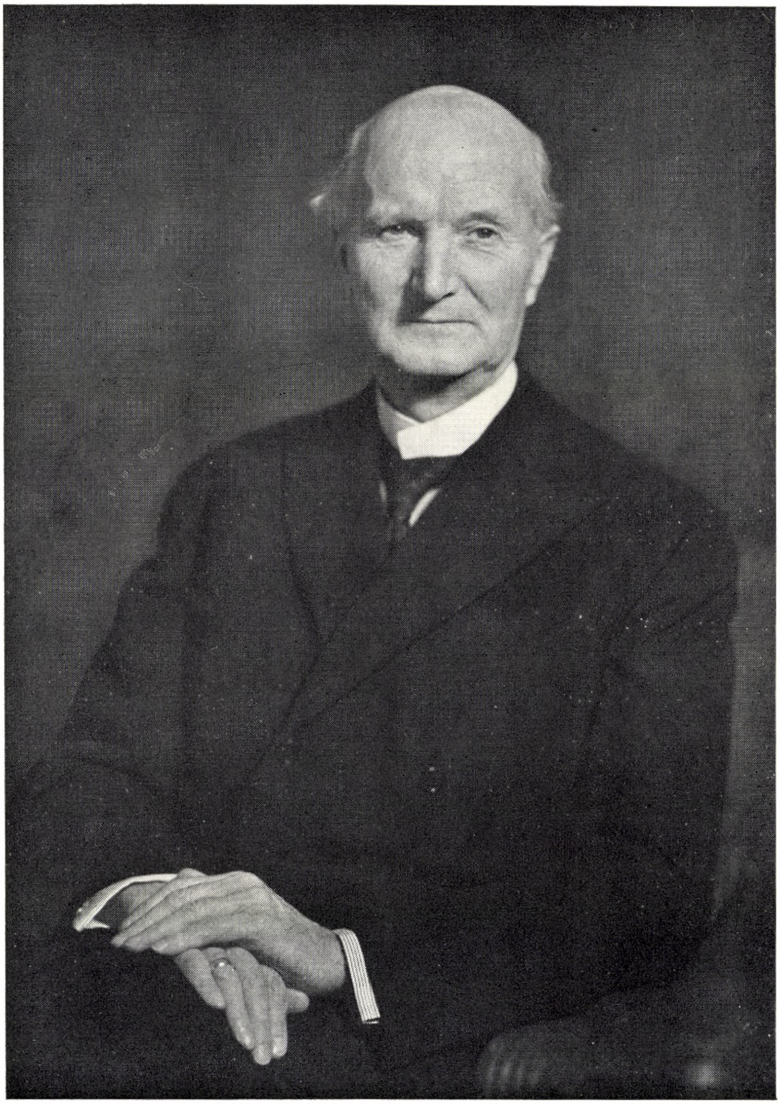

Niels Bjerrum

NIELS BJERRUM

SELECTED PAPERS

Edited by friends and coworkers
on the occasion of his 70th birthday
the 11th of March, 1949

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AALBORG STIFTSBOGTRYKKERI

The scientific publications of Niels Bjerrum have initiated great advances of our knowledge and understanding in many fields of chemistry and physics and bear throughout witness of that same openness of outlook and balance of judgment, which his friends and colleagues admire so highly and which together with his straightforwardness and loyalty has secured him the confidence of the whole Danish community. Many important tasks have been entrusted upon him, and his fertile activities and the encouragement he has given to wide circles will be remembered with deep gratitude from most different sides on his 70th birthday. Deliberating how his colleagues best could contribute on this occasion, the committee has thought that an edition of a selection of the papers of Niels Bjerrum by which he has erected himself a lasting monument in science, would be the most fitting way to express the indebtedness we owe to him, and we feel assured one which will be warmly welcomed by chemists and physicists all over the world.

Niels Bohr.

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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 *p*H 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 *p*H-value at the end-point of the titration, but he also showed how to estimate the error arising from the choice of another *p*H-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 *p*H) 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 physicochemical 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.

J. A. Christiansen.

A Bibliography of Niels Bjerrum's Scientific Publications

The publications are arranged chronologically within each of the two groups, books and papers. The list includes biographical articles on scientists, but not reviews of books and newspaper articles. The abbreviations of the names of the journals are as a rule those used by *Chemical Abstracts*.

A. BOOKS

1. *Studier over basiske Kromiforbindelser. Bidrag til Hydrolysens Teori.* Doctoral dissertation, 170 pp. Prior, Copenhagen (1908).
2. *Vejledning til Brug ved de almene kemiske Øvelser paa Universitetets kemiske Laboratorium*, 17 pp. (1913).
3. *Die Theorie der alkalimetrischen und azidimetrischen Titrierungen*, iv + 128 pp. Enke, Stuttgart (1914). Also in *Samml. Chem. u. chem.-techn. Vorträge* **21.**
4. *Vejledning til indledende Øvelser i Den kgl. Veterinær- og Landbohøjskoles kemiske Laboratorium*, 16 pp. Copenhagen (1916).
5. *Lærebog i uorganisk Kemi for Elever paa Den kgl. Veterinær- og Landbohøjskole*, vi + 281 pp. Copenhagen (1916–17).
6. *Lærebog i uorganisk Kemi* 2nd ed., viii + 315 pp. Copenhagen (1920).
7. *Fysik och Kemi. De exakta Naturvetenskaperna under det nittonde Århundradet* pp. 71–194. Norstedt, Stockholm (1922). Swedish translation of the following book.
8. *Fysik og Kemi i det nittende Aarhundrede. Det nittende Aarhundrede* **18** (1925) 71–192. Gyldendal, Copenhagen.
9. *Lærebog i uorganisk Kemi* 3rd ed., xxiv + 368 pp. Copenhagen (1932).
10. *Kurzes Lehrbuch der anorganischen Chemie.* Translated from the 3rd Danish ed. *(book no. 9)* by L. EBERT, xii + 356 pp. Springer, Berlin (1933).
11. *Kratkiĭ kurs neorganicheskoĭ khimii.* Translated into Russian from the German ed. *(book no. 10)*. Editor I. KAZARNOVSKIĬ 338 pp. Moscow (1935).
12. *Inorganic Chemistry.* Translated from the 3rd Danish ed. *(book no. 9)* by R. P. BELL. x + 317 pp. Heinemann, London (1936).

13. *Lærebog i uorganisk Kemi* 4th ed., xii + 391 pp. Copenhagen (1937).
14. *Lærebog i uorganisk Kemi* 5th ed., xii + 348 pp. Copenhagen (1946).
15. *Inorganic Chemistry* 2nd ed., x + 331 pp. Heinemann, London (1948).

B. PAPERS

1. Om Klorbestemmelse i Havvand. *Foreløbig Meddelelse fra det danske hydrografiske Laboratorium* no. 2 (1903) 11–18.
2. Undersøgelse af den Nøjagtighed, hvormed en Knudsen Pipette afmaaler et Rumfang Havvand. *ibid.* no. 3 (1903) 19–21.
3. On the determination of chlorine in sea-water and examination of the accuracy with which Knudsen's pipette measures a volume of sea-water. *Meddelelser fra Kommissionen for Havundersøgelser. Serie Hydrografi.* **1** no. 3 (1904) 1–11. Translation of *papers nos. 1 and 2.*
4. J. H. van't Hoff. *Fysisk Tids.* **1** (1903) 70–76, 104–113.
5. On the determination of oxygen in sea-water. *Meddelelser fra Kommissionen for Havundersøgelser. Serie Hydrografi* **1** no. 5 (1904) 1–13.
6. Über die Elimination des Diffusionspotentials zwischen zwei verdünnten wässerigen Lösungen durch Einschalten einer konzentrierten Chlorkaliumlösung. *Z. physik. Chem.* **53** (1905) 428-440.
7. Einige Bemerkungen über Chromchloridsulfate. *Ber.* **39** (1906) 1597–1602.
8. Studier over Kromiklorid. *Kgl. Danske Videnskab. Selskab. Skrifter, Naturvidenskab.math. Afdel.* (7) **4** no. 1 (1906) 1–122.
9. Studien über Chromichlorid. Erste Mitteilung. *Z. physik. Chem.* **59** (1907) 336–383. Translation of a part of *paper no. 8.*
10. Studien über Chromichlorid. Zweite Mitteilung. *Z. physik. Chem.* **59** (1907) 581–604. Translation of a part of *paper no. 8.*
11. Über Entwässerungsprodukte des Dichlorochromichlorids. *Ber.* **40** (1907) 2915–2917. Berichtigung. *Ber.* **40** (1907) 3949. Translation of a part of *paper no. 8.*
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13. Nyere og ældre Anskuelser om Grundstoffernes Natur. *Fysisk Tids.* **6** (1907) 71–85.
14. Nyere Anskuelser om vore Grundstoffers Natur. *Tids. Kemi. Farm. Terapi* (1908) 69–75.
15. Physikalisch-chemische Untersuchungen über die Chlorochromisulfate. *Z. anorg. Chem.* **63** (1909) 140–150.

16. Untersuchungen über einige aluminium-, eisen- und vanadinhaltige Halogenochromisalze (with G. HIRSCHFELD-HANSEN). *Z. anorg. Chem.* **63** (1909) 151-159.
17. A new form for the electrolytic dissociation theory. *Proc. Internat. Congr. Appl. Chem.* London. Sect. X (1909) 58–60.
18. Julius Thomsen. *Tids. Industri* **10** (1909) 65-67.
19. Julius Thomsen. *Ber.* **42** (1910) 4971–4988.
20. Studien über Chromichlorid. III. Hydroxoaquochromichloride. *Z. physik. Chem.* **73** (1910) 724-759. An abridged translation of the first half of *book no. 1.*
21. Über die Gültigkeit der Planckschen Formel für das Diffusionspotential. *Z. Elektrochem.* **17** (1911) 58–62.
22. Über die Elimination des Flüssigkeitspotentials bei Messungen von Elektrodenpotentialen. *Z. Elektrochem.* **17** (1911) 389–393.
23. L'agitation moléculaire dans les fluides visqueux (with J. PERRIN). *Compt. rend.* **152** (1911) 1569–1571.
24. Über die spezifische Wärme der Gase. *Z. Elektrochem.* **17** (1911) 731–734.
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26. Antwort an Herrn Richard Swinne. *Z. Elektrochem.* **17** (1911) 994–995.
27. Über die spezifische Wärme der Gase. II. *Z. Elektrochem.* **18** (1912) 101–104.
28. Die Dissoziation und die spezifische Wärme von Wasserdampf bei sehr hohen Temperaturen nach Explosionsversuchen. *Z. physik. Chem.* **79** (1912) 513–536.
29. Die Dissoziation und die spezifische Wärme von Kohlendioxyd bei sehr hohen Temperaturen nach Explosionsversuchen. *Z. physik. Chem.* **79** (1912) 537–550.
30. Über die ultraroten Absorptionsspektren der Gase. *Nernst-Festschrift*, Knapp, Halle (1912) 90–98.
31. Über das Verhalten von Jod und Schwefel bei extrem hohen Temperaturen nach Explosionsversuchen. *Z. physik. Chem.* **81** (1912) 281–297.
32. De galvaniske Elementers Teori. *Fysisk Tids.* **11** (1913) 177–195.
33. Über ultrarote Spektren. II. Eine direkte Messung der Grösse von Energiquanten. *Verhandl. deut. physik. Ges.* **16** (1914) 640–642.
34. Über ultrarote Spektren. III. Die Konfiguration des CO_2-Moleküls und die Gesetze der intramolekularen Kräfte. *Verhandl. deut. physik. Ges.* **16** (1914) 737–753.

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37. De stærke Elektrolyters Dissociation. *Fysisk Tids.* **15** (1916) 59–73.
38. Om sur og basisk Reaktion. *Fysisk Tids.* **16** (1917–18) 53–69, 95–109.
39. Die moderne Auffassung der sauren und basischen Reaktion und ihre Anwendung in der Analyse. *Z. anal. Chem.* **56** (1917) 13–28, 81–95. Translation of *paper no. 38.*
40. Brev til Ingeniør Karsten angaaende Blyrørs Angribelighed af kuldioxydholdigt Vand. *Ingeniøren* **26** (1917) 58–59.
41. De stærke Elektrolyters Dissociation. *Forhandlinger ved de skandinaviske Naturforskeres 16. Møte.* Kristiania (1918) 226–242. The same as *paper no. 37.*
42. Die Dissoziation der starken Elektrolyte. *Z. Elektrochem.* **24** (1918) 321–328. Translation of *paper no. 37.*
43. Die Rhodanide des Goldes und das freie Rhodan mit einem Anhang über das Goldchlorid (with AAGE KIRSCHNER). *Kgl. Danske Videnskab. Selskab. Skrifter, Naturvidenskab. math. Afdel.* (8) **5** (1918) 1–77.
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47. Moderne Atomlære og Kvanteteori. *Naturens Verden* **3** (1919) 529–543.
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53. Über den osmotischen Druck von Elektrolyten. *Z. anorg. Chem.* **129** (1923) 323–340.
54. Tobasiske Syrers Dissociationskonstanter. *Nord. Handelsbl. kem. Industri* **4** (1923) 61–64.
55. Dissoziationskonstanten von mehrbasischen Säuren und ihre Anwendung zur Berechnung molekularer Dimensionen. *Z. physik. Chem.* **106** (1923) 219–242.
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58. Zur Theorie der osmotischen Drucke, der Membranpotentiale und der Ausflockung der Kolloiden. Untersuchungen über kolloides Chromihydroxyd. *Z. physik. Chem.* **100** (1924) 656–684.
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63. Die Entdeckung des Aluminiums. *Z. angew. Chem.* **39** (1926) 316–317.
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67. On the use of Donnan's membrane equilibrium theory for the determination of the charge of colloid particles. *Phil. Mag.* **3** (1927) 22–26.
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The Development of Chemistry in the Nineteenth Century

NIELS BJERRUM

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It is an interesting coincidence that the beginning and end of the nineteenth century open and close a clear cut epoch in the evolution of chemistry. Lavoisier's famous text-book of 1789 may be said to introduce this period. Here for the first time we find in a text-book of chemistry a table of chemical elements closely resembling our present table, and for the first time we see the chemical compounds arranged according to the elements from which they are built instead of place of occurrence or properties. Throughout the nineteenth century order is introduced into chemistry by application of Lavoisier's new system based upon the conception of indestructible elements, and the period comes to a natural close, when Rutherford in 1903 demonstrated the transitoriness of radioactive elements and their transmutation into other elements with changed chemical properties. The task of reviewing the chemistry of this period is an attractive one, for the achievement of the nineteenth century chemists is magnificent. On the other hand one may well hesitate before the task of covering this field in a single lecture, for practically the whole of present day chemistry was developed in this period. However I shall try to give an outline.

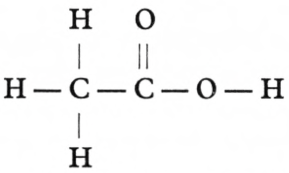
Lavoisier's system set chemists the problem of determining the chemical elements in all matter from the plant, mineral and animal kingdoms. In the first decades of the 19th century this was the central problem. *Chemical analysis* dominated the field. It may be said that the century solved the problem of determining the qualitative and quantitative composition of all kinds of bodies. This included determinations of even the sun's and the fixed stars' compositions by the aid of spectral analysis. About the middle of the century the preparation of old and new compounds, *chemical synthesis* came into the foreground. Chemists have now synthesized, analyzed and described several hundred thousands of compounds.

Towards the close of the century the interest in preparing new compounds ebbed away, except such as had special economic or scientific interest. On the other hand great efforts were now made to lay down laws for chemical phenomena, to express them in numbers and set them to equations. After analysis and synthesis followed the "*mathematization*" of chemistry. Theoretical or physical chemistry has already done important work in this field, but has undoubtedly left plenty for posterity to do. In the chemical laboratory of our college things have developed along the same line. Professor C. T. Barfoed, founder of the laboratory, cultivated analysis and wrote his classical text-books of analytical chemistry. His successor in the chair of chemistry Professor Odin T. Christensen was a synthetist and prepared a large number of new compounds of manganese and chromium. To-day we try in this same laboratory to make chemistry accessible to mathematical treatment. This is for instance our intention in work on the various factors which determine the acidity of soil.

The splendid achievements of the nineteenth century in analysis and synthesis would have been unthinkable had not the atomic theory made it possible to interpret the experimental material and to reduce it to order as it appeared. The nineteenth century can justly be called *the age of atomic chemistry*. Albeit the conception of matter as built of minute indestructible and indivisible atoms is an old one; but it was the famous work of Dalton in the first decade of the nineteenth century which transformed the atomic theory into a scientific hypothesis and made it valuable for chemistry. Dalton assumed that all atoms of an element are alike, and that chemical compounds are built of small identical assemblies of atoms, molecules he called them. From these assumptions he deduced the important laws which govern the quantitative composition of chemical compounds, and he taught us from the results of a chemical analysis to compute the composition of the molecule in terms of atoms. The chemical formula of the atomic theory in the hands of Berzelius proved to be the means to make oneself at home in the mass of results in quantitative analysis which gradually accumulated.

To day any keen first-year student can calculate the nitrogen content of salpeter and ammonium sulphate and he can compute, without special tables, the lime content of a sample of marl from the loss of weight when treated with hydrochloric acid. This is solely due to Daltons atomic theory.

But the atomic theory is very far from being limited to use in cases like those mentioned. It has been an indispensable guide in synthetic work. Chemistry has set up structural formulae in terms of atomic theory and through such formulae has obtained a comprehensive view of the reactions of compounds. Structural formulae show how the atoms are linked together in molecules. To the molecule of acetic acid we ascribe the following structural formula:



$$\begin{array}{ccccccccc} & & H & & O & & & & \\ & & | & & \| & & & & \\ H & - & C & - & C & - & O & - & H \\ & & | & & & & & & \\ & & H & & & & & & \end{array}$$

where H denotes a hydrogen atom, C a carbon atom and O an oxygen atom. The structural formulae are based on experimental knowledge of the behaviour of the compounds when they react chemically. Hence it is possible from the structural formula of a compound to deduce how it will behave when given the chance of reacting. When the reactions take place certain links in the molecule break, after which the fragments combine with molecules of another compound or perhaps with fragments of other molecules. When *bases* or *alcohols* act upon acetic acid the bond between oxygen and hydrogen (O and H) in the molecule is disrupted. *Chlorides of phosphorus* break the bond between carbon and the oxygen atom linked to a hydrogen atom. When acetic acid is heated with *lime* the bond between carbon and carbon is broken, and when *chlorine* reacts with acetic acid the hydrogen atoms linked to carbon are removed.

The system of structural formulae was created in the eighteen fifties. They summarize — in a very compact form — chemistry's knowledge of the creation and destruction of compounds. Nowhere in science has a shorthand notation been developed which summarizes such an abundance of exact knowledge in so small a space. Guided by these formulae chemists have not been content with synthesizing most of the compounds previously isolated from plants and animals. They have conjured up an immense multitude of new substances, drugs more curative and less poisonous than plant drugs, dyes faster and more brilliant than any previously known.

There are still species of vegetable and animal matter such as starch, cellulose and proteins, which have not been produced by the new magic of synthetic chemistry, but one feels sure that the achievement of their synthesis is only a question of time. Preliminary work on the elucidation of their structural formulae has been done, and when the structural formula of a compound has been established it is seldom long before its synthesis has been accomplished.

In the mathematization of chemistry the atomic theory has so far been of less use than one might have expected. In one respect it even proved a total failure. It has not contributed to our understanding of *chemical affinity*. But even if the nineteenth century has been compelled to leave the development of a complete theory of chemical affinity to the future, a preliminary system for the affinity phenomena based on energetics has been constructed. Julius Thomsen in 1852 put forward the hypothesis that the liberation of energy accompanying a chemical process was a measure of the chemical force of the process. This hypothesis has proved to contain a grain of truth, but as put forward the statement is only approximately true. In the years around 1880 it was shown that in order to obtain a true measure of the chemical force we must not take all the energy liberated in the process but only that part of the energy which is available as mechanical work. The chemical force of combustion of petrol is not its entire heat of combustion but the maximum work which can be performed by its combustion in an ideal explosion motor. The failure of the atomic theory when applied to chemical affinity made a group of chemists, led by Ostwald, think that the application of atomic conceptions as realities in chemistry was unwarranted. They sought to remove the symbols and conceptions of atomic theory from chemistry and took great pains to replace them by those of energetics. They did not speak of atomic weights and molecular weights but of equivalent weights and volume weights. They preferred the solid descriptions of energetics to the hypothetical conceptions of atomic theory and did not see that what they gained in confidence they lost in initiative. Because of the brilliance with which the school of energetics advocated its views it came to play a not unimportant rôle for a number of years. Our national adaptability both to good and to evil made its recruiting of proselytes here a matter of course. When I was a student it was fashionable to doubt the existence of atoms, even though such doubt was distressing. The advent of the electronic theory, the discovery of radium and investigations in the Brownian movement in the first years of the 20th century added a series of direct proofs of the existence of atoms to the circumstantial evidence previously amassed by chemists. Effects of processes taking place in single atoms were observed and atoms were counted. In 1908 even Ostwald himself had to admit the existence of atoms and the superiority of the atomic theory.

The vast amount of chemical facts and chemical theories which the nineteenth century produced could not fail to have effects in most of the provinces of human life. *The engineer* builds his structures from materials produced and often analyzed by chemistry. *The physician* diagnoses by methods of chemical analysis and cures with the products of chemical industry. *The physiologist* builds his science on chemistry and from the synthesis of organic chemistry he has learned to dispense with special vital forces as explanations. The *physicist* has taken over the atomic theory from chemistry and has been taught to work with pure substances.

The *world war* has revealed to us the military importance of industrial production of fertilizers and munitions.

To agriculture the development of chemistry has been of paramount importance. In 1840 Liebig developed from a chemical basis the main principles of a nutrition theory for plants and animals which still holds. His work was the foundation of a rational *science of plant fertilizers*. Chemical analyses were used to estimate the fertility of soils and the proper market value of fertilizers and feeding stuffs. The middle of the century was a time when it appeared as if chemistry could solve all problems of plant growth and animal husbandry. In the official report of the commission of 1855 concerning the erection of a Royal Veterinary and Agricultural College in Denmark, chemistry is dealt with in the following words: "It is unquestionably to this science that rural economy mainly owes the advances it has made in the last decades and from which we may expect essential improvements in agriculture in the future".

In the following years chemistry had however difficulties in living up to these intense expectations. Liebig's rationally composed mixed fertilizers did not have the expected effects and soil analyses did not yield adequate estimations of the fertility of soils. Only by degrees it was understood why chemical theories apparently failed, and it was slowly realized that chemistry was not to blame. The explanation of the results of soil analysis is that only such fractions of the plant nutrients in soil have fertilizing value as are sufficiently soluble to be absorbed by the plants. Efforts to estimate the *available* plant nutrients in soil by leaching with a suitable solvent proved futile for a long time but have lately given promising results after having been redirected by improved theoretical chemistry. Chemical analysis, however, is not the only branch of chemistry which has played a rôle in agriculture. The development of synthetic chemistry has also been important. Chemical factories have given to agriculture a series of excellent artificial fertilizers and remedies against plant diseases. But the development of synthetic chemistry has been detrimental as well as beneficial for agriculture. In several fields the synthetic products of chemical industry have entered into successful competition with products of agricultural plant growth. In the years before 1870 the beautiful red dye, with which for instance the red bunting of our Danish flag is dyed, came from madder roots grown in France. The cultivation of the madder plant brought to France an annual revenue amounting to 60 million Danish crowns. In 1869 Graebe and Liebermann found a method for making this red dye from anthracene present in coal tar, and within a few years German factories had destroyed the lucrative cultivation of madder in France. In 1897 the same story was repeated, this time with the indigo dye. Artificial indigo from German factories in few years ruined the indigo cultivation of India which had occupied one million acres of land and brought in an annual revenue equivalent to 70 million Danish crowns.

Over-imaginative writers have depicted a future in which the main products of agriculture, the starch- fat- and protein- containing foodstuffs had been replaced by synthetic products from chemical factories. It can however be said with confidence that in this field the 19th century chemistry will be unable to compete. It is, if I may say so, too clumsy. The 19th century chemists can synthesize organic compounds, but they work with much less agility than the living cells.

They are unable to make artifiical products which can bring about or accelerate chemical processes as easily as can the enzymes of the living cell. The 19th century has failed in its efforts to lift the veil from the secrets of enzymatic action. The running expenses of chemical factories are therefore high. Only those compounds present in very small percentages in the tissue of cultivated plants such as dyes, drugs, scents and stimulants whose agricultural production is very expensive, can at the present be produced more cheaply in factories than on farms or plantations.

A suitable problem for the chemistry of the nineteenth century is the production of a synthetic coffee extract. A German factory has devoted much work to the production of such an extract. The synthesis of coffein, the stimulating alkaloid in coffee, has been accomplished but, as far as we know, the problem of making the substance which is of paramount importance for the sale of the product, I mean the aromatic component, is still unsolved.

Another problem which most likely can be solved by 19th century chemical methods is the synthesis of the aromatic substance in butter. It is not a problem I would recommend to Danish chemists. If chemists could provide margarine factories with butter aroma as well as butter colour, the Danish production of butter would be seriously endangered, and if chemists also succeeded in synthesizing the vitamin of butter, the production would undoubtedly be doomed. So far, however, no work of that kind is known to me.

Time forbids going in detail into the deeply interesting subject of the effect of chemistry upon the pattern of culture, because I wish to say a few words of the general methods by which chemistry in the 19th century has obtained such striking results.

Characteristic of 19th century chemistry as of the culture of the 19th century in general is a strong critical sense. Experimental work as well as hypotheses have benefited from this criticism. In the preface to one of his text-books of analytical chemistry Professor Barfoed writes that he has himself tried out all specifications given in his text-books because "a written account too easily becomes marred by mistakes and inaccuracies if it does not arise from recent personal experience". Probably not many writers on chemistry have been as critical as that. At times the criticism of new hypotheses has been over-severe and clogging in its zeal for making chemistry a purely descriptive science free from assumptions. But the damage inflicted was small in comparison with the benefit, for it was criticism which made chemistry reliable.

In the excellent book on the philosophy of the nineteenth century just published by Professor Høffding, he sets forth the thesis that the most characteristic feature of the century consists in its being a time of realization and empirical confirmation more than a time of creation. To me it appears that Høffding's thesis contains an underestimation of the original thoughts of chemistry (and physics) in the nineteenth century. Lavoisier's conceptions, his new system, mean a new departure for chemistry, and Daltons atomic theory is not a mere *realization* of thoughts from classical antiquity. It is a new-born theory; its elements are new and fundamental thoughts. Of course Lavoisier and Dalton built upon previous work. Everybody, even the greatest genius builds more or less upon previous work. New thoughts have in the nineteenth century infused new life into old conceptions. At no time in the history of chemistry has an explosive development started comparable to that of the early nineteenth century. In addition to calling the nineteenth century a time of realization Høffding speaks of it as a time of empirical confirmation. As for the second characterization I would prefer to call it an age of empirical decision. The century has not merely confirmed earlier views, but it has empirically found decisions where past centuries had stood at a loss. The age has for science been a manhood in which the vague and hazy dreams of childhood become achievements. From weak and tottering thoughts strong and general principles have been created. New thoughts have been conceived from which the twentieth century now is creating a new physics and chemistry.

The nineteenth century chemistry is not completely characterized by its critical sense and its faculty for infusing new life into old conceptions. It is also remarkable for perfect coordination in at least three distinct fields. Coordination of active work and contemplation has been remarkable. Never before has experiment and hypothesis been so happily united as in science in the nineteenth century. Science was not allowed to degenerate into "uninspired research" or into futile speculation devoid of reality.

Secondly the coordination of research and scientific education has been a fine achievement, highly advantageous for both. It was Liebig who created the type of laboratory in which the education of youth is coupled with original scientific research. It was the laboratories created by Liebig and his followers which moved the foci of chemical research from Sweden, England, and France to Germany and made the German universities centres of education for all the world's chemists.

Last but not least the coordination of science and technology, of theory and practice must be mentioned. This concerted action has developed in a capital way. New results obtained by chemistry have promptly been converted in industry into capital values. Industry and governments have therefore found it profitable to subsidize chemistry in order to facilitate its progress. As a consequence the number of chemists has multiplied and their facilities been increased. Technology has perhaps aided chemistry even more in an indirect way by supplying the necessary chemicals and apparatus. To-day industry supplies chemicals and apparatus better and cheaper than those made by the chemists themselves. Technology has provided chemical research with gas, water and electricity, efficient ventilation and drains, facilities the importance of which can hardly be overestimated. New and improved apparatus and accessories have appeared in such rapid succesion, that for purely economic reasons it has been impossible for the laboratories to keep their technique up to date. The laboratories of Europe to-day are behind those of the United States of America. They must seek consolation and hope in remembering that progress in scientific work, in spite of all time-saving gadgets, largely springs from the underlying spiritual force and mental discipline.

Finally I would like to say a few words of the chemistry of the twentieth century and its relation to that of the preceding century. The new chemistry, which was born when Rutherford in 1903 showed us that our chemical elements are not indestructible, builds upon the chemistry of the nineteenth century. The new chemistry supplements the old chemistry, but it does not supersede it. The structure and constitution of atoms had been discussed in the nineteenth century but the new chemistry made it a burning question. Work by J. J. Thomson, Rutherford and our fellow-countryman Niels Bohr has with amazing speed substantiated a theory of atomic structure, according to which atoms are built of two kinds of "electrons": negative electrical particles with a mass equal to one two-thousandth of the mass of a hydrogen atom, and positive electrical particles with a mass equal to that of a hydrogen atom. The problem which the twentieth century now faces is that of reducing the properties of all substances to the properties of these two species of electrons and the laws of their interaction.

According to the views of Bohr it is possible, but extremely difficult and as yet far from realized, to calculate all the chemical and physical properties of an element from one characteristic whole number, the so-called atomic number of the element. When the goal is reached the properties of the elements will simply be mathematical functions of whole numbers from 1 to 92. In the views of Bohr a complete mathematization of chemistry is possible, but even when this has become accomplished, the chemistry of the nineteenth century will be indispensable. Let us remember that we go on adding and subtracting figures long after higher mathematics has developed new methods of calculation. We may be convinced that when the electronic theory has reached perfection the chemical formulae of the nineteenth century will still continue to be the ideal instrument of stating the composition of substances and of understanding their interactions.

On the Specific Heat of Gases

NIELS BJERRUM

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The classical theory of the specific heat of gases, which right at the beginning obtained such a brilliant confirmation through Kundt and Warburg's determination of the specific heat of mercury vapour, has for a long time produced no new results. It has, in particular, proved impossible to explain the variation of the specific heat with the temperature. It has now, however, become possible to give this theory the extension which has for so long been looked forward to, and which enables the theory to explain the variability of the specific heat.

A few years ago Einstein succeeded in enunciating a formula for the specific heat of *solids* on the basis of the quantum theory. And this formula has, after having been modified by Nernst and Lindemann, proved to apply over a very wide temperature range. It therefore seems probable that also for *gases* the correct formula for the specific heat can be obtained by combining the quantum theory with the kinetic theory. A short time ago Nernst has also given an outline of a formulation of this idea.

The derivation is briefly as follows:

A gas molecule possesses three kinds of energy, the amount of which varies with the temperature: the *energy of translation*, due to its translatory movements, the *energy of rotation*, due to the rotatory movement of the molecule, and the *energy of oscillation*, from the oscillations of the atoms in the molecule.

According to the classical kinetic theory of gases the energy of translation is always equal to $^3/_2$ RT per mole, whether the molecule is mono-, di-, tri-, or tetra-atomic. As to the energy of rotation conditions are different. The magnitude of the energy of rotation may be obtained in the following way: According to the laws of classical statistical mechanics the following rule will apply to the kinetic energy of a molecule: the content of energy of a molecule is the same for each degree of freedom, and as the energy of translation possesses three degrees of freedom and is equal to $^3/_2\, RT$, the energy of the molecule must be $^1/_2\, RT$ per degree of freedom. In order to obtain the energy of rotation we therefore only have to multiply the number of degrees of freedom of the energy of rotation by $^1/_2$ RT. The latter number of degrees of freedom is for a monatomic gas 0, for a diatomic gas 2 and for tri- and polyatomic gases 3, because a monatomic molecule may be considered a point-mass, a diatomic molecule can possess energy of rotation about two axes and a tri- or polyatomic gas may possess energy of rotation about all three axes (if it does not happen to be of linear structure).

As regards the energy of oscillation, a monatomic gas molecule cannot possess energy of oscillation. In a diatomic molecule the two atoms may oscillate in relation to each other. There is thus one degree of freedom which, according to the classical theory, corresponds to a kinetic energy of $^1/_2$ RT per mole, and, as an equally large amount of potential energy should be added, a total energy of RT. Here the new theories interfere. According to the quantum hypothesis only a fraction φ of the classical oscillation energy is present, i.e. in this case $RT\varphi$. φ is a function only of the temperature and the frequency of the oscillation in question. According to Einstein we have

$$\varphi = \frac{\frac{\beta\nu}{T}}{e^{\frac{\beta\nu}{T}} - 1}$$

where $\beta = 4.86 \cdot 10^{-11}$ and ν is the frequency (the number of oscillations per second). Nernst and Lindemann have found that Einstein's function does not apply to solids at low temperatures while the formula

$$\varphi = \tfrac{1}{2}\frac{\frac{\beta\nu}{T}}{e^{\frac{\beta\nu}{T}} - 1} + \tfrac{1}{2}\frac{\frac{\beta\nu}{2T}}{e^{\frac{\beta\nu}{2T}} - 1}$$

agrees closely with the observations.

In the following I shall employ both these functions to find out whether the new one is also to be preferred in case of gases.

Both functions of φ are at the absolute zero equal to nil, and they approach 1 at higher temperatures. At higher temperatures the energy content thus approaches that which is required by the classical theory.

In a triatomic gas molecule the three atoms, which may be denoted A, B, and C, can oscillate in pairs, i.e. A and B in relation to each other and likewise B and C as well as C and A. We must thus consider three different oscillations, and the total energy of oscillation will be: $RT(\varphi_1 + \varphi_2 + \varphi_3)$.

Just as a triangle is determined by three elements, the energy of oscillation of a triangular molecule has three degrees of freedom. In analogy with this a tetra-atomic molecule must possess six oscillations, an n-atomic $3n - 6$ oscillations.

Summary

Number of atoms in the molecule	Energy of translation	Energy of rotation	Energy of oscillation
1	$^3/_2\,RT$	0	0
2	$^3/_2\,RT$	RT	$RT\varphi$
3	$^3/_2\,RT$	$^3/_2\,RT$	$RT\,(\varphi_1 + \varphi_2 + \varphi_3)$
4	$^3/_2\,RT$	$^3/_2\,RT$	$RT\,\Sigma_6\varphi$

By adding up energy of translation, energy of rotation and energy of oscillation the total energy is obtained. When the total energy is divided by the temperature we obtain the *mean specific heat* reckoned from the absolute zero, and by differentiating with respect to T, we obtain the true specific heat, in all cases at constant volume. Hereby, we have formulated an expression for the specific heat of gases.

In connection with the above derivation the following should be observed: As shown by Nernst, it also applies to the energy of rotation that at low temperatures only a fraction of the amount calculated according to the classical theory, will be present. However, already at temperatures far below 0° C this amount has practically been reached. For the purpose of the present investigation we need not take this into consideration. Another point neglected is the following: Besides the *kinetic energy of rotation* E_K, the molecule must possess *potential energy of rotation* E_P, as the atoms are more or less removed from each other due to the centrifugal force. This contribution of potential energy of rotation will be the smaller the more rigidly the atoms are linked. For a diatomic gas molecule, the internal frequency of which is ν, it can be calculated that

$$\frac{E_P}{E_K} = \frac{RT}{4\,\pi^2\,\nu^2 M r^2}$$

Here M is the molecular weight and r the radius of the molecule. According to this expression the potential energy of rotation may usually be taken to equal nil. We have, e.g. for oxygen at ordinary temperature, when we substitute $\nu = 10^{14}$, $M = 32$, and $r = 10^{-8}$,

$$\frac{E_P}{E_K} = 0.00002$$

For the purpose of testing the new expressions for the specific heat of gases, monatomic gases cannot be used as Boltzmann's theory remain applicable to these gases. We can therefore at once proceed to the polyatomic gases. In the case of diatomic gases the specific heat has previously been considered to vary linearly with the temperature. However, the values observed are in very good agreement with those calculated from the new exponential formulae, as will be seen from tables 1 and 2.

We have for *hydrogen* and *nitrogen* correlated the observed values of the specific heat with the values (E) calculated from Einstein's φ-function and with the values (N and L) calculated from Nernst and Lindemann's φ-function. *c* denotes the true specific heat at constant volume and $c_m(0°, t°)$ the mean specific heat at constant volume between 0° C and *t*° C.

Table 1. Specific heat of hydrogen

t	Observed value		Calculated E $\lambda = 3.0\mu$	Calculated N and L $\lambda = 2.0\mu$
	c		c	c
18° C	4.9–5.2 from c_p/c_v		4.96	4.96
	$c_m(0°, t°)$		$c_m(0°, t°)$	$c_m(0°, t°)$
1413	5.34	Pier	5.37	5.37
1592	5.42		5.45	5.44
1835	5.52		5.54	5.52
2017	5.61		5.61	5.59
2250	5.72		5.69	5.67

Table 2. Specific heat of nitrogen

t	Observed value		Calculated E $\lambda = 3.6\mu$	Calculated N and L $\lambda = 2.59\mu$
	c		c	c
18° C	4.84 from c_p/c_v		4.96	4.96
	$c_m(0°, t°)$		$c_m(0°, t°)$	$c_m(0°, t°)$
200	4.73	Holborn Hennig	4.97	5.00
630	4.91		5.10	5.19
1000	5.25		5.31	5.38
1347	5.31		5.50	5.53
2000	5.78	Pier	5.78	5.78
2500	5.93		5.93	5.93

When the atoms are electrically charged, we must, according to Einstein, expect to find bands in their absorption and emission spectra at wave-lengths corresponding to the frequencies of the atomic oscillations. In the tables, I have therefore given the wave-lengths λ corresponding to the frequencies used for the calculation.

Hydrogen and nitrogen have no infrared bands and the λ-values which have been calculated according to thermal methods cannot therefore be checked by optical methods. *Carbon monoxide* and *oxygen* seem, however, according to explosion experiments, to have nearly the same specific heat as nitrogen. Their atoms must therefore — as those of nitrogen — oscillate with a frequency corresponding to $\lambda =$ about 3μ. These substances do actually show absorption within this range, namely carbon monoxide at $2.4\ \mu$ and $4.6\ \mu$, and oxygen at $3.2\ \mu$ and $4.7\ \mu$. The oxygen bands are rather weak. The greater the polarity of the molecules the more intense the infrared bands seem to be.

Important material for testing the theory is presented by the triatomic gases, carbon dioxide and water vapour. In the first place the two like atoms can in both gases oscillate in relation to each other. As the forces between these atoms are probably weak, the oscillations will most likely be slow. Secondly, the two oxygen atoms in carbon dioxide can oscillate in relation to the carbon atom and the two hydrogen atoms in water vapour can oscillate in relation to the oxygen atom. We must therefore in these cases expect one slow and two more rapid oscillations, and, considering the uniformity of the valences, the two rapid oscillations are probably identical.

Table 3. Specific heat of carbon dioxide

t	Observed value		Calculated E $\lambda_1 = 14.7\mu$ $\lambda_2 = \lambda_3$ $= 6.2\mu$	Calculated N and L $\lambda_1 = 8.1\mu$ $\lambda_2 = \lambda_3$ $= 5.0\mu$	Calculated N and L $\lambda_1 = 14.7\mu$ $\lambda_2 = 4.3\mu$ $\lambda_3 = 2.7\mu$
	c		c	c	c
18° C	7.09 from c_p/c_v		6.87	6.85	7.24
	$c_m(0°, t°)$		$c_m(0°, t°)$	$c_m(0°, t°)$	$c_m(0°, t°)$
200	7.48	Holborn Hennig	7.44	7.44	7.67
630	8.60		8.66	8.67	8.47
1000	9.33		9.34	9.35	9.00
1364	9.84		9.87	9.80	9.40
1611	9.98	Pier	10.07	10.03	9.62
1839	10.28		10.23	10.21	9.81
2210	10.47		10.45	10.43	10.04

From table 3, columns 3 and 4 we may see the good agreement obtained in the case of *carbon dioxide* under these conditions, both according to Einstein's φ-function and according to Nernst and Lindemann's more recent φ-function. As the absorption spectrum of carbon dioxide consists of three bands at 14.7μ, 4.3μ, and 2.7μ, while the thermally calculated values are 14.7μ and 6.2μ, respectively 8.1μ and 5.0μ, it may be seen that the orders of magnitude of the optically and thermally determined frequencies agree. The last column in table 3, which gives the specific heats calculated according to Nernst and Lindemann's φ-function from the three optical oscillations, shows that the deviations in the λ-values are insignificant to the calculations of the specific heats. *As will be seen, we can calculate the specific heat of carbon dioxide from optical measurements with an accuracy of a few per cent.* When calculating on the basis of the original Einstein φ-function, the deviation is considerably greater.

The applicability of the new theories to *water vapour* will appear from table 4. In this case a comparison between optically and thermally determined values of λ cannot, however, be performed, because water vapour has a complicated infra-red spectrum with bands throughout the range from 1μ to 20μ. It is my opinion that this unexpectedly complicated spectrum is caused by the presence of double-molecules of water. At any rate water vapour has bands within the ranges where they should be expected. A thorough investigation of the spectrum of water vapour at different temperatures and pressures would be of great interest, as the bands originating from the simple H_2O-molecule must become more and more distinctive with decreasing pressure and increasing temperature.

Table 4. Specific heat of water vapour

t	Observed value		Calculated E $\lambda_1 = 5.5\mu$ $\lambda_2 = \lambda_3 = 2.6\mu$	Calculated N and L $\lambda_1 = \lambda_2 = \lambda_3 = 2.4\mu$
	c		c	c
50° C	5.96	Nernst-Levy	6.04	5.98
270	6.40		6.35	6.32
450	6.80		6.78	6.80
	$c_m(110°, t)$		$c_m(110°, t)$	$c_m(110°, t)$
620	6.51	Holborn Hennig	6.59	6.60
1000	6.94		7.13	7.17
1327	7.40		7.53	7.58
	$c_m(0°, t)$		$c_m(0°, t)$	$c_m(0°, t)$
1727	7.96	Pier	7.89	7.94
2027	8.72		8.21	8.27
2327	9.68		8.49	8.53

Measurements have also been performed for a tetra-atomic gas — namely *ammonia*. Among the six oscillations which its molecule, according to theory, must possess I have assumed the five rapid ones to have the same frequency. This assumption is sufficient to obtain agreement with the observations, as shown in table 5.

Table 5. Specific heat of ammonia

t	Observed value	Calculated E $\lambda_1 = 13.0\mu$ $\lambda_2 = \lambda_3 = \lambda_4 = \lambda_5$ $= \lambda_6 = 3.32\mu$	Calculated N and L $\lambda_1 = 8.9\mu$ $\lambda_2 = \lambda_3 = \lambda_4 = \lambda_5$ $= \lambda_6 = 2.1\mu$
18° C	6.61 Nernst	6.61	6.62
112	7.09	6.98	6.91
466	8.4	8.5	8.6
580	9.2	9.2	9.2

The λ-values found by the thermal methods are 13μ and 3.3μ, respectively 8.9μ and 2.1μ. The infrared spectrum of ammonia extends from 14μ to 3μ and comprises about 20 lines and bands. They are likewise within the range in which they should be according to the thermal measurements.

I have now mentioned all the gases for which detailed investigations are available. For other gases only incomplete thermal and optical measurements are available. We are especially short of absorption measurements in the outermost infrared spectrum. There do not seem, however, to be any cases in which the available measurements contradict the theory.

We may establish as a result of the investigation that the available observations confirm the interdependence between specific heat and spectrum which the quantum theory requires. In most cases the observations are equally well reproduced by means of Einstein's and Nernst-Lindemann's φ-function. But just in the case where the data are best, i.e. in the case of carbon dioxide, the new formula by Nernst and Lindemann proves its superiority.

On the Infrared Absorption Spectra of Gases

NIELS BJERRUM

Translated from *Nernst-Festschrift* Verlag von Knapp (1912) pp. 90–98

1. According to Drude[1] the infrared emission and absorption bands found for most substances are caused by vibrations of the electrically charged molecules or atoms. This hypothesis has recently got valuable confirmation through a series of investigations from Nernst's institute[2,3,4]. It was demonstrated that the frequencies of the atomic vibrations calculated on the basis of the quantum theory agree with the frequencies observed in the infrared spectra.

Likewise as an oscillating electrically charged atom emits and absorbs in the infrared it is also to be expected that a rotating polar molecule will emit and absorb infrared radiation. In fact, this has been shown by Rubens and v. Wartenberg[5] who have measured the absorption of gases in the far infrared region (23μ to 314μ).

In the following I shall make an attempt to draw some new consequences from these, as it seems, now well-established theoretical aspects concerning the origin of the infrared spectra.

THE BROADENING OF A SPECTRAL LINE DUE TO THE ROTATION OF THE MOLECULE

2. First we want to ask the following question: How is the nature of the emission of an electrically charged atom which is performing a linear sinusoidal oscillation of frequency ν_1 within a molecule, when this molecule is rotating with a frequency ν_2 *about an axis perpendicular to the linear oscillation?* Already 20 years ago Lord Rayleigh[6] has shown that the light emitted in a direction at right angles to the axis of rotation will split up into a double line. If the linear oscillation is resolved into two rotations about the rotational axis of the molecule it is easily seen that the light emitted in all directions can be resolved into two frequencies $\nu_1 + \nu_2$ and $\nu_1 - \nu_2$. In a direction perpendicular to the rotational axis both frequencies will be linearly polarized, whereas they will be circularly polarized in opposite directions when observed along the rotational axis. In all

intermediate directions the light will appear elliptically polarized. *A rotation of the molecule about an axis coinciding with the direction of the linear oscillation* can not affect the radiation. If, however, the rotation occurs about a random axis forming an angle, α, with the vibrational direction, we can visualize the resulting interaction by resolving the linear vibration into a vibration perpendicular to the axis of rotation (intensity proportional to $\sin^2 \alpha$) and a vibration parallel to the rotational axis (intensity proportional to $\cos^2 \alpha$). The light emitted from the two oscillators will be of the frequencies $\nu_1 \pm \nu_2$ resp. ν_1.

3. If we have a great number of disordered molecules each with a linear vibration of frequency ν_1, and if all these molecules are rotating with the frequency ν_2 the light emitted as a whole must be depolarized and of the frequencies $\nu_1 \pm \nu_2$ and ν_1. Because the two opposite rotations will be equally probable for all orientations of the rotational axis within the molecule it follows that the circularly, resp. elliptically, polarized light rays will combine forming plane polarized light, and furthermore, all directions of polarization will have the same probability. If, however, all orientations of the rotational axis within the molecule are equally probable, it follows, too, that the three frequencies $\nu_1 - \nu_2, \nu_1, \nu_1 + \nu_2$ must appear with the same intensity.

4. In the gas the molecules will have different frequencies of rotation resulting in a broadening of the line. The rotation of a molecule may have two or three degrees of freedom. According to Maxwell's distribution law the different rotational frequencies must be distributed around a definite value of highest probability, so that as well higher as lower frequencies are less probable, and very low rotational frequencies extremely rare. This means that the broadening actually must be a splitting into three components (even if these are unresolved): one sharp central line with two equally intense, diffuse bands at both sides.

