

A Survey of the Scientific Papers of Niels Bjerrum

For the orientation of the reader, it will be attempted in the following to give a short review of Niels Bjerrum's activity in different branches of chemistry. It has been tried to follow the order indicated in the table of contents, without regard to the chronological order. The latter appears from the bibliography which follows this survey.

Most of the papers are translated from Danish, French, or German. The translations have been supervised by members of the editorial committee or have, in a few cases, been made by members. All of them have been revised by the secretary.

History of Chemistry. Bjerrum has written a few articles on the history of chemistry. They are not intended to be historical investigations in the strict sense of the word, but are reviews of the development of chemistry seen with the eyes of one of our outstanding chemists. One of them has been reprinted here as an appropriate introduction to this collection.

Chemical Physics. Early in his career Bjerrum gave contributions to the application of classical mechanics and the quantum theory to the constitution and the optical and thermal properties of molecules. These contributions must now be considered classical, and it only enhances their value that since then an immense number of papers which follow his trend of thought have been published by scientists all over the world. Bjerrum's papers on this subject are reprinted in this book with only one exception.

Physical Chemistry. Physical chemistry has always played a dominant role in Bjerrum's production. In some of his works the theories of physical chemistry are the main object of his studies, while in others physico-chemical measurements are used as tools for the elucidation of problems in chemistry or as an aid in the solution of technical problems in chemistry, analytical or applied, especially to agricultural problems. It may be mentioned in this connection that Bjerrum has been professor of chemistry at the Royal Veterinary and Agricultural College of Denmark since 1914.

First of all Bjerrum is the originator of the idea that many electrolytes, almost all salts, some acids, and some hydroxyl compounds are in the dissolved state practically completely dissociated in ions.

This idea was advocated in 1909 in a paper reprinted here, and in 1916 it was followed up in more detail. The paper, also reprinted here, was read in Kristiania (now Oslo) at the 16th meeting of Scandinavian scientists. Those present on that occasion still remember the attention aroused by the lecture. We also remember that Arrhenius, who was in the chair, did not seem to be very pleased about these new ideas, while to the audience they seemed to be a most beautiful extension of his own ideas from the eighties. Bjerrum's main point was that the thermodynamic "anomalies" of strong electrolytes should be explained by means of the interionic forces, an idea which at that time was not at all obvious to chemists. It may safely be stated that Bjerrum has contributed more to the victory of these ideas than any other single person.

It is unnecessary here to enlarge upon the further development of his views, as this book contains comprehensive papers on the subject by Bjerrum himself.

It may be pointed out that in this group is a series of comprehensive papers by Bjerrum and different coworkers on distribution coefficients of ions, one of which is also to be found in this book. These investigations gave rise to studies on solubilities of gaseous molecules which except for the charge are similar to certain ions whose distribution between the same solvents were studied. Also A. Lannung's studies on the solubilities of inert gases and other gases belong to this group.

In 1923 J. N. Brønsted published his renowned paper: *Zur Theorie der chemischen Reaktionsgeschwindigkeit*, in which the correct way of introducing activity coefficients in the expressions for reaction velocities was stated for the first time. This paper gave rise to a discussion between Bjerrum and Brønsted, not about the result but about the ideas on which the result ought to be founded. The editors of this book have been in doubt whether Bjerrum's contributions to this discussion should be included or not. Finally we decided, however, that notwithstanding their great interest an inclusion of Bjerrum's contributions without Brønsted's would be too one-sided, and we therefore ask readers who may be interested in the views set forth from both sides to look up the papers in the *Zeitschrift für physikalische Chemie*, where they appeared in 1922 and 1923.

It may be mentioned in this connection that in several of the papers on subjects of inorganic chemistry Bjerrum has used kinetic measurements to a great extent to find mechanisms for the reactions involved. A beautiful example will be mentioned at the end of this survey.

Pertaining to the realm of pure physical chemistry is also his paper with Jean

Perrin on Brownian movements in viscous fluids. In this paper it is shown *i.a.* that the equilibrium distribution of particles in the gravitational field is independent of the viscosity of the fluids.

Already in his first papers Bjerrum has applied measurements of hydrogen-ion concentrations. He seems to have been the first in this country to use such measurements, and as a matter of fact S. P. L. Sørensen in his now classical paper (1908) on the measurement and significance of the hydrogen-ion concentration for enzymatic processes (the *pH* paper) explicitly refers to Bjerrum's paper on chromic chloride (1906).

A problem which immediately presents itself when work on these lines is started is the elimination of the diffusion potential. Bjerrum has given very essential contributions to its solution which contain *i.a.* his well known extrapolation method. The reason why these papers have not been included here is that they are rather difficult to read, and that the theory has been further developed and improved by more recent work especially by E. A. Guggenheim, who worked with Bjerrum for several years.

Bjerrum was the first to take up a rational study of the theory and sources of error of acidimetric and alkalimetric titrations. He showed not only how to determine the *pH*-value at the end-point of the titration, but he also showed how to estimate the error arising from the choice of another *pH*-value, a problem which in view of the limited number of indicators is of great practical interest. One of his papers on this subject is included in the present volume.

