new methods of investigating
the constitution of electrolytes have been worked out, the first based upon solubility measurements and the second upon measurements of electrode potential, and a large number of complex ions have been discovered and studied by these methods. Much of this work was carried out by the late Professors Abegg and Bodländer and their pupils.

Such investigations are likely to be of value in framing a theory of chemical combination in the future. For in complex ions we have a class of compounds in which valencies other than the normal valencies of the elements entering into them are exercised, and whose dissociation constants can in some cases be measured, so that we can gain some information about the action of these weaker valencies.

An ingenious theory of valency which is specially applicable to the formation of so-called molecular compounds (including complex ions) has been constructed by Abegg and Bodländer (Abegg and Bodländer, *Zeit. anorg. Chem.*, 20, 471 (1899); Abegg, *Zeit. anorg. Chem.*, 39, 333 (1904)). According to this theory, the tendency which an element exhibits to form complex compounds depends largely upon its electroaffinity, i.e. the free energy with which it takes up an electric charge and becomes converted into an ion. It is assumed that the electrolytic potential is an approximate measure of this quantity, though, as Abegg and Bodländer point out, this would only be true if the concentration of free atoms in saturated solution were the same for all elements. Actually, nothing at all is known of the relative solubilities of the metals in water, and in the case of oxygen and the halogens it is very unlikely that at a given pressure the concentrations of the free atoms in aqueous solutions are equal. It is, however, true that, generally speaking, the less the electrolytic potential (either positive or negative) of an element, the greater is its tendency to enter into complex compounds. The electrolytic potential also shows a certain relationship to the atomic volume, the two quantities being roughly parallel in any given group in the periodic system. In the horizontal rows, the electroaffinity shows a continuous