5. How do these theoretical consequences agree with observations? First we shall apply the theory to hydrogen chloride. According to Rubens and v. Wartenberg gaseous hydrogen chloride absorbs at ordinary temperature in the region round 150μ (50μ — 300μ). This absorption corresponds to a rotation with the mean frequency $2 \cdot 10^{12}$ of the electrically polar molecule. Hydrogen chloride has, however, furthermore an absorption band at 3.5μ which must be caused by a vibration of the atoms against each other with the frequency $86 \cdot 10^{12}$. According to 4, a linear vibration of this frequency in the rotating hydrogen chloride molecules must emit light not only of the frequency $86 \cdot 10^{12}$, but also at higher and lower frequencies. Because the most probable rotational frequency of the molecule is $2 \cdot 10^{12}$ there must be two maxima at the frequencies $(86 \pm 2) \cdot 10^{12}$, i.e. we must expect to observe a sharp line at 3.5μ and two diffuse lines at 3.4 and 3.6μ. From these calculations we see, that the effect should be easily observable. So far, however, only a corresponding broadening of the line has been found.

6. The infrared spectrum of carbon dioxide is thoroughly investigated[7,8,9]. It shows bands at 2.7μ, 4.3μ, and 14.7μ which must be caused by atomic vibrations. This means that the atoms must be electrically charged. Therefore, the molecule must also emit and absorb at its rotational frequency. As Rubens and v. Wartenberg have found no absorption between 23μ and 314μ, it seems safe to conclude that the rotation of the carbon dioxide molecule is rather slow, with a rotational frequency considerably smaller than 10^{12}. From the chemical composition one should expect carbon dioxide to rotate considerably slower than hydrogen chloride because it evidently has the greater moment of inertia of the two molecules.

From the slower rotation of the carbon dioxide molecule it follows that the absorption bands must be rather sharp. In fact, this is the case. I have tried to estimate the rotational frequency of the carbon dioxide molecule from the width of the bands. The difficulty is, however, to find a proper measure for the broadening of the line. I have used the interval between the two points in which the absorption coefficient has just decreased to one half of its maximum value. If the absorption in the maximum is x per cent it will be:

$$(1 - \sqrt{1 - x/100}) \cdot 100 \text{ per cent}$$

for an absorption coefficient of half the magnitude.

In this way I have calculated the width of the bands using Hertz's measurements of the absorption[9]. For the band at 14.7μ the width is about 1μ, and for the band at 4.3μ about 0.1μ. The values found from absorption curves for different partial pressures and different thicknesses of the absorption path agree satisfactorily. If one assumes that the distance between the two components produced by the rotation, is equal to the width, the rotational frequencies are found to be $0.7 \cdot 10^{12}$, resp. $0.8 \cdot 10^{12}$. These frequencies correspond to a band at about 400μ which agrees with the findings of Rubens and v. Wartenberg that the absorption must be at longer wave-lengths than 314μ.

The carbon dioxide band at 2.7μ is much broader than it should be according to the rotational frequency calculated above. On both sides of the principal maximum at 2.67μ it has a secondary maximum. One of these is distinct and situated at 2.75μ, the other is very little pronounced at 2.59μ[9]. These maxima may be explained by assuming a rotation with the mean frequency $3.5 \cdot 10^{12}$. The structure of this band might be explained in another way because it corresponds to such a high rotational frequency. It is possible that the linear vibration, causing the 2.7μ band, is orientated at right angles to an axis in the molecule about which the moment of inertia is particularly small and, consequently, the rotation fast.

7. Owing to the low mass of the hydrogen atom, one must expect the water molecule to rotate rather fast because of its small moment of inertia. Rubens

and v. Wartenberg[5] have found a strong absorption at 52μ in water vapour. I estimate the maximum of the absorption to be at about 60μ because the absorption is weaker at 23μ than it is at 110μ. The position of this maximum corresponds to the rotational frequency $5 \cdot 10^{12}$. This fast rotation must strongly influence the water spectrum in the region between 1 and 10μ (the bands of atomic vibrations). For example, the vibration of the frequency $52 \cdot 10^{12}$ (5.8μ) must absorb light of the frequencies $47 \cdot 10^{12}$ and $57 \cdot 10^{12}$ due to such a rotation. Table 1 shows the wave-lengths of the absorption maxima calculated in this way and the maxima observed in this region[7]. It thus seems as if we are able to explain the absorption of water between 5 and 6μ by assuming a single vibration in the rotating water molecule. The asymmetrical absorption in this region is, however, left unexplained, but it may be due to the superposition of a secondary effect.

Table 1

λ calc.	5.3μ	5.8μ	6.4μ
λ obs.	5.25μ	5.90μ (strong)	6.07μ

The absorption bands of water in the near infrared are, according to the theory, less broadened. There exist, however, no accurate measurements of the structure of these bands. The water bands in the far infrared are probably not caused by vibrations in the water molecule and shall therefore not be dealt with in this connection (cp. 11).

8. I realize fully that the experimental evidence supporting the proposed theory is rather weak. Therefore, I would not have dared to present the above considerations right now had it not been for the reason that they really only are new consequences from old well-established theories derived without the aid of any new hypothesis.

In the following I shall state further consequences which we arrive to, if we proceed in the above way using the quantum hypothesis.

APPLICATION OF THE QUANTUM HYPOTHESIS TO MOLECULAR SPECTRA

9. The problem whether Planck's radiation law and Einstein's formula for the specific heat derived from it, really are to be explained as due to a quantization of the energy, as assumed by Planck, or whether the energy does vary continuously, but that it is the equations of motion of the atoms that must be changed, is one of the most interesting problems of physics at present. A minor contribution to a solution of this question may be given by means of the viewpoints proposed above.

10. As shown by Nernst[10] it is a necessary consequence of the quantum hypothesis that as well the *vibrational energy of the atoms* as the *rotational energy of the molecule* must vary discontinuously. There is, however, at present a certain difficulty in an exact use of the quantum hypothesis to the rotational energy because the quantum distribution of this energy is unknown. It is possible that every fraction of the rotational energy, referring to the different degrees of freedom (momentum coordinates), is quantized. It may be, however, that only the entire rotational energy is quantized. In the following it is assumed that the entire rotational energy is quantized and that the moments of inertia of the molecule about all axes through the centre of gravity are the same. In this case we must have the following equation for the rotational frequency ν

$$\frac{1}{2}\,\mathcal{J}(2\pi\nu)^2 = nh\nu,$$

where $\mathcal{J}$ = moment of inertia, $h = 6.548 \cdot 10^{-27}$ (Planck's constant) and n is any integral number. This equation results in

$$\nu = \frac{nh}{2\pi^2 \cdot \mathcal{J}}$$

According to this the rotational frequencies must vary *discontinuously* and constitute an arithmetical progression*.

If the rotational frequencies are assumed to vary discontinuously it follows that a band originating from a linear vibration of the rotating molecule must consist of a series of fine lines. Many investigators [9, 12, 13, 14, 15, 16] have noticed that the infrared bands of gases possess such a fine structure. This line-structure speaks in favour of a discontinuous rotational energy as claimed by the quantum hypothesis.

11. Some calculations based on measured frequencies in the water vapour bands from 10 to 20μ are of some interest. They seem to confirm that the rotational frequencies of the water molecule really form an arithmetical progression consistent with the formula in 10. The frequencies of these bands actually form an arithmetical progression with the common difference $1.73 \cdot 10^{12}$. If we put

$$\lambda = \frac{3 \cdot 10^{14}}{\nu} = \frac{3 \cdot 10^{14}}{n \cdot 1.73 \cdot 10^{12}}$$

and let n vary from 10 to 16 we get the wave-lengths, λ calc., of table 2. The observed wave-lengths, λ obs., are the band maxima found by Rubens and Aschkinass[8] between 10 and 20μ in the absorption spectrum of water vapour.

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* I want to mention that the interesting work by Eucken[11] on the molecular heat of hydrogen seems to indicate that the rotational frequency is constant. However, the difficulties in the interpretation of the experiments by Eucken are so great that hardly too much emphasis can be given to this.

Table 2

n	16	15	14	13	12	11	10
λ calc.	10.8	11.6	12.4	13.3	14.4	15.8	17.3
λ obs.	10.9	11.6	12.4	13.4	14.3	15.7	17.5

The absorption bands become stronger and stronger toward the long wave-length region and overlap more and more. For wave-lengths higher than 17.5μ, where the experimental technique is less satisfactory, only intensive absorption without structure has so far been found.

Thus it seems permissible to assume that these bands originate from the rotation of the water molecule.

From the difference $1.73 \cdot 10^{12}$, the moment of inertia of the water molecule can be calculated. One has

$$\frac{6.548 \cdot 10^{-27}}{2\pi^2 \cdot \mathcal{J}} = 1.73 \cdot 10^{12}; \quad \mathcal{J} = 1.92 \cdot 10^{-40}$$

A homogeneous sphere of the same mass as the water molecule $(18/[62 \cdot 10^{22}])$ has this moment of inertia if its radius $r = 0.4 \cdot 10^{-8}$ cm.

$$\mathcal{J} = \tfrac{2}{5} r^2 \cdot m = 1.92 \cdot 10^{-40}$$

$$r = 0.4 \cdot 10^{-8}.$$

It is seen that the calculated moment of inertia has a magnitude compatible with molecular dimensions.

It is easy to compute the *rotational energy* of one mole water vapour from the calculated moment of inertia and the observed average rotational frequency $5 \cdot 10^{12}$:

$$\tfrac{1}{2} \cdot 1.92 \cdot 10^{-40}(2\pi \cdot 5 \cdot 10^{12})^2 \cdot 62 \cdot 10^{22}/(0.419 \cdot 10^8) = 1400 \text{ cals.}$$

If it is assumed that the rotational energy of water vapour is ${}^3/_2 RT$ it follows that the temperature must be 200° C. The experiments of Rubens and v. Wartenberg were carried out at 110° C. The agreement must be regarded as satisfactory, considering the somewhat inaccurate determination of the maximum.

The rotational frequency calculated from the bands between 10 and 20μ is 3 to 6-fold greater than the most frequently occurring rotational frequency of the water molecule which corresponds to an absorption near 60μ according to part 7 of this paper. The bands between 10 and 20μ must, therefore, originate from small fractions of the total number of molecules because velocities that are that much in excess of the average are rare, according to the law of distribution of velocities. This explains why these bands have no influence on the broadening of the absorption bands of water vapour from 2 to 6μ.

The rotation of the water molecule does not result in sharp lines, but in bands. This may indicate that the quanta are of different magnitude, or, what seems more likely to me, that there are different moments of inertia about the molecular axes of rotation. The formula

$$\nu = \frac{nh}{2\pi^2 J}$$

shows that rotations about different axes take place with different frequencies.

Thus a closer discussion of the structure of the infrared spectrum of water vapour in two ways leads to the inference that the discontinuity of the rotational energy of the water molecule, as predicted by the quantum hypothesis, seems to be at hand.

12. Before ending the discussion concerning molecular rotation, I may add that it is possible to conclude with great certainty from the sharpness of several spectral lines, resp. from a missing symmetrical arrangement of lines required by the quantum hypothesis, that the radiating *atoms* do not rotate, or, at least not with frequencies comparable with molecular rotational frequencies. In this way we get evidence for the fact, established by investigations of specific heats, that the rotational energy of atoms must be very small.

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On the Infrared Spectra of Gases

III

The Configuration of the Carbon Dioxide Molecule and the Laws of the Intramolecular Forces

NIELS BJERRUM

Translated from *Verhandl. deut. physik. Ges.* **16** (1914) 737–53. The paper was received by the journal 7th July, 1914. A few lines, beginning in the 8th line on page 741 in the original paper, have been left out in the present edition because they contain an incorrect statement, which, however, is of no importance for the conclusions of the paper.

1. According to recent investigations most of the infrared spectral bands are caused by the movements of electrically charged *atoms* or groups of atoms, whereas the lines observed in the visible and in the ultraviolet spectrum are due to oscillations of the *electrons*. Therefore, the study of the infrared spectra must be very useful for our knowledge of the atomic vibrations in the molecules. Although the investigation of infrared spectra reveals only data concerning the movements of electrically charged atoms it is, however, to be expected that the vibrations of neutral atoms are governed by the same laws. In this paper we shall mainly be concerned with the atomic vibrations in the carbon dioxide molecule. The atoms in this molecule are all electrically charged.

2. In a preceding paper[1] it was shown that the three bands at 2.7, 4.3 and $14.7\,\mu$, which are the only bands in the infrared spectrum of carbon dioxide, correspond to three different *vibrations of the atoms*. As a triatomic molecule carbon dioxide has only three internal degrees of freedom. Therefore only three vibrations and, accordingly, three infrared bands are to be expected. From the wave-lengths of these bands the vibrational frequencies of the molecule can be calculated. The interesting question now arises: which properties must we ascribe to the carbon dioxide molecule in order to make it vibrate with just these three frequencies? In the following we will consider this problem.

3. Each of the three possible harmonic vibrations of the carbon dioxide molecule must be a complex movement of the molecule as a whole; if one atom oscillates the two others must necessarily participate in the oscillation. Each of the three harmonic vibrations of the molecule will constitute a co-ordinated synchronous vibration of all three atoms.

According to Rutherford the masses of the atoms are concentrated in the extremely small nuclei. We may therefore consider the carbon dioxide molecule as a simple system of three mass points. The masses will be $\frac{12}{N}, \frac{16}{N}, \frac{16}{N}$, where N is Avogadro's constant. Furthermore we will assume that the two oxygen atoms are fully symmetrically bound in accordance with the chemical properties of the carbon atom. The carbon dioxide molecule consequently forms an isosceles triangle, the shape of which is completely determined by the value of the vertex angle, 2θ.

The equilibrium lengths of the sides of the triangular molecule are denoted as l_1 (base) and l_2 (the two sides), and the changes in these lengths at a certain time as r_1, r_2, and r_3 (cp. fig. 1).

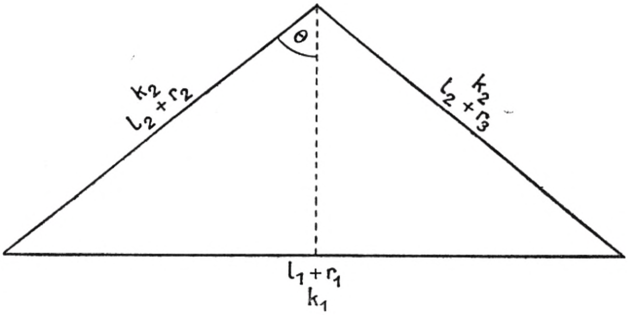


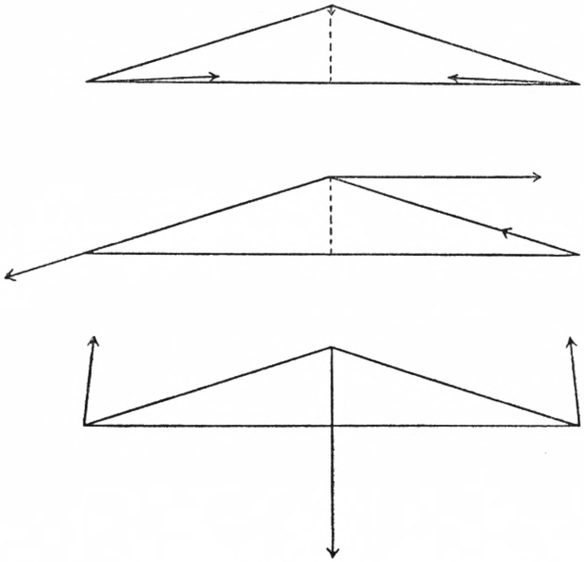
Fig. 1.

Before we can proceed any further we have to make definite assumptions about the nature of the intramolecular forces. We are going to carry through the calculations on the basis of two different hypotheses.

First we will assume that all internal forces are central forces between the three mass points (*Central Force System*). Next we will assume central forces acting between the carbon and the oxygen atoms, but not between the two oxygen atoms. Instead of direct forces between the oxygen atoms we will introduce a deformation (bending) force, which will oppose all changes of the angle θ (*Baeyer's strain theory*). Obviously, the second system agrees with our chemical aspects of the valence forces, and we will therefore nominate it the *Valence Force System.*

4. *Central Force System.* The force caused by a small (infinitesimal) change, r, in the distance between two atoms is represented by kr in the Central Force System, where k is a constant characterizing the strength of the bond between the two atoms. If we know the values of k_1 and k_2 related to the bonds between oxygen and oxygen, resp. carbon and oxygen, and if moreover θ, i.e. the shape

Fig. 2.



$\lambda = 2.7\mu$ $\varphi = 2.0°$

symmetrical $p = 10.9$

$\lambda = 4.3\mu$ $\varphi = 17.5°$

unsymmetrical $p = 0.39$

$\lambda = 14.7\mu$ $\varphi = 83°$

symmetrical $p = 0.37$

1. Solution. Central Force System.
$\theta = 72.5°$, $k_1 = 5.34 \cdot 10^6$ *dyne/cm*, $k_2 = 1.38 \cdot 10^6$ *dyne/cm*

of the molecule, is known we have sufficient data to calculate the three vibrational frequencies of the molecule.

On the other hand, it must be possible to compute k_1, k_2, and θ from the known frequencies, *which means that we are able to calculate the shape and rigidity of the carbon dioxide molecule from the measured positions of the infrared bands.* The details of this calculation will be given in the last part of the paper, but I shall state the results here. Two different solutions are obtained:
Either:

$$\theta = 72.5°,\ k_1 = 5.34 \cdot 10^6 \text{ dyne/cm},\ k_2 = 1.38 \cdot 10^6 \text{ dyne/cm},$$

or

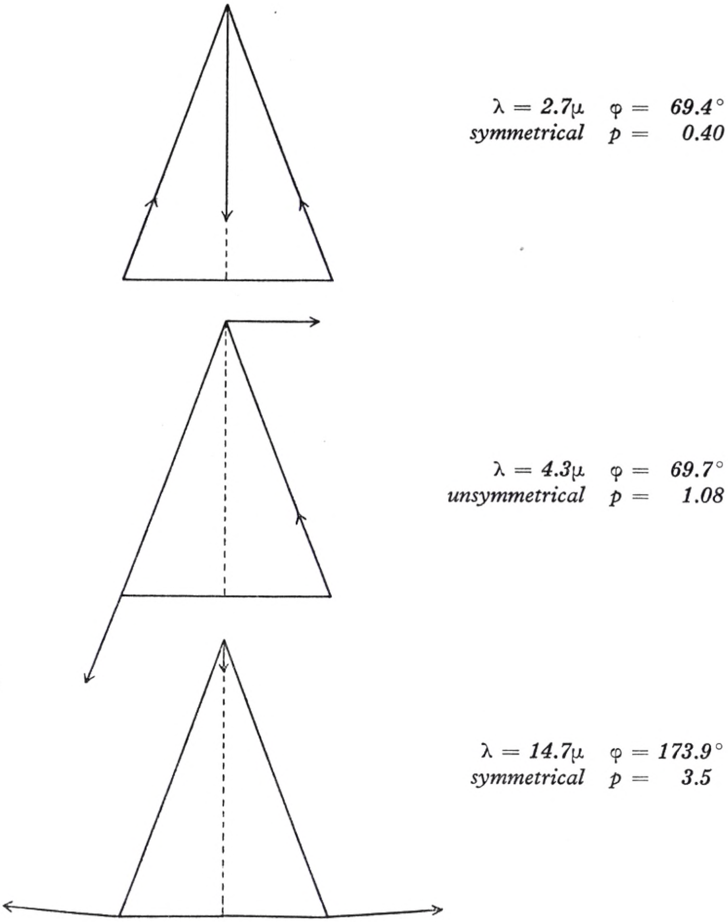
$$\theta = 20.3°,\ k_1 = 0.211 \cdot 10^6 \text{ dyne/cm},\ k_2 = 3.57 \cdot 10^6 \text{ dyne/cm}.$$

Fig. 2 and 3 show a survey of the vibrations of the carbon dioxide molecule in the two cases. The arrows indicate the relative magnitudes and directions of the linear oscillations of the atoms corresponding to the different infrared bands.

φ means the angle between the base (of the triangle) and the direction of oscillation, and p the ratio between the amplitude of the oxygen atoms and the carbon atom.

In both solutions the 4.3μ band corresponds to an unsymmetrical vibration, whereas the two other bands are ascribed to symmetrical vibrations.

Fig. 3.

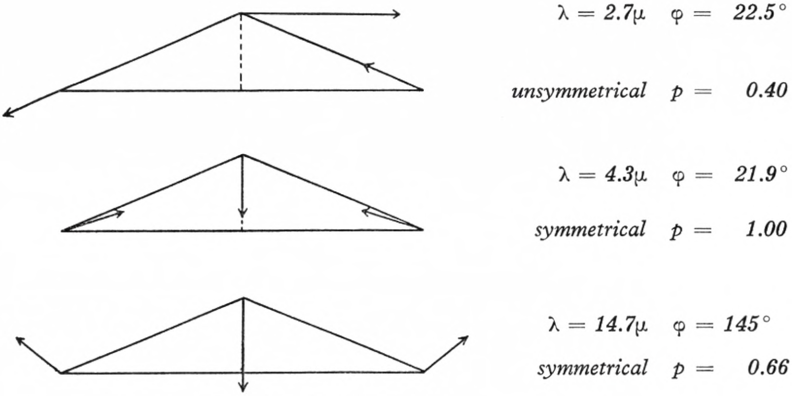


2. Solution. Central Force System.
$\theta = 20.3°$, $k_1 = 0.211 \cdot 10^6$ *dyne/cm*, $k_2 = 3.57 \cdot 10^6$ *dyne/cm.*

However, none of these solutions seems to be plausible on closer consideration. In the first, the oxygen-oxygen bond is 3.87 times stronger than the oxygen-carbon bond ($k_1/k_2 = 3.87$). From a chemical point of view this is extremely improbable. In this respect solution 2 is far better having $k_1/k_2 = 0.059$ which means a rather weak O—O bond. On the other hand, the second solution is very unsatisfactory from a stereochemical point of view because the two oxygen atoms are placed very close together.

For valence-theoretical reasons it is to be expected that no satisfactory solution

Fig. 4.



3. Solution. Valence Force System.
$\theta = 67.5°$, $k_\theta = 0.292 \cdot 10^6$ *dyne/cm*, $k_2 = 3.58 \cdot 10^6$ *dyne/cm.*

for the configuration of the carbon dioxide molecule can be obtained based on the assumption that the forces are all central forces. We are now going to investigate the configurations found on the basis of a Valence Force System.

5. *Valence Force System.* In this case, too, we can characterize the internal force system, governing the oscillations, by two constants k_θ and k_2. As before $k_2 r_2$ is the force acting between carbon and oxygen if the distance is changed with the amount r_2. k_θ is defined by the equation:

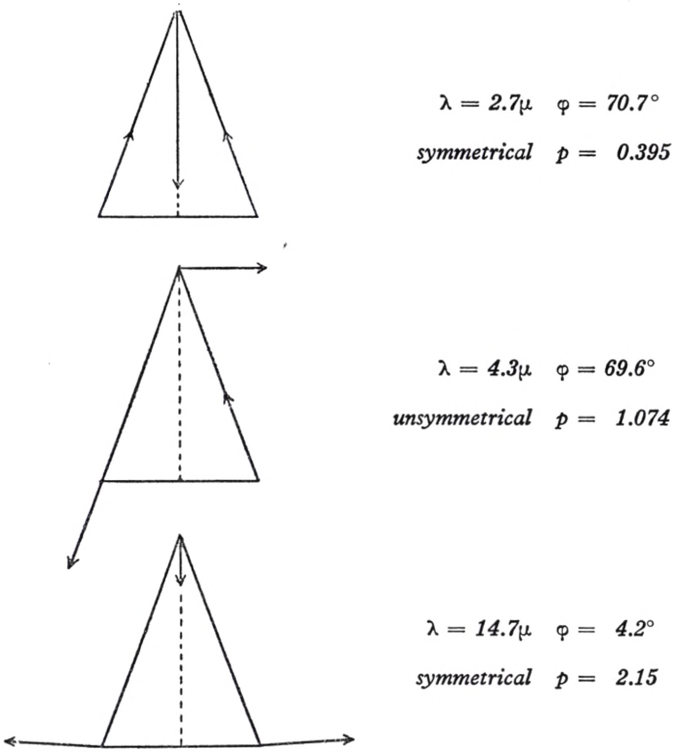
$$P_\theta = k_\theta \cdot l_2 d\theta$$

Here P_θ is the restoring force acting on the oxygen atoms if these are displaced $l_2 d\theta$ from their positions of equilibrium in a direction perpendicular to the sides of the triangle. Again, we can calculate θ, k_θ and k_2 from the (observed) wavelengths of the infrared bands, and two solutions are obtained.

Details concerning these solutions are indicated in fig. 4 and 5.

Of these two "valence-force" solutions the first appears to be the more plausible for several reasons. The two oxygen atoms are not found to be too close together, as $\theta = 67.5°$. Moreover, the constants representing the rigidity of the molecule seem to have plausible values. k_θ is considerably smaller than k_2 which means that it is far more easy to 'bend' the molecule than to diminish the distance between oxygen and carbon, a result that seems most probable. On the other hand, certain features point in favour of the last solution. I only want to point out that investigations of the far infrared spectrum seem to show that the carbon dioxide molecule rotates rather slowly, as there is no absorption between 20μ and 300μ. If the molecule had the extended shape indicated by solution 1 and

Fig. 5.



4. Solution. Valence Force System.
$\theta = 20.4°$, $k_\theta = 0.742 \cdot 10^6$ *dyne/cm*, $k_2 = 3.56 \cdot 10^6$ *dyne/cm*

3, one would expect a fast rotation about the long axis because of the small moment of inertia about this axis.

It would, of course, not be possible to observe the rotation in the far infrared if the molecule did not possess an electrical polarity perpendicular to this axis. It is, however, very probables that the molecule corresponding to solution 3 is polar in this direction.

If one assumes the carbon-oxygen bond to be of the same strength in carbon monoxide as in carbon dioxide one calculates a wave-length 5.2 μ according to solution 1 for the absorption band in carbon monoxide, whereas the other three solutions all give 3.2 μ. As the band in carbon monoxide is situated at 4.7 μ, it follows that our hypothesis leads to a value of the right order of magnitude for the absorption wave-lenght, but nothing more. After all we have no reason for assuming the same bond-strength in carbon monoxide as in carbon dioxide. At the calculation the following relation is used:

$$\lambda = 2\,\pi\, c \sqrt{\frac{C \cdot O}{CO} \cdot \frac{1}{k_2\, N}}$$

$$c = 3 \cdot 10^{14};\; N = 65 \cdot 10^{22}.$$

6. *On the deviation of the carbon dioxide molecule from the linear form.* Although the solutions based upon the "Valence Force" system are more plausible in several respects than those based on the "Central Force" system one can, however, raise one rather serious objection to these. It might be expected that the angle strain force would tend to keep the oxygen atoms in diametrically opposed positions. According to organic chemistry the carbon valencies are all equal and tetrahedrally distributed. Hence, the molecule must be linear. In our solutions, however, we have found it to be non-linear. This result is supported by the specific heat of carbon dioxide as the rotational energy is found to be $\frac{3}{2} RT$, whereas it should be RT for a linear molecule. The valence force system, to which we were led through our calculations, does not quite correspond to the valence force system expected from the organic chemistry.

In order to explain the deviation from the linear form one might assume that there were attractions between the oxygen atoms besides the assumed valence forces. The deviation would then be the result of a competition between this attraction and a Baeyer valence angle strain. Unfortunately, it is not possible in this case to calculate the shape of the molecule and the coefficients of the internal forces without making new arbitrary assumptions with respect to the dependence of the attractive forces on the distance between the oxygen atoms and with respect to the dependence of the valence angle strain on the bending of the molecule. Depending upon whether the attractive force or the valence angle strain changes with the higher power of the variable, the molecule will approach a valence force, respectively central force, molecule.

The bent form of the carbon dioxide molecule might also be explained as a centrifugal effect of the rotation. If the rigidity of the molecule initially is very low, but becomes very high after a certain bending, a resulting bending could be explained. The carbon dioxide molecule was then to be compared with a system of two small sticks connected with a universal joint only allowing a certain limited bending. In this case it would, on the other hand, be difficult to understand why the frequencies of the atomic oscillations are independent of the rotation.

7. *The influence of the rotation on the infrared bands of the carbon dioxide mole-*

cule. As previously shown[2] it is generally to be expected that an infrared band caused by atomic vibrations will appear as a *triplet* comprising two broad components and a sharp central line. For diatomic molecules, however, the band will be simpler. In this case the sharp central line will be missing* because the rotational axis will be perpendicular to the direction of vibration.

This theory for the influence of the rotation has recently been confirmed by the investigations of Burmeister and Eva v. Bahr. In one respect only a certain discrepancy between theory and experiment consists. According to the existing observations the sharp central line seems to be missing also in triatomic molecules like carbon dioxide and water vapour. These molecules seem to obey the theory for diatomic molecules. One must, however, remember that it is only possible to observe a sharp line in the absorption spectrum if a narrow slit is used. New investigations of the emission spectra of these gases would be very desirable for clarifying this point. In the emission spectrum the central line should be observable even if it is ever so sharp.

Quite apart from details the investigations of Burmeister and Eva v. Bahr have proved that the influence of the rotation on the infrared bands is unmistakable. It is furthermore possible to draw important conclusions from its general features.

Generally, it is not to be expected that the influence of the rotation on the three carbon dioxide bands should arise from the same rotation. To get a general survey of the conditions one has to remember that the radiating molecular vibrator has a definite axis of vibration, viz. the direction of a corresponding linear oscillator radiating in the same way. For the two symmetrical vibrations of carbon dioxide this axis of vibration coincides with the symmetry axis of the molecule, and for the unsymmetrical vibration it is an axis perpendicular to it in the plane of the molecule. As the two symmetrical vibrations possess the same axis they must be influenced in the same way by the rotation, whereas one must expect a separate behaviour of the unsymmetrical vibration. Therefore, if we had precise measurements of the structure of the bands it would be possible to decide which

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* W. C. Mandersloot (Diss. p. 51, Amsterdam 1914) who as the first has tried to explain the disappearance of the sharp line, seems to be of the opinion that according to his explanation the central component might disappear for all molecules (cp. p. 58 ff.). The way Mandersloot has treated the problem seems hardly permissible. He separates the actual rotation in rotations about the axis of vibration and perpendicular to it, and only the last rotation is being considered. One must, however, as I previously have done, treat the problem reversely. One must separate the oscillation in two components, one parallel to the rotational axis and one perpendicular to it. The first component will radiate unperturbed of the rotation, whereas the second component will radiate the frequencies $\nu_s \pm \nu_r$. As to Mandersloot's note pag. 51 (resp. Thesis IV) the following may be said. I have not assumed the *axis of oscillation* to have an arbitrary direction within the molecule, but that *the rotational axis* may have any possible orientation within the molecule. Only for linear, i.e. especially diatomic, molecules this assumption is not correct.

band corresponds to the unsymmetrical vibration and to find out if the molecules are rotating faster about the symmetry axis or about a line perpendicular to this axis in the plane of the molecule.

At first glance one might be inclined to think that the decision could be made from the present measurements. Whereas the distance between the components of the double bands at 4.3 μ and 14.7 μ approximately give the same rotational frequency[3] ($2.7 \cdot 10^{11}$, resp. $2.4 \cdot 10^{11}$), the structure of the band at 2.7 μ seems to give a considerably greater frequency of rotation[4] (about $17 \cdot 10^{11}$). This band should therefore correspond to the unsymmetrical vibration and the molecule should have the highest rotational frequency as well as the lowest moment of inertia about an axis perpendicular to the symmetry axis. If we compare these demands with the above four solutions we find that none of them are satisfactory. Only in the third solution does the band at 2.7 μ correspond to the unsymmetrical vibration, but unfortunately the moment of inertia about the symmetry axis here is much smaller than that about an axis at right angles to it.

Eva v. Bahr[4] is, too, of the opinion that the double band at 2.7 μ is not to be explained as due to rotation, but that it is of another, yet unknown, origin. The band is of quite another type than the usual rotational bands. Each of the two bands at 2.7 μ is in all probability a rotational double band. If these were associated with a low rotational frequency this would be in agreement with solution 3.

8. *Absolute size of the amplitudes of the vibrations and the dimension of the molecule.* The above treatment of the problem is permissible only if the amplitudes of the vibrations are really small compared with the dimensions of the molecule.

First, I have verified this for the hydrogen chloride molecule. From the value of the most probable rotational frequency the following moment of inertia is calculated:[5]

$$\mathcal{J} = 0.54 \cdot 10^{-39}$$

From this the distance, l, between the atomic centres is computed by means of the equation:

$$\mathcal{J} = \frac{l^2}{N} \cdot \frac{Cl \cdot H}{HCl}$$

For $N = 65 \cdot 10^{22}$ one gets:

$$l = 1.89 \cdot 10^{-8}$$

This value is of the same order of magnitude as the molecular dimensions of similar molecules calculated on the basis of the kinetic theory of gases.

In order to calculate the amplitudes of the vibrations we compute first the rigidity of the bonds between the atoms. The force, P, acting between the atoms when the distance changes with the amount, r, is equal to

$$P = kr\,.$$

The coefficient, k, is determined by the equation:

$$k = (2\,\pi\,\nu)^2 \cdot \frac{Cl \cdot H}{HCl} \cdot \frac{1}{N} \tag{1}$$

If a denotes the amplitude of the vibration, we have for the vibrational energy (E_v):

$$E_v = \tfrac{1}{2}\,ka^2 \tag{2}$$

Hence, from equations 1 and 2:

$$a = \frac{1}{2\,\pi\,\nu} \cdot \sqrt{\frac{HCl}{H \cdot Cl} \cdot 2E_v \cdot N} \tag{3}$$

If we put the vibration energy equal to one quantum we have

$$E_v = h\nu\,.$$

Further, if we insert the values

$$h = 6.4 \cdot 10^{-27} \text{ and } N = 65 \cdot 10^{22}$$

we get

$$a = 0.158 \cdot 10^{-8}\,.$$

This means that the amplitude of the vibration is 8.3 per cent of the length of the molecule.

If we put

$$E_v = \frac{RT}{N}$$

i.e. we equalize the vibrational energy with the mean value required by the classical theory, we find for 18° C

$$a = 0.041 \cdot 10^{-8}$$

an amplitude corresponding to only about 2 per cent of the length of the molecule.

It is easy in a similar way to calculate the amplitudes of the vibrations for the carbon dioxide molecule if the force constants (k) are known.

I have carried out these calculations for the third solution only; it should, however, suffice to demonstrate the smallness of the amplitudes in a simple case.

The results of the calculation are given in the following table.

Vibrational Amplitudes for CO_2. Third Solution. Valence Force System. $\theta = 67.5°$.

a) The vibrational energy equals one quantum.

As the dimensions of the carbon dioxide molecule certainly exceeds 10^{-8}, it follows from the table that to a good approximation we are entitled to consider the vibrations of the carbon dioxide molecule as infinitesimal.

This is, however, not absolutely correct. It is therefore natural that the vibrational frequencies are not completely independent of the vibrational energy, i.e.

Band at	Ampl. of C-atom	Ampl. of O-atom
14.7μ	$2.8 \cdot 10^{-10}$	$1.84 \cdot 10^{-10}$
4.3μ	$5.8 \cdot 10^{-10}$	$2.6 \cdot 10^{-10}$
2.7μ	$3.4 \cdot 10^{-10}$	$1.36 \cdot 10^{-10}$

b) The vibrational energy equals the classical value for 18° C

Band at	Ampl. of C atom	Ampl. of O atom
14.7μ	$1.49 \cdot 10^{-10}$	$0.98 \cdot 10^{-10}$
4.3μ	$1.66 \cdot 10^{-10}$	$0.75 \cdot 10^{-10}$
2.7μ	$0.77 \cdot 10^{-10}$	$0.31 \cdot 10^{-10}$

that the infrared bands are shifted a little with the temperature. Such a shift is in fact observed for the 6 μ band of water vapour and for the 4.3 μ carbon dioxide band[6] (cf. ref.[7]).

9. The considerations presented above are rather incomplete and have not resulted in unambiguous conclusions. Nevertheless, I believe them to be of a certain interest, because they indicate a way in which we may investigate the limitations of our usual mechanical concepts. If the results of new and more complete investigations of infrared spectra should turn out to be incompatible with considerations like those used above, this might probably indicate that we have to resort to similar revolutionary intuitions for explaining the radiation connected with the vibrations and rotations of the molecules as has been done recently by N. Bohr[8] in the case of electronic radiation.

ON THE METHOD USED FOR THE CALCULATIONS

10. *Calculation of the infinitesimal vibrations of a carbon dioxide molecule assuming central forces (cf. 3 and 4)*. The vibrations have been calculated by means of Lagrange's equations of motion:

$$\frac{\partial (T - U)}{\partial r_i} = \frac{d}{dt}\frac{\partial T}{\partial r_i'}, \quad i = 1, 2, 3. \tag{1}$$

where T is the kinetic energy and U the potential energy. First, expressions for U and T are formed:

$$U = \tfrac{1}{2}k_1 r_1^2 + \tfrac{1}{2}k_2\, r_2^2 + \tfrac{1}{2}k_2 r_3^2 \tag{2}$$

and

$$T = \frac{1}{2\,N}[A\,r_1'^2 + Br_2'^2 + Br_3'^2 + 2Dr_2'r_3' + 2Er_1'r_3' + 2Er_1'r_2'] \tag{3}$$

In equation 3 N is Avogadro's constant and the coefficients A, B, D, E, have the following values:

$$\left.\begin{aligned} &A = \frac{m_2}{2} + \frac{m_1 m_2}{2\,M} \cdot \operatorname{tg}^2 \theta\,, \qquad B = \frac{m_1 m_2}{2\,M \cos^2 \theta} \cdot \frac{M + m_1 \cos^2 \theta}{M - 2m_2 \cos^2 \theta} \\ &D = \frac{m_1 m_2}{2\,M \cos^2 \theta} \cdot \frac{M \sin^2\theta - 2m_2 \cos^2\theta}{M - 2m_2 \cos^2\theta}, \qquad E = -\frac{m_1 m_2}{2M} \cdot \frac{\sin\theta}{\cos^2\theta} \\ &m_1 = 12, \qquad m_2 = 16, \qquad M = m_1 + 2m_2 = 44 \end{aligned}\right\} \tag{4}$$

After insertion of the expressions for T and U the Lagrangian equations take the following form:

$$\left.\begin{aligned} A\frac{d^2r_1}{dt^2} + E\frac{d^2r_2}{dt^2} + E\frac{d^2r_3}{dt^2} + Nk_1r_1 = 0 \\ E\frac{d^2r_1}{dt^2} + B\frac{d^2r_2}{dt^2} + D\frac{d^2r_3}{dt^2} + Nk_2r_2 = 0 \\ E\frac{d^2r_1}{dt^2} + D\frac{d^2r_2}{dt^2} + B\frac{d^2r_3}{dt^2} + Nk_2r_3 = 0 \end{aligned}\right\} \tag{5}$$

The solutions of these equations have the following form:

$$\left.\begin{aligned} r_1 = a_1 \sin\left(t \cdot \frac{2\pi}{T} + \alpha\right) \\ r_2 = a_2 \sin\left(t \cdot \frac{2\pi}{T} + \alpha\right) \\ r_3 = a_3 \sin\left(t \cdot \frac{2\pi}{T} + \alpha\right) \end{aligned}\right\} \tag{6}$$

The period of vibration, T, and the amplitudes, a_1, a_2, a_3 must satisfy the following three equations:

$$\left.\begin{aligned} \left(A - \frac{Nk_1}{4\pi^2} T^2\right) a_1 + Ea_2 + Ea_3 = 0 \\ Ea_1 + \left(B - \frac{Nk_2}{4\pi^2} \cdot T^2\right) a_2 + Da_3 = 0 \\ Ea_1 + Da_2 + \left(B - \frac{Nk_2}{4\pi^2} \cdot T^2\right) a_3 = 0 \end{aligned}\right\} \tag{7}$$

If we introduce

$$\frac{N}{4\pi^2} \cdot T^2 = x \tag{8}$$

and then eliminate a_1, a_2, and a_3, we get:

$$\begin{vmatrix} A - k_1x & E & E \\ E & B - k_2x & D \\ E & D & B - k_2x \end{vmatrix} = 0 \tag{9}$$

This determinant 9 can be transformed as follows:

$$[k_2x - (B - D)] \cdot [x^2k_1k_2 - x(k_1(B + D) + k_2A) + (B + D)A - 2E^2] = 0 \tag{9a}$$

If λ_1, λ_2, and λ_3 are the wave-lengths of the carbon dioxide bands the following values of x must satisfy equation 9a:

$$\lambda_1^2 \cdot \frac{N}{4\pi^2c^2}, \quad \lambda_2^2 \cdot \frac{N}{4\pi^2c^2}, \quad \lambda_3^2 \cdot \frac{N}{4\pi^2c^2} \tag{10}$$

In these expressions c is the velocity of light. We shall denote the numerical values of these three expressions as α_1, α_2, and α_3.

Because α_1, α_2, and α_3 are roots of equation 9a the following three relations are valid:

$$\left.\begin{aligned} k_2\,\alpha_1 &= B - D \\ k_1\,k_2\,\alpha_2\,\alpha_3 &= (B + D)\,A - 2\,E^2 \\ k_1\,k_2\,(\alpha_2 + \alpha_3) &= k_1\,(B + D) + k_2\,A \end{aligned}\right\} \tag{11}$$

One must remember, however, that it is sufficient if a similar set of relations with permuted α-indices are satisfied.

By insertion of the values for A, B, D, E in equations 11 one obtains:

$$\left.\begin{aligned} k_2\,\alpha_1 &= \frac{m_1\,m_2}{M - 2\,m_2\cos^2\theta}\,; \quad k_1\,k_2\,\alpha_2\,\alpha_3 = \frac{m_1\,m_2{}^2}{2\,M\cos^2\theta} \\ k_1\,k_2\,(\alpha_2 + \alpha_3) &= k_2\,\frac{m_2}{2\,M} \cdot \frac{m_1 + 2\,m_2\cos^2\theta}{\cos^2\theta} + k_1\,\frac{m_1\,m_2}{M\cos^2\theta} \end{aligned}\right\} \tag{12}$$

From equations 12 one finds k_1, k_2, and $\cos^2\theta$. After elimination of k_1 and k_2 one gets a second order equation in $\cos^2\theta$. Afterwards α_1 is changed for α_2, resp. α_3, and these equations are solved. In total one would expect six values for $\cos^2\theta$. Four of these are, however, imaginary in θ and only two real solutions are obtained.

After the calculation of k_1, k_2, and θ, the amplitudes are found from the equations 7.

For the root (α_1), which was put equal to $\dfrac{B - D}{k_2}$ (equation 11) one gets:

$$a_1 = 0, \qquad a_2 = -\,a_3. \tag{13}$$

And for the two other roots (α_2 and α_3) one gets:

$$\frac{a_2}{a_1} = \frac{a_3}{a_1} = -\frac{E}{B + D - k_2\,\alpha} = -\frac{A - k_1\,\alpha}{2\,E} \tag{14}$$

Finally, one can calculate the vibrations of each individual atom from the changes of the atomic distances (a_1, a_2, a_3) by means of the following relations.

When $a_1 = 0$ and $a_2 = -a_3$, the carbon atom is vibrating perpendicular to the symmetry axis and the oxygen atoms vibrate along the isosceles of the triangle. To characterize a vibration it is sufficient to know a quantity, p, defined in the following way:

$$p = \frac{\text{amplitude of the O-atoms}}{\text{amplitude of the C-atom}}$$

One can calculate p from the equation:

$$p = \frac{12}{32} \cdot \frac{1}{\sin\theta} \tag{15}$$

For the two other vibrations, where $a_2 = a_3$, the angle between the base of the triangle and the direction of vibration of the oxygen atoms is determined by:

$$\operatorname{tg}\varphi = \frac{12}{44} \cdot \frac{2 \cdot \dfrac{a_2}{a_1} - \sin\theta}{\cos\theta} \tag{16}$$

And p is expressed by:

$$p = \frac{12}{32} \cdot \frac{1}{\sin\varphi} \tag{17}$$

11. *Calculation of the infinitesimal vibrations of a carbon dioxide molecule assuming valence forces* (cf. 5). In this case the expression for T, the kinetic energy, is identical with equation 3. The potential energy, U, is given by:

$$U = \tfrac{1}{2}k_2 r_2^2 + \tfrac{1}{2}k_2 r_3^2 + \tfrac{1}{2}k_\theta l^2 d\theta^2. \tag{18}$$

By transformation, insertion of ν_3 for $d\theta$, we get:

$$\begin{aligned} U = {} & \tfrac{1}{2}k_1 r_1^2 + \tfrac{1}{2}(k_2 + k_1 \sin^2\theta) r_2^2 + \tfrac{1}{2}(k_2 + k_1 \sin^2\theta) r_3^2 \\ & + k_1 \sin^2\theta \; r_2 r_3 - k_1 \sin\theta \; r_1 r_3 - k_1 \sin\theta \; r_1 r_2 \,. \end{aligned} \tag{20}$$

Here, too, $k_1 = \dfrac{k_\theta}{4\cos^2\theta}$ is introduced.

If we integrate the Lagrangian equations as done above we get the following equation, instead of 9a, for the determination of x:

$$\left.\begin{aligned}&[k_2x - (B - D)] \cdot [k_1k_2x^2 - (k_1(B + D) + A(k_2 + 2k_1 \sin^2\theta)\\&+ 4Ek_1 \sin\theta)x + A(B + D) - 2E^2] = 0\end{aligned}\right\} \tag{21}$$

Again if α_1, α_2, α_3 are defined by the relations 10 we get for the evaluation of k_1, k_2, and θ the three equations:

$$\left.\begin{aligned}k_2\alpha_1 = B - D, \quad k_1k_2\alpha_2\alpha_3 = A(B + D) - 2E^2\\k_1k_2(\alpha_2 + \alpha_3) = (B + D + 2A \sin^2\theta + 4E\sin\theta)k_1 + Ak_2\end{aligned}\right\} \tag{22}$$

resp. the corresponding equations with permuted α's.

After insertion of the numerical values for A, B, D, E one gets:

$$\left.\begin{aligned}k_2\alpha_1 = \frac{48}{11 - 8\cos^2\theta}, \qquad k_1k_2\alpha_2\alpha_3 = \frac{384}{11} \cdot \frac{1}{\cos^2\theta}\\k_1k_2(\alpha_2 + \alpha_3) = k_2 \cdot \frac{8}{11} \cdot \frac{3 + 8\cos^2\theta}{\cos^2\theta} + k_1 \cdot \frac{16}{11}(11 - 8\cos^2\theta)\end{aligned}\right\} \tag{23}$$

After elimination of k_1 and k_2 one finally obtains:

$$\frac{\alpha_2\alpha_3}{\alpha_1} \cdot \frac{3 + 8\cos^2\theta}{11 - 8\cos^2\theta} + \alpha_1 \frac{(11 - 8\cos^2\theta)^2}{33} = \alpha_2 + \alpha_3 \tag{24}$$

from which $\cos^2\theta$ is found.

From equations 23 k_1 and k_2, and from 20 k_θ are easily found.

The calculation of the proportions between a_1, a_2, and a_3 is carried through in the following way. For the root (α_1), which is put equal to $\frac{B - D}{k_2}$, one has as before:

$$a_1 = 0, \; a_2 = -a_3. \tag{25}$$

And for the two others (α_2 and α_3):

$$\frac{a_2}{a_1} = \frac{a_3}{a_1} = -\frac{A - k_1\alpha}{2(E + k_1\alpha \sin\theta)} = -\frac{E + k_1 \sin\theta}{B + D - 2\alpha k_1 \sin^2\theta - \alpha k_2}. \tag{26}$$

The calculation of the vibrations of each individual atom from a_1, a_2, and a_3 proceeds in exactly the same way as for central forces.

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A New Form for the Electrolytic Dissociation Theory

NIELS BJERRUM

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Some time ago (1906) I advanced the proposition that a simple electrolytic dissociation is not accompanied by change of colour. I have now tried to establish this hypothesis by new experiments.

It seems to me that experiments with chromium salts are especially adapted for elucidating this question, because the changes between normal and complex salt in the case of these compounds take place only slowly, so that in using them it is possible to work with solutions which are demonstrably free from complex salts, a condition not so easily obtainable in the case of other metallic salts. I have therefore made a number of experiments with chromium chloride, chromium nitrate, and chromium sulphate, and I find that pure normal chromium salts in solution always have exactly the same absorption of light, no matter what the concentration and the acid is, but as soon as the formation of complex salts can be demonstrated, the colour is changed.