Another application of the theory of acidity is to soil science. Bjerrum's works on that subject are represented here by one small paper, a summary of a large paper in Danish.

Of course the subject of these papers: the question which factors determine the reaction (the *pH*) of the soil, is of paramount importance to agriculture everywhere, and indeed especially to a country which, like Denmark, derives a great part of its income from agriculture. The modest number of pages devoted here to this subject is therefore, quite out of proportion to its immense practical value. It may be added that Bjerrum's considerations, being quite general, are also of importance *e.g.* to the public water service in localities with hard water.

On the theoretical side Bjerrum has used his wide knowledge of theory and of the experimental results concerning the strength of acids and bases to alter completely our views on the constitution of ampholytes, especially amino acids, and correspondingly the way in which the experimentally found strength-constants are to be ascribed to the different groups in the molecules. The writer of these lines well remembers the impression it made when 26 years ago Bjerrum explained to the audience in the Danish Chemical Society how naturally his new ideas fitted in with accepted knowledge concerning the variation of the

strength of acids with substitution as contrasted with the complete disagreement between the strength constants of the amino acids calculated in the old way and the constants of the ordinary organic acids.

A paper, also from 1923, on a somewhat similar subject is that on the application of the different strength constants of polybasic acids to the determination of molecular distances. It contains a quantitative formulation of Ostwald's old idea of explaining the difference in strength of the acids in different states of dissociation by electrical forces between the partly ionized molecule and the proton to be removed or taken up. It is well known that extensive experimental work based on these ideas has afterwards been taken up especially by British chemists, a work which has contributed much to our knowledge of molecular architecture.

Inorganic Chemistry. Bjerrum was together with J. N. Brønsted in one of the last groups of advanced students which worked under the personal guidance of the late S. M. Jørgensen on inorganic complex-compounds. But while Jørgensen restricted himself to the application of the methods of classical chemistry, synthesis, and analysis, Bjerrum soon became aware of the numerous problems in inorganic chemistry which could, and could only be solved by means of physico-chemical methods. As early as 1906, when he was 27 years old, he published an extensive work on chromic chlorides, the summary of which is reprinted here. The paper itself comprises about 120 pages in 4to. Among many other things he proved in this paper the existence of a hitherto unknown complex, the monochloropentaquo-complex, and succeeded in isolating it.

Chromium compounds were also the subject of his thesis for the doctorate, in which he investigated *i.a.* the formation of and relations between two kinds of basic complexes, the "true (manifestly) basic" and the "latently basic" complexes, a topic to which he reverted in later publications. I have been told that these papers aroused the interest of the tanning chemists so much indeed that Bjerrum was occasionally invited to their meetings, a distinction which was altogether unexpected to him as he had at that time only a superficial knowledge of the technique of chrome-tanning.

The properties of certain solutions containing chromium salts strongly indicate that they contain high-molecular substances. Consequently Bjerrum became interested in colloid chemistry, which is evident from the bibliography. In this branch he has with a coworker described *i.a.* a method for the preparation of collodion membranes with reproducible permeabilities. This purely technical problem is not at all easy to solve, and it has vexed many scientists working on osmotic pressure, *e.g.* of protein solutions.

In two papers Bjerrum studied the function of the thiocyanate group as a ligand. Summaries of both papers are reprinted here. In the one from 1915

complex compounds of the said ligand with chromic ion are studied. In the other (1918) Bjerrum together with his friend A. Kirschner studied the properties of the gold thiocyanates. In this paper the existence of dithiocyanogen in aqueous solutions is proved about one year before Söderbäck succeeded in preparing it from non-aqueous solutions. In aqueous solution it is very unstable, and Bjerrum set up a sequence of reactions which explained the main features of the rather complicated kinetics of the gross reaction.

The writer of these lines who was at that time getting interested in chemical kinetics well remembers the inspiration he received when Bjerrum read his lecture to the Danish Chemical Society, and also the striking similarity which existed between this sequence and the sequences assumed to explain the kinetics of the oxygen acids of chlorine or their salts.

Recently complex compounds of gold have again been investigated by Bjerrum in a paper read at the 6th Nordic chemist-meeting in Lund (Sweden) 1947, a study of the gold chlorides.

Of course, Bjerrum's influence on the development of chemistry cannot be measured alone by his own production as his many pupils and coworkers from Denmark, from Scandinavia, and from abroad have been inspired by his ideas and contributed to their propagation all over the world. Quite especially to the chemists in Copenhagen and at our neighbouring university in Lund (Sweden) his influence has been immense.

It is impossible to mention here the names of all his pupils and coworkers, and in these lines it has only been done occasionally. However, one more should be named, *viz.* J. Bjerrum, whose name is often mistaken for his father's, the obvious reason being that J. Bjerrum's work is in many ways a continuation of that of Niels Bjerrum.

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