However, it is only in the case of the strong electrolytes that the colour is not changed with the concentration. The colour of the weaker electrolytes depends upon the concentration. I suppose that in the solutions of the weaker electrolytes there is always a greater or smaller quantity of undissociated salt, corresponding in structure to complex salts, and that this salt not only causes the changes in colour but also reduces the electric conductivity.

These colour-relations found in connection with electrolytic dissociation can best be explained by changing Arrhenius's hypothesis in the following manner: We suppose that the strong electrolytes always are completely separated into ions, and that this is the reason why they always have the same colour in all concentrations. If changes of colour take place in solutions of an electrolyte, the ions have more or less entered into combination with each other, the dissociation is not complete.

If this hypothesis is correct, then the decrease in molecular conductivity and in molecular depression of the freezing-point that accompanies the increase in concentration must be due to the action of the electric charges of the ions on each other. The molecular conductivity is diminished not because the number of ions is decreased but because the ions move more slowly. Sutherland has tried to explain the diminution of the molecular conductivity in such a way, but, as it seems to me, without having been quite successful in his attempt. For the explanation it is necessary to have the kinetic theory of liquid, which we still lack. Yet it seems to me there can be no doubt that the electrolytic friction must increase with the ion-concentration, both because the positive and the negative ions will more frequently collide than the neutral molecules and also because the electric field around the ions, increasing with the concentration, will create about the ions a water-mantle of increasing thickness.

It accords well with this new form for the dissociation theory that the "degree of dissociation" which has been calculated from the molecular conductivity is, in the case of strong electrolytes, approximately determined by the valency of the ions (Ostwald-Walden's rule), by the dielectric constant of the solvent (Walden), and by the concentration of the salt. The fact that the so-called "degree of dissociation" depends upon the electric constants of the substances without admitting of any specific influence by chemical affinity becomes quite natural when this quantity in reality is the decrease in electrolytic friction due to the electric forces among the ions. And the fact that the law of mass action does not apply to the influence of the concentration on the degree of dissociation of strong electrolytes will no longer be an inexplicable anomaly. In the case of the dissociation of weak electrolytes, as is well known, the law of mass action has been found to be applicable, but by means of the conductivity we here measure a real dissociation, since the ion-concentration in the solution is so small that we can consider the electrolytic friction as constant.

This new form for the dissociation theory explains just as well as the old Arrhenius form the analytical reactions and the phenomena of electrolysis. The only thing that is not explained so well by the new as by the old theory is the agreement between the decrease in the molecular conductivity and the decrease in the molecular depression of the freezing-point with the increase in concentration. (The agreement between the degrees of dissociation, which are calculated from freezing-point, boiling-point, distribution, electromotive force, etc., is a necessity, since all these quantities can be deduced from osmotic pressure.) But the agreement between the degree of dissociation calculated from the conductivity and that calculated from the freezing-point is not always perfect (*e.g.*, in the case of sodium chloride), and, besides, the approximate agreement may possibly, some time in the future, be explained by the fact that both the decrease in the molecular conductivity and the decrease in the molecular depression of the freezing-point are due to the electric forces at work among the ions.

For all these reasons the new form seems to me to represent a valuable alteration of the Arrhenius dissociation theory.

The Dissociation of Strong Electrolytes

NIELS BJERRUM

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The theory which, during the last decennia, has had the greatest importance for the development of chemistry is undoubtedly the theory of the free ions, which we owe to Arrhenius. It is first through this theory that we have obtained the right understanding of the nature of the acids, bases, and salts, and have learned to know the real difference between strong and weak acids, and between normal and complex salts.

The degree of dissociation α for a *weak* electrolyte calculated from the electrical conductivity by means of the equation $\alpha = \mu/\mu_\infty$ varies with the concentration just as it should according to the mass-action law of Guldberg and Waage. This fact has contributed much to the victory of the theory of ionization in the years following its appearance. However, when one calculates, in the same way, the degree of dissociation for a *strong* electrolyte, there appear a series of anomalies, which have caused considerable difficulties to the theory: the degree of dissociation calculated from the conductivity does, in general, not agree with that computed from osmotic data by means of the equation $\alpha = i - 1$, where i is the so called van't Hoff's coefficient,* and neither of the values agree with the law of mass action. It is the intention with the following considerations to try to show how these and other difficulties for the Arrhenius' theory have arisen because the quantities μ/μ_∞ and $i - 1$ for the strong electrolytes have erroneously been considered as measures of a degree of dissociation. The fact that μ/μ_∞ and $i - 1$ for strong electrolytes decrease more and more below unity with increasing concentration, must not necessarily be explained as a consequence of decreasing

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* The van't Hoff's coefficient i denotes the ratio between the observed osmotic pressure (freezing-point depression, boiling-point elevation) and that calculated without the assumption of dissociation.

dissociation, but may be interpreted in another way. An examination of the available material has led me to the opinion that the strong electrolytes ought to be considered as practically completely dissociated. The new view may therefore appropriately be designated as *the hypothesis of the complete dissociation of the strong electrolytes.*

The reasons for the hypothesis. A series of examinations of the salts of chromium had in 1906 led me to the result that the strong electrolytes, both in dilute and concentrated solution, possess the colour of the ion, if only complex compounds are not formed in the solution[1], and Hantzsch had simultaneously arrived at the same conclusion through other examinations. This fact, that the colour of a strong electrolyte is independent of its concentration, led me in 1909 to propose the hypothesis, that the strong electrolytes in solution are completely dissociated into ions (when complex compounds are not formed)[2]. This hypothesis involves that the influence of the concentration on the molar conductivity and on the van't Hoff's coefficient i must be explained in another way than hitherto. It was already then pointed out that it should probably be possible to explain these effects as a consequence of the electrical forces between the ions. In favour of this explanation spoke the fact, otherwise difficult to understand, that the effect is mainly determined by the electrical properties of the system (number of ions, magnitude of the electric charge of the system, and dielectric constant of the solvent). It was further emphasized that the anomalies of the strong electrolytes would disappear when μ/μ_∞ and $i - 1$ were no longer considered as measures of a degree of dissociation. But it is of course evident that the justification for assuming the hypothesis of the complete dissociation of the strong electrolytes depends upon whether it is possible, in a plausible way, to explain the values of μ/μ_∞ and $i - 1$ as a consequence of the electric charges of the ions.

Some time ago, I resumed working with the hypothesis, and I succeeded in calculating approximately how much the electric forces between the ions must reduce the osmotic pressure. In this way I found that the effect was approximately as great as it should be. Having reached so far, I discovered, however, that Milner[3] in the years 1912–13 had carried through a similar calculation. I have based the following statements on his results because his calculations have been carried out with a considerably greater degree of accuracy than my own.

The lowering of the osmotic pressure which the electric charges of the ions produce, and which may appropriately be called the *Milner effect,* is in Fig. 1 represented by the continuous curve. The curve shows the lowering for an electrolyte consisting of two monovalent ions. For comparison is given, by means of crosses, the lowering which has been found experimentally for potassium chloride from freezing-point determinations. It is seen that the Milner effect has the right order of magnitude, especially at concentrations which are neither

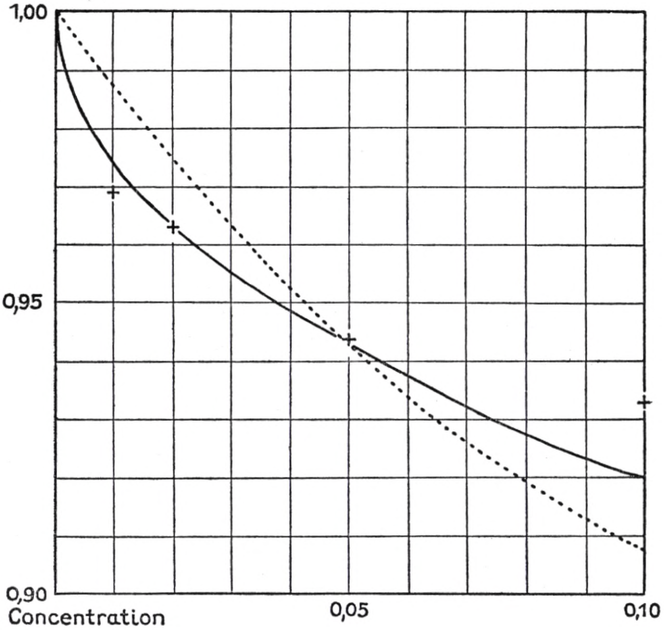

Fig. 1. The decrease of the osmotic pressure.

——————— *according to Milner*

- - - - - - - - - - - - - - *according to the mass-action law*

+ + *from freezing-point determinations.*

so small that the experimental determinations are too uncertain, nor so great that Milner's calculations, the accuracy of which decreases with increasing concentration, are too unreliable. The dotted curve shows how the osmotic pressure would decrease if it should be explained from the assumption of undissociated molecules formed according to the law of Guldberg and Waage. This curve makes a much poorer fit than that of Milner although a suitably chosen dissociation constant has been used for its calculation, while the Milner curve has been calculated without any arbitrarily chosen constant.

The Milner effect is a direct consequence of the mutual attraction and repulsion of the ions according to Coulomb's laws, and if the variation of the osmotic pressure is to be interpreted from the assumption of incomplete dissociation, one must first explain why the Milner effect may be neglected.

If one will assume that the strong electrolytes are completely ionized, one ought also to be able to explain the variation of the conductivity with the concentration as a consequence of the electric charges of the ions. Hertz[4] has in 1912 examined how the conductivity of the ions is affected by the electric forces which are active between them, and he has found that this effect, which appropriately may be called the *Hertz effect*, must produce a decrease of the conductivity of the ions with increasing concentration. He has also deduced a formula for this effect and shown that it may be used for explaining the observed variation of the conductivity, *e. g.* for sodium chloride. His formula contains, however, quantities which are only little known (thus, the free path of the ions in the solution), and the values which he must use for these quantities are not the most probable. For this reason, more work is needed before it may be considered to be certain that the Hertz effect is fully able to account for the change of the conductivity of strong electrolytes with concentration.

We have now seen that measurements of freezing-points and conductivities, owing to the Milner and the Hertz effect, respectively, are not suitable for the determination of the degree of dissociation of the strong electrolytes. A third method which has been used for this purpose, and which is based upon the catalytic effect of the ions, remains yet to be examined. It is especially the hydrogen ions which have a catalytic effect. It is therefore primarily the dissociation constants of the acids which one has tried to determine in this way. Most investigators who have examined strong acids by this method have found that the catalytic activity of the acid is proportional to its gross concentration, irrespective of the fact that the molar conductivity of the acid varies within wide limits. As an example I shall refer to some measurements by Goldschmidt and Thuesen[5] of the esterifying effect of hydrogen chloride on organic acids dissolved in methyl alcohol.

The esterifying effect of hydrogen chloride in methyl alcohol
c is the molar concentration of hydrogen chloride, and k the velocity constant for the esterification

c	k/c for			μ/μ_∞ for hydrochloric acid
	i-butyric acid	benzoic acid	acetic acid	
0.1		0.308		0.601
0.05	31.0	0.311	97.1	0.672
0.025	31.7		100.2	0.734
0.01			92.7	0.806

Snethlage[6] has with special strength emphasized the peculiarity in this result, and he has pointed out that it indicates that the strong electrolytes are either not dissociated at all, or they are completely dissociated. But while Snethlage, for reasons to which I cannot attach any importance, prefers the former alternative, I am of the opinion that one should prefer the assumption that the strong electrolytes are completely dissociated, because it seems impossible to me to abandon the Arrhenius conception of the free ions. If one will maintain that $i - 1$

and μ/μ_∞ are measures of a degree of dissociation of the strong acid, one must, in order to explain the catalytic measurements, assume that not only the hydrogen ions, but also the undissociated acid molecules catalyze the esterification, an auxiliary hypothesis which does away with all the beauty in the application of the ionic theory to the phenomena of catalysis.

Our present knowledge of the degree of dissociation of the strong electrolytes may therefore be summarized in the following few words:

The osmotic and the catalytic measurements indicate complete dissociation, and the conductivity measurements do not speak against complete dissociation.

Everyone who will maintain that $i - 1$ and μ/μ_∞ are measures of the degree of dissociation of a strong electrolyte must first explain why the Milner effect and the Hertz effect should fail to appear, and must then, as an explanation of the catalytic measurements, make the auxiliary hypothesis of the catalytic activity of the undissociated acid molecules, and, having cleared these rocks, he has yet left to find applicable explanations of all the many "anomalies of the strong electrolytes" by means of new auxiliary hypotheses suitable for the purpose.

The working programme of the hypothesis. If one will assume that the strong electrolytes are completely dissociated, one may no longer by μ/μ_∞ understand the degree of dissociation of a strong electrolyte. The quantity μ/μ_∞ will only be a coefficient expressing the ratio between the conductivity of the ions in the solution considered and their conductivity in infinitely dilute solution. One may appropriately call it the *conductivity coefficient* and designate it as f_μ. The van't Hoff coefficient i, which expresses the osmotic effect of an electrolyte (*e. g.* its influence on the freezing-point) may no longer be put equal to $1 + x$ where x is the degree of dissociation. One must introduce an *osmotic coefficient*, $f_o = p/p_0$, where p is the osmotic pressure of the solution, and p_0 is the osmotic pressure which one should have if the ions behaved like uncharged molecules (for binary electrolytes, $f_o = i/2$). Finally, it is necessary to introduce an *activity coefficient* f_a which expresses the ratio between the active mass of the ion and its concentration, because one must not assume that this ratio is equal to the degree of dissociation defined by the conductivity coefficient. (Instead of the activity coefficient f_a, it may, in certain cases, be useful to introduce -log f_a, and this quantity may appropriately be called the exponential or potential deviation).

$$f_\mu = \mu/\mu_\infty;\ f_o = p/p_0\ (= i/2);$$
$$f_a = \text{active mass/concentration.}$$

The hypothesis places us before the task, by experimental examinations and by theoretical considerations, to determine the values of these coefficients and to discover the laws holding for them, thus, among other things, to find out if there are relations between the different coefficients. As far as I have hitherto been able to judge from the material, all these coefficients depend mainly upon the concentration of ions in the solution, the valency of the ions, and the dielectric constant of the solvent, but they are only to a small degree dependent upon the other properties of the ions, *e. g.* their weight and volume. Owing to these results, it is easy to obtain a survey of the values of these coefficients in a solution of an electrolyte. A formula as the following

$$-\log f_a = 26 \frac{n^2}{K} \sqrt[3]{c_{\text{ion}}},$$

where n is the valency of the ions, K the dielectric constant of the solvent, and c_{ion} the concentration of ions in the solution, gives with approximation the value of the activity coefficient in a large number of cases.

As to the value of the conductivity coefficient, an immense experimental material is, as is well known, available, and we are, especially through the investigations of Walden and Noyes, well acquainted with the laws for its magnitude. This coefficient has hitherto been used in a multitude of calculations where one really ought to have used the activity coefficient, *e. g.* in calculations of equilibrium constants of homogeneous and heterogeneous equilibria, and in calculations of electromotive forces. It has hitherto been assumed that the two coefficients are identical, but this is far from being the case, and at least a considerable part of the anomalies, for the explanation of which one has had to put forward the hypothesis of the effect of neutral salts on chemical equilibria, disappear when the correct value of the activity coefficient is applied instead of the conductivity coefficient.

Methods for the calculation of the activity coefficient. In the following, some examples of how the activity coefficient may be calculated will be given as an illustration of what one may expect to obtain by carrying out one's calculations on the basis of the new hypothesis. Although the activity coefficient, from a chemical point of view, is the most interesting of the coefficients mentioned, it has hitherto been overlooked. By the calculations we get an opportunity of seeing, how anomalies found by earlier calculations everywhere disappear when the values calculated for the activity coefficients are applied.

1. The activity coefficient may be determined from the osmotic coefficient by means of the following relation which may be deduced thermodynamically*

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* For a mixture of x moles of the component 1 and $1-x$ moles of the component 2, the following equation holds

$$x \frac{dA_1}{dx} + (1-x) \frac{dA_2}{dx} = 0$$

where A_1 and A_2 are the free energies which may be gained by adding one mole of the corresponding component to a large amount of the mixture. For ideal mixtures one has

$$A_1 = -RT \ln x \quad \text{and} \quad A_2 = -RT \ln(1-x).$$

(continues)

$$f_o + c\,\frac{df_o}{dc} = 1 + c\,\frac{d\ln f_a}{dc}\,.$$

This thermodynamic relation is very interesting and it possesses many curious properties. We shall, however, not discuss the equation further at this occasion but only use it for the calculation of the activity coefficient of potassium chloride, for which salt the osmotic coefficient is known from freezing-point measurements. According to the statements of Noyes and Falk[7], the available determinations may be summarized in the following interpolation formula (c is the molar concentration)

$$f_o = 1 - 0.146\,\sqrt[3]{c}\ .$$

When this expression is introduced into the thermodynamic equation, one obtains

$$\ln f_a = -4 \cdot 0.146\,\sqrt[3]{c}$$

or

$$\log f_a = -0.253\,\sqrt[3]{c}\,.$$

In the following small table, the values of f_o, f_a, and f_μ for potassium chloride have been compared.

Deviation coefficients for potassium chloride

Molar conc.	f_o	f_a	$f_\mu (= \mu/\mu_\infty)$
0.001	0.985	0.943	0.979
0.01	0.969	0.882	0.941
0.1	0.932	0.762	0.861
1.0	0.854	0.558	0.755

For non-ideal mixtures, the deviation from ideality is expressed by means of the osmotic coefficient and the activity coefficient in the following equations:

$$A_1 = -RT\ln(xf_a) \quad\text{and}\quad A_2 = -RTf_o\ln(1-x),$$

where the component 1 of the concentration x is considered as solute and the component 2 as solvent. When these expressions are substituted into the first equation, we obtain

$$f_o - (1-x)\ln(1-x)\,\frac{df_o}{dx} = 1 + x\,\frac{d\ln f_a}{dx}.$$

For dilute solutions (small values of x), $(1-x)\ln(1-x)$ is approximately equal to $-x$, and the equation may therefore be written as follows

$$f_o + x\,\frac{df_o}{dx} = 1 + x\,\frac{d\ln f_a}{dx}.$$

It follows from the form of this equation that one may, instead of x-concentrations, introduce other concentrations which are proportional to them, for dilute solutions, for instance, molar concentrations c.

Although the equation between f_a and f_o deduced here is only exact for dilute solutions, it may, as shown by a closer analysis, be used even at rather great concentrations without introducing any appreciable error.

The table shows that the activity coefficient, at all the concentrations, deviates more from unity than the conductivity coefficient. It is therefore not surprising that one has formerly found anomalies when the conductivity coefficient has been applied where one ought to have used the activity coefficient.

The osmotic coefficient is nearly the same for all monovalent electrolytes. The value is, however, according to the compilation of Noyes and Falk, on an average a little greater than for potassium chloride. For a binary, monovalent strong electrolyte in aqueous solution one may use the formula

$$f_o = 1 - 0.17 \sqrt[3]{c},$$

from which we deduce

$$\log f_a = -0.3 \sqrt[3]{c}.$$

2. The activity coefficient may be determined from measurements of electromotive force, and it is this coefficient, and not the conductivity coefficient, which must be used in the calculation of the electromotive force of concentration cells and other galvanic elements. As an illustration, we shall use an earlier measurement[8] of the cell

$$\mathrm{Hg} \mid \mathrm{HgCl},\ 0.1\ \mathrm{n\ KCl} \mid 0.01\ \mathrm{n\ KCl},\ \mathrm{HgCl} \mid \mathrm{Hg}.$$

After elimination of the diffusion potential, the electrode potential was found to be $\varepsilon = 0.0548$ volts. By means of the Nernst formula

$$\varepsilon = 0.0591 \log \frac{c_2}{c_1},$$

we calculate,

from the gross concentrations, $\varepsilon = 0.0591$,
applying the conductivity coefficient f_μ, $\varepsilon = 0.0569$,
applying the activity coefficient f_a, $\varepsilon = 0.0553$.

The deviation of the last value from that found by experiment is so small that it is without any importance.*

3. A very important method for the determination of the activity coefficient is the examination of chemical equilibria. One may thus find the activity coefficient for the ions of picric acid in methyl alcohol by determining how the degree of dissociation of picric acid in that solvent changes with the concentration. The degree of dissociation of picric acid may be calculated from some conductivity

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* It is the activity coefficient of the chloride ion that enters into the calculation of the electromotive force. From the determinations of the freezing-points of solutions of potassium chloride, one finds the average of the activity coefficients for the potassium and the chloride ion. The above calculation is therefore only exact if we may assume that the two coefficients are equal; but we may expect that this assumption holds with good approximation.

measurements which have been published by Goldschmidt and Thuesen[5]. This example will also illustrate how, according to the new hypothesis, the degree of dissociation of a weak electrolyte may be calculated from its conductivity. The fact is that the formula usually applied, according to which the degree of dissociation is equal to μ/μ_∞, ought no more to be used, because we cannot expect to get correct results from it except for the weakest electrolytes. It ought to be noticed that Goldschmidt and Thuesen, calculating in the old way, have obtained values for the degree of dissociation of picric acid which do not agree with the mas-action law but show anomalies of the kind which has been characterized as neutral salt effect.

Picric acid dissolved in methyl alcohol is a weak electrolyte, and its molar conductivity deviates from the conductivity at infinite dilution, partly because it is only incompletely dissociated, and partly because the ions, just as in strong electrolytes, affect one another. If α denotes the degree of dissociation, and if the conductivity coefficient, which expresses the influence of the mutual interaction of the ions, is designated as f_μ, the following formula must hold

$$\mu/\mu_\infty = \alpha f_\mu .$$

By means of this equation we may calculate α when μ/μ_∞ is taken from the conductivity measurements, and for f_μ is used the value found for hydrochloric acid in methyl alcohol at the same ionic concentration. The values used for μ/μ_∞ and f_μ, and those calculated for α, are given in the following table.

Molar conc.	μ/μ_∞	f_μ	α	K_c	f_a	f_a (calcd.)
0.2	0.0372	0.81	0.046	$4.44 \cdot 10^{-4}$	0.673	0.679
0.1	0.0512	0.84	0.061	3.96 –	0.712	0.714
0.05	0.0700	0.86	0.0815	3.615 –	0.746	0.745
0.025	0.0960	0.875	0.1095	3.4 –	0.769	0.773
0.0125	0.1309	0.89	0.147	3.17 –	0.797	0.802
0.00625	0.1760	0.90	0.195	2.95 –	0.825	0.822
0.003125	0.2358	0.91	0.259	2.83 –	0.843	0.843
0.001562	0.3117	0.92	0.339	2.72 –	0.860	0.861
0				2.01 –		

K_c given in the fifth column is the value of the expression

$$K_c = \frac{c\alpha \cdot c\alpha}{c\,(1-\alpha)} = c\,\frac{\alpha^2}{1-\alpha}.$$

If the activity coefficient of the ions were equal to unity, this expression would have a constant value. The table shows, however, that the value varies considerably with the concentration of picric acid, and from this variation we may calculate the activity coefficient of the ions in the following way. From the mass-action law we obtain, when the activity coefficients are introduced,

$$K = \frac{c\,\alpha f_a \cdot c\,\alpha f_a}{c\,(1-\alpha)} = c\,\frac{\alpha^2}{1-\alpha} f_a^{\,2} = K_c f_a^{\,2},$$

where K is a constant. Hence, one has

$$f_a = \sqrt{\frac{K}{K_c}}\,.$$

The value of K is equal to K_c at infinite dilution and may be calculated by extrapolation of the values of K_c. We find $K = 2.01 \cdot 10^{-4}$, and obtain for f_a the values given in the next to the last column of the table. These values for the activity coefficient in methyl alcohol agree excellently with those for aqueous solutions as it is seen from the following considerations.

The values found for the activity coefficient of the ions of picric acid in methyl alcohol may be summarized in the following interpolation formula

$$\log f_a = -0.8 \cdot \sqrt[3]{c_{\text{ion}}}\,.$$

Values of f_a calculated from this formula are presented in the last column of the table. The good agreement between the values in the two last columns shows how well the variation of the activity coefficient is expressed by the formula. As previously stated, we may, on an average, for water set

$$\log f_a = -0.3 \cdot \sqrt[3]{c_{\text{ion}}}\,.$$

Hence, $-\log f_a$ is for methyl alcohol $^8/_3$ times as great as for water, and this result agrees excellently with the fact that the dielectric constant of water is $^8/_3$ times as great as that of methyl alcohol.

4. As a last example of the application of the hypothesis of the complete dissociation of the strong electrolytes, we shall discuss the interpretation of the important measurements, carried out by Goldschmidt and Thuesen, of the velocity of esterification of the organic acids in methyl alcohol with picric acid as a catalyst. When an acid, say acetic acid, is dissolved in methyl alcohol, the esterification, *i. e.* the formation of methyl acetate, will proceed extremely slowly, and it does not quicken until a moderately strong, or a strong acid, *e. g.* picric acid or hydrochloric acid, is added. One must, from the standpoint of the ionic theory, assume that it is the hydrogen ions, which are common to all acids, that accelerate the esterification. This view has, in fact, been embraced since the first days of the ionic theory. It has, however, been impossible to account for the newest and most accurate measurements of the velocity of esterification in this way. It has been

found that the velocity constant for the esterification is not exactly proportional to that hydrogen-ion concentration which is found when the degree of dissociation of the catalyzing acid is calculated by means of the formula $\alpha = \mu/\mu_\infty$. It has thus been stated by Goldschmidt and Thuesen that the esterification of organic acids is 8.24 times as fast in 0.05 n hydrochloric acid as in 0.1 n picric acid, while the ratio between the hydrogen-ion concentrations, when calculated from the conductivity measurements, is 6.56. In order to explain this discrepancy they must resort to the unsatisfactory auxiliary hypothesis that also the undissociated acid molecules catalyze the esterification.

The measurements of Goldschmidt and Thuesen present, however, no anomalies when the new hypothesis of the dissociation of the strong electrolytes is applied. This is shown in the following table.

	0.05 n HCl	0.1 n picric acid		0.1 n picric acid + 0.15 n picrate	
	k	k	α	k	α
Phenyl-acetic acid	2.23	0.265	0.0595	0.047	0.0105
Acetic acid	4.86	0.590	0.0607	0.100	0.0103
n-Butyric acid	2.23	0.277	0.0621	0.0535	0.0120
i-Butyric acid	1.55	0.196	0.0632	0.0353	0.0114
i-Valeric acid	0.583	0.0735	0.0630	0.00144	0.0123
Benzoic acid	0.0156	0.00175	0.0561	0.00026	0.0084
			0.0606		0.0108

In this table, we have first given the velocity constants (k) for the esterification of different weak organic acids with, respectively, 0.05 n hydrochloric acid and 0.1 n picric acid as catalysts. If it is assumed that the hydrochloric acid is completely dissociated, and that the velocity of esterification is proportional to the hydrogen ion concentration, one may calculate the degree of dissociation (α) of 0.1 n picric acid in methyl alcohol. The average of the values found is 0.0606, in excellent agreement with the value 0.061 which has previously (page 66) been found for the degree of dissociation of 0.1 n picric acid in methyl alcohol by a correct method of calculation from conductivity measurements. The explanation of the somewhat deviating value of the degree of dissociation found for benzoic acid is possibly that this acid is esterified so slowly that it may not be permissible to neglect the esterification of the hydrochloric acid during the experiment.

Goldschmidt and Thuesen find an important support for the hypothesis of the catalytic activity of the undissociated acid molecules in some experiments on the esterifying effect of 0.1 n picric acid to which had been added 0.15 n aniline picrate. The velocity constants for the esterification with this mixture are given in the table. From the velocity constants we calculate that the degree of dissociation of picric acid in the presence of 0.15 n picrate is 0.0108. Goldschmidt and Thuesen, thinking that the addition of the picrate must have depressed the dissociation of the picric acid much more, conclude that the observed catalytic effect must mainly be due to the undissociated picric acid. When we, however, conversely, from the value found for the degree of dissociation of picric acid, calculate the activity coefficient for the ions of picric acid in the picrate solution by means of the mass-action equation

$$f_a \cdot c_{\mathrm{H}+} \cdot f_a \cdot c_{\text{picrate ion}} / c_{\text{picric acid}} = K,$$

we obtain

$$f_a^2 \cdot 0.0108 \cdot 0.15 = 2.01 \cdot 10^{-4},$$

and, hence,

$$f_a = 0.353.$$

This value must be considered very plausible, for, when the activity coefficient in methyl alcohol at the ionic concentration 0.15 is calculated from the formula given before:

$$\log f_a = -0.8 \sqrt[3]{c_{\text{ion}}}\,,$$

we obtain $f_a = 0.376$. The agreement is as good as one would dare to expect, considering that the formula has been derived on the basis of experiments at much lower ionic concentrations.

In the preceding calculations, it has been assumed that the catalytic effect of the hydrogen ion is proportional to its concentration, but otherwise independent of the concentration of ions in the solution. The agreement found demonstrates the justification of these assumptions. It would, in itself, not have been unreasonable if it had been found to be necessary to introduce into the calculation of the catalytic effect a coefficient expressing the influence of the concentration of ions upon the catalysis, a *catalytic coefficient*. This seems, however, not to be necessary.

It seems to me that the examples considered in the preceding, and many other similar examples, show conclusively, that it would be of the greatest importance for the development of our knowledge of the behaviour of the electrolytes if one, in future calculations, would cease using degrees of dissociation determined by conductivity where one, in reality, should apply activity coefficients. I feel sure, that the difficulties in calculating with activity coefficients, when one gets used to it, will not be greater than those in calculating with conductivity ratios, although it at first, as long as tables of activity coefficients as comprehensive as those of conductivities are not available, will give a little more trouble. The old method of calculating degrees of dissociation will surely, as long as it is still in use, act as a clog on the development.

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On the Activity Coefficient for Ions

NIELS BJERRUM

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1. In the year 1887 Arrhenius presented his famous hypothesis according to which the ions in a solution of electrolytes are present in the free state. During the next three decades this hypothesis has become an indispensable part of physics and chemistry, and even to-day it is a fruitful working hypothesis, which shows the power of the original conception. In the course of time, however, the hypothesis has encountered some difficulties, especially in the explanation of the properties of strong electrolytes. In view of recent work (*cf.*ref.[1]), these difficulties have been resolved on consideration of the effects that must be produced on the properties of the solutions of electrolytes by the electric forces between ions. These effects may be taken into account by means of coefficients expressing the relation between the real value of the property in question and the value the property should have had supposing the electric forces did not act between the ions. Thus the *activity coefficient* f_a is a measure of the effect of the interionic forces on the activity of the ions; the *conductivity coefficient* f_μ is a measure of the influence of the interionic forces on the conductivity; the *osmotic coefficient* f_o is a measure of the influence of the interionic forces on the osmotic pressure, etc.

2. It is of great importance to calculate the values of these coefficients from the point of view of our kinetic conceptions of the solutions and to deduce relations between them. And it is of no less importance to determine the values of these coefficients experimentally.

Milner[2] has formed a theory for the osmotic coefficient. This theory does not lead to a simple expression for the coefficient, but it has enabled Milner by numerical calculation to determine approximately the value of the coefficient in case of an electrolyte composed of monovalent ions up to the concentration 0.2 molar. Milner's calculated values are with a fair approximation rendered by the formula

$$1 - f_o = 0.27 \sqrt{c}, \tag{1}$$

in which c is the molar concentration. This may be seen from table 1.

If we suppose that the strong electrolytes are completely dissociated into ions we may determine the value of the osmotic coefficient by means of freezing-point determinations. From Noyes's and Falk's excellent exposition[3] it thus appears that the osmotic coefficient of all electrolytes with monovalent ions may, with a fair approximation, be given by the formula

$$1 - f_o = k\sqrt[3]{c}, \tag{2}$$

Table 1. Value of $1 - f_o$

c	$1 - f_o$ Milner	$0.27\sqrt{c}$	$0.17\sqrt[3]{c}$
0.0001	0.0028	0.0027	
0.001	0.0087	0.0085	
0.01	0.0265	0.027	0.037
0.1	0.081	0.085	0.079
0.2	0.112	0.121	0.099

in which k varies between 0.146 and 0.225 the mean being 0.17. Although this formula and Milner's are different in form they both give approximately the same values for f_o within the limits of concentration where both experiments and Milner's calculation are fairly reliable, viz. 0.01 M — 0.1 M (see table 1). This fact must be looked upon as a support for the assumption that the strong electrolytes are *completely dissociated* or, at any rate, are much more dissociated than originally assumed.

When the expression for the osmotic coefficient is known, the formula for the activity coefficient may be deduced by means of the following thermodynamic relation:

$$f_o + c\frac{df_o}{dc} = 1 + c\frac{d\ln f_a}{dc}. \tag{3}$$

If this be combined with equation 2 the following expression is obtained:

$$\ln f_a = -4k\sqrt[3]{c}. \tag{4}$$

In the case of potassium chloride we have

$$1 - f_o = 0.146\sqrt[3]{c}. \tag{5}$$

From this we obtain:

$$\log f_a = -0.25\sqrt[3]{c}.$$

This formula can be controlled by measurements of concentration cells. In the case of potassium chloride I obtained, in this way, a confirmation of the formula as far as 0.01 and 0.1 molar solutions are concerned.

3. It would be of great value to obtain a relation between the conductivity coefficient and the other two coefficients. Last year this was tried from two different quarters. But to my judgement the results obtained are not correct.

Milner[4] has tried to show that the conductivity coefficient must equal P/P_0, where P is a quantity which he calls the pressure of the free ions, and P_0 the osmotic pressure in the absence of ionic forces. Milner was unable to see clearly the experimental significance of his P; but in my opinion there is no doubt but that P/P_0 must equal the activity coefficient. If Milner's result were right then the conductivity coefficient had to be equal to the activity coefficient, and the hitherto general use of the conductivity coefficient, "conductivity degree of dissociation", in calculating chemical equilibria, etc., would be justified not only in the case of weak electrolytes, which actually are incompletely dissociated, but also in the case of strong, completely dissociated electrolytes. However, this result seems rather doubtful. Although it appears from the available experimental data that a certain proportionality exists between f_μ and f_a, f_μ is as a rule somewhat nearer to 1 than f_a. A critical examination of Milner's considerations, at which Professor N. Bohr lent me valuable assistance, convinced me that the line of argument is not right. In the first place Milner's expressions for the number of "views" which enter and leave the configuration P in the time τ are wrong. Secondly, Milner is not right in identifying u_0 with the experimentally determined conductivity at zero concentration. It is hardly possible, I think, to obtain a result by pursuing Milner's path.

Another attempt was made by Inanendra Chandra Ghosh.[5] He tries to show that

$$i = n(1 + {}^1/_3 \ln f_\mu), \tag{6}$$

in which i is van Hoff's old coefficient and n the number of ions in the electrolyte. Since f_0 equals $\frac{i}{n}$, Ghosh's equation may be written

$$f_0 = 1 + {}^1/_3 \ln f_\mu . \tag{7}$$

Ghosh assumes that the electricity is conducted only by those ions the kinetic energy of which is greater than the average potential of the interionic forces per ion. Here "potential" is the work which must be *done* to separate the ions. This bold and, in my opinion, unwarranted assumption gives Ghosh

$$f_\mu = e^{-\frac{A}{nRT}}, \tag{8}$$

where A is the potential of the ionic forces per gram-molecule. Since A further is equal to the virial of the interionic forces we have according to Clausius, for the osmotic pressure of the ions, P:

$$PV = nRT - {}^1/_3\,A, \tag{9}$$

which by combination with equation 8 gives:

$$i = \frac{PV}{RT} = n(1 + {}^1/_3\,\ln f_\mu). \tag{10}$$

On combining formulae 7, 2, and 4, the following formula may be deduced:

$$\ln f_a = {}^4/_3\,\ln f_\mu \tag{11}$$

This result agrees better with the experiments than $f_a = f_\mu$; this better agreement, however, can hardly make Ghosh's bold assumptions probable.

Ghosh shows that formula 8 gives the proper value of f_μ when calculating A in the following way: We imagine the ions in a binary electrolyte arranged like the atoms in a potassium chloride crystal, and the ions in a ternary electrolyte like the ions in fluorspar, and we further assume that the ions of each salt-molecule form a completely saturated ionic pair. I am not, on this occasion, going to enter more fully into these singular assumptions; I only want to state that the formulae for f_μ as established by Ghosh fit so well, that we may hope, perhaps, to be able to deduce them from more reasonable assumptions than those of Ghosh. I cannot but think that the right theory of the influence of the interionic forces on the conductivity of ions is still wanting. Of the theories so far proposed, that of Hertz[6] is in my opinion the only reliable one, but it has not been thoroughly worked out.

4. When trying to determine experimentally the value of the activity coefficient f_a for an ion, various difficulties are encountered.

Firstly, it is difficult to make sure that the electrolyte is *really completely ionized* or, if that is not the case, to determine its degree of dissociation. If the molar conductivity of the electrolyte increases with decreasing concentration according to Ostwald-Walden's valence rule it will, however, be natural, as I have formerly pointed out, to assume complete dissociation. In many cases this point may be investigated by means of spectrophotometric measurements, the colour of the ions being, to a rather high degree, independent of the interionic forces and, on the other hand, greatly influenced by chemical combination of the ions.

Secondly, it is not possible, even if the ion concentration is known, to state with certainty *what the activity of the ion would have been if the interionic forces did not exist*. This difficulty particularly manifests itself in concentrated solutions. As the measure of the activity one should, most likely, take neither the mole number per litre nor the mole number per 1000 g of water but what is known as the mole fraction

$$x = \frac{n}{n + n'}, \tag{12}$$

where n is the mole number of the solute and n' the mole number of the solvent. We shall designate this mole fraction as x-concentration. As to the justification of putting the activity equal to the x-concentration we may for instance refer to the excellent treatment of ideal solutions in Alex. Findlay's book: *The osmotic pressure*.

Thirdly, *the water content of the ions* in the solution must be considered. When the ions form hydrates in solution the consequence is that the x-concentrations of the ions will be larger than they would have been without the hydration. This effect of hydration is well known and frequently discussed. There is, however, another effect of hydration which has not as yet been taken into account; although it is rather of greater importance than the former effect. If we want to determine the activity of an ion by means of potential measurements, say with metal or hydrogen electrodes or with mercurous chloride electrodes, we obtain for a hydrated ion by means of the ordinary Nernst formula not a measure of the activity of the ion itself but only of the activity of the ion without water. If the ion contains $m\,H_2O$, we must multiply the activity of the ion, which we may call A, by the activity of the water to the m-th power in order to obtain the activity of ion hydrate. We have a good measure of the activity of the water in the vapour pressure of the solution p divided by the vapour pressure of pure water p_0. Hence the activity of the actual (hydrated) ion may be written

$$a = A\left(\frac{p}{p_0}\right)^m . \tag{13}$$

Strangely enough, no account has until now been taken of this correction, in spite of the fact that, in the electrometric determination of hydrogen-ion concentration so frequently used recently, it is of considerable magnitude, since the hydrogen ion is very strongly hydrated. The measurement of the potential of a hydrogen electrode in a solution does not directly give us either the hydrogen-ion concentration or the hydrogen-ion activity, but only a fictive quantity which may be designated as the activity of the dehydrated hydrogen ion. Lack of knowledge of this fact has led to the conclusion that the hydrogen-ion activity increases on addition of liberal amounts of neutral salts to hydrochloric and other strong acids (comp. for instance[7]). A similar correction should also be made in the case of activity determinations based on the solubility of salts.

Fourthly, the exact determination of ion activities in concentrated solutions is rendered difficult by the *association of the water*, which is of importance in calculating the x-concentration, and which is not properly known. In the following this association is, as a rule, left out of consideration. To illustrate the error thus committed, the calculation is carried through in a single case on the supposition of complete association into double molecules.

5. If the apparent activity coefficient F_a is defined as the ratio between the activity of the dehydrated ion and the concentration c expressed in moles per 1000 g of water, and if f_a is the true activity coefficient taking account of the electric ionic forces, then:

$$F_a \cdot c \cdot \left(\frac{p}{p_0}\right)^m = x \cdot 55.5 \cdot f_a. \tag{14}$$

Both the right and the left side of the equation are expressions for the activity of the ion hydrate. The factor 55.5 arises from the fact that at zero concentration when F_a, f_a, and p/p_0 equal 1, we have

$$c = x\,\frac{1000}{18.02} = x \cdot 55.5.$$

If we consider a completely dissociated binary electrolyte and call the activity coefficients of the two ions F'_a and F''_a and f'_a and f''_a respectively and the number of water molecules in the ions m' and m'', we get by insertion in equation 14

$$F'_a \cdot c \cdot (p/p_0)^{m'} = \frac{c}{55.5 + 2c - (m' + m'')c} \cdot 55.5 \cdot f'_a \tag{15}$$

$$F''_a \cdot c\,(p/p_0)^{m''} = \frac{c}{55.5 + 2c - (m' + m'')c} \cdot 55.5 \cdot f''_a. \tag{16}$$

By logarithmic transformation these expressions give:

$$\ln F'_a + m' \ln p/p_0 = \ln f'_a - \ln\left(1 - \frac{m' + m'' - 2}{55.5} \cdot c\right) \tag{17}$$

$$\ln F''_a + m'' \ln p/p_0 = \ln f''_a - \ln\left(1 - \frac{m' + m'' - 2}{55.5} \cdot c\right). \tag{18}$$

Many of the experimental methods do not determine F'_a and F''_a separately but the square root of their product

$$F_a = \sqrt{F'_a \cdot F''_a}. \tag{19}$$

By adding equations 17 and 18, introducing F_a, and further putting

$$f_a = \sqrt{f'_a \cdot f''_a} \quad \text{and} \quad m = m' + m'', \tag{20}$$

we get

$$\ln F_a + \frac{m}{2} \ln p/p_0 = \ln f_a - \ln\left(1 - \frac{m - 2}{55.5}\, c\right). \tag{21}$$

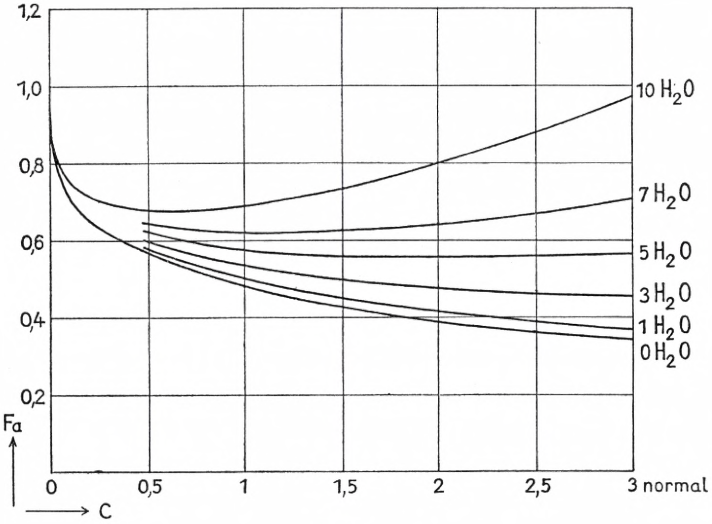

Fig. 1.

This universally valid equation may be simplified by introducing the following approximately valid relations:

$$\ln p/p_0 = -\frac{2c}{55.5} \quad \text{and} \quad -\ln\left(1 - \frac{m-2}{55.5}\,c\right) = \frac{m-2}{55.5}\,c\,, \tag{22}$$

and we get:

$$\ln F_a = \ln f_a + \frac{2m-2}{55.5}\,c\,. \tag{23}$$

Fig. 1 gives an impression of the variations of the apparent activity coefficient F_a for a salt in the case that m assumes the values 0, 1, 3, 5, 7, 10. In the calculation the assumption $\log f_a = -0.3\sqrt[3]{c}$ is made use of. We see that some of these curves show a minimum, and that the concentration at which this minimum is reached is lower the more hydrated the salt is.

6. At present the degree of hydration of the ions is unknown, and hence it is not possible to use the above equations for the purpose of determining f_a from measurements of F_a. Starting from measurements of F_a, an attempt has been made to calculate the hydration of some electrolytes and ions on the assumption that it is permissible to extend the use of the formula for f_a applicable to dilute solutions:

$$\ln f_a = -k\sqrt[3]{c}\,. \tag{24}$$

also to concentrated solutions. A further assumption used below is that the electrolytes are completely ionized.

The calculations themselves give us a certain opportunity of testing the accuracy of our assumptions, as we ought to find a content of water decreasing very slightly with the concentration, or remaining constant. Even if the calculations include solutions up to 4 normal, the activity of water in the solutions will vary only 10 to 20 per cent, which cannot alter the degree of hydration to any extent. In order that a change of the degree of hydration shall take place at all the ion must exist in more than one form in the solution. Supposing, for instance, that at infinite dilution the hydration $m\,H_2O$ results from there being 25 per cent ions with $(m - 1)\,H_2O$, 50 per cent with $m\,H_2O$ and 25 per cent with $(m + 1)\,H_2O$, it is easy from the law of mass action to calculate that there will, when the activity of water falls by 20 per cent, be 31 per cent with $(m - 1)\,H_2O$, 49 per cent with $m\,H_2O$ and 20 per cent with $(m + 1)\,H_2O$, and the average degree of hydration will have altered only from m to $(m - 0.11)$. The greater the difference in the water contents of the different hydrates existing in the solution, the greater the changes of the average degree of hydration, but the above calculation may serve as an example of the order of magnitude of the effect.

7. The result of the following calculations is that the ions of hydrochloric acid contain about 9 H_2O and the ions of potassium chloride about 2 H_2O. A calculation made for the hydrogen ion alone gave 9 H_2O and for the chloride ion alone 2 H_2O. Since the sum of these results is 11 H_2O, while the direct estimation gave 9 H_2O for the ions of hydrochloric acid, the calculations cannot be quite exact; but this was not to be expected either. According to our calculations the following formulae for the composition of the ions may be used with fair approximation:

$$H^+, 8\,H_2O, \quad Cl^-, 2\,H_2O, \quad K^+, 0\,H_2O.$$

If the association of the water is taken into consideration somewhat higher values for the hydration are found. The particulars of the calculations will be given below.

THE CALCULATIONS

8. Table 2 contains calculations of the hydration of hydrochloric acid. First column c gives the concentrations of hydrochloric acid in moles per 1000 g of water; second column, F_a (Ellis), contains the values of the apparent activity coefficient of the ions of hydrochloric acid as calculated by Ellis[8] from potential measurements. On calculating these values Ellis assumed F_a in the most dilute solution to equal f_a. I have preferred to attribute to F_a in the most dilute solution such a value as to make the formula $\log F_a = - k \sqrt[3]{c}$, fit as well as possible for the values of c below 0.1. In this way I got the values of $- \log F_a$ given in

the third column. The determination of log p/p_o is made from the values of the apparent activity coefficient in the following way.

If the activity of each of the ions of hydrochloric acid were equal to c, then

$$p/p_o = e^{-2c/55.5} \qquad (25)$$

would apply thermodynamically.

The activity of the ions being $c \cdot F_a$ a tension coefficient F_p defined by the following expression may be introduced:

$$p/p_o = F_p \cdot e^{-2c/55.5}. \qquad (26)$$

F_a and F_p are thermodynamically connected through the equation:

$$2c \frac{d\ln F_a}{dc} + 55.5 \frac{d\ln F_p}{dc} = 0. \qquad (27)$$

If F_p is determined by means of this equation, we shall at once have p/p_o by means of equation 26.

Starting from Ellis's figures corrected as indicated above, the following interpolation formulae have been established for $-\log F_a$:

for $c < 0.1$: $\quad -\log F_a = 0.2 \sqrt[3]{c}$ (28)

for $0.1 < c < 1$: $\quad -\log F_a = 0.0810 + 0.141\, c - 0.138\, c^2$ (29)

for $1 < c$: $\quad -\log F_a = 0.247 - 0.170\, c + 0.0092\, c^2$ (30)

In column 4 (table 2) the corresponding values of $-\log F_a$ are found. When introducing expressions 28–30 in equation 27, integrating and using 26 the following formulae for $\log p/p_o$ are obtained:

for $c < 0.1$: $\quad -\log p/p_o = 0.01566\, c\, (1 - 0.115 \sqrt[3]{c})$ (31)

for $0.1 < c < 1$: $\quad -\log p/p_o = 0.01566\, c\, (1 - 0.161\, c + 0.212\, c^2) - 0.00006$ (32)

for $1 < c$: $\quad -\log p/p_o = 0.01566\, c\, (1 + 0.196\, c - 0.0141\, c^2) - 0.0022$ (33)

The values of $-\log p/p_o$ calculated by means of these formulae are given in column 5. In column 6 are given the values of $-\log f_a$ calculated according to the formula $-\log f_a = 0.2 \sqrt[3]{c}$. According to expression 28 this formula applies to f_a at low concentrations since in this case we may put $f_a = F_a$, and we shall suppose that the same formula may be used at high concentrations. Finally, column 7 shows m, the number of H_2O which, according to equation 21, must be bound to the ions of hydrochloric acid. It will be seen that the average number of bound water molecules is 9. Thus the hydrogen ion and the chloride ion bind 9 H_2O in all.

Table 2. Hydration of hydrochloric acid according to activity measurements by Ellis at 25° C.

c	F_a (Ellis)	$-\log F_a$	$-\log F_a$ calc.	$-\log p/p_o$	$-\log f_a$	m
0.00168	0.988	0.0238	0.0238			
0.002	0.987	0.0242	0.0252			
0.005	0.971	0.0313	0.0342			
0.01	0.947	0.0422	0.0430			
0.02	0.918	0.0557	0.0542			
0.05	0.874	0.0770	0.0736			
0.10	0.843	0.0927	0.0930			
0.20	0.818	0.1057	0.1037			
0.30	0.804	0.1132	0.1132			
0.50	0.793	0.1192	0.1170	0.00756	0.159	8.5
0.75	0.820	0.1047	0.1090	0.01168	0.182	9.0
1.00	0.857	0.086	0.086	0.01634	0.200	9.0
2.00	1.186	-0.056	-0.057	0.0398	0.252	9.5
4.484	2.228	-0.329	-0.329	0.1098	0.330	7.6
						mean 8.7

9. In order to determine the *hydration of potassium chloride* we must proceed in another way since the apparent activity coefficient of the ions in this salt has not been measured. The hydration is calculated from the freezing point lowering of potassium chloride. Determinations of freezing points give us the activity of water and, as this will allow us to calculate thermodynamically the apparent activity of the ions, the possibility of such calculations follows from the above considerations. It is true that Jones and Biltz have long ago determined the hydration of electrolytes, starting from determinations of freezing points, but their procedure was rather inexact. The following method is better: Starting from the expression

$$Q = 18.02\,(79.65 - 0.53t) \tag{34}$$

in which Q is the heat of fusion of ice and t the freezing point lowering, we obtain by integration of the equation

$$\frac{d\ln p/p_o}{dt} = -\frac{Q}{R\,(273.1 - t)^2} \tag{35}$$

the following formula for $\log p/p_o$

$$\log p/p_o = -0.00421 \cdot t \cdot (1 + 0.00033\,t)\,. \tag{36}$$

In the case of an ideal solution of neutral molecules we have:

$$p/p_o = 1 - x. \tag{37}$$

In the case of an ideal solution of ions we may put:

$$p/p_o = (1 - x) f_p. \tag{38}$$

Here f_p is the tension coefficient due to the interionic electric forces. f_p is thermodynamically connected with f_a by the following relation:

$$x\frac{d\ln f_a}{dx} + (1-x)\frac{d\ln f_p}{dx} = 0. \tag{39}$$

If $\ln f_a = -k\sqrt[3]{x}$ we obtain by integration:

$$\ln f_p = \frac{k}{4}x^{\frac{4}{3}}(1 + \frac{4}{7}x + \frac{4}{10}x^2 + \ldots.). \tag{40}$$

For the ions of the potassium chloride we may put $\log f_a = -0.25\sqrt[3]{c}$; by introducing $c = x \cdot 55.5/2$ and by discarding higher powers of x in equation 40 we have:

$$\log f_p = 0.00225\, c^{\frac{4}{3}}. \tag{41}$$

From the equations 36, 38, and 41 we obtain:

$$-\log(1-x) = 0.00421\,(1 + 0.00033\,t)\,t + 0.00225 \cdot c^{\frac{4}{3}}. \tag{42}$$

If x is calculated by means of this equation, m, the number of H_2O bound to the ions of potassium chloride, may be obtained from the equation

$$x = \frac{2c}{55.5 + 2c - mc} \tag{43}$$

giving

$$m = 2 + \frac{55.5}{c} - \frac{2}{x}. \tag{44}$$

Table 3 contains the results of such a calculation.

Table 3. Hydration of potassium chloride according to determinations of freezing points

c	t*	x	m
0.339	1.130	0.01212	(1.0)
0.428	1.404	0.01529	(—0.2)
0.476	1.605	0.01755	(3.7)
0.704	2.283	0.02503	0.9
0.772	2.529	0.02821	2.1
1.00	3.286	0.03640	2.5
1.03	3.37	0.03811	3.4
1.989	6.46	0.07295	2.5
3.269	10.61	0.1204	2.4
			mean 2.3

* Values taken from Landolt-Börnstein's tables.

The values for m in the most dilute solutions vary greatly; but it is also seen from formula 44 that a small error in the determination of c or t will have an influence on m that will be greater the more dilute the solution. On calculating a mean value of m leaving out the results for the three most dilute solutions, we obtain $m = 2.3$. According to this potassium chloride contains about 2 H_2O.

10. Table 4 shows the results of a calculation of the hydration of hydrochloric acid from determinations of the freezing points. We assume that f_a for the ions of hydrochloric acid at the freezing point is determined by $-\log f_a = 0.25 \sqrt[3]{c}$. According to Milner's theory $-\log f_a$ at the freezing point should be greater than at 25° C, where we used $-\log f_a = 0.20 \sqrt[3]{c}$. The calculation gives as a mean $m = 7.9$. This is somewhat less than calculated above from Ellis's activity measurements ($m = 8.7$). Since experimental errors no doubt exert a greater influence on the calculation based on determinations of freezing points than on that based on measurements of activity, I attach little importance to the smaller value.

Table 4. Hydration of hydrochloric acid according to determinations of freezing points

c	t	x	m	m for $\log f_a = -0.20\sqrt[3]{c}$	m for t 1% greater	m for $(H_2O)_2$
0.2443	0.888	0.00936	(15.6)	(12.0)	(20.0)	(16.8)
0.4598	1.67	0.01789	(10.9)	(8.6)	(13.1)	(11.6)
1.017	4.04	0.04356	10.7	9.5	11.6	11.6
1.563	6.57	0.07061	9.2	8.4	9.7	10.1
3.052	14.97	0.1546	7.2	6.9	7.5	7.9
4.064	23.05	0.2253	6.8	6.5	7.0	7.2
4.656	28.84	0.2704	6.5	6.3	6.7	6.8
			mean 7.9	7.5	8.5	8.7

In order to be able to evaluate the assumptions made in the calculation of m, we give in table 4 values of m which are calculated on somewhat altered assumptions, viz, that $\log f_a = -0.20 \sqrt[3]{c}$ instead of $-0.25 \sqrt[3]{c}$, that t is 1 per cent greater, and that all molecules of water are associated to $(H_2O)_2$. In none of these cases the mean value of m will change by more than 0.8.

The calculation of m for water associated to $(H_2O)_2$ is undertaken in the following way. As the water consists of double molecules $(H_2O)_2$ and the vapour consists of single molecules we have:

$$p/p_o = \sqrt{1 - x}\, f_p \,. \tag{45}$$

By combination with equations 36 and 41 this expression gives:

$$-\log (1-x) = 2\,(0.00421\,t\,(1+0.00033\,t) + 0.00225\,c^{\frac{4}{3}}). \qquad (46)$$

When x is determined by this equation, m is obtained from the equation

$$x = \frac{2c}{27.75 + 2c - \frac{m}{2}c} \qquad (47)$$

which gives

$$m = 4 + \frac{55.5}{c} - \frac{4}{x}. \qquad (48)$$

11. As yet only the *total* hydration of electrolytes has been calculated. It is, however, possible to calculate the hydration of the *single* ions if only the apparent activity coefficients of the single ions are known. These can be determined by means of measurements of the e.m.f. of cells of the following types:

metal/salt-solution I/salt-solution II/metal.

The difficulty in calculating the activity from such measurements lies in the elimination of the diffusion potential between the solutions. The calculation of the hydration of the hydrogen ion is made by means of Harned's[7] measurements of cells of the type:

Hg/HgCl, 1 M KCl/saturated KCl/c M KCl in 0.1 M HCl/H_2.

Harned eliminated the diffusion potential between saturated KCl and c M KCl in 0.1 M HCl by an empiric and, in my opinion, unwarranted method. I have preferred to calculate the diffusion potential according to Henderson's formula. If E is the electrode potential corrected for the diffusion potential and E_o the value of this potential for $c = 0$ (hydrochloric acid without potassium chloride) the following equation serves for the determination of the apparent activity coefficient F_a of the hydrogen ion,

$$\log F_a - \log\,[F_a]_o = (E_o - E)/0.0591. \qquad (49)$$

Here $[F_a]_o$ is the value of the activity coefficient in hydrochloric acid without potassium chloride.

If we consider a solution containing c_1 moles of HCl and c_2 moles of KCl per 1000 g of H_2O, and if we suppose that the ions of the hydrochloric acid contain 9 H_2O and the ions of the potassium chloride 2 H_2O as found above, we have the following equation:

$$F_a \cdot c_1 \cdot (p/p_o)^m = c_1 \cdot \frac{55.5}{55.5 + 2c_1 + 2c_2 - 9c_1 - 2c_2} \cdot f_a. \qquad (50)$$

Here F_a is the apparent activity coefficient of the hydrogen ion, f_a the activity coefficient originating from the interionic electric forces and m the number of water molecules in the hydrogen ion. Both right and left sides of the equation express the activity of the hydrogen-ion hydrate. From equation 50 we easily get:

$$\log F_a + m \log p/p_o = \log f_a - \log\left(1 - \frac{7c_1}{55.5}\right). \tag{51}$$

Applied to the solution of hydrochloric acid without potassium chloride, equation 51 gives

$$\log [F_a]_o + m \log [p/p_o]_o = \log [f_a]_o - \log\left(1 - \frac{7c_1}{55.5}\right). \tag{52}$$

By subtraction of equation 52 from 51 and isolation of m we get:

$$m = \frac{\log F_a - \log [F_a]_o - \log f_a + \log [f_a]_o}{\log [p/p_o]_o - \log p/p_o}. \tag{53}$$

From this equation m is calculated. $\log F_a - \log [F_a]_o$ is obtained by means of formula 49 from Harned's potential measurements. For the calculation of $\log f_a$ and $\log [f_a]_o$ the following formula is used:

$$\log f_a = -0.2 \sqrt[3]{c_1 + c_2}\ ; \tag{54}$$

$\log p/p_o$ and $\log [p/p_o]_o$ are calculated from the freezing points of the solutions by means of equation 36. By the latter calculation it is assumed that a solution with the concentrations 0.1 M HCl and c M KCl freezes at the same temperature as a $(c + 0.1)$ M KCl solution. Table 5 shows the results of the calculation.

Table 5. Hydration of the hydrogen ion according to activity measurements at 25° C.

c	c_1	c_2	E	Diff.-potential	$\log F_a - \log[F_a]_o$	$-\log f_a$	$-\log p/p_o$	m
0	0.1004	0	0.3495	0.0048		0.093	0.0015	
1.100	0.1004	1.143	0.3459	0.0024	0.020	0.212	0.0172	8.9
1.376	0.1004	1.441	0.3443	0.0022	0.044	0.238	0.0212	9.6
3.134	0.1004	3.474	0.3326	0.0014	0.229	0.296	0.0492	9.1
								mean 9.2

Harned makes up his solution by dissolving c moles of KCl in 1 litre of 0.1 M HCl. The values of c are given in column 1; in columns 2 and 3, c_1 and c_2, the numbers of moles of HCl and KCl per 1000 g of H_2O are given, calculated from c on the assumption that the apparent molar volumes are 18 cc. for HCl and 30 cc. for KCl. Column 4, E, gives the potentials as found by Harned; column 5 the diffusion potentials calculated according to Henderson (*cf.* Bjerrum[9]); column 6 the values of log F_a — log $[F_a]_0$ calculated according to formula 49; column 7 — log f_a calculated from expression 54, and column 8 — log p/p_0 calculated according to formula 36. Finally in the last column the values of m calculated according to formula 53 are shown. The mean value of m, 9.2, shows that the greater part of the water bound by the ions of hydrochloric acid, must be ascribed to the hydrogen ion.

12. For the determination of the hydration of the chloride ion Harned's potential measurements with cells of the following type may be used:

$$\mathrm{Hg/HgCl},\ c\ M\ \mathrm{KCl}/0.1\ M\ \mathrm{KCl},\ \mathrm{HgCl/Hg}.$$

From these measurements Harned rightly eliminated the diffusion potential by means of Nernst's formula. For the determination of the apparent activity coefficient of the chloride ion we have

$$\log\,[F_a]_{c_1} - \log\,[F_a]_{c_1'} = \frac{E}{0.0591}\log\frac{c_1}{c_1'}. \tag{55}$$

Here c_1 and c_1' indicate the concentrations of the solutions used in moles of KCl per 1000 g of H_2O, and E is the potential corrected for the diffusion potential. The calculation of m for the chloride ion may be made according to the same formula 53 as used in the case of the hydrogen ion. Table 6 contains the results of the calculations.

Table 6. Hydration of the chloride ion according to activity measurements at 25° C.

c	c_2	E corr. for Diff.-Pot.	$\log\,[F_a]_o$ $-\log\,[F_a]_{0.1}$	$-\log f_a$	$-\log p/p_0$	m
0.1	0.1005	0	0	0.116	0.0014	–
1.0	1.038	0.05340	—0.109	0.250	0.0143	1.9
1.9	2.020	0.06912	—0.133	0.310	0.0276	2.3
3.1	3.427	0.08247	—0.136	0.364	0.0468	2.5
					mean	2.2

In column 1, c, the molar concentrations of potassium chloride (moles per litre) are given according to Harned. Column 2 shows the values of c_2, the concentration of potassium chloride in moles per 1000 g of water. In this calculation of c_2 the apparent molar volume in the solution of potassium chloride is put equal to 30 cc. Column 3 contains the results of Harned's potential measurements corrected for the diffusion potential. Column 4 contains the values of log $[F_a]_c$ — log $[F_a]_{0.1}$, calculated by means of eq. 55; column 5 the values of — log f_a calculated from the expression $0.25\sqrt[3]{c}$; column 6 the values of — log p/p_0 calculated from determinations of freezing points according to formula 36. Finally the last column contains the values of m calculated according to formula 53. The mean value is 2.2 and hence the formula for the chloride ion must be supposed to be $Cl^-, 2H_2O$.

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On Electric Forces Between Ions and Their Effects

NIELS BJERRUM

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After the enunciation in 1887 by Svante Arrhenius of his famous theory of electrolytic dissociation much work was devoted to the further development of this theory. Nevertheless one aspect of the theory was not taken up for further discussion until fairly late, viz. the study of the interionic forces. For many years the effects of the electric forces between the ionic charges were neglected. The existence of such *interionic forces* was hardly questioned, but most emphasis was justly laid upon the feature which is so characteristic of the theory, namely that the behaviour of free ions is essentially like that of neutral molecules, while the small difference between free ions and neutral molecules caused by the interionic forces was neglected. During the last decennium work on the interionic forces has, however, gathered momentum and has resulted in an interesting development of the classical ionization theory, and in the following we shall consider the results of these investigations more closely.

I

1. When applying Coulomb's and Faraday's laws to the forces acting between two ions, each having an electric charge E, and being a distance r apart, in a solvent with a dielectric constant D, we find the following formula for the force,

$$K = \frac{E^2}{Dr^2} \tag{1}$$

For large values of r this formula is no doubt justified, but when r is of molecular dimensions, i. e. when only a few, a single or perhaps none of the molecules of the solvent occur between the ions, the justification is more questionable. Without going further into a theory about the dielectric constant D and the application of the usual value of D even to small values of r, I shall state a number of experimental results which indicate that the above formula maintains — if not its correctness — at least its applicability even down to very small distances.

2. The first scientist to direct his attention to the effect of interionic electric forces was probably W. Ostwald. In 1892 he drew attention to the fact that the second-stage dissociation constant of a dibasic acid is always less than the first-stage constant, and explained this condition as a consequence of the fact that the electric attraction between the hydrogen ion and the single negative charge on the acid ion (HR^-) impedes the dissociation of the second hydrogen atom. In agreement with this view it was ascertained by Ostwald that the difference between the two dissociation constants is the larger the closer the two hydrogen atoms in the acid are to each other, e. g. greater in oxalic acid than in glutaric acid.

Ostwald's qualitative consideration may be given a quantitative form[1]. Let us consider a solution of a dibasic symmetrical acid H_2R. In the proximity of a negative ion HR^- the hydrogen-ion concentration will be greater than in the proximity of H_2R. According to Boltzmann the concentration is proportional to

$$\mathrm{e}^{\frac{\varphi}{kT}}$$

(where k is Boltzmann's constant, T the absolute temperature, and φ the work required to remove the ions HR^- and H^+ from each other). According to Coulomb's law (equation 1), this work (in a sufficiently dilute solution) is equal to

$$\varphi = \frac{E^2}{Dr}$$

(where r is the distance between the charges on the ions). According to this the ratio of the concentrations of hydrogen ions close to HR^- and H_2R respectively will be equal to

$$\mathrm{e}^{\frac{E^2}{kTDr}}$$

Hence we find the following formula for the ratio between the first and the second dissociation constants of the acid:

$$\frac{K_1}{K_2} = 4 \cdot \mathrm{e}^{\frac{E^2}{kTDr}} \qquad (2)$$

In this formula r will denote the intramolecular distance between the hydrogen atom and the negative charge of the ion HR^-. The factor 4 is a statistical factor which is a result firstly of the fact that the acid H_2R has two hydrogen ions which may be dissociated, and secondly of the fact that in the anion R^{--} there are two points to which the hydrogen ions may link themselves. The exponential term represents the actual electrostatic effect caused by the interionic forces between the free charges. For water at 18° C $D = 81$ and equation 2 may be written

$$\log \frac{K_1}{K_2} = \log 4 + \frac{3.1}{r} \qquad (3)$$

In this formula r is to be measured in Ångström.

When calculating r according to this formula for a series of normal dibasic acids of the oxalic acid series, the following values are obtained (table 1, column 4).

Table 1. Dimensions of molecules of normal dicarboxylic acids of the oxalic acid series

	Length of chain $(2 + 1.5\,(n-1))$	$1.3\,n$	r in H_2O	r in CH_3OH	r saponification
C_2	3.5	2.6	1.33	—	0.8
C_3	5.0	3.9	1.35	—	1.8
C_4	6.5	5.2	3.8	5.0	4.4
C_5	8.0	6.5	5.3	—	—
C_8	12.5	10.4	7.2	—	—
C_9	14.0	11.7	8.6	—	—
C_{10}	15.5	13.0	7.4	8.9	—

From the structure of the diamond crystal we know that the distance between carbon atoms linked by single bonds is about 1.5 Å. If we add 1 Å for each of the oxygen atoms we can obtain figures for the length of the molecular chain measured along the carbon chain for the different acids; these figures have been stated in column 2 (under the heading: length of chain). The actual length of the molecules must on account of their curved or zig-zag formation be smaller. Langmuir[2] has, on the basis of his experiments on oil films on water, calculated the length of the acid molecules to be 1.3 Å per carbon atom (3rd column).

Apart from the lowest members of the acid series (C_2 and C_3) the r-values calculated from the dissociation constants seem very acceptable. The figures for oxalic acid and malonic acid seem to indicate that we ought to base the calculation on a smaller value of the dielectric constant (e. g. half as great). However, these deviations should not — or at any rate not exclusively — be explained by the assumption that it is incorrect to use the usual dielectric constant of water as, besides the actual electrostatic effect, we must also expect an effect through the atomic chain (by displacement of electrons). The effect of the introduction of hydroxyl and halogen on the strength of organic acids prove that even if the effect through the atomic chain is small in γ-positions and more remote positions, it has a considerable value in α- and β-positions, and may therefore explain why the calculated values of r for oxalic acid and malonic acid are too small.

3. An interesting confirmation of the applicability of formula 3 is obtained by means of *phenolphthalein*. For this dibasic acid Rosenstein has found $K_1/K_2 = 4$

As r on the basis of the formula of phenolphthalein must be assumed to be about 8 Å, we find from equation 3 that

$$\frac{K_1}{K_2} = \text{about } 10.$$

I have therefore concluded[1] that the double-charged phenolphthalein ion is only present to an extent of 40 per cent in a colourless form corresponding to the undissociated acid. If we take only the concentration of this form into account, we have $K_1/K_2 = 10$. The remaining 60 per cent must thus be present in the rearranged, red, quinoidal form. Acree and Birge[3] have on the basis of colorimetrical investigations considered it a warrantable conclusion that about 44 per cent of the double-charged ion is present as a coloured, rearranged ion. This result suggests a confirmation of my theory.

In alcohol, the dielectric constant of which is lower than that of water, the difference between the first and the second dissociation constants of the same acid (same value of r) is, according to the theory, greater than in water. For methyl alcohol ($D = 35$) the following equation should thus hold,

$$\log \frac{K_1}{K_2} = \log 4 + \frac{7.2}{r} \tag{4}$$

From Ebert's[4] determinations of the dissociation constants for succinic acid and suberic acid it is possible to calculate r according to formula 4. The values found (table 1, column 5) are almost the same as those applying to water, but they are slightly larger. This might be expected, as the effect through the carbon chain on account of the greater influence of the free charges in the alcoholic solution must play a relatively smaller part than in aqueous solution.

5. Analogous to the fact that a *negative charge* impedes the dissociation of a positive hydrogen ion, a *positive charge* will facilitate such a dissociation. Positive charges will thus make an acid stronger. It is of course also possible to apply equation 3 to this effect; it should be borne in mind, however, that the statistical factor is not always 4, but should be determined in each individual case. The following examples may be mentioned.

The first and second hydrolysis constants of the *hexaquochromic ion* have previously been determined to be about $1 \cdot 10^{-4}$ and $0.006 \cdot 10^{-4}$, respectively, at 17° C[5]. These two constants are measures of the dissociation of hydrogen ion from $Cr(H_2O)_6^{+++}$ and $Cr(H_2O)_5OH^{++}$, respectively.

As the statistical factor in this case should probably be ascribed the value $^{12}/_{1} \cdot {}^{2}/_{10}$, we find, from the ratio of the hydrolysis constants, r to be equal to 1.7 Å for the distance between the ionizing hydrogen atoms and the electrical centre of gravity of the complexes — a fairly reasonable value.

The hydrolysis constant of the *dichlorotetraquochromic ion* was determined to be $4 \cdot 10^{-6}$ at 25° C. This ion is consequently a much weaker acid (compare Brønsted's definition of an acid [6]) than the hexaquochromic ion, in spite of the fact that it contains two electronegative chlorine atoms, but in agreement with its single positive charge as against the three charges of the hexaquochromic ion.

6. The above electrostatic reasoning may also be applied to *ampholytes*.

I have previously [7] derived the formula:

$$\frac{K_S \cdot K_B}{K_{H_2O}} = \frac{n}{x\,(1-x)} \tag{5}$$

where K_S and K_B are the dissociation constants for the acid and basic groups of an ampholyte, x is the fraction of the undissociated ampholyte which is present as a "zwitter-ion" or ampho-ion, and n is a factor which indicates the ratio between the dissociation constants of the *acids*:

$$NH_2 \cdot R \cdot COOH \text{ and } NH_3^+ \cdot R \cdot COOH$$

or, which may be shown to be the same thing, of the *amines*

$$NH_2 \cdot R \cdot COOH \text{ and } NH_2 \cdot R \cdot COO^-.$$

If we substitute the electrostatic expression for n and take the logarithms, we obtain

$$\log \frac{K_S K_B}{K_{H_2O}} = \frac{3.1}{r} - \log x(1-x) \tag{6}$$

The difficulty experienced in testing the correctness of this formula is caused by the fact that x is usually not known.

As regards amino-benzoic acids reasons have previously been given for the opinion that x is between 0.1 and 0.9. According to Rørdam's[8] investigations, which, however, as regards this point, is somewhat uncertain, $x = 0.6$ for the *ortho*-acid and $x = 0.4$ for the *para*-acid. Euler has recently found that x must be fairly small, but it is hardly less than $^1/_4$. If we substitute $x(1-x) = 0.2$, we find from the known dissociation constants

	o-acid	*m*-acid	*p*-acid
r (amino-benzoic acid)	1.4	3.3	1.5
r (phthalic acid)	1.6	6.7	—

For comparison the r-values for phthalic acid and *iso*-phthalic acid calculated from formula 3 have been stated.

Considering the uncertainty of this material the values found for the *o*- and *m*-acids must be said to be acceptable, while the small value of r found for the *p*-acid suggests that a renewed determination of the dissociation constants and x of this amino-acid is required. An explanation of the higher values of r for *m*-phthalic acid than for *m*-amino-benzoic acid may be found in the fact that the ionized carboxyl groups in a phthalic acid have like charges and thus repel each other, while the ionized amino and carboxyl groups have opposite charges and attract each other. In the former case the molecule will be stretched, and in the latter it will be more or less doubled up.

The above treatment of amino-acids gives an example of the way in which it is possible to calculate electrostatic effects in asymmetrical molecules the ionizing hydrogen atoms of which are *linked in different ways.*

7. The electrostatic reasoning may also be applied to the *consecutive dissociation of other ions* than hydrogen ions. As an example we may use the complexity constants of the chromic thiocyanates[9]. This is a question of dissociation of the six thiocyanate groups in the complex $Cr(CNS)_6^{---}$ and addition of H_2O instead of $(CNS)^-$ so that the end-result will be a hexaquochromic ion:

$$Cr(CNS)_6^{---} \rightarrow Cr(CNS)_5(H_2O)^{--} \rightarrow Cr(CNS)_4(H_2O)_2^{-} \rightarrow Cr(CNS)_3(H_2O)_3$$
$$\rightarrow Cr(CNS)_2(H_2O)_4^{+} \rightarrow CrCNS(H_2O)_5^{++} \rightarrow Cr(H_2O)_6^{+++}$$

Column 2 in the following table gives the values of the six dissociation constants previously published by me.

Table 2. The dissociation constants for the hexathiocyanato-chromiate complex at 50° C.

	Bjerrum	Corrected to $C_{\text{Ion}}=0$	Statistical factor	Corrected for stat. factor	Diff. $(=\frac{3.3}{r})$
$\log K_1$	0.39	1.6	${}^6/_1$	0.8	
$\log K_2$	0.09	0.7	${}^5/_2$	0.3	0.5
$\log K_3$	—0.29	—0.3	${}^4/_3$	—0.4	0.7
$\log K_4$	—0.66	—1.0	${}^3/_4$	—0.9	0.5
$\log K_5$	—1.24	—1.7	${}^2/_5$	—1.3	0.4
$\log K_6$	—2.52	—3.1	${}^1/_6$	—2.3	1.0
				mean value:	0.6 $r = 5.5$ Å

The calculation of these values is based on concentrations, not on activities. When these values are converted — as best we can for the time being — into activitie, whisch means that the values are extrapolated to an ionic concentration equal to zero, the figures of column 3 are obtained. For statistical reasons the ratio of the constants must be as the fractions of column 4. If we correct for the statistical effect, we obtain the values given in column 5. When we explain the decrease of these values with increasing index figure exclusively as a consequence of the increasing positive charge of the complex caused by the dissociation of the thiocyanate ion, the effect of the individual charge will be measured by the differences stated in the 6th. column. From the mean value of these differences, r is calculated to be 5.5 Å. This value appears somewhat large, but the order of magnitude is acceptable. The fact that it is too large does not at any rate suggest that the value of D used should be lower than the usual D of water, not even in case of thiocyanate ions which, so to speak, touch the complex.

8. The interionic forces does not only influence chemical equilibria, but also the *velocity of chemical reactions.*

In 1898 it was stated by Emil Fischer in a paper that he had observed that the saponifying or decomposing effect of hydroxyl ions is usually greater towards a neutral substance than towards an analogous acid substance. Thus the saponification of dimethylacetoacetic ester proceeds much more rapidly than that of the acid acetoacetic ester. He adds that van't Hoff has drawn his attention to the fact that this may be explained by assuming the *acid forms* to occur in the basic solution as negative ions, e. g.:

$$CH_3CO^-:CHCOOC_2H_5$$

The negative charges of these ions repel the hydroxyl ions and thus impede the decomposing effect of the latter.

In 1909 Julius Meyer again expounded this view. As it had already been shown, it is always more difficult to saponify the second alkyl than the first alkyl in the esters of dibasic acids. Meyer explained this by assuming that the semi-ester anion repels the hydroxyl ion electrically.

When formulating the electrostatic theory quantitatively the following equation is obtained

$$\log \frac{k_1}{k_2} = \log 2 + \frac{3.1}{r} \tag{7}$$

(where k_1 and k_2 are the velocity constants of the saponification of 1. and 2. alkyl).

The following equation holds, as previously mentioned, for the dissociation constants

$$\log \frac{K_1}{K_2} = \log 4 + \frac{3.1}{r} \tag{8}$$

The actual electrostatic effect is the same on the saponification constant and on the dissociation constant according to equations 7 and 8. The difference between these formulae are caused by the fact that the statistical factor in case of the saponification constants is 2, while in case of the dissociation constants it is 4.

Skrabal, who has lately carried on comprehensive studies of the saponification processes, has, on a purely empirical basis, concluded from his experiments that there is a certain parallelism between the ratio of the equilibrium constants of dibasic acids and the velocity constants of the saponification of the corresponding esters. He has also pointed out that with increasing distance between the acid groups in the molecule the ratio of the saponification constants approaches 2. (compare especially[10]). These observations agree closely with formulae 7 and 8.

Unfortunately Skrabal has performed most of his experiments in solutions the ionic concentration of which was above 0.1 normal, and as the ionic concentration has a great influence, especially on the 2. saponification constant (Holmberg's cation catalysis) it is not possible with certainty to estimate the value of the velocity constants at zero ionic concentration on the basis of Skrabal's measurements. Skrabal's experiments have moreover in a number of cases been performed in a mixture of 50 per cent alcohol and 50 per cent water. These conditions render a quantitative application of Skrabal's comprehensive and interesting experimental material very difficult.

When using, preferably, the determinations at low salt concentrations, the following values of the ratio of 1. to 2. saponification constants in water are obtained from measurements performed by Goldschmidt and Scholz, Jul. Meyer and Skrabal:

Oxalic acid: 19000 (high salt concentration).
Malonic acid: about 100. Succinic acid: about 10.

Using these values and formula 7 we find the r-values of the last column in table 1. These values are in good agreement with values determined by other methods.

9. Altogether it may be said that the material which has been referred to on the preceding pages show that we are entitled to consider the calculation of the forces between two ions based on Coulomb's law and the usual dielectric constants of the solvent to be a useful approximation even for ions very close to each other.

II.

10. Some of the especially interesting effects of the interionic forces are their influence on the *osmotic pressure* of the ions, on their active mass or *activity*, and on their *conductivity*. Already van Laar, Malmstrøm, Sutherland, Bjerrum and Kjellin have realized the importance of the interionic forces in this connection. But Milner (1913) was the first to grasp the essential characteristic of this phenomenon, namely the grouping of the ions in solution in such a manner that ions of opposite charges are on an average closer to each other than ions of like charges.

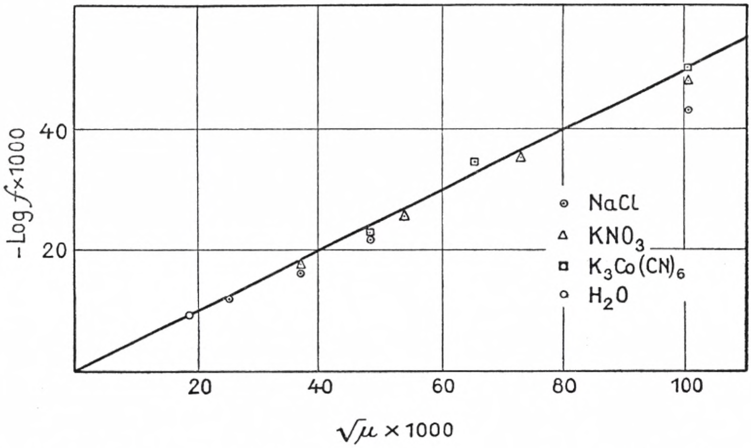

Fig. 1. Connection between activity coefficient f and ionic strength of the uni-univalent salt $[(NO_2)(CNS)(NH_3)_4Co][(C_2O_4)(NO_2)_2(NH_3)_2Co]$ *in the presence of other salts. The line drawn represents the theoretical values according to Debye and Hückel. After Brønsted and La Mer.*

And it was not until 1923 that Debye and Hückel[11] succeeded in enunciating formulae for these effects which were applicable in practice and quite exact as regards sufficiently dilute solutions.

These scientists base their work on Coulomb-Faraday's law, assume the ions to be spherical with a diameter *a* and with the charge located in the centre, and thus find the following formula for the *activity coefficient f* (= activity/concentration) of an ion,

$$-\log f = 0.50 \frac{z^2 \sqrt{\mu}}{1 + 0.327 \sqrt{\mu}\, a} \tag{9}$$

In this formula the numerical values are those applying to water at 18° C, z is the valency of the ion, and $\mu = {}^1/_2 \Sigma\, cz^2$ is the *ionic strength,* introduced in the theory of electrolytes by Lewis and Randall. In case of low ionic strengths (small ionic concentrations) the denominator may be neglected and it will be found that $-\log f$ (which is positive) with increasing dilution will approach zero according to a simple square root law; f is thus smaller than 1 and approaches 1 with decreasing concentration according to a square root law. A corresponding formula was proposed by Debye and Hückel for the osmotic pressure of the ions and a similar, although more complicated, formula for their conductivity (mobility).

11. Milner's and Debye and Hückel's investigations show that on account of the existence of the interionic forces it is not permissible to assume that the ratio of the osmotic effect (or the activity) of the ions to their concentration is constant. Nor is the mobility independent of the concentration. We must, on the contrary, expect all these quantities to decrease with increasing ionic concentration.

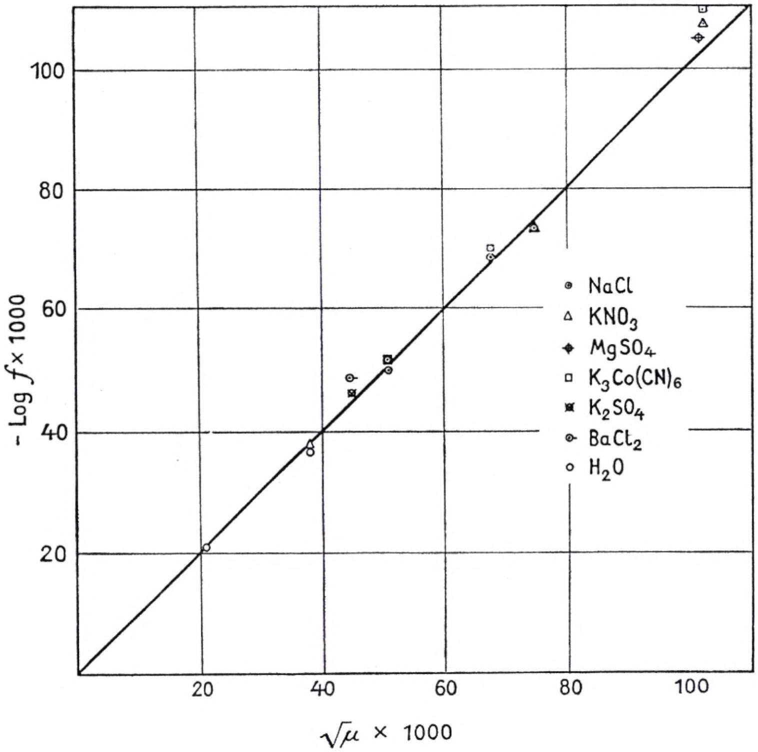

Fig. 2. Connection between the activity coefficient f and ionic strength of the uni-bivalent salt $[(C_2O_4)(NH_3)_4Co]_2S_2O_6$ *in the presence of other salts. The line drawn represents the theoretical values according to Debye and Hückel. After Brønsted and La Mer.*

It is well known that these quantities are observed to decrease with increasing ionic concentration in all electrolytes. This was originally — both with regard to strong and weak electrolytes — interpreted as an indication of incomplete dissociation. If, however, the decrease which is observed experimentally is compared with the decrease according to Debye and Hückel, it will appear that in the case of *strong electrolytes* the agreement is so good that there is no necessity of explaining anything by incomplete dissociation. I shall mention a number of examples of the agreement observed.

The most accurate method of measuring the activity of ions available at present is probably determination of salt solubilities. According to this method Brønsted and La Mer[12] have found values for $-\log f$ which in dilute solutions, up to 0.01 molar, agree excellently with Debye and Hückel's formula. This may be seen from figs. 1–3.

This summer Rodebush and Hovorka[13] have performed a number of exceedingly accurate cryoscopic determinations in very dilute aqueous salt solutions (0.001–

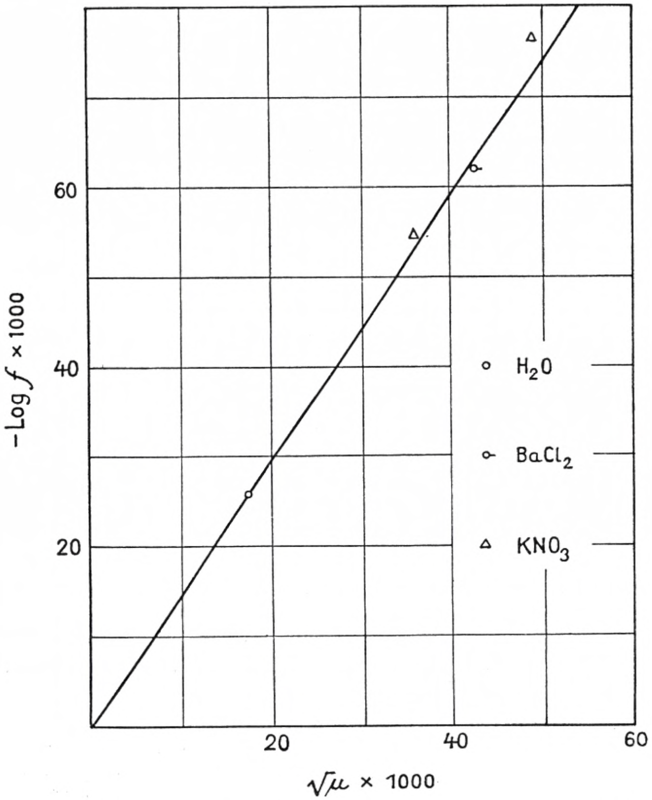

Fig. 3. Connection between the activity coefficient f and ionic strength of the tri-univalent salt $[(NH_3)_6Co][(C_2O_4)(NO_2)_2(NH_3)_2Co]_3$ *in the presence of other salts. The line drawn represents the theoretical values according to Debye and Hückel. After Brønsted and La Mer.*

0.01 molar). Figs. 4 and 5 show their results. The curves drawn represents the values according to Debye and Hückel. The slight curvature of these curves show that Rodebush and Hovorka have allowed for the diameter of the ions. Otherwise the curves would have been rectilinear (tangents to the curves at the point corresponding to concentration zero). The diameters (*a*) which they have allowed for are chosen so as to make the curves pass through the point corresponding to the highest concentration measured.

The ionic diameters used are:

Salt	KCl	$CsNO_3$	K_2SO_4	$Ba(NO_3)_2$	$MgSO_4$	$CuSO_4$	$La_2(SO_4)_3$
a in Å	2.32	2.32	1.09	1.01	2.22	1.59	3.00

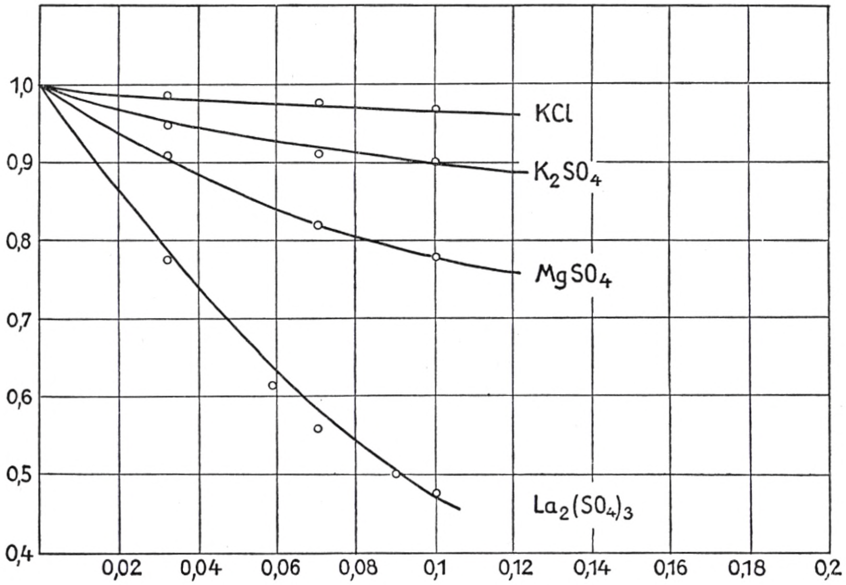

Fig. 4. The dependence of the osmotic coefficient on $\sqrt{\mu}$, *after Rodebush and Hovorka.*

Figs. 4 and 5 show that it is also possible to understand the osmotic behaviour of the ions if it is assumed that there is no perceptible amount of undissociated molecules in the salt solutions examined.

This also appears in an interesting manner from a recently published paper by Schreiner and Frivold[14] on the freezing-point lowering of lithium chloride in cyclohexanol.

As regards the conductivity the theory is more complicated, but also in this case Debye and Hückel's theory can account for the conditions in dilute solutions of strong electrolytes without the assumption of incomplete ionization.

12. As well known, it has previously[15] been concluded that the so-called strong electrolytes are practically completely dissociated. This was indicated especially by the results of investigations on the optic and catalytic properties of salt solutions and by the peculiar uniformity of the degrees of dissociation of all strong electrolytes as calculated according to classical methods. These degrees of dissociation are mainly determined by the electric properties of the system (the charge and concentration of the ions, the dielectric constant of the solvent). Through the investigations by Debye and Hückel the hypothesis of the practically complete ionization of strong electrolytes has now become a fact which can hardly be questioned.

With our present knowledge it must be considered very unfortunate in the case of a strong electrolyte to consider the conductivity coefficient, μ/μ_∞, as a degree of dissociation and to try to apply the law of mass action to it.

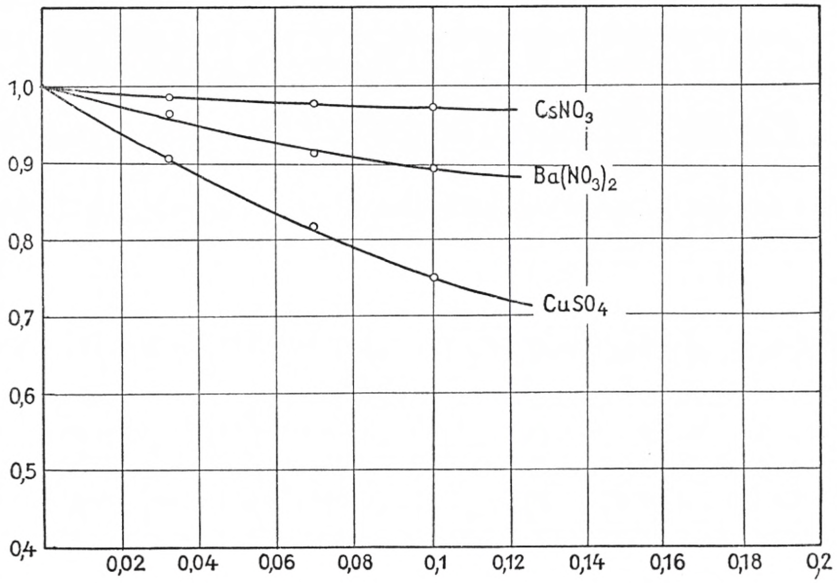

Fig. 5. The dependence of the osmotic coefficient on $\sqrt{\mu}$, *after Rodebush and Hovorka.*

For very weak electrolytes μ/μ_∞ should on the other hand be considered a degree of dissociation. For in this case the ionic concentration is so small that we may neglect the effect of interionic forces and assume the mobility of the ions to be constant.

For electrolytes of medium strength it is possible (as already shown in 1916 for picric acid in alcohol[16]) to calculate the actual degree of dissociation from the conductivity coefficient by correcting the latter for the influence of the interionic forces. The stronger the electrolyte the greater this correction and the more uncertain the calculated degree of dissociation.

13. As we have now discussed the importance of the interionic forces to the activity of the ions, it will be of interest to return to the importance of these forces to the velocity of the ionic reactions.

It has already previously been mentioned that it is possible by means of the interionic forces to explain why a negative ion, as e. g. the hydroxyl ion, has a smaller effect on a group in a negative ion than on the same group in a neutral molecule or a positive ion. We shall now consider another aspect, namely *the influence of the ionic concentration on the velocity constant.*

Holmberg has in a very interesting series of papers shown that a number of reactions, in which *hydroxyl ions* or other negative ions react with *ions with a negative charge*, is catalyzed by the addition of salt and is particularly accelerated by salts with polyvalent cations (cation catalysis). As stated by Holmberg[17] in

1921 this must, on the basis of the hypothesis on the complete dissociation of the salts, be explained by the fact that the interionic forces increase the velocity of reaction, although this author has not attempted any further elaboration of the idea.

Brønsted[18] has in 1922 in a very interesting paper shown that the influence of the salt concentration, not only on the ionic reactions dealt with by Holmberg, but also on other ionic reactions examined, may be formulated in the following equation:

$$k = k_o \frac{f_1 f_2}{f_{12}} \tag{10}$$

Here k and k_o are the velocity constants in the salt solution considered and at an infinitely small ionic concentration, respectively, f_1 and f_2 are the activity coefficients of the interacting ions (molecules) and f_{12} is the activity coefficient of an ion the charge on which is equal to the sum of the charges on the interacting ions. As regards the derivation and meaning of this important formula Brønsted and I do not agree completely, but none of us have any doubt that numerically the formula gives a correct explanation of the influence of the salt concentration on the velocity of the ionic reaction.

When Debye and Hückel's expression for the activity coefficients according to formula 9 is substituted in Brønsted's formula, the latter will assume the following form:

$$\log \frac{k}{k_o} = 0.50 \frac{2\, z_1 z_2 \sqrt{\mu}}{1 + 0.327 \sqrt{\mu}\, a} \tag{11}$$

(z_1 and z_2 being the number of electrical charges, with the correct sign, on the two interacting complexes).

14. The influence of the ionic concentration is perhaps most clearly realized through the following considerations (as an example we shall use one of Holmberg's cation catalyses). We shall consider the influence of hydroxyl ions on the anion of dibromopropionic acid, $CH_2BrCHBrCOO^-$. Close to this ion the concentration of hydroxyl ions will, due to interionic forces, be smaller than elsewhere in the liquid. Assuming that the point of the molecule which is attacked is the β-bromine*) and that the distance of this atom from the negative charge is r Å, we find that the concentration of hydroxyl ions in the vicinity of the β-bromine is

$$e^{\frac{E^2}{kTDr}} = 10^{\frac{3.1}{r}}$$

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*) After the reading of this paper Professor Holmberg informed me that the point of attack is probably the α-hydrogen, and I quite agree with this view. Hereby the tenor of the reasoning is not altered, however.

times lower than elsewhere in the solution. When the ionic concentration of the solution increases, the electric force emanating from the dibromopropionate ion will alter the distribution not only of the hydroxyl ions, but of all ions present. The greater the number of ions present the smaller the effect on the individual ion and the larger the concentration of hydroxyl ions in the vicinity of the dibromopropionate ion. The influence of the salt can thus be ascribed to a reduction of the electrostatic effect. A quantitative calculation will show that in dilute salt solutions the effect of the salt is independent of r, provided that r is not too large.

For large salt concentrations and large values of r the magnitude of r will, however, be significant, and it will be impossible to use the simple formula 11. It will probably be possible in the case of substances with a high value of r (i. e. great distance between charge and reacting group) to ascertain that the ratio of the velocity of reaction in a medium with a small number of ions to that in a medium rich in ions will, with increasing ionic concentration, approach the limiting value $10^{\frac{3.1}{r}}$. In that case it will also be possible to determine the molecular dimension r in this way.

III.

15. It has sometimes been considered possible to contest the new views on strong electrolytes by proving the existence of undissociated molecules in some strong electrolyte or other. This opinion is, however, unjustified.

It might beforehand be expected that in nature we could meet with all the transition forms from the 100 per cent dissociated strong electrolyte through medium-strong and weak electrolytes down to the typical non-electrolytes.

That the green dichlorochromic chloride contains undissociated chloride may be ascertained by means of silver nitrate. That concentrated solutions of cupric chloride contains chloro-complexes is seen from the colour.

Particular interest is attached to the degree of dissociation of the hydrogen halogenides. As regards hydrogen chloride Schreiner[19] has, from its catalytic action in alcohol, calculated the dissociation constant in alcoholic solution to be about 10^{-2}, and as the dissociation constant of acids in water is usually about 10^6 times larger than in alcohol, he has concluded that it must be about 10^4 in water. According to Schreiner, the index of refraction of concentrated hydrochloric acid also suggests an incomplete dissociation, and in this way he has calculated a dissociation constant of about 10^6. A third method for an approximate estimation of the dissociation constant of hydrogen chloride has been devised by Ebert[20]. By extrapolating from the series C_3H_7Cl, C_2H_5Cl, CH_3Cl to HCl he calculates the solubility of undissociated hydrogen chloride in water. As the vapour pressure of hydrogen chloride, e. g. over 1 normal hydrochloric acid, is known, it is now possible for Ebert to calculate the concentration of undissociated hydrogen chloride in this acid and thus the dissociation constant of hydrochloric acid. The result he finds in this way is about 10^7. On account of the nature of the extrapolation this method must, however, as emphasized by Ebert, produce a result which is too large.

Along different ways we have thus reached the result that hydrochloric acid is not completely dissociated, but even in 1 normal hydrochloric acid the amount of undissociated hydrogen chloride is only small (about 10^{-5} to 10^{-6} moles per litre).

Measured by means of the conductivity coefficient μ/μ_∞ HCl, HBr, and HJ are all equally strong, but measured according to Ebert the ratio of the dissociation constants are 1:100:250. Such a great difference agrees very well with the considerable differences in the "acid" properties of these substances when anhydrous, as ascertained by Hantzsch[21]. When the dissociation constant of hydrogen iodide is about 250 times that of hydrogen chloride, this means that the difference in strength between hydrogen chloride and hydrogen iodide is greater than between acetic and monochloroacetic acid.

While the dissociation constants of strong electrolytes previously calculated from the conductivity were not at all specific and were chiefly determined by the valency of the ions, the new dissociation constants distinguish themselves by their specificity, their variation from electrolyte to electrolyte, which is such a characteristic property of chemical equilibrium constants.

I ascribe great importance to the fact that the new views have drawn our attention towards the problem of *determining the dissociation constants for almost strong electrolytes* and thus obtaining a measure of the true strength also of these electrolytes.

Interesting problems are in this connection presented by sulphuric acid and the sulphonic acids.

As a last example of a strong electrolyte which is hardly completely dissociated, I shall mention *sodium hydroxide*. The activity of the hydroxyl ion is in solutions of sodium hydroxide considerably lower than in potassium hydroxide solutions*). If the dissociation were complete, it should be the other way round as the activity of the ions in sodium salts is usually greater than in potassium salts, in accordance with the fact that the sodium ion is hydrated and consequently larger than the potassium ion. I therefore assume that the small activity of the hydroxyl

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*) Measurements by Miss A. Unmack, not yet published. Harned[22] has shown that the activity of sodium hydroxide is smaller than that of potassium hydroxide.

ion in sodium hydroxide may be explained by an incomplete dissociation in aqueous solution of sodium hydroxide. Harned has drawn a similar conclusion from his measurements[23].

When considering the similarity in structure between H_2O and OH^-, it is quite obvious that an ion, as the sodium ion, which tends to form hydrates can also combine with hydroxyl ions. Indeed a parallelism between the hydration of the cations and the weakness of their bases might be expected. In this connection I should like to point out that both Kolthoff[24] and Gjaldbæk[25] have recently shown that magnesium hydroxide is incompletely dissociated in solution. For the second dissociation constant of magnesium hydroxide Gjaldbæk finds a value of about $10^{-2.1}$ when assuming the first dissociation constant to be infinite.

A number of determinations of the conductivity of magnesium methylate and various magnesium salts in methyl alcohol carried out by L. Zechmeister in my laboratory, but not published, show that magnesium methylate in methyl alcoholic solution is also rather incompletely dissociated as its conductivity is much lower than that of magnesium chloride and similar ternary electrolytes in methyl alcohol. The magnesium ion thus combines not only with H_2O and OH^-, but also with the CH_3O^--ion which is related to H_2O.

16. In his otherwise excellent book: *The Properties of Electrolytically conducting Systems*, New York 1922, Ch. A. Kraus has attacked the modern views on electrolytes chiefly for the following reasons: He is of the opinion that the interionic forces cannot explain the great variations of the conductivity coefficient μ/μ_∞ with the concentration, which is observed even in very strong electrolytes in a solvent with a very low dielectric constant, e. g. in water at high temperatures approaching the critical temperature. It appears to him to be particularly impossible to explain why the conductivity coefficient in media with a very low dielectric constant at high concentrations increases in an abnormal manner — and often increases considerably — with the concentration.

Actually it is possible by means of the interionic forces also to account for this behaviour, if the *ionic association* produced by these forces is duly allowed for.

It is immediately evident that ions of opposite charges will, due to interionic forces, more frequently be found close together than will neutral molecules, provided the concentration is the same. The former attract each other, which the latter do not. In order to estimate the significance of this fact, a quantitative consideration should, however, be made.

An elementary consideration shows that the number of neutral molecules in a given solution between which the distance varies from r to $r + dr$ for small values of r (small compared with the average distance between the molecules) may be assumed to be proportional to r^2dr. For ions of opposite charges the corresponding number is proportional to $r^2dr\ e^{\frac{E^2}{kTDr}}$ and for ions of like charges it is proportional to $r^2dr\ e^{-\frac{E^2}{kTDr}}$.

The curves plotted in fig. 1 on page (109) shows the frequency of molecular pairs without charge (I), of ionic pairs with like charges (III) and of ionic pairs with opposite charges (II) in aqueous solution at ordinary temperature. The abscissa is the distance between the components of the pairs (in Ångström), and the ordinate represents the frequency of pairs with this distance.

In the curve applying to ionic pairs consisting of ions of opposite charges (II) a pronounced minimum is observed at 3.5 Å. A similar minimum will of course occur in other solvents. It will always be located at the distance at which the work of separating the ions amounts to $2kT$, i. e. is equal to 4 times the average kinetic energy per degree of freedom. Ionic pairs with this distance are less frequent than those with greater or smaller distances. When in a solution the ions are so small that they can get perceptibly closer to each other than this, the frequency of closely associated ionic pairs will according to the figure increase considerably, and to obtain a correct picture of the influence of the interionic forces due regard must be had to this association. In aqueous solutions of sodium chloride and potassium chloride the charges of the ions cannot approach each other so closely. But when the ions are considerably smaller or have several charges, or if the dielectric constant of the solvent is considerably smaller than that of water this will be the case.

In Debye and Hückel's formula sufficient allowance has not been made for this association. I have tried to perform a more exact calculation by applying special considerations to the ions between which the distance is smaller than the distance corresponding to the minimum in the association curve and omitting to include them among the free ions. It seems actually possible to proceed along this line, which I shall endeavour to show elsewhere; it is particularly interesting that according to this point of view it is possible to account for the fact that the interionic forces can reduce the active mass of the ions, the osmotic effect and conductivity of their solutions to a tiny fraction of the values which would apply to perfectly free ions.

By applying this method of calculation we make the modern picture of an electrolytic solution approach the classical picture, as we are dealing with a degree of association which resembles the old degree of dissociation.

It must not, however, be forgotten that the separation between free and associated ions is so to speak of a calculatory nature, and does not possess the sharpness which characterizes chemical transformations. On the other hand it is not without interest that this new picture explains why the classical picture with its degree of dissociation does not become completely useless under conditions where the interionic forces result in extensive association, but on the contrary seem to obtain increased applicability.

The applicability of the picture of ions associated in pairs does not, however, continue to increase with the above mentioned external "associating" factors (large charge on the ion and high concentration, small dimensions of the ion and low dielectric constant). When the association in pairs is extensive, the interionic forces will namely also necessarily produce association into higher complexes, unless the solution is extremely dilute. This explains the high degree of association ascertained by Walden for strong electrolytes in media with very low dielectric constants.

In case of pronounced association *in pairs* the conductivity of the ions will be very small. In solvents with a very low dielectric constant the ions will probably, theoretically speaking, be free, not associated, in case of infinite dilution, but at the lowest measurable concentrations (0.0001–0.01 molar) the association in pairs will be very extensive and the conductivity consequently low. In more concentrated solutions the interionic forces may under such circumstances set up a conductivity increasing with the concentration. With increasing concentration the ionic pairs will approach each other, the interaction between them will tend to loosen them, ternary and higher products of association will become more frequent, and this will increase the conductivity. With increasing concentration we are approaching the state which is characteristic of melted salts, in which the ions are no doubt highly associated, but not in pairs, and thus able to move about and conduct the electric current.

The diagrams below give a schematical representation of the condition in a dilute, ionized solution with association in pairs (diagram I), that in a melted salt with high association, but not in pairs (diagram III), and an intermediate state in a relatively concentrated solution.

I: + — + — + —
II: + — + — + — + — + —
III: + — + — + — + — + — + — + — + — + — + — + — + — + —

Within a range in which association in pairs prevails the conductivity will be low and the osmotic effect comparatively high. When the association is of a higher order (multi-ionic complexes), a considerable conductivity may occur simultaneously with low osmotic effect.

17. A summary of the above will give the result that *the property which characterizes strong electrolytes* is not the freedom of the ions. In a potassium chloride crystal the ions are very closely attached to each other, but also in crystalline condition potassium chloride is a typically strong electrolyte. Nay — the strong electrolytes are characterized by the fact that the combination of their ions into

chemical molecules is not accompanied by any considerable change in the properties of the ions. *On the contrary, their ions can approach each other very closely without the occurrence of perceptible deformation. An ideal strong electrolyte* would, according to my view, be an electrolyte the ions of which do not cause any mutual deformation. It is for such electrolytes that endeavours have recently been made to formulate a theory and compare the latter with experience.

As Kossel and many other scientists — especially physicists — have assumed, a *smooth transition* may be expected to occur from large, slightly deformable and slightly associating ions, through smaller ions which are to some extent associating and deformable, to small ions which form typical chemical complexes while altering their properties considerably. According to this we should find a smooth transition from the practically non-associating KCl, through the somewhat associating KNO_3, to complex ions as $Cr(CNS)_6^{---}$ and so on to SO_4^{--} in which the hexavalent positive sulphur ion is assumed to be linked to four divalent negative oxygen ions. On the basis of the available experimental material it appears to me, however, to be more probable that there is a more or less sharp line of demarcation between *products of association* of only slightly deformable ions on one hand and more or less stable *chemical complexes*, built up of highly deformed or completely vanished ions on the other hand.

Presumably the formation of chemical complexes is associated with a change in the arrangement of certain electrons which after having been attached to one nucleus will become common to two nuclei. As far as I can see, it is most probable that such a change does not occur gradually, but when an electron in a certain state suddenly jumps from its original orbit into a new one associating it with both nuclei.

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Investigations on Association of Ions. I.

The Influence of Association of Ions on the Activity of the Ions at Intermediate Degrees of Association

NIELS BJERRUM

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A. INTRODUCTORY SURVEY

The modern theory for the strong electrolytes explains their properties in terms of the electrical forces between the ionic charges, without assuming any formation of un-dissociated molecules. This conception, which was founded by Bjerrum, Hertz, Milner, and further developed by Brønsted, Lorenz and Schreiner, has recently been crowned by the beautiful works of Debye and co-workers[1].

In my opinion several of the difficulties which beset this theory have been caused by the fact that, so far, too little attention has been paid to the association of ions caused by inter-ionic forces between the electrical charges of the ions.

The effect of the inter-ionic forces must be that oppositely charged ions are more often found in the proximity of each other than is the case with ions of like charge. In order to obtain an idea of the importance of this phenomenon of association, it is necessary to calculate its order of magnitude.

Let us calculate the probability H that an ion of the i-th kind is present at a distance between r and $r + dr$ from a chosen ion of the k-th kind and forms with this an ion pair, in which the distance between the electrical charges is r.

For dilute solutions and for small values of r we can write:

$$H = \frac{Nc_i}{1000} \cdot 4\,\pi\, r^2\, dr \cdot e^{\frac{\varphi}{k\,T}} \qquad (1)$$

in which c_i is the molarity and $Nc_i/1000$ the number of ions of the i-th kind per cc.; $4\,\pi\, r^2\, dr$ is the volume of a spherical shell with the radii r and $r + dr$; φ is

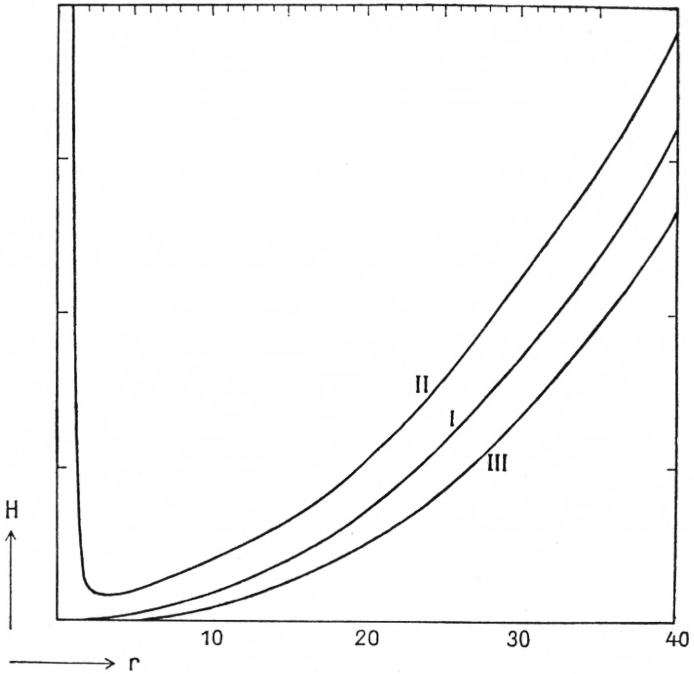

Fig. 1. Frequency (H) of ion pairs with internal distance r as a function of r (monovalent ions in water at 18° C, r small compared with the mean distance between the ions in the solution).

the work required for separating the two ions, and $e^{\frac{\varphi}{kT}}$ is a factor which according to Boltzmann, expresses the extent to which the electrical forces favour the configuration in question. If the solvent is considered as a homogeneous medium with a dielectric constant of D, it follows from Coulomb's law that

$$\varphi = -\frac{z_i \; z_k \; \varepsilon^2}{D \cdot r} \tag{2}$$

It is presupposed here that the ions are spheres with the charges placed centrally. The valencies of the ions, z_i and z_k, are considered positive or negative, according to whether the ions are positively or negatively charged.

From fig. 1 it is seen how, for monovalent ions in water at 18° C, the ion pairs present are distributed over the range of different ionic distances, according to equations 1 and 2, H being in this case expressed as a function of r. Curve 1 shows the number of ion pairs if no electrical forces were present ($\varphi = 0$). Curve 3 shows the frequency of ion pairs composed of like charged ions (φ negative). The occurrence of ion pairs of this kind is of course considerably more rare than it would be if no electrical forces were present. Finally, curve 2, the most important and most interesting, shows that the number of ion pairs composed of oppositely charged ions first decreases with diminishing distance, then passes a minimum and finally increases rapidly.

If q represents the ionic distance corresponding to the minimum frequency in this association curve (curve 2), the position of the minimum can be found by a simple calculation:

$$q = \frac{\varepsilon^2 z_i z_k}{2\,DkT} \tag{3}$$

As is easily seen, the work of separating two oppositely charged ions being this distance apart is equal to $2kT$. That means *that the energy necessary for separating the ion pair is four times as great as the average kinetic energy per degree of freedom.*

In water at 18° C, the minimum for monovalent ions lies at $q = 3.5$ Ångström (Å $= 10^{-8}$ cm). Hence, ions, which are so large that the sum of the ionic radii exceeds 3.5 Å, will associate into pairs only to an inconsiderable extent; but in the case of smaller ions, the association will become more and more marked with diminishing radii.

Ions, such as K^+ and Cl^-, are so large that their charges cannot come closer to each other than 3.5 Å. For this reason the association in water does not play any important rôle for these ions. In the case of smaller ions or ions of the same size, but polyvalent, the inter-ionic forces will, even in water, produce a considerable association and in non-aqueous solvents with a small dielectric constant the association into smaller or larger groups may be very great.

Let us tentatively affirm *that ion pairs, with an internal distance of less than that corresponding to the minimum, are to be denoted as associated and all other ion pairs as free.* Naturally this distinction between free and associated ions is rather arbitrary. The association phenomena induced by the Coulomb forces between the charges of the ions do not display the discontinuity which is in general considered characteristic for chemical processes. While it is possible clearly and unambiguously to state the degree of dissociation in the thermic dissociation of hydrogen iodide into iodine and hydrogen, because transitional forms between un-dissociated and dissociated molecules are not present in finite concentrations (at least, this has so far been considered as correct — compare however Lewis and Randall[2]), the problem is quite a different one in the present case, where transitional forms between free and associated ions appear in finite amounts, *although in the smallest number, when the line of distinction is placed at the minimum of the frequency curve.*

The theory of Debye and Hückel does not pay sufficient attention to the presence of associated ions in general. This is connected with the fact that Debye and Hückel in their differential equation, had to substitute $\frac{\varphi}{kT}$ for $\sinh \frac{\varphi}{kT}$ in order to carry through the integration. Since at the present moment, it seems impossible to integrate the unsimplified equation, an attempt will be made in the paper presented here, to achieve a somewhat more accurate, even if not completely exact, calculation of the degree of association and its effect upon the activity of the ions.

For very dilute solutions and small degrees of association, a simple integration of equation 1 from a to q ($a =$ the sum of the ionic radii) will give the degree of association.

For higher concentrations, the mass-action law is used in the determination of the degree of association. From a thermodynamic point of view, it is permissible to apply this law to the equilibrium between associated and free ions, provided suitable expressions for the activity of these particles are introduced.

It was supposed that the association is exclusively binary, and the activity of the product of association was put equal to its concentration. For the free ions an activity coefficient was taken into account, calculated according to Debye and Hückel for ions with a diameter q (corresponding to the minimum of the association curve), and at the same concentration of ions as that of the free ions.

By subtracting the calculated degree of association from 1, and multiplying by the above mentioned activity coefficient for the free ions after Debye-Hückel, the required composite activity coefficient f is found.

The details of these calculations are dealt with in the special part of this paper.

Fig. 2 shows the result of such calculations. The dependence of the activity coefficient f for the ions on the ion concentration c at different ion diameters is here given, partly according to the older Debye-Hückel formulae (fully drawn curves) and partly according to the new calculation (dashed curves).

For monovalent ions, with a diameter equal to or greater than 3.52 Ångström in the solvent water, associated ions are excluded by definition, and the new curves coincide with those of Debye-Hückel. Even at an ionic diameter down to 1.76 Å, the two systems of curves follow each other approximately. But with further decrease of the ionic diameter greater differences appear: the Debye-Hückel curves slowly converge towards a limiting curve corresponding to the ionic diameter $=$ 0 Å, while the new curves clearly demonstrate a strongly increasing diminution of the activity coefficient f with decreasing size of the ion.

Besides the dashed curve for the ion diameter $a =$ 1.01 Å, another has been drawn of alternating dashes and dots. This curve has been calculated by considering only ions with a distance of less than 1.76 Å as associated and all other ions as free. The small difference between the results of the two different methods of calculation shows, as also was to be expected, that the choice of distinction between free and associated ions can be made rather arbitrarily.

By means of fig. 2 it is possible to obtain an impression of the effect of the

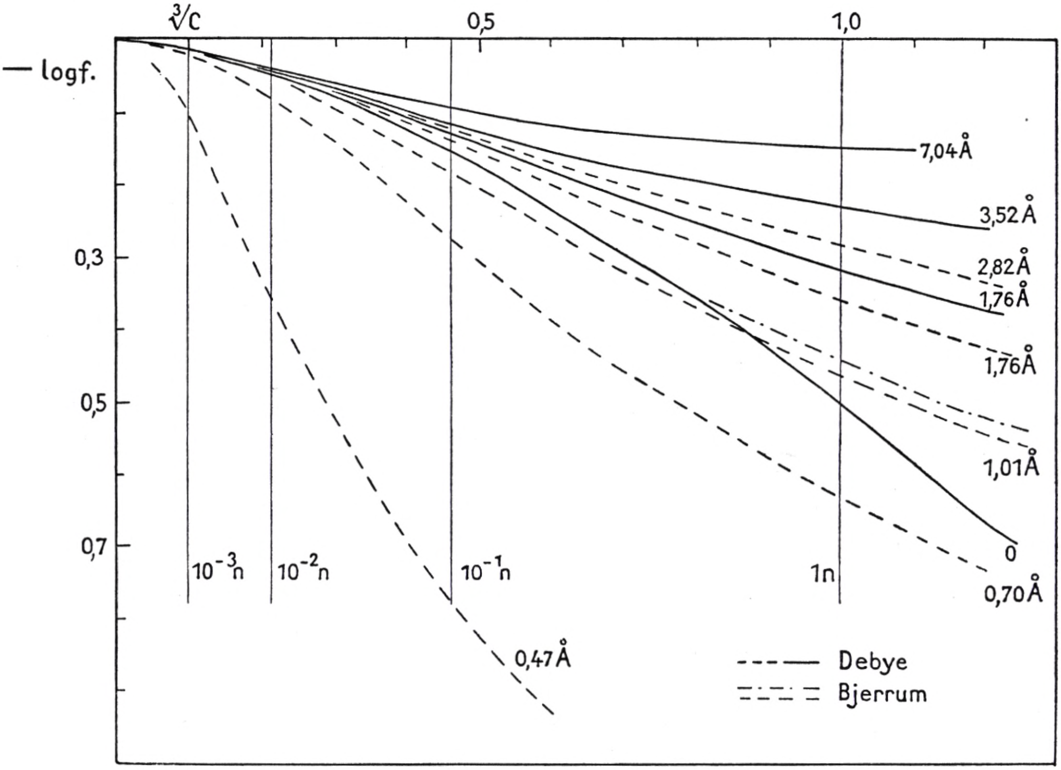

Fig. 2. Relation between activity coefficient (f) and ionic concentration (c) for monovalent ions of different size in water at 18° C.

simplification ($\sinh \frac{\varphi}{kT} = \frac{\varphi}{kT}$), introduced by Debye and Hückel in their differential equation. It is seen that under unfavorable circumstances this simplification can lead to a considerable distortion of the results.

The validity of the formulae presented depends upon the supposition that only binary association occurs, that means that aggregates composed of three or more ions are not present in significant amounts. As long as the binary association is not large and the solution is dilute this supposition can be maintained. However, it is necessary to be careful, especially if the cation and anion are of different valencies.

In order to get an impression of the order of magnitude of the ternary association, the following considerations are put forward.

Let $[M^+]$ and $[S^-]$ denote the molar concentrations of the ions M^+ and S^-, and $[MS]$ and $[MS_2^-]$, the molar concentrations of the association products MS and MS_2^-, and let us suppose that the solution is so dilute that "the volume of association" of the S^--ions constitutes only a small fraction K of the total volume of the solution. By the volume of association is here understood the volume in the vicinity of the S^--ions inside which the M^+ can be considered as associated with S^-. The following expression is then obtained:

$$\frac{[MS]}{[M^+]} = Ke^{\frac{\varphi}{kT}}, \tag{4}$$

φ denoting the mean value of the work of separation of the two ions inside the association volume.

In the case of spherical ions with the charge in the centre the work of separation for the second S^--ion in MS_2^- will be only half of the corresponding work for the first, presupposing that both ions are at the same distance from M^+, but diametrically opposite, and that the ions can not be deformed. With some approximation we may therefore put:

$$\frac{[MS_2^-]}{[MS]} = Ke^{\frac{1}{2}\frac{\varphi}{kT}}. \tag{5}$$

From equations 4 and 5 it can be estimated under which circumstances it is possible to neglect the ternary association for the binary. If, for example, in a 0.1 molar solution of certain monovalent ions in water at 18° C the degree of binary association is 0.2 and if we put K equal to 0.0014, equation 4 gives the value of 179 for $e^{\frac{\varphi}{kT}}$. From equation 5 furthermore follows that the concentration of the ternary product of association is 0.019 times that of the binary, i. e. only a few parts per mil.

If the valency of one of the ions is greater than that of the other, the circumstances are somewhat less favourable, as compared with the case of ions with valencies of the same value. Considering for example, the association of monovalent ions with a trivalent ion, the work of separation for the second ion (same assumptions as above) is not $\varphi/2$, but $\varphi \cdot 5/6$. If the degree of binary association of the trivalent ion in 0.01 mol. solutions is 0.2, then the degree of ternary association of the same ion is calculated to 0.02.

From equations 4 and 5 it follows in general that in sufficiently dilute solutions the importance of the ternary association is small as compared with the binary. From equations 4 and 5 we get namely:

$$\frac{[MS_2^-]}{[M^+]} = \left(\frac{[MS]}{[M^+]}\right)^2 \cdot e^{-\frac{1}{2}\frac{\varphi}{kT}}. \tag{6}$$

If the degree of binary association expressed by $\frac{[MS]}{[M^+]}$ is in itself small, the degree of ternary association calculated from equation 6 and measured by $\frac{[MS_2^-]}{[M^+]}$

is even smaller. If the degree of binary association in a dilute solution is still so great that $\frac{[MS]}{[M^+]}$ is about 1 then, according to equation 4, $e^{\frac{\varphi}{kT}} >> 1$ (since in dilute solution $K << 1$.). Consequently, following equation 6, the degree of ternary association will also be small.

The comparison, in the special part of this paper, between the new calculations and the experimental data shows that, in general by taking the ionic association into account, a striking agreement between observation and calculation is obtained. It is true that a satisfactory agreement may also be obtained by applying the formulae of Debye and Hückel, but the superiority of the new method is evident from the more reasonable values for the ionic dimensions obtained in this way.

In the following table 1, some calculated ionic dimensions are given as the distances of nearest approach of the ionic charges (Ångström).

Table 1. Ionic dimensions (distances of nearest approach in Å), calculated from the activity coefficients.

In water :

	KIO_3 $NaIO_3$	KNO_3	KCl	NaCl	K_2SO_4	$MgSO_4$ $CdSO_4$ $CuSO_4$	$BaCl_2$	La- $(NO_3)_3$
New calculation	1.33	1.57	3.40	4.02	3.8	4.2	5.8	6.4
Debye & Hückel	0	0.43	3.40	4.02	2.69	3.0		4.97

In alcohols :

New calculation: In CH_3OH 4.1–6.5. In C_2H_5OH 2.4–7.8.

It is evident that the new calculations has made the figures for the ionic dimensions more probable. Especially the values for iodates and nitrates are more reasonable than the earlier, impossible, small values.

Against the view put forward in this paper, the objection can be raised that we possess only little information about the laws of force prevailing under conditions where small ions are close to each other, and that the assumptions made concerning this question are not very convincing. It is therefore not without interest to emphasize that the *f*-curves will remain approximately the same, even if Coulomb's law is invalid in the neighbourhood of the ions, and even if the ions cannot be considered as spheres with the charge in the centre. The ionic dimensions, ascribed to the different curves, however, will no longer be the true dimensions, but only represent effective dimensions, i. e. such dimensions as must be assigned to spherical ions with a central charge in order that they, under the influence of the assumed laws of force, show the properties of the actual ions under the prevailing conditions.

In reality, however, the calculated dimensions of the ions are quite reasonable, and we may therefore conclude that the assumptions made have been justified. Naturally this does not imply that the ions of the strong electrolytes do not become at all deformed or that Coulomb's law of force is strictly valid in the vicinity of the ions, but only that these assumptions give, in this case, useful approximations.

By the methods applied here a distinction can be made between the influence of the forces between remote ions (which can be calculated according to Debye and Hückel) and the influence of the forces between adjacent ions. The latter forces are only little known. In spite of this, the dependence of their influence upon concentration can be calculated fairly exactly on the basis of the thermodynamic principles in the law of mass action.

While in the calculations so far mentioned, it has been sufficient to take into account the binary association, it is necessary also to consider the higher association types in *solvents with very small dielectric constants.* If that is done, there is in my opinion, a possibility of explaining the characteristic phenomena, observed in these solvents, by means of the inter-ionic forces only.

In this connection, I think especially of the high molecular weights found cryoscopically by Walden, and of the anomalous properties of the molar conductance at high electrolyte concentrations, discussed in details by Kraus.

Probably it will also be possible in many cases to explain the absorption of small ions on large, highly charged *colloidal ions*, by means of the inter-ionic electrical forces alone. The osmotic and conductometric behaviour of large colloidal ions offer a very interesting field for investigation, in which the consideration of ionic association promises new results. In fused salts and in ionic lattices we find systems of the highest degree of association which in part have already been dealt with in a way similar to that implied in our association hypothesis.

In later publications I hope to be able to return to these phenomena and their explanation by inter-ionic forces.

The introduction of a degree of association brings the new conceptions nearer to the classical ideas involving an incomplete dissociation. The similarity is especially pronounced at higher degrees of association. This association explains why in earlier works often useful, if not completely exact, pictures were obtained by introducing the degree of dissociation in the classical sense.

The difference between the old and the new view is, however, still considerable. Firstly, even at high association, the classical clarity of distinction between free and bound ions is missing in our picture. As previously mentioned the definition of free and associated ions by means of the minimum of the association curve is somewhat arbitrary. Secondly, according to the new point of view the ions are supposed to enter the association products without essential alteration of their properties, a point that is inconsistent with the classical conception of un-dissociated molecules, composed of chemically bound ions.

Modern views on strong electrolytes are often briefly characterized as the hypothesis of 100 per cent dissociation of strong electrolytes. The marked phenomena of association, mentioned above, so characteristic for many solutions of strong electrolytes, make this definition less appropriate. I would prefer to speak about a 100 per cent ionization of strong electrolytes. This definition can be used not only for solutions, but also for solids. According to this definition, potassium chloride is even in the crystalline state a strong electrolyte.

The fundamental property of strong electrolytes is not the freedom of their ions. This freedom can be much restricted as in the crystals of potassium chloride. The essential point is that the oppositely charged ions can be in close contact without reacting chemically with one another, indeed without any considerable change of their properties. The typical strong electrolyte, is an electrolyte consisting of rigid and unchangeable ions. This picture has been in the centre of the discussions during recent years, and an attempt has been made to deduce all the properties of electrolytes from the properties of such ions by means of the inter-ionic forces.

By comparing the theory of the typical strong electrolytes with experiments on real electrolytes it can be seen how far it is justifiable, in the theory for strong electrolytes, to neglect ionic deformation.

It must still be considered an open question, whether it is possible to maintain a sharp distinction between associated ions and ions which are chemically bound to each other. From the *physicist's* point of view, it may be natural to assume a *gradual transition* from association products in which the ions are but slightly deformed, through intermediary steps with increasing deformation, to true chemical compounds. The *chemist*, on the other hand, will be inclined to maintain the existence of a *discontinuity* in the formation of the chemical compound between the ions.

In a future paper this important question will be dealt with in further detail. On this occasion, I would only like to stress the fact that the properties of a great number of electrolytes in solution are strong evidence that their ions are not, or only to a small degree, chemically bound, and that *deformation is even but little pronounced.* The clearest indication of this fact is the independence of the salt concentration shown by so many ionic properties, among which the colour of the ions may be especially mentioned (Hantzsch[3] and Bjerrum[4]). This constancy of colour is so convincing because here we deal with a property that is quite sensitive to changes in constitution. The recent, very exact investigations on light absorption that we owe to Ebert and v. Halban[5] have on the whole confirmed the older investigations, although some small corrections were found in several cases.

Table 2. The degree of association α *for monovalent ions in water at 18° C.* ($q = 3.52$ *Å*).

	Sum of the ionic radii:					
	2.82 Å	2.35 Å	1.76 Å	1.01 Å	0.70 Å	0.47 Å
0.0001 *M*	0	0	0	0	0.001	0.027
0.0002 –	0	0	0	0	0.002	0.049
0.0005 –	0	0	0	0.002	0.006	0.106
0.001 –	0	0.001	0.001	0.004	0.011	0.177
0.002 –	0.002	0.002	0.003	0.007	0.021	0.274
0.005 –	0.002	0.004	0.007	0.016	0.048	0.418
0.01 –	0.005	0.008	0.012	0.030	0.083	0.529
0.02 –	0.008	0.013	0.022	0.053	0.137	0.632
0.05 –	0.017	0.028	0.046	0.105	0.240	0.741
0.1 –	0.029	0.048	0.072	0.163	0.336	0.804
0.2 –	0.048	0.079	0.121	0.240	0.437	0.854
0.5 –	0.090	0.140	0.204	0.360	0.568	0.901
1 –	0.138	0.206	0.286	0.457	0.651	0.928
2 –	0.204	0.289	0.383	0.554	0.725	0.946

Table 2a. Values of $-\log f$ *according to Bjerrum for monovalent ions in water at 18° C.* ($q=3.52$ *Å*)

	Sum of the ionic radii:					
	2.82 Å	2.35 Å	1.76 Å	1.01 Å	0.70 Å	0.47 Å
0.0001 *M*	0.005	0.005	0.005	0.005	0.005	0.017
0.0002 –	0.007	0.007	0.007	0.007	0.008	0.028
0.0005 –	0.011	0.011	0.011	0.012	0.013	0.059
0.001 –	0.015	0.016	0.016	0.017	0.020	0.098
0.002 –	0.022	0.022	0.023	0.025	0.030	0.157
0.005 –	0.034	0.035	0.036	0.040	0.053	0.262
0.01 –	0.047	0.048	0.050	0.057	0.081	0.360
0.02 –	0.064	0.066	0.070	0.085	0.121	0.474
0.05 –	0.095	0.100	0.107	0.133	0.200	0.637
0.1 –	0.127	0.135	0.146	0.188	0.278	0.769
0.2 –	0.164	0.179	0.198	0.255	0.371	0.907
0.5 –	0.230	0.251	0.282	0.366	0.516	1.092
1 –	0.285	0.317	0.360	0.463	0.635	1.244
2 –	0.351	0.395	0.447	0.574	0.760	1.387

SUMMARY

According to modern views, an electrolyte belongs to the class of *strong electrolytes* if its ions do not combine chemically under the conditions considered.

Since in general the mutual interaction between the ions of strong electrolytes does not give rise to pronounced deformations, it would seem natural to apply the term *ideal strong electrolyte* to an electrolyte composed of ions which cannot be deformed. It is the properties of such a type of electrolyte, which are dealt with theoretically in most of the recent papers on strong electrolytes, and which have also been studied in this paper.

The electrical forces between the ionic charges of an ideal strong electrolyte must cause a considerable association of ions in many cases. It is possible to predict that this association of ions must be especially great in the case of small ions and ions with high valencies. Furthermore it can be foreseen that it will be larger in non-aqueous solvents with a small dielectric constant than in water. This association can be considered as a purely physical process. Its existence makes it more correct to speak about 100 per cent ionization than about 100 per cent dissociation in the case of strong electrolytes.

In weak association, the ions will mainly associate in pairs, in stronger association — especially at higher concentrations — ternary and higher complexes are also formed to a considerable extent. In the present paper, the intermediary states of association have been studied, where it is sufficient to consider binary association. The effect of the association on the activity of the ions has especially been studied.

It is shown that the formulae derived by Debye and Hückel for the calculation of ionic activity from ionic concentration and size, do not give a good approximation in the case of small ions or ions with high valencies, and a method for obtaining more exact values has been developed.

The new values for the activity coefficients (f) for different ionic concentrations are given for monovalent ions in water at 18° C in table 2a, and in fig. 2 these new values can be compared with the old ones.

By means of a simple transformation, table 2a can be used for all solutions of electrolytes. The activity coefficient possesses, namely, the same value in all solutions for which the expressions

$$c\left(\frac{z_1 z_2}{DT}\right)^3 \quad \text{and} \quad a\frac{DT}{z_1 z_2}$$

have the same values (c = mean molar ionic concentration, D = dielectric constant, T = abs. temperature, z_1 and z_2 the valencies of the two ions and a the sum of their ionic radii, indicating the distance between the charges, when the ions are in mutual contact).

On the basis of the available experimental material the sums of the ionic radii were determined for some electrolytes in water and in methyl and ethyl alcohol, using the above described principle (see table 1).

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The Theory of Ion-Distribution Coefficients, Their Determination and Use

NIELS BJERRUM

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One of the subjects which have always commanded the interest of chemists is the question of the *solubility* of the substances. What forces are here at work, and how may solubility be computed quantitatively?

In the 19th century, *thermodynamics* led us many paces forward along the way, but did not lead us to the core of the problem. The true understanding of the problems of solubility will not be gained from thermodynamics, but only from the more comprehensive atomistics, of which thermodynamics, in spite of its own great importance, is but a single side issue.

The problem of the solubility of a solid substance in a liquid divides naturally into two parts. The first deals with the *structure of the solid substance*, the second with the *properties of the solution*. This becomes apparent when the solution process takes place through evaporation. To compute the vapour pressure of the solid substance, it is necessary to know the work required to transform one molecule of the solid substance into the vapour state. This work depends on the crystalline structure of the substance. Going further, to determine the solubility from the vapour pressure, it is necessary to know the work required to transfer one molecule from the solution to the vapour state. This work depends on the properties of the solution.

Limiting our considerations to the strong electrolytes built up from stable ions, we find in the modern ion-lattice theory, especially developed by Born, an approximate theory for the work done when ions are transferred from the solid crystal into the vapour state. When, in what follows, we study the distribution of ions between two liquids, we are in reality studying the last mentioned work. The distribution between a liquid and its vapour may be considered a simple example of distribution between two liquids.

I

Let us first look more closely at the *definition and determination of the distribution coefficients.*

The definition of a distribution coefficient is simple enough in the case of two immiscible media. However, if the two media are miscible, as for instance, water and alcohol, the definition is slightly more difficult. We may define thus: *The distribution coefficient is the ratio between the concentrations of the soluble substance in solutions in which the dissolved substance has the same activity.* Solutions, in which the dissolved substance has the same activity, are, for instance, solutions saturated with the same solid substance, or in which the dissolved substance has the same vapour tension.

Each of the ions in an electrolyte has its own special distribution coefficient. The distribution coefficient of an electrolyte, which can be computed from its solubility in two media, lies between those of the two ions, and in the case of binary electrolytes, it equals the square root of the product of the individual distribution coefficients.

Table 1. The sum of the ion-distribution exponents between water and alcohol for different salts, computed from the solubilities of the salts in water and alcohol

	Li	Na	K	Rb	Cs	NH_4	$N(CH_3)_4$	$N(C_2H_5)_4$	Ag
Cl		6.0	6.6	6.4		5.2			
Br			5.8			(5.1)			
J			5.5			(5.9)	4.4	4.1	
ClO_4	(5.1)	4.6	4.6	4.6	4.7	4.1			
Benzoate	4.1	4.8				3.6			2.3
Salicylate		4.9				(5.2)			
Laurate	0.4								
Myristate	—0.7								0.1
Palmitate	—0.9								—0.2
Stearate	—1.2								—0.2

In table 1, Dr. Larsson and I have compiled a number of results about the ion-distribution coefficients between water and alcohol. The figures are computed from the results of *solubility experiments* (concentration in water in the numerator). Instead of the actual distribution coefficient V, its logarithm is given in the table; this is designated P and named the distribution exponent:

$$P = \log V$$

From solubility determinations it is impossible to calculate the distribution exponents of the individual ions, but the *sum of the distribution exponents of the ions* may be calculated; it is this sum which is given in the table.

The figures make no great claim to exactitude. In the first place many of the solubility determinations are uncertain. Often the alcohol used contained water; neither is it absolutely certain in all cases that the solid form, whose solubility was determined, was the anhydrous unsolvated salt which is a presupposition for the exactness of the calculations. However our attention has been drawn to this point (moreover, through determinations of the vapour pressure of the solvates, it is possible to utilize also solubility determinations of solid hydrated salts in determining distribution coefficients).

The greatest inexactitude of the computations is due to a special characteristic of the distribution coefficients of the electrolytes. On account of inter-ionic forces, and in contrast to the case of non-electrolytes, the distribution coefficient of the electrolytes *depends greatly upon concentration.*

The value listed in the table, is when possible that limiting value which the distribution exponent approaches under increasing dilution.

If the distribution coefficient between water and alcohol, calculated directly from the solubilities, is called V, it is possible to compute the limiting value for infinitely dilute solutions (V_o) according to the following equation:

$$V_o = V \frac{F_{H_2O}}{F_A}$$

in which F_{H_2O} and F_A are the activity coefficients in the saturated aqueous and saturated alcoholic solutions, respectively.

Potassium chloride is that salt for which the sum of the ion-distribution exponents has the highest value (6.6). An aqueous solution of this salt must be

$$10^{\frac{6.6}{2}} = 2000$$

times more concentrated than an alcoholic solution, before distribution equilibrium (the same activity of the salt in the two solutions) is attained.

On the other hand, lithium stearate is that salt, for which the sum of the distribution exponents has the lowest value (—1.2). The alcoholic solution of this salt must be 4 times as concentrated as the aqueous solution, before distribution equilibrium between the solutions is established.

The figures in parenthesis in table 1 are especially uncertain.

By measuring *the electromotive force* of such a chain as

$$H_2 \mid HCl \text{ in water}, AgCl \mid Ag—Ag \mid AgCl, HCl \text{ in alcohol} \mid H_2,$$

in which an element with aqueous electrolyte is combined against the same element with alcoholic electrolyte, it is also possible to determine sums of ion-distribution exponents. In this way, from Fleysher's electrometric measurements, we have computed the sum of the distribution exponents of the hydrogen and chloride ion to 4.8.

For a weak acid one is able to compute the sum of the distribution exponents of the ions ($P_H + P_{anion}$) when the dissociation constants of the acid in the two media (K_{H_2O} and K_A) are known. As Larsson demonstrated in his doctor's thesis, we find:

$$P_H + P_{anion} - P_{undiss.\ acid} = \log K_{H_2O} - \log K_A = \Delta \log K.$$

It is therefore possible to determine the sum of the distribution exponents of the ions by adding the distribution exponent for the undissociated acid to the difference between the logarithms of the dissociation constants of the acids in the two media. This last distribution coefficient may be determined by means of the solubility of the acid in water and alcohol. This method is used in determining the distribution exponent of the ions of benzoic acid, salicylic acid, and the three nitrobenzoic acids (see table 2).

Table 2. The sum of the ion-distribution exponents between water and alcohol for different weak acids, calculated from the dissociation constants of the acids in water and in alcohol

Benzoic acid	3.91
Salicylic acid	3.47
o-Nitrobenzoic acid	4.25
m- — -	3.17
p- — -	3.33

It is of course of special interest to determine the *distribution exponents of the individual ions.* Larsson has attempted this in his doctor's thesis. It is known that *a saturated aqueous solution of potassium chloride* possesses only a very small diffusion potential against dilute aqueous solutions. He assumes that it also shows *a negligibly small potential against alcoholic solutions.* I shall discuss the justification of this assumption later.

By measuring the potential in a cell such as,

$$H_2 \mid HCl \text{ in } H_2O \mid 3.5\ M \text{ KCl in } H_2O \mid HCl \text{ in alcohol} \mid H_2$$

and using his above-mentioned assumption, Larsson computes the distribution exponent of the hydrogen ion to 2.52, and, in a similar way, that of the silver ion, the benzoate ion and the chloride ion to 2.06, 1.27, and 2.51, respectively. Continuing in the same way, we have computed the distribution exponent of the bromide ion to 1.84.

By means of these distribution exponents of the individual ions and our other material of distribution-exponent sums, it has been possible to list in table 3 a few ion-distribution exponents. The values vary from 4.1 for the potassium ion to —3.9 for the stearate ion.

Table 3. Distribution exponents of ions between water and alcohol

H^+	2.5	Cl^-	2.5
Li^+	2.8	Br^-	1.8
Na^+	3.5	J^-	1.4
K^+	4.1	ClO_4^-	0.7
Rb^+	3.9	Benzoate ion	1.3
Cs^+	4.0	Salicylate ion	1.2
Ag^+	2.1	*o*-Nitrobenzoate ion	1.7
NH_4^+	2.7	*m*- — –	0.7
$N(CH_3)_4^+$	3.0	*p*- — –	0.8
$N(C_2H_5)_4^+$	2.7	Laurate ion	—2.4
		Myristate ion	—3.5
		Palmitate ion	—3.7
		Stearate ion	—3.9

II

Roughly speaking, it may be said, that the way in which ions distribute themselves indicates that they prefer to be in water. Even though not all salts are soluble in water, yet they are almost all more soluble in water than in alcohol and in other non-aqueous solvents. This fact is the basis of the definition of salts by the ancient chemists as substances soluble in water.

The preference of ions for water is due to the large dielectric constant of that medium. When an electrically charged body is transferred from a dielectric to a vacuum, a certain (electric) work must be overcome. At the moment the body, for instance, is just above the surface of the dielectric, that surface will possess an opposite electric charge, and will therefore try to prevent the removal. Some years ago, Born showed that this work for a spherical z-valent ion, with radius r, may be expressed by $\frac{(z\varepsilon)^2}{2r}\left(1-\frac{1}{D}\right)$ (ε denotes the charge of the electron and D the dielectric constant of the medium). He discovered, moreover, that this expression for reasonable values of r leads to plausible values for the development of heat by the transference of ions from vacuum into aqueous solution. Fajans had already earlier computed such *heats of solution* from experimental data and named them heats of hydration of the ions, a name, which to me seems somewhat misleading. Hückel followed the same principle in developing his formula for ion-activity coefficients in concentrated solutions, and also Scatchard has used this principle in his theory of the e. m. f. of cells with aqueous-alcoholic electrolytes.

Transferring a z-valent ion with radius r from water (with $D = 81$) to alcohol (with $D = 26$), the *electric work* to be overcome may be expressed as follows:

$$\frac{(z\varepsilon)^2}{2r}\left(\frac{1}{26}-\frac{1}{81}\right).$$

This electric work introduces in the distribution exponent between water and alcohol an electric term: $P_e = \frac{(z\varepsilon)^2}{2rKT} \log e \left(\frac{1}{26} - \frac{1}{81}\right)$ which when solved gives $P_e = 3.15 \frac{z^2}{r}$ (z denotes the valency and r the radius in Å of the ion). For monovalent ions with radii 1, 2, and 3 Å, P_e is, respectively, 3.15, 1.6, and 1.05.

If the distribution exponent for the same atom group, when uncharged, is P_u, the distribution exponent P for the ion will be

$$P = P_e + P_u = 3.15 \frac{z^2}{r} + P_u.$$

As is well-known, ions like K^+ and Cl^- are supposed to possess an external electronic structure, similar to that of argon. Therefore the above formula could be tested by adding to the distribution exponent of argon between water and alcohol, the electric term P_e, and thus finding out whether, by that means, the distribution exponents of the potassium and the chloride ions were obtained. Unfortunately, in so far as I know, the solubility in alcohol of rare gases has not yet been measured, but we are now planning experiments along those lines.

If P is known for the entire series of rare gases, He, Ne, A, Kr, X, it may be possible to make a more exact calculation, by considering that K^+ and Cl^- are, respectively, a little smaller and a little larger than the argon atom, and, in calculating the non-electric part of the distribution exponents of the ions to interpolate between the distribution exponents of the rare gases.

For a larger organic ion, as for instance the benzoate ion, we may assume that the non-electric part is nearly the same as the entire value for the undissociated benzoic acid. Hence, we have

$$P(\text{benzoate}) = P_e + P(\text{benzoic acid}).$$

If this equation is combined with the previously mentioned equation from Larsson's thesis:

$$P_H + P(\text{benzoate}) - P(\text{benzoic acid}) = \Delta \log K,$$

we find,

$$P_H + P_e = \Delta \log K.$$

($\Delta \log K$ expresses the difference between the value of $\log K$ in water and in alcohol).

Heinrich Goldschmidt has found that $\Delta \log K$ is nearly constant for organic carboxylic acids. This agrees well with the above formula. According to Goldschmidt, $\Delta \log K =$ about 6. If we set $P_H = 2.5$, we find $P_e =$ about 3.5, corresponding to an effective radius for the carboxyl group of about 0.8 Å.

For phenols, $\Delta \log K$ is smaller than for carboxylic acids; P_e is therefore also smaller. The effective radius of the phenolate group is consequently larger. This may be explained by the location of the electric charge less close to the surface.

When we remember that the electric part of the distribution exponent of carboxylate ions is about 3.5, whereas the entire distribution exponent for a laurate ion is only —2.4 and that for a stearate ion is but —3.9, we see that the paraffine end of these ions reduces the distribution exponent with 5.9 and 7.4 respectively, a proof of the power with which the paraffine part of the molecule shuns water.

It is comprehensible that ions with so different reactions to water in their two ends, must energetically orientate themselves in the surface of an aqueous solution with the paraffine end outwards and the carboxyl end inwards; moreover, they must have a tendency to form aggregates, "micells", with the paraffine tails inwards, and the carboxyl ends outwards, towards the water.

The ability of soaps to lather, as well as their colloidal characteristics, may perhaps be approximately measured by the difference between the distribution exponents of their carboxyl ends ($= P_e$) and their paraffine ends ($= P - P_e$).

In the case of polyvalent ions, the electric term in the distribution exponent increases with the second power of the magnitude of the charge. Therefore, in the case of the di- and tri-valent ions, the difference between the solubility in water and in alcohol is, on the average, much larger than in the case of monovalent ions. In practice, this is illustrated by the difficulty that exists in finding salts with polyvalent ions, with even an appreciable solubility in alcohol.

Therefore, when salts are precipitated from aqueous solutions by the addition of alcohol, the solubility of salts with polyvalent ions decreases more rapidly under the addition of alcohol, than that of salts with monovalent ions.

In an other connection, Gjaldbæk has recently determined the solubility of three different salts in a series of mixtures of water and alcohol.

Table 4 shows his results which he communicated to me privately.

Table 4. The solubility of three different salts in alcohol of various strengths at about 22° C, according to Gjaldbæk

Strength of alcohol	Solubility in g. per l. saturated solution of:		
	$NaCl$ uni-univalent	$Na_2S_4O_6,2H_2O$ uni-divalent	$Na_3Au\,(S_2O_3)_2,2H_2O$ uni-trivalent
50 % Tralles	114	382	77
60 – –	76	252	29
70 – –	45	160	8
80 – –	40	66	2
90 – –	4	10	0

The figures demonstrate clearly how the influence of the percentage of alcohol on the solubility increases with the valency of the ions. The very concentrated solutions of sodium tetrathionate in 50 per cent and 60 per cent alcohol shows this less clearly than the solutions of sodium chloride; however, in these strongly concentrated solutions, the activity of the ions increases undoubtedly much more rapidly than their concentration. The third salt is the complex sodium aurothiosulphate containing the trivalent aurothiosulphate ion.

As a matter of fact, water is not a continuous dielectric, but an aggregate of dipole molecules. Therefore the formula for the electric part of the distribution exponent of an ion expressed by

$$P_e = \frac{z^2}{r}\,3.15$$

is only approximate. The smaller the ion, the more uncertain the formula becomes. The orientation of the dipole molecules of the water around an ion assumes, when the ion is very small, the character of a chemical hydration, and Born's formula is certainly not applicable. This, for instance, is true of the hydrogen ion; this ion is present in water as H^+,H_2O and in alcohol as H^+,C_2H_5OH. In mixtures of water and alcohol it appears in both forms. In the theory of P, this must be taken into account.

In mixtures of water and alcohol, we have the following chemical equilibrium for the hydrogen ion

$$H^+, C_2H_5OH + H_2O \rightleftarrows H^+, H_2O + C_2H_5OH$$

The equilibrium constant for this process has been determined by H. Goldschmidt. If we introduce molar concentrations of the ions and the vapour tensions of water and alcohol expressed in fractions of the vapour tensions of the pure liquids, we find $K =$ about 100 in solutions rich in alcohol.

It is possible to demonstrate that the gross distribution exponent P_H, which we, in the preceding, have computed without taking the solvation into account, may be expressed by the following equation

$$P_H = \log K + P(H^+, H_2O),$$

in which $P(H^+, H_2O)$ indicates the distribution coefficient of the hydrated ion. K varies, depending on whether the value of the equilibrium constant has been determined in alcohol containing a little water, or in water containing a little alcohol. It is the former value we must use. As previously stated, it is about 100. If we introduce this value of K we obtain for the distribution coefficient of the hydrated hydrogen ion the surprisingly small value 0.5. However this is supported by the fact that a similar small value seems to hold for the hydroxyl ion, which, considering the smallness of the hydrogen nucleus must be assumed to resemble the hydrogen ion a great deal. As the formulae H_3O^+ and HO^- show, the difference between them is merely two hydrogen nuclei.

III

Knowledge about the ion-distribution coefficients is of value in many respects. With the help of these coefficients it is possible, when the solubility of a salt in one medium is known, to determine the solubility of the salt in other media, or, when the e.m.f. of a cell with one solvent is known, to calculate the e.m.f. of the same cell with other solvents.

Of special interest is the connection between the ion-distribution coefficient and the so-called *phase-boundary potentials.*

Between two immiscible media, which contain an electrolyte in distribution equilibrium, a phase-boundary potential always exists, provided the distribution exponents for the cation and anion, P_K and P_A, are not equal. Only by means of this potential is it possible to have distribution equilibrium with the same ratio of the concentrations of both cation and anion. The phase-boundary potential will influence the distribution of oppositely charged ions in opposite directions, and can thus make the distribution of the ions in equilibrium uniform, in spite of different distribution exponents.

This phase-boundary potential is (at 25° C and in the case of monovalent ions) expressed by the equation:

$$\pi_F = \tfrac{1}{2} \cdot 0.0591\,(P_K - P_A)$$

The potential is independent of the mobility of the ions and is solely determined by their distribution exponents.

If the electrolyte is not in distribution equilibrium between the two phases, a diffusion from one phase into the other will take place. It is natural to assume that distribution equilibrium will most often occur at the phase boundary itself, and that the very phase-boundary potential will be determined by the above formula. To this is added the diffusion potentials π_D on both sides of the phase boundary, determined according to Nernst's formula from the mobilities of the ions. The following equation designates the entire phase potential:

$$\pi = \pi_D + \pi_F = \pi_D + \tfrac{1}{2} \cdot 0.0591\,(P_K - P_A).$$

It is possible with some degree of approximation to use the same formula for the potential between salt solutions in two intermiscible media as water and alcohol. The entire potential is the sum of a *phase-boundary potential* which is determined by the distribution exponents of the ions, and *diffusion potentials* which depend on the mobilities of the ions, and which are the greater, the further the solutions are from being in distribution equilibrium with each other as regards the electrolyte.

We will use this theory in investigating the justification of assuming the potential between saturated aqueous KCl-solution and dilute alcoholic solutions to be zero.

Let us assume that the potential has the value x. Then the distribution exponent of the potassium ion, instead of 4.1 as computed earlier, will be $4.1 + \frac{x}{0.0591}$, and in a similar way for the chloride ion $2.5 - \frac{x}{0.0591}$. According to these formulae, the entire potential may be expressed by the equation

$$x = \frac{0.0591}{2}\left[4.1 + \frac{x}{0.0591} - \left(2.5 - \frac{x}{0.0591}\right)\right] + \pi_D$$

As is readily seen, x vanishes and the equation is simplified to

$$\tfrac{1}{2} \cdot 0.0591 \cdot 1.6 + \pi_D = 0$$

Let us first consider the fact that x vanishes. As a result of this, we are unable to say anything on the basis of our experiments about the absolute value of the phase-boundary potential, nor, indeed, anything about the absolute magnitude of the distribution exponents. Possibly P_K is larger (or smaller) than 4.1, but if this be the case, all distribution exponents of the cations are, likewise, just as much larger (or smaller) and all the distribution exponents of the anions just as much smaller (or larger).

Another conclusion may be drawn from the above equation. Accepting Larsson's assumption about the potential 0 between saturated aqueous potassium chloride solution and dilute alcoholic solutions, we find the distribution exponents for K^+ and Cl^- to have a difference of 1.6. This shows that π_D must equal $-\frac{1}{2}\, 0.0591 \cdot 1.6 = -0.047$ volts, and that therefore it was not permissible to ignore the diffusion potentials. The explanation for this must lie in the fact that the migration velocities of K^+ and Cl^- differ so much that the diffusion potentials in water and especially in alcohol are not negligible. For the present I have, however, refrained from correcting the given distribution coefficients, since, even after such a correction, the values would still be relative, as is described above, because we do not know the value of x.

However, certain considerations indicate that the distribution exponents of individual ions shown in table 3, are not far from being correct. Theoretically, it is most probable that the distribution exponent of the large chloride ion will be smaller than that of the structurally similar, smaller potassium ion, just as the values, 2.5 and 4.1, in table 3, show. Therefore Larsson's assumption, that the potential difference between a saturated, aqueous potassium chloride solution and a dilute alcoholic solution is equal to zero, is also, perhaps, not far from the truth.

If *the temperature of a medium changes*, it may be considered a different medium. We may therefore speak of distribution coefficients between water of 25° C and water of 75° C. It is this kind of thermal distribution coefficients, which Soret, in his days, determined by placing the salt solution in a vertical tube and keeping the upper end of the tube at a higher temperature for a considerable time, and then analyzing the solution at the top and at the bottom of the tube. As found by van't Hoff and Arrhenius, it is impossible to explain Soret's experiment by merely taking into account the change in osmotic pressure with temperature. Other forces must be at work, and based on the above, the change in the dielectric constant of the water must produce one such force. We have found, however, that for the present, it is not enough to take this force into consideration, though certain main lines in the experimental results of Soret's effect may be explained in this way, especially the fact that it is electrolytes with polyvalent ions (as $CuSO_4$) which show strong Soret effects.

Because of the different distribution coefficients of the ions between cold and hot water, and their different migration velocities, *thermo-electric forces* must arise when one end of a salt solution is heated. Nernst and his pupils have studied these electromotive forces. Their investigations show that special forces come into play here, too. Both in Soret's phenomenon and in the thermo-electric forces arising in electrolyte solutions of different temperature, there are possibilities for experimental investigations, which will give us information about ion-distribution coefficients.

As I hope I have made plain in the above, the ion-distribution coefficients are figures which procure us a comprehensive survey of a series of very different properties of electrolyte solutions. In the theory of ion-distribution coefficients advanced here, we have a theory applicable to all these properties. This theory leads us an essential step closer to the solution of the important problem of calculating in advance the solubility of salts in water and other solvents.

For the further development and extension of the theory, a considerable increase of the available experimental material is, however, necessary. It is to be hoped that such material will be at hand in the years which lie just ahead.

This lecture is, in the main, based on a paper in which Dr. E. Larsson, Lund, was my collaborator, and which is not yet published.

Recent Views on Electrolytes

NIELS BJERRUM

Summarizing lecture given at *Kemisk Forening*, Copenhagen, 15th of January, 1929, and at the *Deutschen Chemischen Gesellschaft*, Berlin, 26th of January, 1929. Translated from *Ber*. **62** (1929) 1091–1103. A Danish translation is to be found in *Kem. Maanedsblad* **10** (1929) 92–99.

I

In the years around 1908, Hantzsch and I were simultaneously occupied with investigations upon the *light absorption of electrolytes*[1,2]. We both obtained the same experimental result, namely, that *the colour of many electrolytes within a considerable range of concentration is independent of the concentration.* The conclusions, which we drew from this result, were however rather different. Hantzsch considered that the ionization was without importance for the colour. If an acid showed a colour different from that of its salts, he assumed that it had a different constitution and called it a *pseudo acid.* According to my opinion, however, the constancy of colour could be only satisfactorily explained by assuming *complete* (or almost complete) *ionization.* If an acid showed a colour different from that of its salts, this was taken simply as an indication of incomplete ionization.

The idea of a complete ionization of many electrolytes has proved very profitable. Many properties of strong electrolytes can be explained as being due to an effect of the ionic charges of the completely ionized electrolyte. Only because this effect of the ionic charges was not sufficiently considered in the first decades of the dissociation theory, was the complete ionization of many electrolytes not discovered at that time.

In the calculation of the effects of the ionic charges the forces between the ionic charges themselves, the so called *inter-ionic forces,* must first be taken into account.

For these the validity of Coulomb's law is generally accepted:

$$K = \frac{\varepsilon_1 \varepsilon_2}{Da^2}$$

(ε_1 and ε_2 the ionic charges, a the inter-ionic distance, D the dielectric constant of the solvent).

Secondly, the *forces between the ionic charges and the solvent* have to be taken into consideration. These forces are of special interest when the properties in different solvents are compared.

In the calculation, it is of course essential, to ascribe to the ions molecular properties, as possessed by molecules of non-electrolytes. In many cases, it is sufficient to treat the ions as rigid spheres with a constant diameter. If a more exact calculation is required, one can, with Born[3], instead of a constant diameter, introduce *repulsive forces*, which are inversely proportional to a high power of the inter-ionic distance. For ions in a cubic lattice, Born rendered the exponent 9 probable. If a still more exact calculation is required, the *deformability* of the ions may be taken into consideration. An electrical force produces a dipole moment in a "soft" ion, the magnitude of which can be estimated by measurements of refraction or by spectroscopic investigations, and the presence of which produces forces, which can be taken into account in the calculation[4].

II

We will examine in further detail a few typical examples from the results obtained. Let us consider an *ionic vapour* of stable, monovalent positive and negative ions of radius 1 Ångström. At extremely high temperatures, only known in astronomy, of 100000° C and more, the ions will move almost independently of each other, the thermic movements being so strong that the inter-ionic forces exert little influence. The picture is quite different, however, when experimentally realizable temperatures, such as 2000° C are considered. The inter-ionic forces will here cause the ions to associate completely to pairs. This is conceivable, considering that the energy necessary to separate the ionic pairs is about 250 kcal per mole, and that the mean translatory energy of an ion at 2000° only reaches about 7 kcal per mole. In agreement with this, Nernst[5] has found normal vapour density for NaCl vapour. Further evidence of the extreme force by which the ions are held together in the pairs may be found in the fact that *the electrical conductivity of salt vapours is indeed very low.*

By further lowering of the temperature, a point will be reached where the inter-ionic forces, at a still very high temperature, will cause the ions to associate and form a liquid phase. In the condensed liquid, the association of ions assumes a character, which is quite different from that in vapour. The ions no longer form ionic pairs, but one ion is associated with several other ions at the same time. The whole fluid may be regarded as a single aggregate of ions. Under these conditions the association should not prevent the movements of the ions relative to one another, which is confirmed by Arndt's[6] finding that many salts show a molar conductivity in the fluid state similar to that in aqueous solution.

If the temperature is still further lowered, it is to be expected that the ions will associate to form an *ionic lattice crystal* and X-ray investigations by Bragg[8] and by Debye and Scherrer[9] have unambiguously shown that salts are really built up as ionic lattices. The ions have *lost their free mobility* in the ionic lattices. For this reason salts in the solid state are as a rule poor conductors. The physics of the ionic crystal lattices has especially been developed by Born[3]. He has shown, for example, that it is possible to calculate accurately the considerable hardness of many salts from the assumption that the ions in the lattice are held together only by the inter-ionic Coulomb forces. It is especially interesting that Born[4] together with Heisenberg has succeeded in calculating the *heat of vaporization of the alkali halides*. Table 1 shows how well the calculated values agree with the experimental values estimated by v. Wartenberg. In this calculation the work necessary for separating the ions, the so called *lattice energy*, was first determined. To obtain the heat of vaporization, the energy, liberated in the process of building up ionic pairs from the separate ions, was subtracted. Since the volatility is closely connected with the heat of vaporization, these calculations by Born and Heisenberg show that the low volatility of the alkali halides, built up of small ions, is completely explained by the existence of inter-ionic forces.

Table 1. Heat of vaporization (kcal per mole) theoretically calculated by Born and Heisenberg[4]. Figures in brackets experimentally found values of v. Wartenberg and co-workers

	F	Cl	Br	I
Na	61 (57)	43 (44)	39 (39)	32 (37)
K	51 (42)	40 (40)	36 (38)	32 (37)
Rb	41 (40)	37 (38)	34 (37)	30 (37)
Cs	41 (35)	31 (37)	29 (37)	26 (37)

For electrolytes built up of simpler ions, it is possible, as especially shown by V. M. Goldschmidt[10], to predict the lattice form, and therefore also the crystal structure. For only slightly deformable ions, it is determined by the relative amounts and the ratio of the radii of the ions. For more strongly deformable ions, the influence of the deformability is added.

In conclusion we can say that typical properties of salts, like their power of crystal formation, their hardness, their high melting point and low volatility support the idea of their complete ionization in all three states of aggregation.

III

Passing now to *aqueous solutions*, we must, with Nernst and J. J. Thomsen, take into account that the dielectric constant (D) of water is about 80. In aqueous solutions, the inter-ionic forces are therefore about 80 times smaller than in ionic vapour, and hence in dilute solutions of not too small ions, the inter-ionic forces will give rise to no significant association of ions. However, this does not mean that the effect of the forces is negligible. An ion picked at random will, by virtue of *the long range of the inter-ionic forces*, have an appreciable effect on a great number of the surrounding ions, attracting those with opposite charges and repulsing those with charges of the same sign. As a result of this, the ion considered will be surrounded by a kind of atmosphere of ions with opposite charge. This situation was already perceived in 1913 by Milner[11] but first in 1923 Debye and Hückel[12] succeeded on this basis in formulating the laws for the effect of the inter-ionic forces.

The main problem is to find expressions for the empirical *coefficients* by which the changes with concentration of the conductivity, the osmotic properties, and of the active mass of the ions were registered after abandoning the use of a "degree of dissociation" as impracticable for this purpose (Bjerrum[13]).

A long series of experimental works by many authors has shown that the *formulae of Debye and Hückel* in an excellent way describe the conditions in sufficiently dilute solutions of electrolytes (the expression for the conductivity coefficient in fact only after a small alteration by Onsager[14]). The formulae given represent the limiting laws, approached with increasing dilution. In the case of dilute salt solutions, there remains no decrease in conductivity, osmotic effect or ionic activity, which can be ascribed to incomplete dissociation.

The *heat of dilution* caused some difficulties in the beginning. A negative heat of dilution was first expected, since it was argued that the overcoming of the inter-ionic forces in the process of dilution would absorb thermal energy from the solution. This is, however, not correct.

According to Debye[15] the dielectric properties are explained by the dipolar structure of the water molecule. Now, the dipoles of water have a *mutual potential energy* which depends upon the field of force. On dilution of an ionic solution, this potential energy decreases, and an amount of energy is released which is more than sufficient to overcome the inter-ionic forces. The total result is therefore a heat formation of about 3/10 of the heat absorption first expected (Bjerrum[16]). Recent, very exact measurements from Nernst's laboratory[17 18] together with experiments by Lange[19] and co-workers, clearly show an approach to this theoretical limiting law on increasing dilution. Table 2 gives a survey of the values for high dilutions, found in Nernst's laboratory.

The theoretical values given are calculated according to the following expression:

$$U_c = 418 \frac{\sqrt{c}}{1 + 0.327\, a \sqrt{c}}$$

In this expression, the ionic diameter a was taken as 4 Ångström. U_c is the heat of dilution for one mole of salt at 18° C on diluting from c to 0.

Table 2. Heats of dilution after Naudé[18] at 18° C, the values expressed in gcal. per mole

From	0.004 *N*	0.0133 *N*	0.1 *N*	0.333 *N*
to	0.002 *N*	0.0067 *N*	0.002 *N*	0.0067 *N*
theoretically	6.7	10.9	76	107
LiCl	7.7	8.6	83	128
NaCl	5.0	8.1	41	10.6
KCl	–	7.6	–	5.4
$NaNO_3$	6.5	0.2	—10	—154
KNO_3	4.0	—2.5	—94	—353

For concentrated aqueous solutions — whereby often must be understood solutions above 0.01 *N* — it has so far been impossible to carry out satisfactory calculations of the ionic coefficients and the heats of dilution. Firstly, we do not know with what *D* we have to reckon. The experimental determination of *D* of salt solutions is so difficult, owing to the conductivity of these solutions, that it has so far not been possible to obtain agreement with regard to the change in *D* of water upon addition of salt (*cf.*[20]). Besides, in more concentrated solutions the conditions prevailing in the vicinity of the ions play an important role, and it is for this reason necessary to take into account the ionic radii. Debye and Hückel have deduced an expression for the activity coefficient, in which the radius of the ions is introduced, and which in many cases leads to radii of the expected size. It follows, however, from their mathematical treatment that the expressions cannot be correct for small ions (Bjerrum[21]). It is possible to proceed further by distinguishing between the ions which are in the immediate proximity of each other and the rest of the ions[21]. Such a distinction between *associated* and *free* ions is, however, only to be considered as a mathematical artifice, with no chemical meaning, and neither this treatment, nor the use of elaborate graphical integration (H. Müller[22]), nor integration by power series (Gronwall, La Mer and Sandved[23]) met with definite success. The physical basis for all these calculations is, namely, the validity of Coulomb's law: $K = \varepsilon_1 \varepsilon_2 / Da^2$; and for ions in close proximity to each other, it is certainly not permissible to introduce in this equation the macroscopically determined *D* of the solvent. For this reason

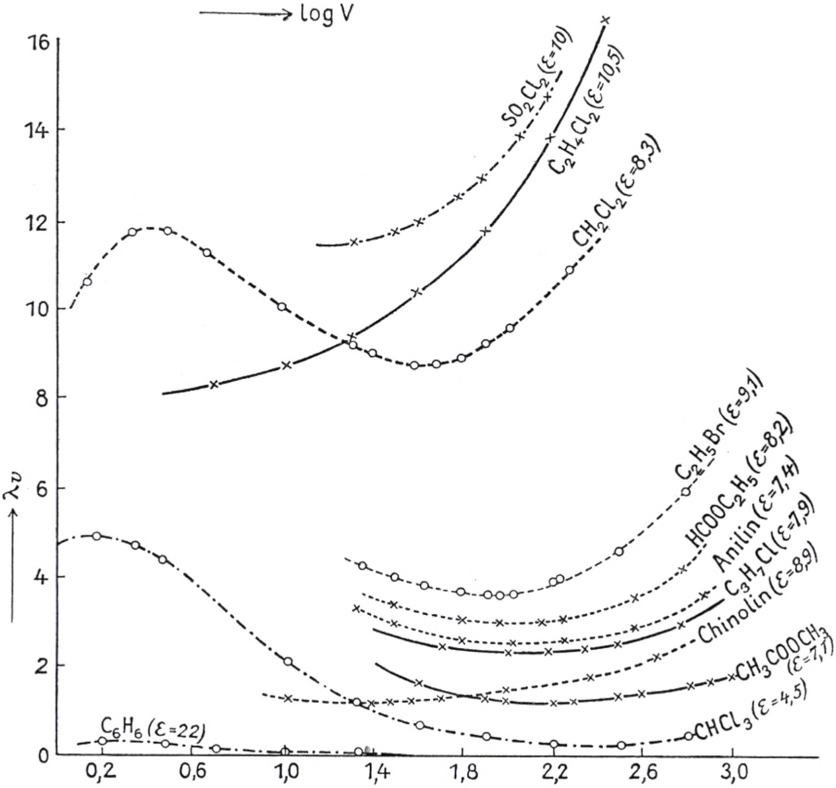

Fig. 1. Curves for the molar conductivity λ_ν *as a function of the dilution V and the nature of the solvent (after Walden*[25]*).*

we cannot consider the ionic radii so far calculated as the true ionic radii. In agreement with this conclusion they are extremely dependent on the temperature. That in many cases, ionic radii of reasonable sizes have been calculated, is, in my opinion, partly a result of an accidental compensation of several disturbing factors. In case of the heats of dilution, large deviations from the theory appear even at very small concentrations (comp. table 2). No compensation occurs here.

Passing from water to *solvents with lower dielectric constants,* the inter-ionic forces increase and the above difficulties for an exact theory appear at even smaller ionic concentrations than in water. The Debye-Hückel limiting laws have, however, also proved useful here (Schreiner and Frivold[24]).

In *solvents with very small dielectric constants* the molar conductivity as a rule has a rather anomalous course. Fig. 1 shows according to Walden[25], the molar conductivity of tetra-amyl-ammonium iodide in a series of solvents with $D \leqq 10.5$. The conductivity first decreases normally with decreasing dilution, but then passes a minimum and begins to rise again. The smaller the D, the smaller as a rule is the conductivity at the minimum, and the earlier is the minimum reached. This minimum has been the cause of much speculation and it has, a little unjustly, been considered an argument against the validity of modern electrolyte theories (Kraus[26]). In fact it should have been possible to predict the existence of this minimum from the new conceptions. In the vicinity of the minimum we have mainly binary ionic association, similar to that in salt vapour, and consequently a small conductivity. With decreasing concentration, the ions associate to a lesser degree and hence they conduct better. But also with increasing concentration does the conductivity rise, since here the ionic association becomes more general, ion aggregates of increasing size being formed as we approach the state of melted tetra-amyl-ammonium iodide, which shows the high conductivity characteristic of molten salts (*cf.*[21]).

Unfortunately it has so far been impossible to overcome the mathematical difficulties in developing a quantitative theory for these phenomena. The same is true of the quantitative calculation of the influences of inter-ionic forces on the properties of large colloid ions with many charges. But we can deduce qualitatively the laws of ion absorption on large colloid ions and the inhibitory effect of their charges upon coagulation, on the basis of the conception of the inter-ionic forces as put forward here.

IV

The explanation of the phenomenon of *solubility* is one of the most important problems in recent theories on electrolytes. The solubility is closely connected with the heat of solution and according to Fajans[27] the heat of solution in water can be expressed as the difference between the heat of hydration of the ions and the lattice energy of the solid salt. The lattice energy is the work expended in the dissolution of the ionic lattice into its individual ions, and the heat of hydration — or as I prefer to call it — the *heat of solution* of the ions is the heat evolved in the transfer of the separated ions to water.

This idea of Fajans can be further developed by combination with some expressions put forward by Born[28].

On transferring a sphere of radius r and charge $z\varepsilon$ from vacuum to a dielectric, work is gained since the sphere is attracted by the dielectric. This work is equal to:

$$\frac{(z\varepsilon)^2}{2r}\left(1 - \frac{1}{D}\right).$$

Born now identifies this work with the experimental heats of solutions of the ions, and calculates their radii on this basis. Table 3 gives for 11 ions the experimentally found heats of solution (W) in water (Fajans's values, recalculated by Born) and the ionic radii calculated from these (r is given in Ångström). Below are the radii estimated by V. M. Goldschmidt[10] from measurements of crystals (r observed). Although the agreement between the calculated and the observed radii is not complete (the calculated values are on an average about 0.6 Å too large), it seems justifiable to explain the large heats of solution of the ions in water in terms of an effect of their electrical charge.

Table 3

	H+	Li+	Na+	K+	Rb+	Cs+	Tl+	Ca++	Cl−	Br−	I−
W (kcal)	262	110	103	82	73	74	82	344	77	68	57
r calc.	0.625	1.49	1.59	2.00	2.24	2.22	2.00	1.91	2.13	2.41	2.88
r obs.	0	0.78	0.98	1.33	1.49	1.65	1.49	1.06	1.81	1.96	2.20

In the case of an electrolyte composed of two z-valent ions with radii r_1 and r_2 the ionic charges determine a work of solution of the magnitude:

$$\left(\frac{(z\varepsilon)^2}{2r_1} + \frac{(z\varepsilon)^2}{2r_2}\right)\left(1 - \frac{1}{D}\right) K_1$$

We have taken the approximate nature of Born's expression into account by introducing a coefficient K_1. According to the data in table 3 this coefficient, for most ions in water, lies between 0.75 and 0.5.

The lattice energy of the salt is:

$$\frac{2(z\varepsilon)^2}{r_1 + r_2} K_2$$

where K_2 is a coefficient somewhat less than 1 and dependent upon the nature of the lattice.

Typical binary electrolytes can crystallize in three different lattices like those of cesium chloride, sodium chloride and zinc sulphide (zincblende). The structure of these three lattices is shown in fig. 2. According to Born the coefficient K_2 is for the CsCl lattice 0.783, for the NaCl lattice 0.777 and for the zincblende lattice 0.72.

The work of solution due to the ionic charges, or as it can also be expressed, the *affinity of solution* due to the ionic charges, is given by:

$$\left(\frac{(z\varepsilon)^2}{2r_1} + \frac{(z\varepsilon^2)}{2r_2}\right)\left(1 - \frac{1}{D}\right) K_1 - \frac{2(z\varepsilon)^2}{r_1 + r_2} K_2$$

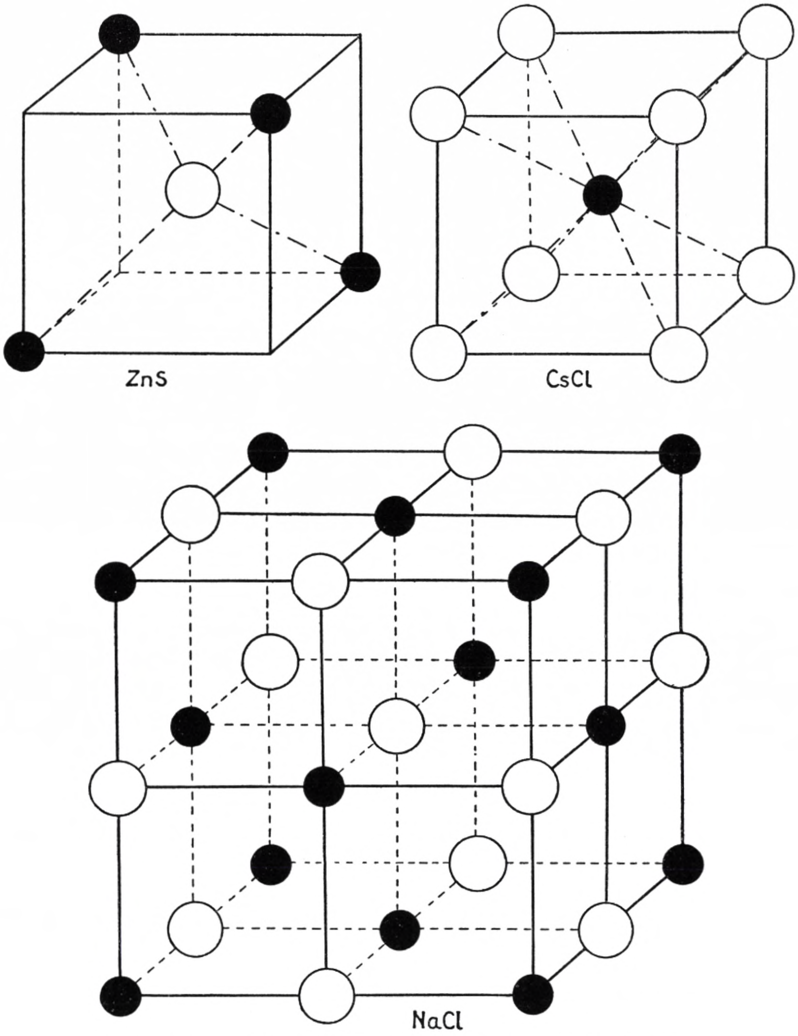

Fig. 2. Crystal lattices of CsCl, NaCl and ZnS (zincblende).

For water $1 - \frac{1}{D}$ is approximately equal to 1. In this formula therefore the work of solution appears as a small difference between two large, insufficiently known figures, and hence it is difficult in this way to obtain a value for the electrical affinity of solution, which is accurate enough to enable an estimation of the solubility.

However, the formula is very valuable, all the same. The fact that its two terms are approximately of the same size for aqueous solutions explains the old observation that *water is a good solvent for most salts.* In solvents with D less than that of water, the work of solution of the ions will be less than in water. Therefore with decreasing D, these solvents will have a decreasing capacity to dissolve salts.

If we confine ourselves to calculating the *relative solubilities in different solvents* (partition coefficients) the lattice energy is cancelled and only the variations of the work of solution of the ions have to be considered. If we assume that the ionic charges alone determine the solubilities, we arrive at the following expression[29]:

$$p = \log \frac{C_{H_2O}}{C_A} = \frac{z^2 \cdot 1{\cdot}5}{r} \quad \frac{D_{H_2O} - D_A}{D_A}$$

(p partition exponent, C_{H_2O} and C_A solubilities in water and in A, z and r valency and radius (mean value in Ångström) of the ions, D_{H_2O} and D_A, D of water and of A).

For potassium chloride in alcohol ($z = 1$, $r = 1.55$Å, $D = 26$) p is found equal to 2.0 against the experimental value 3.3. Considering that in the deduction of the formula we have neglected K_1 and its variations, a better agreement can scarcely be expected. According to the formula the solubility of salts composed of ions with higher valencies should be especially diminished on passing from water to alcohol. This is also known to be the case, as the slight solubility in alcohol of sulphates and most other salts of di- and polyvalent ions would call to mind. We are at present carrying out investigations with the purpose of testing the above formula extensively. In these investigations, we take into consideration in the following way the presence of molecular forces other than those due to the electrical charges: we add to the above expression for the partition exponent p a term:

$$\log \frac{C_{H_2O'}}{C_{A'}} ,$$

in which $C_{H_2O'}$ and $C_{A'}$ are the solubilities in water and in A of a substance composed of particles similar to the ions, but uncharged. For the alkali and halogen ions, which have an electronic configuration like that of the inert gases, we may reckon with the solubilities of the corresponding inert gases, for a quaternary ammonium ion NR_4^+ with the solubility of CR_4 (SiR_4 or SnR_4), for large organic ions $R.COO^-$ with the solubilities of the undissociated acids $R.COOH$ etc.

As regards the difference between the solubilities of different salts only little indication of regularity has been found so far. Ephraim[30] and Fajans[27] have, however, both observed that *salts composed of ions of approximately the same size are comparatively slightly soluble.* Ephraim came to this conclusion by detailed studies on complex salts, and Fajans by consideration of the solubility of alkali halides. In table 4 the solubilities of the alkali halides are surveyed. If we look at the solubilities of the potassium and rubidium salts, minima occur at KCl and RbBr, corresponding to the similar sizes of K^+ and Cl^- and of Rb^+ and Br^-. The least soluble of lithium and sodium salts are the fluorides, and of cesium salts the iodides, all in agreement with the Ephraim-Fajans's rule.

Table 4. Solubility of alkali halides. Moles per 1000 g H_2O at 18° C. If the solid salt contains water, its water content is given in parenthesis

	Li	Na	K	Rb	Cs
F	0.11	1.06	15.9 (2 aq)	12.7 (?)	24.2 (1.5 aq)
Cl	18.5 (1 aq)	6.14	4.6	7.34	10.9
Br	19.7 (2 aq)	8.6 (2 aq)	5.6	6.4	5.8
J	12.1 (3 aq)	11.9 (2 aq)	8.35	7.2	2.9

This *rule of Ephraim-Fajans* can be derived from our general expression for the electrical affinity of solution. If $r_1 + r_2$ is kept constant, the work of solution of the ions is minimum and the lattice energy maximum for $r_1 = r_2$. Consequently the solubility must also be minimum when the ratio of the radii is equal to one.

That the work of solution of the ions is minimum when $r_1 = r_2$ follows mathematically from the fact that it is in the form $(1/r_1 + 1/r_2)$. That the lattice energy reaches its highest value for $r_1 = r_2$ is seen from the fact that preference is then given to the CsCl lattice which has the greatest lattice energy ($K_2 = 0.783$). When r_1/r_2 diverges from 1, first the NaCl lattice ($K_2 = 0.777$) and later the zincblende lattice appears ($K_2 = 0.72$). For $r_1 + r_2$ constant, the lattice energy becomes smaller the more r_1/r_2 deviates from 1. The connection between the lattice type and ratio of the radii has been pointed out mainly by V. M. Goldschmidt[10].

In conclusion it can be stated, I think, that all the more general features of the solubility of strong electrolytes can be freely deduced from their ionic structure. Before, however, a direct calculation of the solubilities of the individual salts is possible there is much to be done. Firstly we must be able to take into account the more or less hypothetical solubility of the ions deprived of their charge, secondly the deformability of the ions in the lattices must be taken into consideration and thirdly, we must obtain a more detailed knowledge of the coefficient K_1 in the expression for the electrical work of solution of the ions.

V

Besides the strong electrolytes, the properties of which indicate complete dissociation, there are a large number of *weak electrolytes*, for which incomplete ionization has to be assumed. In order to describe their properties, we use at the same time chemical degrees of dissociation and *physical coefficients*, which express the effects of the ionic charges.

Thus we write for the conductivity:

$$\frac{\mu}{\mu_\infty} = \alpha f_\mu$$

where α is the degree of dissociation and f_μ a coefficient accounting for the inter-ionic forces. For the active mass (the activity) we write:

$$\frac{A}{c} = \alpha f_A$$

where A is the active mass of the ion, c the concentration of the electrolyte, α the degree of dissociation and f_A a coefficient accounting for the inter-ionic forces.

This treatment has been used since 1916 in my laboratory with good results[13].

In the case of weak electrolytes, we therefore use at the same time a physical and a chemical method. It is difficult to draw a *completely sharp boundary* between the ranges of application of these two methods. As long as the physical method has only been slightly developed, we must be content with the more *summary chemical method*, even when it is probable that the physical treatment will later on be carried through. It was in such a boundary case, that I myself[21], some years ago resorted to the *introduction of a degree of association* for nitrates and other salts. A similar case it is perhaps when Nernst in his recent paper on the heat of dilution of salt solutions, assumes the *existance of undissociated molecules* in the alkali chlorides and nitrates[31].

In their interpretation of the refraction and light absorption in concentrated ionic solutions, Fajans[32] and v. Halban[33] have encountered difficulties in distinguishing between physical and chemical phenomena. Their investigations show that we have to expect the interionic forces to exert a considerable influence on the refraction and light absorption of the ions in concentrated solutions, and it has not been possible to distinguish with certainty between these influences and the effect of a possible incomplete ionization.

When, however, Kossel[34] considers even the *sulphate ion as a physical aggregate* of four negative oxygen ions and one positive sulphur ion, it is certainly going too far. In the sulphate ion, the properties of oxygen and sulphur ions have almost completely disappeared. Not only the reaction to light, which implies the configuration of the outer electrons, but also the reaction to X-rays, which implies the configuration of the inner electrons, show that the sulphur in the sulphate ion does not possess the properties of an independent positive sulphur ion. The K and L levels in the sulphur atom of the sulphate ion correspond more nearly to those in sulphide, and do not at all possess the values which would have been expected for a free positive sulphur ion. The electrons from the oxygen ions in the sulphate ion must therefore in their penetration approach the positive sulphur nucleus almost as much as the eight external electrons in the sulphide ion[35].

It is quite natural that the recent conquest by phycisists of regions which had previously belonged to chemists, gives rise to the thought that the use of chemical methods is only an indication of the limitation of our physical understanding. The more able the phycisists, the further they extend the boundaries of physics and the less remains for the chemists. I believe, however, that the situation is not so unstable. The contrast between the rigid or slightly deformable ions of the strong electrolytes, and the ionic rudiments in complex ions, such as the sulphate ion, is so sharp that it is possible to maintain that there is a natural distinction between the two fields.

Table 5. Equivalent conductance of the chlorides of the elements of the main groups at the melting point (after W. Biltz and W. Klemm [37]).

HCl $\sim 10^{-8}$					
LiCl 166	$BeCl_2$ 0.086	BCl_3 0	CCl_4 0		
NaCl 133.5	$MgCl_2$ 28.8	$AlCl_3$ 15.10^{-6}	$SiCl_4$ 0	PCl_5 0	
KCl 103.5	$CaCl_2$ 57.9	$ScCl_3$ 15	$TiCl_4$ 0	VCl_4 0	
RbCl 78.2	$SrCl_2$ 55.7	YCl_3 9.5	$ZrCl_4$	$NbCl_5$ $\varkappa = 2 \cdot 10^{-7}$	$MoCl_5$ $\varkappa = 1.8 \times 10^{-6}$
CsCl 66.7	$BaCl_2$ 64.6	$LaCl_3$ 29.0	$HfCl_4$	$TaCl_5$ $\varkappa = 3 \cdot 10^{-7}$	WCl_6 $\varkappa = 2 \cdot 10^{-6}$
			$ThCl_4$ 16		UCl_4 $\varkappa = 0.34$

For salt vapours Franck and his co-workers[38] have been able, on the basis of absorption spectra, to distinguish clearly between the vapour of the alkali halides, which is composed of ion pairs, and that of silver halide, which is not composed of ions.

In table 5, the molar conductivities of the molten chlorides of the elements of the main groups are presented (after Biltz and Klemm[37]).

By looking at the table, it is easy to see, as Biltz himself stresses, that the chlorides fall into two big groups, the ionic fluids with high conductivity and the molecular fluids with low conductivity.

Also in crystal lattices, we can seldom be in doubt as to whether an ionic lattice or a lattice of atoms or molecules is present, and in the same way the chemists are able in most cases to distinguish with considerable certainty between ionized double salts, such as the alums, and complex compounds, such as the iron cyanides.

Even in solution where the distinction is perhaps most difficult, the error in the determination of the degree of ionization seldom exceeds a few per cent.

On the other hand, I do not wish to maintain that it is impossible to describe the formation of a chemical compound from ions as a continuous, *physical process*. Water for one thing may be continuously transformed into vapour without our abandoning, for this reason, the clear distinction between liquid and vapour under normal conditions. In the same way it will certainly also be possible in the future to distinguish physical aggregates of ions from chemical compounds between ions.

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On Acid and Basic Reaction

NIELS BJERRUM

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The following short article aims at giving a survey of recent views on acid and basic reaction. We shall see how a rational method for measuring the reaction of a solution has been found by introducing the so-called "*hydrogen-ion exponent*", how the *reaction in solutions* of acids, bases, and salts can be computed, when the strength of the acids and bases is known, and how solutions with well-defined reaction (*buffer mixtures*) can be made. The theory of *dye-stuff indicators* will likewise be discussed, and we shall finally demonstrate, how *the error in an acid or alkali titration* depends on the strength of the acid or base, as well as on the properties of the indicator.

1. THE REACTION SCALE

According to the theory of electrolytic dissociation, the acid reaction of a solution depends on its content of hydrogen ions, and the basic reaction on its content of hydroxyl ions. It is customary to say that a solution cannot at the same time show both acid and basic reaction; this is correct in so far as it is impossible for hydrogen ions and hydroxyl ions to be simultaneously present in appreciable quantities in a solution without combining with each other to form water according to the equation:

$$H^+ + OH^- = H_2O\,.$$

This process takes place when acid and basic solutions are mixed and causes the acid or the basic reaction to disappear. When the two solutions are mixed in a definite proportion, both reactions disappear and the solution becomes *neutral.*

Accurate investigations have revealed, however, that hydrogen ions and hydroxyl ions do not combine completely; every aqueous solution, in fact, contains both kinds of ions, but one of them is always present in extremely small quantity. If one of them is totally absent in an aqueous solution, some water molecules will immediately dissociate according to the equation:

$$H_2O = H^+ + OH^-.$$

The reaction of hydrogen ions and hydroxyl ions to form water is therefore reversible and mobile at room temperature. Hence, it follows from the law of mass action that the product of the hydrogen-ion and hydroxyl-ion concentrations in all dilute aqueous solutions must have one and the same value. This value is called the *dissociation constant of water*. We shall designate it as K_{H_2O}. If the molar concentration of a substance is designated as C with the formula for the substance as suffix, we may write

$$C_{H^+} \cdot C_{OH^-} = K_{H_2O}$$

The dissociation equation for water.

At 20° C the numerical value of the dissociation constant of water is about 10^{-14}; the constant increases about 7 per cent per degree centigrade, and at 100° C it is about 60 times as large as at 20° C. In what follows we shall use the value 10^{-14}.

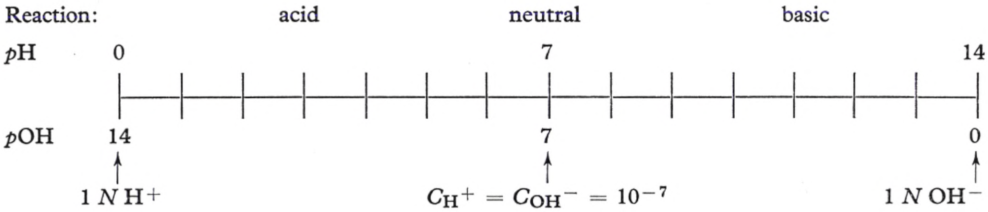
As a result of the connection between the hydrogen-ion and the hydroxyl-ion concentrations, the hydroxyl-ion concentration in a 1 molar hydrogen-ion solution has the very small value 10^{-14}. With decreasing hydrogen-ion concentration, the hydroxyl-ion concentration increases. When the hydrogen-ion concentration has decreased to 10^{-7} the two concentrations are equal, and when the hydrogen-ion concentration becomes even smaller, the hydroxyl-ion concentration is the larger. We find then, that in strongly acid solutions the hydroxyl-ion content is very small, and in strongly alkaline solutions the reverse is true and the content of hydrogen ions is very small.

As suggested by Friedenthal, the reaction of all solutions may be expressed by their hydrogen-ion concentration. If a solution shows basic reaction, it is easy from the hydrogen-ion concentration by means of the equation for the dissociation of water to compute the hydroxyl-ion concentration, and *vice versa*. This suggestion of Friedenthal makes it possible to measure the reaction in all solutions by the same scale.

It is often unpractical to express the reaction of a solution by means of the hydrogen-ion concentration, especially in graphical representations, for it varies over a very great interval, from about 1 to about 10^{-14}. A great improvement was therefore introduced when Professor S. P. L. Sørensen suggested substituting for the hydrogen-ion concentration, the negative value of its logarithm. Sørensen calls this value the *hydrogen-ion exponent* and designates it as pH. The relation between pH and C_{H^+} may be expressed by one of the two following equations:

$$C_{H^+} = 10^{-pH}\,; \qquad pH = -\log C_{H^+}$$

The first of the two equations explains the name hydrogen-ion exponent.



When the hydrogen-ion exponent decreases with 1, the hydrogen-ion concentration is correspondingly multiplied by 10 ($\log 10 = 1$), and a decrease in the hydrogen-ion exponent of 0.3 corresponds very nearly to doubling the hydrogen-ion concentration ($\log 2 = 0.301$) etc.

At ordinary temperature, the *p*H scale extends from about 0 to about 14. The value 0 corresponds to a 1 molar hydrogen-ion solution. The figures 0 to 7 represent acid solutions. The figure 7 indicates a completely neutral solution, in which hydrogen-ion and hydroxyl-ion concentrations are equal. The figures 7 to 14 represent alkaline solutions. The closer the hydrogen-ion exponent approaches 7, the closer the solution approaches neutrality. (This is only true at room temperature; at other temperatures, instead of 7, $-\frac{1}{2}\log K_{H_2O}$ should be inserted).

Under certain conditions it is practical to indicate the reaction by a *hydroxyl-ion exponent* *p*OH. Its definition is quite analogous to that of the hydrogen-ion exponent. Hence, we have

$$C_{OH^-} = 10^{-p\mathrm{OH}}\,; \qquad p\mathrm{OH} = -\log C_{OH^-}\,.$$

From the dissociation equation of water

$$C_{H^+} \cdot C_{OH^-} = K_{H_2O}\,,$$

the following simple relation between *p*H and *p*OH may be deduced by taking the logarithms:

$$p\mathrm{H} + p\mathrm{OH} = 14\,.$$

The following diagram gives a survey of the relation between the *p*H scale and the *p*OH scale.

2. THE STRENGTH OF ACIDS AND BASES

Strong acids and bases like most salts are highly dissociated in solution. In computing hydrogen-ion exponents of solutions of strong acids and bases we may with good approximation assume that these compounds are completely split into ions. Throughout this paper we will therefore assume that strong acids and bases and all salts are completely dissociated into their ions. The inaccuracy thereby introduced, is irrelevant in presenting the main features of the phenomena.

In the case of weak acids and bases, the conditions are totally different. Let us consider a weak monobasic acid HS. In solution, it is but slightly split into ions, according to the equation:

$$HS = H^+ + S^- .$$

The more an acid splits into ions, the more acid is the solution, and therefore the stronger the acid. Yet the degree of dissociation is not a good measure of the strength of an acid, because it changes with the concentration. The best measure of the *strength of an acid* is to be found in the so-called *dissociation constant.*

For any solution containing the acid radical S in one or the other form, we have according to the mass-action law that the expression

$$\frac{C_{H^+} \cdot C_{S^-}}{C_{HS}} = K_S$$

The dissociation equation for the acid HS

has the same constant value K_S which we call the dissociation constant of the acid.

This important equation is the basis for almost all that follows. It is perhaps not superfluous to emphasize the fact, that the validity of the above equation in no way depends on whether the hydrogen ions or the anions of the acid have been formed by the dissociation of one compound or another. The validity of the equation is totally independent of the past history of the ions.

If we wish to determine the dissociation constant of an acid, it is only necessary to determine its degree of dissociation at a single concentration. This can be done by measuring the electrical conductance of the solution of the acid. From the corresponding values of degree of dissociation and concentration, the dissociation constant may be calculated as follows.

In a solution of the acid, of which the molar concentration is C, and in which the degree of dissociation is γ, the ions and undissociated acid molecules have the following molar concentrations:

$$C_{H^+} = C_{S^-} = \gamma\, C, \qquad C_{HS} = (1 - \gamma)\, C$$

The dissociation equation of the acid may then be transformed to read

$$C \cdot \frac{\gamma^2}{1 - \gamma} = K_S \text{ (Ostwald's law of dilution)}$$

This equation enables us, from the corresponding values of C and γ, to compute the dissociation constant. Table 1 shows some values of the dissociation constant of acetic acid calculated by this method.

Table 1. Dissociation of acetic acid at 18° C.

C	100 γ	K_S
1/8	1.19 per cent	0.0000179
1/16	1.68 – –	179
1/32	2.38 – –	181
1/64	3.33 – –	179
1/128	4.68 – –	179
1/1024	12.66 – –	179

The uniformity of the values of the dissociation constant in the last column prove experimentally the correctness of our dissociation equation.

The larger the dissociation constant of the acid, the larger the degree of dissociation of the acid at a given concentration, and therefore, the stronger the acid reaction at the concentration considered. The dissociation constant of the acid is therefore a measure of the strength of the acid.

Analogously, the *strength of a base* may be measured by its dissociation constant.

A tabulation of the dissociation constants of a large number of acids is found in *Landolt-Börnstein-Roth's Tables* 4th Edition (1912).

Table 2 shows dissociation constants of a selected series of acids and bases. I have endeavoured to select acids and bases with chemical properties with which one is familiar and of whose strength one already has a notion.

This table should enable us to obtain an idea of the strength of an acid (base) when its dissociation constant is known; for, using the table, the acid (base) in question can be placed between two acids (bases) of whose strengths one already has a definite notion.

In the table, the dissociation constants are expressed as powers of 10. This is convenient when the reaction is expressed by the hydrogen-ion exponent. In this case the strength of an acid is simply given by naming the numerical value of the exponent, the strength exponent of the acid in question, using the symbol pS (for bases pB).

$$K_S = 10^{-pS}$$

We note, that in the table, more than one dissociation constant is given for the polybasic acids. Each of these corresponds to one special hydrogen atom in the acid. With a dibasic acid account must be taken of two reversible dissociation processes

$$H_2S = H^+ + HS^- \text{ and } HS^- = H^+ + S^{--}.$$

The corresponding mass-action equations are:

$$\frac{C_{H^+} \cdot C_{HS^-}}{C_{H_2S}} = K_1 \text{ and } \frac{C_{H^+} \cdot C_{S^{--}}}{C_{HS^-}} = K_2.$$

*Table 2. Dissociation constants for selected acids and bases at room temperature about 18° C.**

	K_1	K_2	K_3		K_1
Strong acids	about 1			Strong bases	about 1
Sulphurous acid	$10^{-1.78}$	$10^{-5.3}$		Piperidine	$10^{-2.82}$
Phosphoric acid	$10^{-1.92}$	$10^{-6.7}$	$10^{-12.44}$	Methylamine	$10^{-3.3}$
Monochloro acetic acid	$10^{-2.82}$			Ammonia	$10^{-4.75}$
Formic acid	$10^{-3.67}$			Hydrazine	$10^{-5.52}$
Acetic acid	$10^{-4.75}$			Pyridine	$10^{-8.8}$
Carbonic acid	$10^{-6.52}$	$10^{-10.22}$		Aniline	$10^{-9.4}$
Hydrogen sulphide	$10^{-7.0}$			*p*-Nitroaniline	10^{-12}
Boric acid	$10^{-8.77}$			Urea	$10^{-13.92}$
Hydrocyanic acid	$10^{-9.3}$				
Phenol	10^{-10}				
Hydrogen peroxide	$10^{-11.7}$				

* Dissociation constants are in general not very accurately known; therefore too much reliance should not be placed on the decimals.

These two equations show the significance of the two dissociation constants K_1 and K_2 for a dibasic acid.

3. THE REACTION IN SOLUTIONS OF ACIDS, BASES, AND SALTS

Having shown how the dissociation constant and the strength exponent are measures of the strength of an acid or a base, we shall proceed to show how these figures make it possible to calculate the reaction not only of solutions of the free acid but also of solutions containing salts of the acid, and of mixtures containing the free acid and its salts.

a) *The reaction of a mixture of an acid and its salt.* In a mixture of a weak acid and one of its salts, the dissociation of the acid is very small and the dissociation of the salt large. The concentration of the undissociated acid molecules HS is therefore approximately equal to the concentration of the acid in the mixture, and the concentration of the anion S^- is approximately equal to the salt concentration in the mixture:

$$C_{HS} = C_{acid} \text{ and } C_{S^-} = C_{salt}$$

According to the dissociation equation of the acid, the hydrogen-ion concentration is determined by the concentration of undissociated acid molecules and the concentration of anions of the acid:

$$C_{H^+} = K_S \cdot \frac{C_{HS}}{C_{S^-}}$$

From the above equations we obtain:

$$C_{H^+} = K_S \cdot \frac{C_{acid}}{C_{salt}}$$

In a mixture of equivalent quantities of acid and salt, the hydrogen-ion concentration therefore equals the dissociation constant of the acid.

By taking logarithms we come to the following equation

$$pH = pS + \log \frac{C_{\text{salt}}}{C_{\text{acid}}}$$

It follows from this equation, that the hydrogen-ion exponent is equal to the strength exponent of the acid when acid and salt are present in equivalent amounts. When acid and salt are not present in equivalent amounts, but in amounts of the same order of magnitude, the last term of the equation, though not zero, is yet very small, and therefore the hydrogen-ion exponent in such a mixture, must always come close to the strength exponent of the acid. Each time the salt to acid ratio increases 10 times, the hydrogen-ion exponent increases one unit.

Example: The strength exponent of acetic acid is 4.75. Therefore a mixture of acetic acid and sodium acetate has a hydrogen-ion exponent close to 4.75. If the solution contains 10 times as many molecules of acetic acid as of sodium acetate, $pH = 3.75$. If, on the other hand, the acetate concentration is 10 times larger than the acetic acid concentration, $pH = 5.75$. By adding acetic acid and sodium acetate to a solution, a weakly acid reaction of the solution may be obtained with a pH value close to 4.75. This procedure is used in inorganic analysis to produce a very weakly acid reaction, at which ferric and aluminium phosphate precipitate completely, while phosphates of zinc, manganese, calcium and magnesium remain in solution.

b) *The reaction in a solution of an acid.* We shall now compute the reaction in a pure aqueous solution of a weak acid. As the acid is but slightly dissociated, we may consider the concentration of the undissociated acid molecules to be equal to the total concentration of the acid: $C_{HS} = C_{\text{acid}}$. Moreover as the two ions, by dissociation, are formed in equally large quantities the equation: $C_{H^+} = C_{S^-}$ holds. By introducing these values into the dissociation equation for the acid

$$\frac{C_{H^+} C_{S^-}}{C_{HS}} = K_S ,$$

we find the following expression for the hydrogen-ion concentration of the solution of the acid:

$$C_{H^+} = \sqrt{K_S \cdot C_{\text{acid}}} .$$

Hence, on taking the logarithms,

$$pH = \tfrac{1}{2}\, pS - \tfrac{1}{2} \log C_{\text{acid}} .$$

In a 1 molar solution of an acid we see that the hydrogen-ion exponent is equal to half the acid-strength exponent, and as the hydrogen-ion exponent only changes one half unit each time the concentration of the acid becomes ten times smaller, we may say that the value of the hydrogen-ion exponent in a non-dilute solution, is always close to half the value of the acid-strength exponent.

Example : In a 1 molar solution of acetic acid, the hydrogen-ion exponent will be $\frac{1}{2} \cdot 4.75 = 2.375$, i.e. the hydrogen-ion concentration will be $10^{-2.375} = 0.0042$. In a 0.1 molar solution of acetic acid, the hydrogen-ion exponent will be $\frac{1}{2} \cdot 4.75 + \frac{1}{2} = 2.875$, i.e. the hydrogen-ion concentration will be $10^{-2.875} = 0.0013$.

In a mixture of a free acid and one of its salts, the reaction may well be alkaline, even if the free acid is present in great quantities. According to the above, this anomaly may be shown by all the acids, whose strength exponents are close to 7 or even have higher values, f. inst. boric acid, hydrocyanic acid, phenol. On the other hand, the reaction of a pure solution of an acid in which no salt of the acid is present, is always acid, however weak the acid may be, for a hydrogen compound with a dissociation constant smaller than 10^{-14} would hardly be called an acid.

c) *The reaction in a salt solution. Hydrolysis.* When salts are dissolved in water, they split to a larger or lesser degree into free acids and bases, i.e. they *hydrolyze.* The extent of the hydrolysis process is determined by the fact that the hydrogen ions from the acid formed, and the hydroxyl ions from the base formed, must perforce possess concentrations whose product equals the dissociation constant of water. The less the acid and the base dissociate, the greater must be the extent of the hydrolysis in order to fulfill this requirement.

Let us calculate the *p*H and *p*OH for a solution of the salt of a weak acid HS with a strong base BOH. We take the following equations:

$$C_{\mathrm{H}^+} \cdot C_{\mathrm{OH}^-} = K_{\mathrm{H_2O}} \text{ (the dissociation equation for water)}$$

$$\frac{C_{\mathrm{H}^+} \cdot C_{\mathrm{S}^-}}{C_{\mathrm{HS}}} = K_{\mathrm{S}} \text{ (the dissociation equation for the acid).}$$

Since the quantities of acid and base formed by hydrolysis must be equivalent, and since the strong base formed is completely dissociated, while the weak acid formed dissociates only to a small degree, we have further:

$$C_{\mathrm{HS}} = C_{\mathrm{OH}^-} \text{ (equivalence of acid and base).}$$

If we assume that the salt is completely ionized, but only slightly hydrolyzed, which is approximately true in most cases, we may set the concentration of the ion S^- equal to the concentration of the salt solution:

$$C_{\mathrm{S}^-} = C_{\mathrm{salt}} \, .$$

From the above four equations we derive:

$$C_{OH^-} = \sqrt{\frac{K_{H_2O}}{K_S} C_{salt}}\,.$$

By taking the logarithms and substituting for K_{H_2O} the value 10^{-14} we find:

$$pOH = -\tfrac{1}{2}\,pS + 7 - \tfrac{1}{2}\log C_{salt}, \text{ or}$$

$$pH = \tfrac{1}{2}\,pS + 7 + \tfrac{1}{2}\log C_{salt}$$

In a 1 molar salt solution the hydrogen-ion exponent will therefore be 7 units larger than half the value of the acid-strength exponent, and the hydrogen-ion exponent varies with only $\frac{1}{2}$ unit each time the concentration of the salt solution decreases ten times.

Example: In a 1 molar solution of sodium acetate the hydrogen-ion exponent is $\frac{1}{2}\,4.75 + 7 = 9.375$, and in a 0.1 molar solution of the same substance it is $\frac{1}{2}$ unit smaller, i.e. 8.875. Since both of these hydrogen-ion exponents are larger than 7, both solutions show an alkaline reaction, but the hydroxyl-ion concentrations in the solutions are only small:

$$C_{OH^-} = 10^{-(14-9.375)} = 0.000024$$

$$C_{OH^-} = 10^{-(14-8.875)} = 0.0000075$$

All salts in which the acid is weaker than the base, show an alkaline reaction in solution.

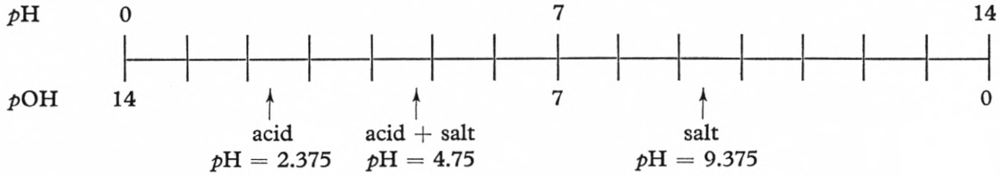
In the case of a dibasic acid the first strength exponent determines the reaction in solution of the free acid, while the second strength exponent determines the basic reaction of its salt. Therefore a polybasic acid may well, as free acid be stronger than a monobasic acid, and still, judged by the hydrolysis of its sodium salt, be weaker than the same monobasic acid. This is true in the case of sulphurous acid (first $pS = 1.78$, second $pS = 5.3$) and acetic acid ($pS = 4.75$).

Graphic representation. If we, in a pH scale, plot the reactions

a) of a mixture of equivalent amounts of acid and salt
b) of a 1 molar acid solution
c) of a 1 molar salt solution

we obtain a comprehensive survey of the system.

To find the point representing the reaction of the acid-salt mixture, we have only to introduce the strength exponent of the acid in the hydrogen-ion exponent scale. Halving the distance between this acid-salt-point and the point $pH = 0$ gives the reaction point for the solution of the acid; halving the distance between the acid-salt-point and the point $pH = 14$ (or more generally $pOH = 0$), gives the reaction point for the salt solution. In the following reaction scale, these 3 points are shown for acetic acid:



Acetic acid, $pS = 4.75$

The *acid-point* moves $\frac{1}{2}$ unit to the right each time the solution becomes 10 times weaker. The *salt-point* moves $\frac{1}{2}$ unit to the left each time the solution becomes 10 times weaker, and the *salt-acid-point* moves one full unit to the right, each time the acid to salt ratio decreases 10 times.

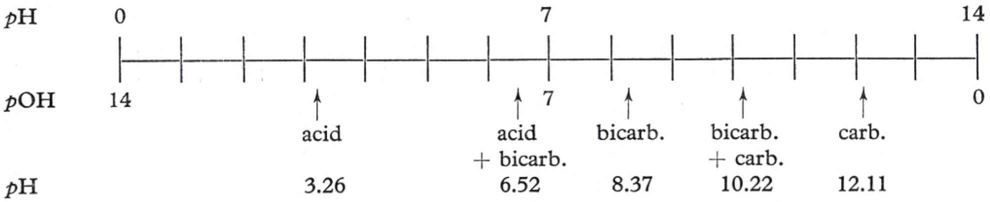
In the case of a weak base an analogous procedure can be followed to find the reaction points for the base, for its salt with a strong acid, and for a mixture of base and salt; however, instead of the hydrogen-ion exponent scale the hydroxyl-ion exponent scale should be used.

This graphic method may be extended to polybasic acids. It is sufficient to show how to proceed for a dibasic acid as carbonic acid. It is easy to extend the method to acids of still higher basicity.

Carbonic acid has 2 strength exponents, 6.52 and 10.22. The first value represents ionization of the first hydrogen atom by which a bicarbonate ion is formed from undissociated carbonic acid. The second exponent represents ionization of the second hydrogen atom, by which a carbonate ion is formed from a bicarbonate ion. A mixture of free carbonic acid and bicarbonate has a hydrogen-ion exponent close to the first strength exponent, and a mixture of bicarbonate and carbonate has a hydrogen-ion exponent close to the second strength exponent. When the mixtures contain equivalent amounts, the reactions (pH values) will exactly equal the strength exponents. In other cases they will be displaced from these points according to the above rules, valid for an acetic acid-acetate mixture. By halving the distance between the point $p\text{H} = 0$ and the acid-bicarbonate point, the reaction point for the pure carbonic acid is found; by halving the distance between the acid-bicarbonate point and the bicarbonate-carbonate point the reaction point for a pure bicarbonate solution is found; and halving the distance between the bicarbonate-carbonate point and $p\text{H} = 14$ (or more generally $p\text{OH} = 0$) we finally obtain the reaction point for a soda solution. All these points are marked in the following reaction scale.

The reaction in the solution of free carbonic acid and in the solution of soda varies with dilution according to the rules governing a monobasic acid, and the points shown are exactly valid only for 1 molar solutions. The reaction of a bicarbonate solution, on the other hand, is independent of the concentration. In this case the point marked applies to all concentrations.

Carbonic acid, first $pS = 6.52$, second $pS = 10.22$



At this juncture let us remember that in all the discussions and results in this paper, complete dissociation of the salts has been taken for granted. This causes a slight inaccuracy in the results obtained. However, when the degree of dissociation of the salts is known, the inaccuracy may easily be corrected in each case by considering the incomplete dissociation. This correction, indeed, slightly changes the figures in the results, but the main features of the phenomena here described are not changed.

4. BUFFER MIXTURES

When hydrochloric acid is added drop by drop to a mixture of acetic acid and sodium acetate, the reaction in the mixture will, at first, hardly change at all. This is because the hydrochloric acid is consumed by the sodium acetate in forming acetic acid. Since the hydrogen-ion exponent of the mixture is determined by the ratio of free acetic acid to sodium acetate according to the equation mentioned earlier:

$$pH = pS + \log \frac{C_{\text{salt}}}{C_{\text{acid}}},$$

the reaction of the solution will change but little as long as the quantity of hydrochloric acid added is small compared with the quantities present of acetic acid and acetate. Not until the acetic acid is completely released does the solution become strongly acid. The addition of bases will likewise change the reaction but only little at first. The mixture of acetic acid and sodium acetate acts as a kind of "buffer" against change in reaction from the addition of strong acids and bases. How pronounced this buffer effect is, may be seen from the following example. If 1 per cent of 1 normal hydrochloric acid is added to pure water, the solution becomes 0.01 normal hydrochloric acid and the hydrogen-ion exponent drops from 7 to 2 — i.e. 5 units. If, on the other hand, 1 per cent of 1 normal hydrochloric acid is added to a solution which is 0.1 normal with respect to both acetic acid and sodium acetate, the hydrogen-ion exponent only falls from 4.75 to 4.66 — not even 0.1 unit.

Any mixture of a weak acid and one of its salts will act as a buffer, the same is true of mixtures of weak bases and their salts. In a mixture of ammonia and ammonium chloride, the reaction lies close to $pH = 9.25$. The strength exponent of the ammonia base is 4.75, consequently the hydroxyl-ion exponent of the solution lies close to 4.75. From this the hydrogen-ion exponent is calculated by subtraction from 14.

$$pH = 14 - pOH = 14 - 4.75 = 9.25.$$

Since the reaction of a solution is of decisive importance to numerous properties of the solution and to many of the processes taking place within the solution, it is in many investigations necessary to ensure that the solution one investigates has a definite and well-defined reaction. Such a reaction may be obtained by adding a suitable buffer mixture. By this addition the solution attains a known hydrogen-ion exponent not appreciably influenced by accidental small quantities of impurities or by eventual new substances formed in the solution. A solution of the purest potassium chloride in ordinary distilled water has no well-defined reaction. The reaction is of course close to the neutral point $pH = 7$, but accidental impurities such as carbonic acid from the atmosphere, or alkali from the glass, may alter the hydrogen-ion exponent to 6 or 8, or even to 5 or 9 although the solutions have been prepared with great care. In many investigations results are only reproducible when the reaction of the solutions in question are fixed by means of buffer mixtures. This is true, for instance, in many enzymatic investigations, in solubility determinations of many so-called insoluble substances, and in investigations on reaction velocity of chemical processes. In living organisms the reaction of fluids is regulated by phosphate- and especially carbonate- containing buffer mixtures. The reaction of blood, for example, is regulated by a carbonic acid-bicarbonate buffer.

In a good buffer mixture both components must be present in not too small concentrations. Therefore, a definite pair of components, such as acetic acid and sodium acetate, cover only a rather small interval, generally not more than 2 units on the *p*H scale. It is therefore important to have recourse to a series of different component pairs to cover the entire reaction interval.

We are indebted to S. P. L. Sørensen for the most detailed and accurate directions for the preparation of good buffer mixtures. Following his directions, it is easy to produce any hydrogen-ion concentration with an accuracy of one or two per cent. Table 3 gives the composition of a series of solutions with round values of the hydrogen-ion exponent computed from the statements of S. P. L. Sørensen.

The standard solutions used in preparing these solutions are: 1) "*Hydrochloric acid*", a 0.1 N HCl, 2) "*Sodium hydroxide*", a 0.1 N (carbon-dioxide-free) solution of NaOH, 3) "*Glycine*", a 0.1 M glycine, which is also 0.1 M with respect to NaCl, 4) "*Secondary phosphate*", a $\frac{1}{15}$ M Na_2HPO_4, 5) "*Primary phosphate*", a

Table 3. Solutions with well-defined hydrogen-ion exponents

*p*H	Hydrochloric acid	Citrate	*p*H	Hydrochloric acid	Borate
1.04	10.00 cc.	0.00 cc.	8	4.43 cc.	5.57 cc.
1.5	7.77 –	2.23 –	8.5	3.51 –	6.49 –
2	6.93 –	3.07 –	9	1.49 –	8.51 –
2.5	6.45 –	3.55 –			
3	5.96 –	4.04 –		Sodium hydroxide	Borate
3.5	5.31 –	4.69 –			
4	4.38 –	5.62 –	9.5	2.03 cc.	7.97 cc.
4.5	2.79 –	7.21 –	10	4.06 –	5.94 –
			10.5	4.69 –	5.31 –
	Sodium hydroxide	Citrate	11	4.98 –	5.02 –
5	0.39 cc.	9.61 cc.		Sodium hydroxide	Glycine
5.5	2.78 –	7.22 –			
6	4.06 –	5.94 –	11.5	5.07 cc.	4.93 cc.
(6.5)	4.65 –	5.35 –	12	5.39 –	4.61 –
			12.5	6.32 –	3.68 –
	Primary phosphate	Secondary phosphate	13	9.23 –	0.77 –
(6)	8.77 cc.	1.23 cc.			
6.5	6.86 –	3.14 –			
7	3.90 –	6.10 –			
7.5	1.60 –	8.40 –			
(8)	0.54 –	9.46 –			

$\frac{1}{15}$ *M* KH_2PO_4, 6) "*Borate*", a $\frac{1}{20}$ *M* borax, $Na_2B_4O_7$, prepared from 1 *N* sodium hydroxide and boric acid, 7) "*Citrate*", a 0.1 *M* solution of secondary sodium citrate, prepared from 1 *N* sodium hydroxide and citric acid. The solutions should be prepared from pure reagents and great care taken to prevent contamination by carbon dioxide.

5. THE DYE-STUFF INDICATORS

According to W. Ostwald dye-stuff indicators such as litmus and phenolphthalein *are weak acids or bases which show different colours in undissociated and in ionized state*. The free indicators are only little ionized and show the colours of the undissociated molecules, but when neutralized and transformed into salts, their colours change to those of their ions.

According to this theory, indicators may be divided into acid and basic indicators. This classification has, however, nothing to do with their sphere of applicability, their sensitivity, or their quality. In the following the indicator theory will be discussed for an acid indicator. A corresponding theory may be developed for a basic indicator with exactly corresponding results.

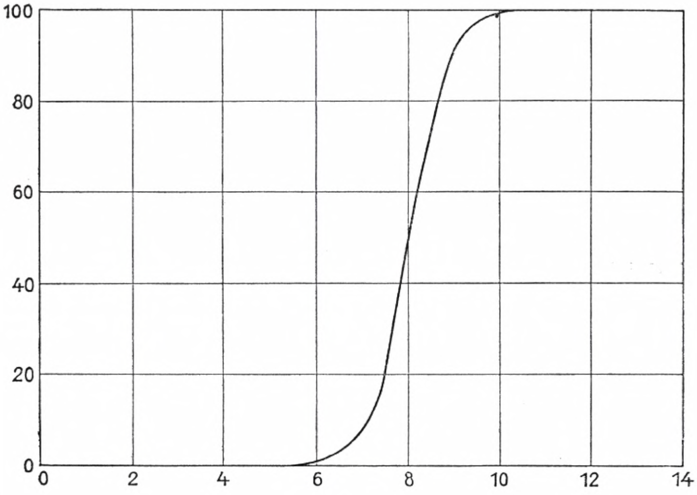


Fig. 1.

An indicator acting as a monobasic acid may be written HI; in solution it will be present, either as free indicator acid HI with "acid" colour, or as indicator-ion I^-, with "alkaline" colour. The ratio between the concentrations of the two differently coloured indicator forms is determined by the hydrogen-ion concentration in the solution, and the dissociation constant, K_I, of the indicator; this follows from the dissociation equation of the indicator acid:

$$C_{H^+} \cdot \frac{C_{I^-}}{C_{HI}} = K_I \, .$$

On taking logarithms, and designating the strength exponent of the indicator acid as pI:

$$\log \frac{C_{I^-}}{C_{HI}} = p\mathrm{H} - p\mathrm{I} \, .$$

It appears from these equations that the colour shown by an indicator depends only on the reaction of the solution. When the hydrogen-ion concentration in the solution is equal to the dissociation constant of the indicator-acid, the indicator is half-way transformed; when the hydrogen-ion concentration is larger, the indicator is mainly present with acid colour, and when smaller, the alkaline colour predominates. The curve drawn, fig. 1, shows how the dissociation of the indicator changes with the reaction. As abscissa is used the hydrogen-ion exponent and as ordinate the quantity of the basic form of the indicator, expressed in per cent of the total quantity of indicator present: $100\ C_{I^-}/(C_{HI} + C_{I^-})$.

The curve is drawn for an indicator with strength exponent 8. For an indicator with another strength exponent the curve will be congruent with the one drawn,

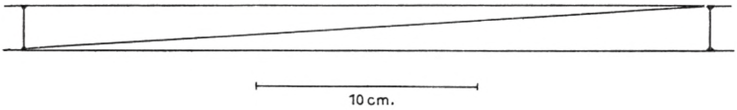


Fig 2.

only displaced the proper distance parallel to the abscissa axis. The colour-transformation interval, expressed in *p*H units, is the same for all indicators.

When both indicator forms are coloured, as in the case of litmus, it will hardly be possible with the naked eye to distinguish the presence of $\frac{1}{20}$ of the one colour in $\frac{19}{20}$ of the other colour. In other words, as soon as the hydrogen-ion exponent in the solution is $\log\frac{\frac{19}{20}}{\frac{1}{20}} = 1.28$ larger or smaller than the strength exponent of the indicator, the indicator will be outside the interval within which its colour markedly changes with reaction. The entire change-interval will then only comprise 2.6 *p*H units, i.e. 1.3 units on each side of the strength exponent of the indicator.

Demonstration of the theory. To prove the correctness of the formulae for indicator change given here, colorimetric measurements are used to determine the ratio between the two indicator forms in solutions with known hydrogen-ion exponents. Such a measurement may be made, for instance as follows:

Using thin glass plates joined together with pitch, a cuvette, 30 cm long, 10 cm high, and 2 cm wide, is made. In this a long vertically placed glass plate is fastened diagonally. Fig. 2 shows the cuvette seen from above. The diagonal plate divides the cuvette into two wedge-shaped containers. One of these is filled with a solution of the indicator, so acid that it shows the pure acid colour of the indicator, the other container is filled with an alkaline solution of the indicator which shows the pure alkaline colour. The concentration of the indicator in both these solutions must equal the concentration of the indicator in the solution to be tested. Looking through the cuvette in different places, we always look through the same quantity of indicator, but the ratio between the quantities of the two forms is different. It is a simple matter to place a small graduated scale so that this ratio can be directly read. The indicator solution in which the ratio between the two indicator forms is to be determined is poured into a small cuvette, whose width equals the combined widths of the two sections of the large cuvette. In moving this small cuvette along the top of the large one, a point may be found where the large cuvette shows the same colour tone as the small cuvette. This is easily done by shading off and comparing the colour of a narrow section in the large cuvette with the colour in the small cuvette standing on top of it.

This arrangement is well-suited for demonstration in a small lecture room. Using it in a lecture, I was able to find the results given in table 4 and from those to calculate the strength exponents $p\mathrm{I}$ for methyl orange according to the formula

$$p\mathrm{I} = p\mathrm{H} + \log \frac{a}{1 - a}\,.$$

In this formula a denotes the fraction of the indicator present with red colour. The agreement between the strength exponent values listed in the last column proves the correctness of the formula used.

Table 4. State of methyl orange in solution

$p\mathrm{H}$	C_{H^+}	Percentage of yellow colour	Percentage of red colour	$p\mathrm{I}$
3	10^{-3}	20	80	3.60
3.5	$10^{-3.5}$	45	55	3.59
4	10^{-4}	70	30	3.64

Table 5 shows the transformation intervals of 22 indicators. S. P. L. Sørensen determined these transformation intervals by adding the indicator in question to different solutions with known hydrogen exponents and compared the colour of the indicators in these solutions with each other. The $p\mathrm{H}$ intervals given comprise the hydrogen-ion exponents within which the colour of the indicator is so sensitive to changes in the reaction, that, by comparing the colour tone of the indicator in the solution with the colour tone in the standard solutions with known hydrogen-ion exponents, it is possible to determine the unknown hydrogen-ion exponent in the solution with an accuracy of 0.02—0.05 units *(colorimetric reaction determination)*. Outside the intervals stated here, the colour of the indicator only shows that the reaction of the solution is more acid or more alkaline than corresponding to the transformation interval, without permitting quantitative statements.

Table 6 contains transformation intervals according to Salm for some indicators not found in S. P. L. Sørensens table.

The titration exponent. The indicators are chiefly used in titrating acids and bases. If an indicator is always used with the same concentration and titrated to the same colour tone, the titrated solutions will also have the same reaction, i.e. they have been titrated to a definite hydrogen-ion exponent. This exponent we call the *titration exponent* of the indicator and designate as $p\mathrm{T}$. For an acid

Table 5. Transformation intervals for indicators according to Sørensen

Indicator	*p*H	Amount of indicator to 10 cc.
Methyl violet	0.1 - 1.5	8 — 3 drops 0.05 per cent
— —	1.5 - 3.2	10 — 4 - 0.01 - -
Mauveine	0.1 - 1.5	8 — 3 - 0.05 - -
—	1.5 - 2.9	10 — 4 - 0.01 - -
Benzene-azo-diphenylamine	1.2 - 2.1	15 — 6 - 0.01 - -
m-Benzenesulphonic acid-azo-diphenyl-amine	1.2 - 2.3	5 — 3 - 0.01 - -
p-Benzenesulphonic acid-azo-diphenyl-amine	1.4 - 2.6	5 — 3 - 0.01 - -
p-Benzenesulphonic acid-azo-benzyl-amine	1.9 - 3.3	6 — 3 - 0.01 - -
Benzene-azo-benzyl-aniline	2.3 - 3.3	10 — 5 - 0.02 - -
p-Benzenesulphonic acid-azo-*m*-chlorodiethylaniline	2.6 - 4.0	5 — 3 - 0.01 - -
Benzene-azo-dimethylaniline	2.9 - 4.0	10 — 5 - 0.01 - -
Methyl orange	3.1 - 4.4	5 — 3 - 0.01 - -
Benzene-azo-α-naphthylamine	3.7 - 5.0	20 —10 - 0.01 - -
p-Benzenesulphonic acid-azo-α-naphthylamine	3.5 - 5.7	12 — 8 - 0.01 - -
Methyl red	4.2 - 6.3	4 — 2 - 0.02 - -
p-Nitrophenol	5.0 - 7.0	20 — 3 - 0.04 - -
Neutral red	6.8 - 8.0	20 —10 - 0.01 - -
Rosolic acid	6.9 - 8.0	15 — 6 - 0.04 - -
p-Benzenesulphonic acid-azo-α-naphthol	7.6 - 8.9	10 — 4 - 0.01 - -
α-Naphtholphthalein	7.3 - 8.7	12 — 4 - 0.04 - -
Phenolphthalein	8.3 -10.0	20 — 3 - 0.05 - -
Thymolphthalein	9.3 -10.5	10 — 3 - 0.04 - -
p-Nitrobenzene-azo-salicylic acid	10.1 -12.1	10 — 5 - 0.01 - -
p-Benzenesulphonic acid-azo-resorcinol	11.1 -12.7	10 — 5 - 0.01 - -

Table 6. Transformation intervals for indicators according to Salm

Indicator	*p*H	Indicator	*p*H
Congo red	4	α-Naphthol benzoin	10
Sodium alizarine sulphonate	5	Tropaeolin O	12
Cochineal	5.5	Trinitrobenzene	13.5
Lacmoid	6	Benzopurpurin B	13.5
Litmus	7	Safranin	15.5
Cyanin	7.5		

indicator the titration exponent will always be close to the strength exponent of the indicator but in certain cases it may deviate more than 1 unit from it. In table 7 the approximate titration exponents for some of the most important indicators are shown.

Table 7. Approximate values for the titration exponents of the most important indicators

Indicator	pT	Colour tone to which is titrated	Amount of indicator per 100 cc.
Methyl orange	4	yellow with reddish tone	0.1 cc. 0.1 per cent
Methyl red	5.5	— — — —	0.1 — 0.1 - -
Rosolic acid	6.5	pale brown with rosa tone	1 — 0.1 - -
Litmus	6 7	red with bluish tone blue with reddish tone	1 cc. of 2 per cent solution of Kahlbaum's extract
Phenolphthalein	8	weakly red	0.7 cc. 1 per cent
	9	— —	0.04 — 0.1 - -

In titration analysis the titration exponents of the indicators are of fundamental interest. It is their values which determine the *useful ranges* of the indicators. On the other hand, the value of the titration exponent does not determine the general usefulness of an indicator. The usefulness of an indicator which, judged from its titration exponent, seems suitable for the titration in question, depends upon the accuracy with which a definite hydrogen-ion exponent may be fixed by means of the indicator. The more abrupt and contrasting the colour change, the better is the indicator. Under ordinary conditions we cannot expect to hit the pH value with a greater accuracy than 0.3 pH units, even when a good indicator is used.

6. THEORY OF TITRATION

When the amount of an acid is to be determined by titration it is natural to ask: *To what reaction is it best to titrate?* The answer must be: titrate to the reaction characteristic for the salt of the acid in question. We are, however, not told whether it is also necessary to use an indicator which changes colour at just that reaction, or whether other indicators can be used as well. We are led somewhat further by asking: *How great is the error when titrating with a definite indicator?* When this question is answered for the different indicators it is easy enough to decide which indicators are suitable and which are unsuitable for our purpose.

The titration error and formulae for computing it. We assume that we are to titrate an acid HS with strength exponent pS using an indicator with titration exponent pT. When titrating a weak acid a strong base should always be used, sodium hydroxide for instance. We will therefore compute the error under this assumption. The source of error in a titration is due to the fact that the solution, when completely titrated, should only contain the salt, but actually, contains some acid or base or both. Free acid may be present in our solution both as hydrogen ions and as undissociated acid molecules, free base must chiefly be present as hydroxyl ion, since sodium hydroxide is strongly ionized. Therefore there are three kinds of error to take into account:

1. Hydrogen-ion error (H^+ – error)
2. Hydroxyl-ion error (OH^- – error)
3. Acid error (HS – error)

A closer consideration will show that each of the three errors must be small if the titration shall be exact. Even though some of the errors are positive and others negative we cannot be sure that they compensate each other to any great extent.

We will first write the formulae for these three kinds of error. In the case of the *hydrogen-ion error*, when the total volume at the close of the titration is designated v and the standard solution is n normal:

$$H^+ \text{ – error} = C_{H^+} \cdot \frac{v}{n} = 10^{-pT} \cdot \frac{v}{n} \text{ cc. standard solution.}$$

This expression is found by computing the amount of n normal solution, corresponding to v cc. of normality C_{H^+}. Analogously the hydroxyl-ion error may be expressed:

$$OH^- \text{ – error} = C_{OH^-} \cdot \frac{v}{n} = 10^{-(14-pT)} \cdot \frac{v}{n} \text{ cc. standard solution.}$$

In dealing with the *acid error* it is easiest to give its relative value, i.e. its value in relation to the total amount of acid to be titrated. Since the main part of the acid at the end of the titration is present in the solution as S^--ions, the relative value of the acid error is found by computing the ratio between the number of undissociated molecules and anions, in the completely titrated solution. This is found from the dissociation equation of the acid:

$$\frac{C_{HS}}{C_{S^-}} = \frac{C_{H^+}}{K_S} = \frac{10^{-pT}}{10^{-pS}} = 10^{pS-pT} .$$

Hence, the relative acid error $= \dfrac{C_{H^+}}{K_S} = 10^{pS-pT}$.

Examples. Let us compute these three kinds of error in certain definite cases using the formulae found.

Example 1. Titration of acetic acid ($pS = 4.75$) with phenophthalein in small quantities ($pT = 9$) in a total volume of 100 cc. ($v = 100$) with 0.1 normal sodium hydroxide ($n = 0.1$).

H^+ – error: negligible, since the reaction at the end point of the titration is alkaline.

$$\text{OH}^- - \text{error: } 10^{-(14-9)} \cdot \frac{100}{0.1} = 0.01 \text{ cc.}$$

$$\text{relative HS} - \text{error: } 10^{4.75-9} = 10^{-4.25} = \frac{1}{18000} = \frac{1}{180} \text{ per cent.}$$

From this we conclude that the titration of the acid with phenolphthalein as indicator, is extremely exact.

Example 2. Same titration with litmus as indicator to distinct blue colour (pT = 7).

$$\text{H}^+ - \text{error} = 10^{-7} \cdot \frac{100}{0.1} = 10^{-4} \text{ cc.}$$

$$\text{OH}^- - \text{error} = 10^{-7} \cdot \frac{100}{0.1} = 10^{-4} \text{ cc.}$$

$$\text{relative HS} - \text{error} = 10^{4.75-7} = 10^{-2.25} = \frac{1}{180}.$$

Titrating acetic acid with litmus as indicator, by which one titrates very close to the true neutral point, the acid error is 1/180 of the entire amount of acid. At the close of titration this fraction of the acid is present in the solution as free acid. Titrating acetic acid with litmus indicator is not as exact as titrating it with phenolphthalein.

Example 3. The same titration using methyl orange (pT = 4) as indicator.

$$\text{H}^+ - \text{error} = 10^{-4} \cdot \frac{100}{0.1} = 0.1 \text{ cc.}$$

$$\text{OH}^- - \text{error: negligible.}$$

$$\text{relative HS} - \text{error} = 10^{4.75-4} = 10^{0.75} = \text{about } 6.$$

With methyl orange as indicator, the acid error is very large and the hydrogen-ion error is appreciable. Methyl orange is of no use at all for the titration of acetic acid. The value 6 for the acid error indicates that methyl orange changes from red to yellow when only 1/7 of the acetic acid is changed to acetate, i.e. when 6/7 of the total acetic acid is still in solution as free acid.

The factors determining the value and influence of titration errors. The values of hydrogen-ion and hydroxyl-ion errors are quite independent of the strenght of the acid. The errors are constant, as long as the same indicator is used, whether one titrates hydrochloric acid, acetic acid or boric acid. To keep these errors under 0.01 cc. in titrations with 0.1 normal sodium hydroxide in 100 cc. solution ("normal titration"), *the titration exponent of the indicator must lie between 5 and 9.* Methyl red, litmus, and phenolphthalein fulfill these requirements. If the titration exponent of the indicator lies outside the interval 5 to 9, as does that of methyl orange, it is necessary either to titrate in a smaller volume than 100 cc., or titrate with a solution stronger than 0.1 normal. Otherwise we must expect a larger error than 0.01 cc.

It is characteristic of the *acid error* that it does *not* depend on the volume of the solution, but depends solely on the strength of the acid and the transition point of the indicator. If the acid error must be less than 0.1 per cent, the titration exponent of the indicator must be 3 units larger than the strength exponent of the acid; we have the equation:

$$\text{relative HS-error} = 10^{p\text{S}-p\text{T}}$$

This result may be expressed as follows: *At the end of the titration, the reaction must lie at least 3 units in the pH scale to the right of the strength exponent of the acid.* If an accuracy of 1 per cent is sufficient, the titration exponent may lie only 2 units to the right of the strength exponent of the acid etc.

When titrating weak acids, it is accordingly best to select an indicator with a transition point so far beyond on the alkaline side of the neutral point as is compatible with a small hydroxyl-ion error. In accord with this condition we prefer an indicator with titration exponent 9 when titrating weak acids. Since phenolphthalein has just this titration exponent, it is particularly well-adapted to the titration of weak acids. Using phenolphthalein as indicator, it is possible, in 100 cc. solution with 0.1 *N* sodium hydroxide to titrate acids with dissociation constants down to 10^{-6} with an accuracy of 0.1 per cent. In titrating weaker acids we must either tolerate an error above 0.1 per cent, or use stronger titration solutions in smaller volumes with an indicator whose titration exponent is larger than 9. As yet, no indicator with titration exponent 9.5—10, and well adapted to this use, seems to have been found.

When titrating *weak bases* a strong acid should be used as titrating solution. The errors to be expected in titrating weak bases with strong acids are subject to the same rules as the errors in titrating strong acids with weak bases. There is nothing new to be said in regard to the hydrogen-ion error and hydroxyl-ion error. Instead of an acid error, in this case a *base error* occurs, dependent on the hydroxyl-ion exponent and the strength exponent of the base, in the same way as the acid error depends on the hydrogen-ion exponent and the strength exponent of the acid. If titration is to be accurate to 0.1 per cent the hydroxyl-ion exponent must, at the end point of titration, be at least 3 units larger than the strength exponent of the base i.e. the *reaction at the end point of the titration, must lie at least 3 units in the hydroxyl-ion exponent scale to the right of the strength exponent for the base.*

Titration of ammonia, with $p\text{B} = 4.75$, requires the use of an indicator, for which, at the transition point the hydroxyl-ion exponent is larger than $4.75 + 3 = 7.75$. Its titration exponent must consequently be less than $14 - 7.75 = 6.25$. When titrating with litmus to clear red, the titration exponent will be about 6 and thus fulfill the requirement, consequently litmus may be used in ammonia titration.

The smaller the titration exponent of the indicator, the smaller the "*base error*" in titrations of weak bases. The smallest titration exponent which should be used in ordinary titration is $pT = 5$. If the titration exponent is smaller the hydrogen-ion error will be too large. The end point of titration $pH = 5$ is obtained using methyl red; this indicator is just as advantageous in titrating weak bases as is phenolphthalein in titrating weak acids. With no difficulty whatsoever, methyl red can be used to titrate bases with strength exponents up to 6. Ammonia ($pB = 4.75$) is very satisfactorily titrated with this indicator, and hydrazine ($pB = 5.5$) as well, but we are here close to the limit. For even weaker bases, methyl orange, with titration exponent 4, can be used. If by using a sufficiently small volume, and sufficiently strong titration solution, the hydrogen-ion error is kept sufficiently small, methyl orange may be used with an accuracy of 0.1 per cent for titrating bases with dissociation constants down to 10^{-7}, and even weaker bases with an accuracy of 1 per cent.

Example. The strength exponent of the base pyridine is 8.8. To keep the base error in a titration of pyridine below 1 per cent the hydroxyl-ion exponent must, at the end point of titration, be equal to, or larger than 10.8. Consequently, the titration exponent must be equal to, or smaller than 3.2. When we titrate with methyl orange to so strong red colour, that more than one half of the methyl orange is changed to the red form, we are approximately working with this titration exponent. When we furthermore titrate with 1/5 normal hydrochloric acid and keep the volume below 50 cc. the hydrogen-ion error may be expressed:

$$H^+ - \text{error} = 10^{-3.2} \cdot \frac{50}{0.2} = \frac{1}{16}\,\text{cc.}$$

This estimate shows the accuracy which may be expected in titrations of pyridine. The simplest way to determine the colour tone at which titration should end, is to make a solution of the pyridine salt formed in the titration, and then titrate to the colour of methyl orange in that solution.

Insensitivity of indicators to very weak acids. The use of methyl orange in titrating alkali hydroxydes which contain carbonates is important and interesting from a theoretical point of view. This use depends on the insensitivity of methyl orange to carbonic acid. When hydrochloric acid is added to sodium carbonate, methyl orange first changes to red when all the carbonate has been transformed to chloride.

We shall consider how weak an acid must be, in order that it should not be affected by the titration. The requirement is that, at the end point of the titration, the acid must mainly be present as an undissociated hydrogen compound. The fraction present as ion causes an acid error.

If we designate an acid, which we wish should not be affected, as Hs, the relative value of the acid error is C_{s^-}/C_{Hs}.

On introducing the dissociation equation for the acid, we find:

$$\text{relative Hs} - \text{error} = \frac{C_{s}}{C_{Hs}} = \frac{K_s}{C_H} = 10^{pT - ps}$$

If this error is to be small, the dissociation constant of the acid must be less than the hydrogen-ion concentration at the end point of the titration, or, as it may otherwise be expressed: the strength exponent of the acid must be larger than the titration exponent of the indicator. If the strength exponent is 2 units larger than the titration exponent, the acid error may be estimated to 1 per cent, if it is 3 units larger the value of the error is reduced to 0.1 per cent.

Example. The titration exponent of methyl orange is 4; the smaller of the two strength exponents of carbonic acid is 6.52. To the difference 2.52, corresponds a relative acid error of $10^{-2.52} = 0.003$, i.e. when a titration with methyl orange as indicator is made, 0.003 part = 0.3 per cent of the carbonic acid present is titrated as monobasic acid, the rest of the carbonic acid remains as free acid at the end of the titration. If the titration of acid is continued until methyl orange shows an orange colour, the titration is carried to $pT = 3.5$ instead of $pT = 4$, and in that case only $10^{3.5-6.5} = 0.001$ part of the amount of carbonic acid is affected by the titration. The greater accuracy attained in this way will, however, in many instances be lost by an increase of the hydrogen-ion error.

The following little table shows the carbonic-acid sensitivity of the most important indicators. The figures indicate how many equivalents base each carbonic-acid molecule present binds.

Methyl orange	$pT = 3.5$	0.001
	$pT = 4$	0.003
Methyl red	$pT = 5$	0.03
	$pT = 5.5$	0.1
Litmus	$pT = 6$	0.3
	$pT = 7$	1
Phenolphthalein	$pT = 8$	1
	$pT = 9$	1.5

As seen from the table *methyl red* is but slightly sensitive to carbonic acid in comparison with litmus and phenolphthalein. When this indicator is used, the amounts of carbonic acid present in ordinary distilled water and in acid solutions made from it, are, as a rule, no cause for error; this is not the case with litmus and phenolphthalein. When these two indicators are used, it is necessary to boil away the carbonic acid. *Methyl orange* is even less sensitive to carbonic acid than methyl red.

Titration of mixtures. When a mixture of several acids and bases is to be titrated, it is necessary to take into account not only the hydrogen-ion error and hydroxyl-ion error but also a base and acid error for each base and acid present in the mixture. Therefore, for the sake of accuracy in the titration, the hydrogen-ion exponent, at the end of titration must not lie near to the strength exponent of anyone of the acids present in the solution, (nor must the hydroxyl-ion exponent at the end of titration lie close to the strength exponent of any of the bases present in the solution). The problem is to locate a point on the reaction scale, sufficiently removed from the strength exponents of the acids and bases present, and to select an indicator which changes at this point. It is hardly necessary to state that the smaller the quantity of acid present, the closer may the hydrogen-ion exponent be to the strength exponent of the acid, and it is evident that only those acids (bases) whose strength points on the reaction scale lie to the left (right) of the end point of the titration are included in the titration, whereas the acids (bases) whose strength points lie to the right (left) of the end point of the titration are not affected by the titration.

A *polybasic acid* behaves during titration almost like a mixture of monobasic acids with the same strength exponents as the polybasic acid. In a titration in which the titration exponent is less than all the strength exponents of the polybasic acid, the acid is not included in the titration; if the titration exponent lies between the first and second strength exponent, preferably just in the middle, the acid is titrated as a monobasic acid; if the titration exponent lies between the second and third strength exponent, the acid is titrated as dibasic; if the titration exponent is larger than all the strength exponents of the acid, the acid is titrated with its complete basicity.

1. Example. The strength exponents of carbonic acid are 6.52 and 10.22. If a titration exponent is selected half-way between these two figures, i.e. about 8.4, the carbonic acid is titrated as a monobasic acid. To the end point $p\mathrm{T} = 8.4$, phenolphthalein can be used as indicator, and carbonic acid will react with this indicator as a *monobasic acid.* As the interval between 8.4 and the two strength exponents of the carbonic acid 6.52 and 10.22 hardly equals 2, the accuracy to be expected from titrating carbonic acid with phenolphthalein is not very great, less than 1 per cent.

2. Example. The strength exponents of phosphoric acid are 1.96, 6.7 and 12.44. When titration is performed with methyl orange as indicator ($p\mathrm{T} = 4$) the titration exponent lies between the 1st and 2nd strength exponent, and the phosphoric acid is titrated as a *monobasic acid.* In this titration, the distance of the titration exponent from the strength exponents is larger than 2, and the accuracy obtainable is somewhat greater than 1 per cent. If phosphoric acid is titrated with phenolphthalein, the titration exponent is about 9, and it lies between the 2nd and 3rd strength exponent of phosphoric acid; phosphoric acid, then, is titrated as a *dibasic acid.* It is best to titrate to a hydrogen-ion exponent located exactly half-way between the two strength exponents, that is to 9.6. Titration must therefore continue to strong red colour. With this titration it is possible to obtain an accuracy of nearly 0.1 per cent, for the distance between 9.6 and each of the two strength exponents (6.7 and 12.44) is here almost 3. However, we must remember, that when working with a titration exponent larger than 9, the hydroxyl-ion error may easily decrease the accuracy of the titration.

The important subject whose main points are outlined in this little paper, has been more thoroughly discussed in several larger articles. The hydrogen-ion exponent, its experimental determination and importance especially in the field of biology is described by S. P. L. Sørensen (in *Compt. rend. trav. lab. Carlsberg* **8** (1909) and in *Asher-Spiros Ergeb. Physiol.* **12** (1912) 393) and by L. Michaelis (in *Die Wasserstoffionenkoncentration*, Verlag Springer, Berlin). Titration analysis and the theory of indicators are discussed in a paper by A. A. Noyes (*J. Am. Chem. Soc.* **32** (1910) 815). The author of the present article has written a monograph on the subject which may be consulted by those who wish a more comprehensive treatment of the subject along the same lines as those followed in the present paper (*Die Theorie der alkalimetrischen and acidimetrischen Titrierungen. Sammlung chemischer und chemisch-technischer Vorträge.* **21** (1914)).

Investigations on the Factors Which Determine the Reaction of the Soil

I. On the Determination of the Acid and Basic Properties of a Soil

II. On the Reaction of Solutions Saturated With Calcium Carbonate

NIELS BJERRUM AND J. K. GJALDBÆK

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SUMMARY

For the purpose of describing the acid and basic properties of a soil various quantities may be employed. Firstly, a statement of the *reaction* may be used. However, it is not sufficient by observing the colour of an indicator to obtain a qualitative statement as to the reaction. The best thing to do is to describe the reaction by stating the hydrogen-ion concentration or the hydrogen-ion exponent (p_H), and these quantities may be determined either in the soil water or in an extract of the soil prepared according to a standardized method. The reaction determined will vary somewhat according to the mode of preparation of the solution used. Secondly, the acid nature of a soil may be described by means of a determination of the *acidity*, i.e. by determining the amount of base required to neutralize the soil. Thirdly, it is possible to obtain a figure describing the basic properties of the soil by means of a corresponding determination of the *basicity*.

It is essential not to confuse the concepts thus defined, namely reaction, acidity and basicity; because determinations of these quantities cannot replace each other, each of them having a separate meaning.

It appears from a summary of the methods which have hitherto been used for the purpose of determining the acid or basic nature of a soil that, when con-

sidered more closely, all the methods aim at a determination of either reaction, acidity or basicity.

The result of a determination of the acidity or basicity of a sample of soil can vary highly according to the method used. Besides several other reasons, it is of great importance that the so-called neutral point to which the soil is brought by addition of base or acid is not characterized by the same reaction in the different methods. In order to obtain a thorough knowledge of a soil, it is a useful procedure to perform the determinations of acidity and basicity according to several different methods, because the various methods will often each supply separate contributions towards the knowledge of the soil. The best thing would be if, for each reaction (p_H), the amount of acid or base, respectively, required to produce this reaction in the soil was determined. By means of electrometric titration it is possible to obtain a series of such results which may be illustrated by means of a *titration curve*.

The exact form of the titration curve is — to an extent which should not be underestimated — dependent on the method of titration used (time, temperature, whether CO_2 has been present or not, the solution used for titration etc.), and it appears from this that a complete picture of the acid and basic properties of a soil is only obtained by means of several titration curves and is consequently of a very complicated nature.

If we could succeed in finding the laws according to which the individual acid and basic constituents of the soil determine the reaction, the amount of these constituents would provide a simple measurement of the acid and basic properties of the soil, because it would then be possible by means of these laws and from the content of such constituents in the soil to calculate all its acid and basic properties. We have therefore set ourselves the task of investigating these laws and have, in the second part of this paper, made a beginning by investigating the influence of calcium carbonate on the reaction.

It follows from the law of mass action that the hydrogen ion concentration (c_{H^+}) in an aqueous solution saturated with calcium carbonate is determined according to the following equation by the calcium ion concentration ($C_{Ca^{++}}$) and the carbon dioxide pressure (p_{CO_2}):

$$C_{H^+} = K \cdot \sqrt{C_{Ca^{++}}} \cdot \sqrt{p_{CO_2}}$$

Whence, by taking the logarithms, we obtain the following expression for p_H:

$$p_H = -\log K - \tfrac{1}{2}\log C_{Ca^{++}} - \tfrac{1}{2}\log p_{CO_2}$$

The above formulae are limiting laws which are exactly valid only for infinitely dilute solutions. For ionic concentrations (C_{ion}) up to 0.2 normal the following formula gives a more exact result:

$$p_H = -\log K - \tfrac{1}{2}\log C_{Ca^{++}} - \tfrac{1}{2}\log p_{CO_2} + 0.3\sqrt[3]{C_{ion}}\,.$$

For ionic concentrations higher than 0.2 normal this formula does not apply either, as the hydration of the calcium ion has a disturbing influence.

The value of K, the reaction constant of calcium carbonate, has been determined according to two different methods.

By electrometrical measurements of p_H in solutions of calcium chloride saturated with calcium carbonate at different carbon dioxide pressures we have found $\log K$ at 18° C to be -5.02.

In these measurements *precipitated* calcium carbonate was employed. By a number of measurements with *Iceland spar* results were obtained which agreed within the experimental error with the above measurements. *Aragonite*, however, gave hydrogen-electrode potentials which on an average were 3.5 millivolts larger, which means a value of $\log K$ increased by 0.06. This higher value of $\log K$ for aragonite is in agreement with available measurements of the relationship between the solubilities of aragonite and Iceland spar.

By combining Schlösing's determinations of the solubility of calcium carbonate in water containing carbon dioxide with Bohr's determinations of the solubility of carbon dioxide in water and with Walker and Cormack's and Kendall's determinations of the conductivity of water containing carbon dioxide, it is possible to calculate the value of $\log K$, and in this way we have obtained a value of -5.05.

The temperature coefficient of $\log K$ has, according to the same determinations been calculated to be $+0.0045$. This value can also be obtained by means of thermo-chemical measurements performed by Julius Thomsen.

In all our calculations we have assumed that the calcium salts were completely dissociated, and we have calculated p_H according to the following equation:

$$p_H = (E - E_0)/0.0577,$$

where E is the potential of a hydrogen electrode in the solution, and E_0 the potential of a hydrogen electrode in a solution with an apparent hydrogen ion activity of 1. When the measurement is performed with a 3.5 M potassium chloride calomel electrode as reference half-cell, $E_0 = 0.252$, and when using a 0.1 M potassium chloride calomel electrode, $E_0 = 0.335$.

According to our formulae it is quite possible for a soil which contains calcium carbonate to have a p_H which is less than 7 and consequently to have an acid reaction. The greater the amount of carbon dioxide in the air of the soil and the greater the calcium ion concentration in the soil water, the more acid the reaction of the soil will be.

As the reaction of a saturated solution of calcium carbonate is only dependent on the carbon dioxide pressure and the calcium ion content of the solution, it is natural to detect and to estimate calcium carbonate present in a soil by measuring the p_H in a solution of calcium chloride saturated with the soil in question at a certain carbon dioxide pressure. Under these circumstances the presence of calcium carbonate in a soil will manifest itself through the maintenance of a constant p_H even after addition of hydrochloric acid and stirring, the value of p_H only decreasing when all the calcium carbonate present has been dissolved by the acid added.

The Constitution of Ampholytes, Particularly That of Amino Acids, and Their Dissociation Constants

NIELS BJERRUM

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1. Bredig[1] is probably the first to have called attention to the fact that an amphoteric electrolyte, and particularly betaine, is an internal salt, i. e. that the same molecule may contain a positive and a negative charge which neutralize each other. A few years later Küster[2] put forward a theory to explain the colour change of methyl orange. According to this theory methyl orange may exist in an electrically charged and yet electrically neutral form. For according to Küster yellow methyl orange is:

$$(CH_3)_2N.C_6H_4.N_2.C_6H_4.SO_3^-$$

and the red form, existing in acid solutions:

$$^+H(CH_3)_2N.C_6H_4.N_2.C_6H_4.SO_3^- \;.$$

Küster gives the name "Zwitterionen" ("ampho-ions") to "ions" like red methyl orange which carry a positive and a negative charge at the same time and consequently cannot contribute to the conduction of current. It is usually supposed that such forms of ions only exist in small quantities, and up to now the dissociation constants of amino acids have always been calculated on the assumption that these forms of ions are unimportant. Thus Walker[3] writes: "Die weitere Komplikation durch Annahme eines Zwitterions,

$$^+NH_3.R.COO^- \;,$$

braucht nicht betrachtet zu werden, da bei dem gegenwärtigen Stand unserer Kenntnisse über amphotere Elektrolyte, diese Annahme nicht zur Erklärung der beobachteten Erscheinungen nötig ist." Michaelis[8] is even more emphatic in the new edition of his excellent book on concentration of hydrogen ions (p. 62). He writes of the amino acid ampho-ion: "Seine Menge ist zweifellos auch stets verschwindend klein", and later: "Wir haben bisher kein Mittel, die Existenz der Zwitterionen nachzuweisen. Wegen ihrer stets sehr geringen Konzentration sind diese auch nicht imstande, das Gleichgewicht zwischen den anderen, bekannten Dissoziationsformen der Aminosäure messbar zu verschieben."

But as I shall try to show in the following, the situation is entirely the reverse. *For in all physiologically important amino acids the non-ionised (i.e. not as cations or anions existing) part of the dissolved matter occurs mainly as ampho-ions.* Only the dissociation constants which are calculated on the basis of this assumption will obtain really plausible values. Fortunately it does not matter whether the old or the new view is taken as a basis for calculating the equilibrium between cations, anions, and electrically neutral molecules. The important results obtained by Bredig, Walker, Michaelis and others in this field will still hold and only become clearer.

2. Küster arrived at his idea of the state of methyl orange in acid red solutions through the following considerations, which are still convincing. As all sulphonic acids are strong acids, the sulphonic group of methyl orange must always be strongly dissociated; the ionisation in the sulphonic group cannot, therefore, have anything to do with the colour change. Accordingly methyl orange must be supposed to act as an indicator because it contains an *amino* group. The colour changes when the latter group is turned into an electrically charged ammonium group by a hydrogen ion. This is also in accordance with the fact that methyl orange as an indicator is very similar to its mother substance dimethylamino-azo-benzene, which has no sulphonic group. The colours of both indicators are alike, and their colour change occurs in the same range of hydrogen-ion concentration (colour transformation range according to Sørensen[4] for methyl orange $p_H = 3.1 - 4.4$, for dimethylamino-azo-benzene $p_H = 2.9 - 4.0$). Thus according to Küster the red form of methyl orange is not:

$$(CH_3)_2N.C_6H_4.N_2.C_6H_4.SO_3H \ ,$$

but

$$^{+}HN(CH_3)_2.C_6H_4.N_2.C_6H_4.SO_3^{-} \ .$$

According to the views of organic chemists a quinoid transformation takes place giving:

$$^{+}(CH_3)_2N\!:\!C_6H_4\!:\!N.NH.C_6H_4.SO_3^{-} \ .$$

However, this is of no importance here.

Küster's train of thought seems very convincing. But it can only be applied to amino acids which are indicators, consequently for example not to amino-acetic acid. But as it is necessary in certain cases, as shown by Küster, to assume that the ampho-ion is the main form, it is likely that the same would occur in many other cases. And furthermore when it is remembered that 99.5 per cent of ammonium acetate in aqueous solution exists as:

$$NH_4^+ + CH_3COO^- \ ,$$

and only 0.5 per cent is hydrolysed into:

$$NH_3 + CH_3COOH \ ,$$

it seems simplest to assume that amino-acetic acid exists mainly in aqueous solution as:

$$^+NH_3.CH_2.COO^- \ .$$

We must expect the carboxyl group of amino-acetic acid to possess acidic properties, almost like those of acetic acid, and the amino group to possess basic properties, almost like those of ammonia. We shall, therefore, assume that the undissociated molecules of amino acids have a positive and a negative charge at the same time. On this assumption we shall calculate the dissociation constants of amino acids numerically.

3. According to the old view an amino acid $NH_2.R.COOH$ exists in aqueous solutions in three forms: as a cation $^+NH_3.R.COOH$, as an uncharged molecule $NH_2.R.COOH$, and as an anion $NH_2.R.COO^-$. The ratio between the three forms varies with the hydrogen-ion concentration of the solution. Let A^+, A, and A^- be the concentrations of these forms, and H^+ and OH^- the concentrations of the hydrogen ions and hydroxyl ions, respectively. The acidic dissociation constant k_a will then be defined by:

$$\frac{A^- \cdot H^+}{A} = k_a \qquad (1)$$

and the basic dissociation constant k_b by:

$$\frac{A^+ \cdot OH^-}{A} = k_b \ . \qquad (2)$$

According to the new view an amino acid in solution exists partly as the cation $^+NH_3.R.COOH$, and partly as the anion $NH_2.R.COO^-$ as above, but moreover as the ampho-ion $^+NH_3.R.COO^-$. We shall name the concentration of the latter form A^{+-}.* The dissociation of the carboxyl group then occurs according to the equation:

$$^+NH_3.R.COOH = {}^+NH_3.R.COO^- + H^+ \ ,$$

and for the corresponding acidic dissociation constant K_S we have:

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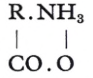
* In agreement with the hypothesis according to which neutral salts like NaCl, NH_4NO_3 are completely ionised, we shall not take into consideration the form:



$$\begin{array}{c} R.NH_3 \\ | \quad\ | \\ CO.O \end{array}$$

and in accordance with the predominant views we assume that the hydration of $—NH_2$ to $—NH_3.OH$ is slight.

$$\frac{A^{+-} \cdot H^+}{A^+} = K_S \ . \tag{3}$$

The dissociation of the amino group occurs according to:

$$H_2O + NH_2.R.COO^- = OH^- + {}^+NH_3.R.COO^-$$

and for the corresponding basic dissociation constant K_B we have:

$$\frac{A^{+-} \cdot OH^-}{A^-} = K_B \ . \tag{4}$$

If the old k_a- and k_b-values are known, it is easy to calculate the new dissociation constants, for A of the old exposition is equal to A^{+-} of the new; from the equations 1, 2, 3, and 4 we obtain:

$$K_S = K_{H_2O}/k_b \ , \qquad K_B = K_{H_2O}/k_a \ . \tag{5}$$

Here K_{H_2O} is the dissociation constant of water: $K_{H_2O} = H^+ \cdot OH^-$.

When an acid or a base has the dissociation constant K, it is well known that the hydrolysis constant of its salts is equal to K_{H_2O}/K. Thus it appears from equation 5 that the new dissociation constant K_S, which *characterizes the carboxyl group*, is identical with the hydrolysis constant which corresponds to the old basic dissociation constant k_b, and furthermore that the new dissociation constant K_B, which *characterizes the amino group*, is identical with the hydrolysis constant which corresponds to the old acidic dissociation constant k_a. By this change in the conception of the constitution of the amino acid molecule *the constant which formerly described the function of the amino group becomes a constant which characterizes the carboxyl group, and vice-versa.*

4. In table 1 the values of the old and new dissociation constants for a number of amino acids are collected, mainly according to the above-mentioned book by Michaelis. All constants are given as powers of 10 as this mode of writing is usually the most convenient. Actually it is sufficient to state the numerical value of the powers (—log K), for which I have previously proposed the term *dissociation exponent*[5]. To avoid misunderstandings the K-values themselves will, however, be stated in table 1. For the dissociation constant of water at 25° C the value $10^{-13.90}$ was used.

On converting the old k-value into the new K-value a difficulty is encountered in *lysine*, *arginine*, and *histidine*. The structural formulae of these substances show that they have one acidic function and two basic functions. Consequently it is not permissible to convert both old basicity constants into acidity constants. The first basicity constant has been transferred unchanged to the new system; the acidity constant was converted into the second basicity constant, and the second basicity constant into the acidity constant. The following consideration has been guiding for this procedure:

It always appears *unambiguously* from the experimental data, at which hydrogen-ion concentrations (a_1, a_2, $a_3 \ldots$) the ampholyte possesses a buffer effect and changes its state of dissociation with the hydrogen-ion concentration. When the buffer effect at $H^+ = a$ is caused by an acidic group in the molecule, the acidity constant of this group is equal to a, and when it is caused by a basic group, the basicity constant equals $\frac{K_{H_2O}}{a}$. According to this principle the a-value can be calculated from the constants of the literature, and then it may be converted at pleasure into acidity or basicity constants.

Table 1. Dissociation Constants of Some Amino Acids at 25° C.

		k_a	k_b	K_S	K_B
Glycine		$10^{-9.75}$	$10^{-11.57}$	$10^{-2.33}$	$10^{-4.15}$
Methyl-glycine		$10^{-9.89}$	$10^{-11.75}$	$10^{-2.15}$	$10^{-4.01}$
Dimethyl-glycine		$10^{-9.85}$	$10^{-11.97}$	$10^{-1.93}$	$10^{-4.05}$
Betaine		abt. 10^{-14}	$10^{-12.66}$	$10^{-1.34}$	abt. 1
Alanine		$10^{-9.72}$	$10^{-11.29}$	$10^{-2.61}$	$10^{-4.18}$
Leucine		$10^{-9.75}$	$10^{-11.64}$	$10^{-2.26}$	$10^{-4.15}$
Phenylalanine		$10^{-8.60}$	$10^{-11.89}$	$10^{-2.01}$	$10^{-5.30}$
Tyrosine		$10^{-8.40}$	$10^{-11.39}$	$10^{-2.51}$	$10^{-5.50}$
Glycyl-glycine		$10^{-7.74}$	$10^{-10.70}$	$10^{-3.20}$	$10^{-6.16}$
Alanyl-glycine		$10^{-7.74}$	$10^{-10.70}$	$10^{-3.20}$	$10^{-6.16}$
Leucyl-glycine		$10^{-7.82}$	$10^{-10.52}$	$10^{-3.38}$	$10^{-6.08}$
Taurine		$10^{-8.8}$	abt. 10^{-14}	abt. 1	$10^{-5.1}$
Asparagine		$10^{-8.87}$	$10^{-11.82}$	$10^{-2.08}$	$10^{-5.03}$
Lysine	1st stage dissociation	10^{-12}	$<10^{-6.96}$	$10^{-1.94}$	$10^{-1.9}$
	2nd stage dissociation	—	$10^{-11.96}$	—	$10^{-6.96}$
Arginine	1st stage dissociation	$<10^{-13.96}$	$10^{-7.0}$	$10^{-2.24}$	> 1
	2nd stage dissociation	—	$10^{-11.66}$	—	$10^{-6.9}$
Histidine	1st stage dissociation	$10^{-8.66}$	$10^{-8.24}$	$10^{-1.60}$	$10^{-5.24}$
	2nd stage dissociation	—	$10^{-12.30}$	—	$10^{-8.24}$
Aspartic acid	1st stage dissociation	$10^{-3.82}$	$10^{-11.92}$	$10^{-1.98}$	$10^{-1.8}$
	2nd stage dissociation	$10^{-12.1}$	—	$10^{-3.82}$	—

For *lysine* we find in the literature:

$$k_b \text{ (2nd stage dissociation)} = 10^{-11.96},$$

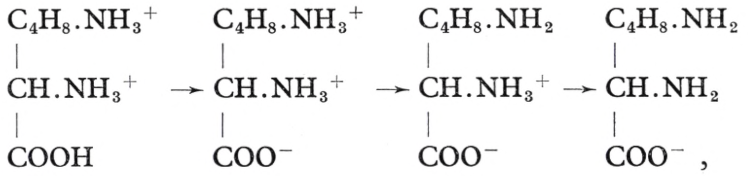
$$k_b \text{ (1st stage dissociation)} < 10^{-6.96},$$

$$k_a = 10^{-12}.$$

Hence:

$$a_1 = 10^{-1.94}, \qquad a_2 > 10^{-6.94}, \qquad a_3 = 10^{-12}.$$

The values are arranged according to falling hydrogen-ion concentrations. When it is assumed that the hydrogen ions of lysine are split off at these values in the following sequence:

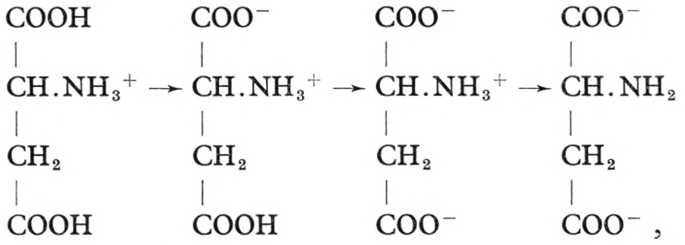


$$\begin{array}{ccccccc} C_4H_8.NH_3^+ & & C_4H_8.NH_3^+ & & C_4H_8.NH_2 & & C_4H_8.NH_2 \\ | & & | & & | & & | \\ CH.NH_3^+ & \rightarrow & CH.NH_3^+ & \rightarrow & CH.NH_3^+ & \rightarrow & CH.NH_2 \\ | & & | & & | & & | \\ COOH & & COO^- & & COO^- & & COO^- , \end{array}$$

the corresponding dissociation constants are:

$$K_S = 10^{-1.94} ,$$
$$K_B \text{ (2nd stage dissociation) } < 10^{-6.96} ,$$
$$K_B \text{ (1st stage dissociation) } = 10^{-1.9} .$$

For the tervalent ampholyte *aspartic acid* only two constants are given in the literature: an acidity constant k_a and a basicity constant k_b. The two a-values corresponding to these constants are $a_1 = 10^{-1.98}$ and $a_2 = 10^{-3.82}$. Winkelblech[6] has, however, published results which permit the calculation of the hydrogen-ion concentration for a third p_H-range. Winkelblech has measured the conductivity of aspartic acid + 2NaOH, but interpreted the result wrongly. By calculation from his measurements, I find k_a (2nd stage dissociation) $= 10^{-12.1}$, and so $a_3 = 10^{-12.1}$. When it is assumed that the hydrogen ions are split off from the cation of aspartic acid in the following sequence:



$$\begin{array}{ccccccc} COOH & & COO^- & & COO^- & & COO^- \\ | & & | & & | & & | \\ CH.NH_3^+ & \rightarrow & CH.NH_3^+ & \rightarrow & CH.NH_3^+ & \rightarrow & CH.NH_2 \\ | & & | & & | & & | \\ CH_2 & & CH_2 & & CH_2 & & CH_2 \\ | & & | & & | & & | \\ COOH & & COOH & & COO^- & & COO^- , \end{array}$$

we obtain from the above three a-values:

$$K_S \text{ (1st stage dissociation) } = 10^{-1.98} ,$$
$$K_S \text{ (2nd stage dissociation) } = 10^{-3.82} ,$$
$$K_B = 10^{-1.8} .$$

5. We shall now consider the numerical values of the old and the new *acidity constants*. The acidity constants computed from the old k_a-values for most of the amino acids mentioned range from about 10^{-8} to 10^{-10}; arginine and betaine are still less, and only aspartic acid more acid. But these values are very improbable;

for all these acids with the exception of taurine are *carboxylic acids*, and most of the known carboxylic acids have acidity constants of the magnitude 10^{-2} to 10^{-5}. Taurine is a sulphonic acid, and as these acids are usually just as strong as sulphuric acid ($k =$ about 1), the value ($10^{-8.8}$) found for taurine is also very strange. It has already been observed by Winkelblech[6] that the numerical values of k_a and k_b are hard to understand.

According to the new view the acidity constants get values from about $10^{-1.5}$ to $10^{-3.5}$. These values are certainly a little higher than those usually met with in carboxylic acids, but a certain increase in the acidic function of the carboxyl group is to be expected in these amino acids. When the dissociation scheme of acetic acid is compared with that of the carboxyl group of glycine

$$\mathrm{CH_3.COOH = CH_3.COO^- + H^+}$$
$$\mathrm{{}^+NH_3.CH_2.COOH = {}^+NH_3.CH_2.COO^- + H^+} ,$$

it becomes at once obvious that the positively charged ammonium group of glycine must facilitate the dissociation of the hydrogen ion by its electric repulsion, and consequently increase the acidity of the carboxyl group. In the dibasic acids we have the opposite effect, namely that of a negative electrical charge. The second dissociation constant in these acids is usually from 10 to 10000 times smaller than the first. Comparing the two dissociation equations, e.g. of malonic acid:

$$\mathrm{COOH.CH_2.COOH = COOH.CH_2.COO^- + H^+}$$
$$\mathrm{COOH.CH_2.COO^- = COO^-.CH_2.COO^- + H^+} ,$$

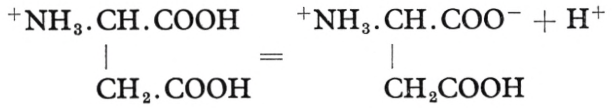
we see that the smallness of the second dissociation constant may be regarded as a consequence of the attractive effect of the first negatively charged carboxyl group on the hydrogen ion of the second.

It is interesting to see that the acidic function of an amino carboxylic acid is the stronger the nearer the carboxyl group is situated to the positively charged amino group, just as it was to be expected. For dipeptides, e.g. glycyl-glycine:

$$\mathrm{{}^+NH_3.CH_2.CO.NH.CH_2.COO^-}$$

with its widely interspaced groups, K_S is approximately 10 times smaller than for the α-amino acids with neighbouring COOH- and NH_2-groups.

The explanation of the high value of the first dissociation constant in *aspartic acid* is as follows: At the dissociation of the first carboxyl group:



$$\begin{array}{ccc} \mathrm{{}^+NH_3.CH.COOH} & & \mathrm{{}^+NH_3.CH.COO^- + H^+} \\ | & = & | \\ \mathrm{CH_2.COOH} & & \mathrm{CH_2COOH} \end{array}$$

we have to take into account not only the increment in acidic strength due to the positive charge of the ammonium group, but also the increment due to the second non-dissociated carboxyl group. That the carboxyl group in diaminomonocarboxylic acids like *lysine*, *arginine*, *histidine* is so strongly acidic ($K_S = 10^{-1.6}$ to $10^{-2.2}$) is due to the fact that in this case we have two positively charged ammonium groups, e.g. in lysine:

$$^{+}NH_3.C_4H_8.CHNH_3^{+}.COOH = {}^{+}NH_3.C_4H_8.CHNH_3^{+}.COO^{-} + H^{+}\ .$$

It agrees well with the sulphonic acid nature of *taurine* that it has a K_S of about 1.

The only unexpected thing is the increase in the acidic function of the carboxyl group through the introduction of methyl groups in the amino group of glycine.

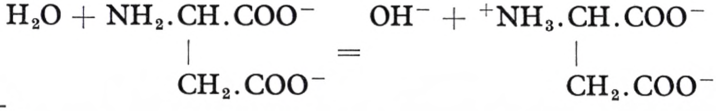
6. Having discussed the advantages of the new view with regard to the acidity constants, we shall proceed to consider the *basicity constants*. The old k_b-value for most aliphatic amino acids lies between 10^{-10} and 10^{-12}; for taurine we have $k_b = 10^{-14}$. According to this the amino groups should be 10^6 to 10^{10} times less basic than ammonia and aliphatic amines, the dissociation constants of which are in the vicinity of 10^{-4}. Even betaine, which has a quaternary ammonium group, and arginine, which is a derivative of the alkali-like base *guanidine*, should thus have very weakly basic properties.

The situation becomes, however, quite clear when we consider the new K_B-values. For in this case the alkali-like character of the basic groups of *betaine* and *arginine* is expressed by the K_B-values being equal to 1 or even greater. *Glycine* and the other aliphatic α-amino acids have basicity constants from about 10^{-4} to 10^{-5}, that is about the same as ammonia and aliphatic amines. In *dipeptides*, e.g. glycyl-glycine:

$$\begin{gathered} H_2O + NH_2.CH_2.CO.NH.CH_2.COO^{-} = \\ OH^{-} + {}^{+}NH_3.CH_2.CO.NH.CH_2.COO^{-} \end{gathered}$$

the peptide binding evidently has a fairly strong electronegative* effect, because K_B is less than 10^{-6} for this substance. In *phenylalanine* and *tyrosine* it is the benzene nucleus which has an electronegative effect ($K_B = 10^{-5.3}$ and $10^{-5.5}$, respectively).

In *aspartic acid* K_B is exceptionally great (about $10^{-1.9}$). Here the dissociation scheme is:



$$H_2O + \begin{array}{l} NH_2.CH.COO^{-} \\ \quad\quad\ \ | \\ \quad\ \ CH_2.COO^{-} \end{array} = OH^{-} + \begin{array}{l} ^{+}NH_3.CH.COO^{-} \\ \quad\quad\ \ | \\ \quad\ \ CH_2.COO^{-}\ . \end{array}$$

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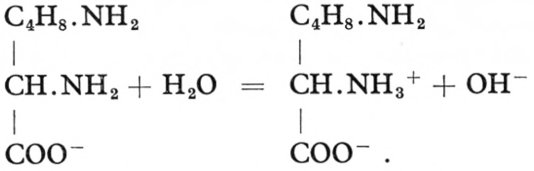
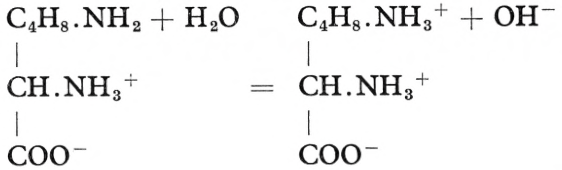
* "Electronegative" is used here as usual in chemistry in the meaning: increasing the acidic properties or decreasing the basic properties.

The two negatively charged carboxyl groups must facilitate the admission of a hydrogen ion into the amino group considerably and thereby make it more strongly basic. Also for *lysine* the first basicity constant is very great ($K_{B1} = 10^{-1.94}$). Its dissociation scheme is:



$$\begin{array}{lcl} C_4H_8.NH_2 & & C_4H_8.NH_2 \\ | & & | \\ CH.NH_2 + H_2O & = & CH.NH_3^+ + OH^- \\ | & & | \\ COO^- & & COO^- . \end{array}$$

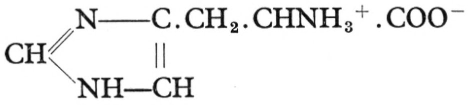
Besides the negatively charged carboxyl group the terminal amino group also acts electropositively here and increases K_{B1}. Conversely at the ionisation of the second amino group:



$$\begin{array}{lcl} C_4H_8.NH_2 + H_2O & & C_4H_8.NH_3^+ + OH^- \\ | & & | \\ CH.NH_3^+ & = & CH.NH_3^+ \\ | & & | \\ COO^- & & COO^- \end{array}$$

the positively charged α-ammonium group must decrease the value of K_{B2} ($K_{B2} = 10^{-6.94}$). It should not surprise that the amino group has an electropositive, but the ammonium group an electronegative effect as a similar phenomenon is well known from the behaviour of dicarboxylic acids. For malonic acid for instance the first dissociation constant is greater and the second smaller than for acetic acid. Thus an undissociated carboxyl group has an electronegative effect while on the other hand an ionised carboxyl group has an electropositive effect.

That the second basicity constant of *histidine*:



is small ($10^{-8.24}$) was to be expected as the second basic function derives from the but weakly basic glyoxaline ring. That the first basicity constant is rather small, too, ($10^{-6.9}$) shows that the glyoxaline ring exerts a pronounced electronegative influence on the α-amino group.

7. On the whole it may be said that the assumption of the ampho-ion constitution results in dissociation constant values of the considered amino acids which conform excellently with their structural formulae, which was not the case with the old dissociation constants. From this it can be concluded that these amino acids must exist mainly as ampho-ions, just as Küster has already previously found it to be the case for methyl orange.

Why this conclusion was not drawn before can be explained as follows: It has been calculated that salts of acids and bases with dissociation constants like k_a and k_b should be almost completely hydrolysed, and consequently it was concluded that there could be no ampho-ions as they represent the non-hydrolysed salt form. But thereby it has been overlooked that the dissociation constants obtain quite different values when an ampho-ion constitution is assumed (cp. Walker[7], Winkelblech[6], and Michaelis[8]).

The aliphatic amino acids are *internal salts* of an acidic group with a basic group in the same molecule. They are closely related to a salt like ammonium acetate. But *acetates* having an alkaline reaction are not regarded as bases, and *ammonium salts* having an acidic reaction are not regarded as acids. Similarly *amino acids* should not be regarded as acids and bases at the same time. All these compounds are substances in which acidic and basic groups have interacted to form salts, and their respective acidic and alkaline reactions are to be explained by *hydrolysis*.

The old acidity constant of amino acids k_a is not the dissociation constant of a carboxyl group, but a hydrolysis constant corresponding to the amino group, and the former basicity constant k_b is not the dissociation constant of the amino group, but a hydrolysis constant corresponding to the carboxyl group.

When it is desired to calculate the influence of the hydrogen-ion concentration on the ratio between the quantities of free undissociated amino acid and its cation and anion, equations 1 and 2 with k_a and k_b may just as well be used as equations 3 and 4 with K_S and K_B. Mathematically the two systems are completely equivalent. The advantage of equations 3 and 4 and the constants K_S and K_B is only that in this system the values of the constants conform with the dissociation constants found for other carboxylic acids (respectively sulphonic acids) and amines. If we were used to express the strength of an acid by the hydrolysis constant of its sodium salt and the strength of a base by the hydrolysis constant of its chloride, it would also come most natural to use k_a and k_b, and not K_S and K_B, to indicate the acidic and basic functions of amino acids.

8. Already in the year 1867 Erlenmeyer has proposed a cyclic formula with quinquevalent nitrogen for *taurine*, and in 1875 he[9] has ascribed a similar cyclic formula to the amino carboxylic acids, anyway for the α-amino carboxylic acids.

Later on other scientists have also come to the conclusion of a cyclic formula of the amino acids from chemical evidence. An interesting work by Marckwald, Neumark and Stelzner[10] should especially be noted. In this work Marckwald concludes that as the amino acids of the fatty series do not react easily and smoothly with mustard oils, while all other primary amines usually react violently with mustard oils at ordinary temperature, amino acids contain no free amino group, but are salt-like substances of a cyclic constitution. He finds this view borne out by the fact that even at ordinary temperature all amino acids investigated by him react upon all mustard oils in alkaline solution under generation of a considerable heat. For there is no doubt that they exist in alkaline solution as salts with the free amino group:

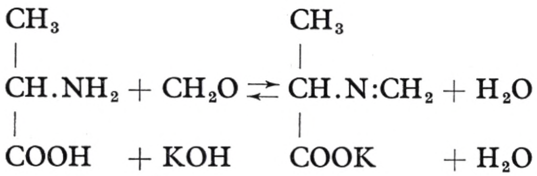
$$NH_2.R.COO.Na\ .$$

Translated into the terms of the ionic theory the cyclic formula becomes the ampho-ion formula of Bredig and Küster, and consequently we can regard Marckwald's work as an important argument for the ampho-ion nature of the aliphatic amines.

A certain corroboration of the ampho-ion formula is also derived from the behaviour of amino acids towards formaldehyde at Sørensen's "formol titration"[11]. At this titration the solution is first neutralised against litmus, then extra formaldehyde is added, and a titration with a base is performed with phenolphthalein as indicator until a deep red colour is obtained ($p_H > 9$). The consumption of base will be a measure of the amino groups present. By this method of determination formaldehyde reacts, forming methylene compounds with the amino groups, thus concealing the basic properties of the latter.

The aliphatic amino acids have two p_H-ranges in which they have a buffer effect. One is in the acid region at $p_H =$ about 4, the other in the basic region at $\mathrm{p_H} =$ about 10. According to the old view which is expressed in the formula $NH_2.R.COOH$, the buffer effect is caused by the *amino group* at $p_H =$ about 4, and by the *carboxyl group* at $p_H =$ about 10. According to the new view, which assigns the formula $^+NH_3.R.COO^-$ to the free amino acids, it is exactly in the reverse. On addition of formaldehyde the buffer effect disappears at $p_H =$ about 10; otherwise it would not have been possible to titrate to $p_H \geqq 9$ according to Sørensen and find a sufficiently sharp colour change. Consequently it comes more natural to assume that the amino group causes the buffer effect at $p_H =$ about 10, and accordingly that the formula of the free amino acid is $^+NH_3.R.COO^-$.

The following consideration is even more convincing: Sørensen has shown that at the formol titration it is necessary to titrate to a strongly alkaline reaction because the binding of the amino group through formaldehyde only becomes complete in a strongly alkaline solution. He formulates the transformation for alanine:



$$\begin{array}{llll} CH_3 & & CH_3 & \\ | & & | & \\ CH.NH_2 & + CH_2O \rightleftarrows & CH.N{:}CH_2 & + H_2O \\ | & & | & \\ COOH & + KOH & COOK & + H_2O \end{array}$$

It is not immediately obvious from this scheme why the amino group only at strongly alkaline reaction is completely saturated by an excess of formaldehyde.

If there were a free amino group in the amino acid, one would expect the formation of a methylene compound to occur in neutral solution almost as completely as in alkaline solution. For potassium hydroxide does not attack the amino group as formaldehyde does, but reacts with another part of the molecule.

The behaviour of amino acids becomes, however, intelligible when the formula $^{+}NH_3.R.COO^{-}$ is assumed. According to this conception the free amino group does not appear until the amino acid in alkaline solution changes into the anion $NH_2.R.COO^{-}$. Before this release of the amino group has taken place the formation of the methylene compound cannot be complete.

The partial formation of the formaldehyde compound even without addition of base is probably to be explained by the presence of some $NH_2.R.COOH$ besides $^{+}NH_3.R.COO^{-}$.

9. Strictly speaking the solution of an amino acid contains $^{+}NH_3.R.COO^{-}$ as well as $NH_3.R.COOH$. What we have ascertained is only that the amphoion is by far the predominant form in the amino acids in question. It might be of interest to ascertain the numerical ratio between the quantities of these forms. According to the law of mass action this ratio is a constant for each amino acid in a diluted aqueous solution, irrespective of the other dissolved substances, particularly irrespective of the hydrogen-ion concentration.

In order to estimate the value of this constant from the dissociation constants we shall begin by assuming that the acidic character of the carboxyl group is not essentially dependent on the state of ionisation of the amino group. This assumption means that the acids:

$$^{+}NH_3.CH_2.COOH \quad \text{and} \quad NH_2.CH_2.COOH$$

should be almost equally strong. However, this will certainly only hold to a rough approximation, because the closer the amino group is situated to the carboxyl group, the more will the acidic function increase by the transformation of the amino group into a positively charged ammonium group. If K_1 is the dissociation constant of the acid $^{+}NH_3.CH_2.COOH$ and K_2 the dissociation constant of the acid $NH_2.CH_2.COOH$, we can write:

$$K_1 = n \cdot K_2\,, \tag{6}$$

where n is a number between 1 and 10000. So far we are only able to estimate n roughly for the various amino acids.

If it is assumed that $NH_2.CH_2.COOH$ as well as $^{+}NH_3.CH_2.COO^{-}$ are to be found in the solution, the equations by which k_a, k_b, K_S, and K_B are determined must be written as follows

$$k_a = \frac{A^{-} \cdot H^{+}}{A + A^{+-}}, \tag{7}$$

$$k_b = \frac{A^{+} \cdot OH^{-}}{A + A^{+-}}, \tag{8}$$

$$K_S = \frac{(A + A^{+-})\, H^{+}}{A^{+}}, \tag{9}$$

$$K_B = \frac{(A + A^{+-}) OH^{-}}{A^{-}} \tag{10}$$

The ratio between the quantities of the two forms of the undissociated amino acid we shall name x:

$$x = \frac{A}{A + A^{+-}}, \qquad 1 - x = \frac{A^{+-}}{A + A^{+-}}. \tag{11}$$

For the dissociation constant K_1 of the acid $^{+}NH_3.CH_2.COOH$ we then obtain:

$$K_1 = \frac{A^{+-} \cdot H^{+}}{A^{+}} = (1 - x) K_S \tag{12}$$

and for the dissociation constant K_2 of the acid $NH_2.CH_2.COOH$:

$$K_2 = \frac{A^{-} \cdot H^{+}}{A} = \frac{A^{-} \cdot K_{H_2O}}{A \cdot OH^{-}} = \frac{K_{H_2O}}{x \cdot K_B}. \tag{13}$$

From equations 6, 12, and 13 we obtain:

$$x(1 - x) = n \frac{K_{H_2O}}{K_S K_B} \tag{14}$$

and by introducing k_a and k_b:

$$x(1 - x) = n \cdot \frac{k_a \cdot k_b}{K_{H_2O}}. \tag{15}$$

It is evident that equation 14 has no unambiguous solution. When a satisfies the equation, 1—a will do it, too. If for instance we find $x = 0.001$, $x = 0.999$ will also satisfy the equation. In order to decide between these two values, we must examine whether k_a and k_b or K_S and K_B are the better expressions for the acidic and basic properties of a substance of the constitution considered. Not till then can we decide whether 99.9 per cent occurs as $^{+}NH_3.R.COO^{-}$ or as $NH_2.R.COOH$.

Equation 15 affords an explanation of an observation by Michaelis[8] according to which ampholytes with $k_a . k_b$ equal to or greater than $K_{H_2O}(= 10^{-14})$ are not to be found in nature. According to equation 15 we have:

$$k_a \cdot k_b = \frac{x(1 - x)}{n} \cdot K_{H_2O}.$$

As $x(1-x)$ can at most become $\frac{1}{4}$, and n must be greater than 1 according to our theoretical molecular considerations, the product $k_a \cdot k_b$ can at most rise to $\frac{1}{4} K_{H_2O}$. Analogously it holds for $K_S \cdot K_B$ that it cannot be less than $4\, K_{H_2O}$. In an α-amino acid in which the amino group and the carboxyl group are neighbours, and n consequently is large, $k_a \cdot k_b$ must be much less than $\frac{1}{4} K_{H_2O}$. In polypeptides and albumins amino groups and carboxyl groups may be situated so far from each other that they hardly influence each other. Here n will approach 1, and $k_a \cdot k_b$ may rise to $\frac{1}{4} K_{H_2O}$. But this does not mean that they must rise to that value.

The significance of the two identical expressions:

$$\frac{K_S \cdot K_B}{4K_{H_2O}} \quad \text{and} \quad \frac{K_{H_2O}}{4k_a \cdot k_b}$$

which are always greater than one, is illustrated by the following. Their square root gives the ratio at the isoelectric point between the concentrations of the free undissociated ampholyte $(A + A^{+-})$ and that part $(A^{+} + A^{-})$ which occurs as cation or anion. So neither this fraction can fall below 1. Consequently at least 50 per cent of the ampholytes are undissociated at the isoelectric point.

10. In table 2 the values of K_S, K_B, and $K_{H_2O}/(K_S \cdot K_B)$ are stated for some amino acids; furthermore the estimated values of n and the values of x calculated according to equation 14. It follows from our previous considerations that all the amino acids of the table occur mainly as $^{+}NH_3.R.COO^{-}$. The smaller of the two mathematically possible values should, therefore, be chosen.

Table 2

	K_S	K_B	$\frac{K_{H_2O}}{K_S K_B}$	n	x
Dimethyl-glycine	$10^{-1.93}$	$10^{-4.05}$	$10^{-7.92}$	10^4	$10^{-3.92}$
Glycine	$10^{-2.33}$	$10^{-4.15}$	$10^{-7.42}$	10^4	$10^{-3.42}$
Phenylalanine	$10^{-2.01}$	$10^{-5.30}$	$10^{-6.59}$	10^4	$10^{-2.59}$
Glycyl-glycine	$10^{-3.20}$	$10^{-6.16}$	$10^{-4.54}$	10^2	$10^{-2.54}$

In table 2 n is given the value 10^4 for α-amino acids, and 10^2 for dipeptides. These values were estimated as follows: By considering the dissociation constants of the dicarboxylic acids, particularly those of the symmetrical ones, we can observe the effect of a *negative* charge on the dissociation constants of a carboxyl group. In these acids the dissociating molecule is neutral at the dissociation of the first carboxyl group, and at the dissociation of the second group it is negatively charged*. We may assume that the acidity constant of a carboxyl group will be increased approximately as much by the *positive* charging which accompanies the transition of an NH_2-group to a $^+NH_3$-group as it will be decreased by the *negative* charging which accompanies the transition of a COOH-group to a COO^--group. Now the ratio K_1/K_2 of the two acidity constants in dicarboxylic acids is never greater than 54000 (value for maleic acid). The ratio is 780 for oxalic acid, and only 25 for succinic acid. Accordingly we may be justified in regarding the n-value of table 2 as the upper limit. Even when using these high values for n, $^+NH_3.R.COO^-$ is found to prevail to such an extent that only 0.01 to 0.3 per cent of the form $NH_2.R.COOH$ is present.

When K_S or K_B *are approximately 1*, equation 14 may only be used with a certain qualification. In such cases we have to do with strong electrolytes the actual dissociation constants of which are much higher than those calculated according to the methods generally used up to now. Consequently the amphoion is more prevalent than it is calculated with the usual constants according to equation 14. Such conditions prevail in *betaine* and *taurine*. Indeed, the only possible form for betaine is $^+N(CH_3)_3.CH_2.COO^-$ as the other form $(CH_3)_2N.CH_2.COO.CH_3$, which is well known, shows properties quite different from those of betaine.

The preceding considerations were derived from an investigation of the *acidic function* of the compounds:

$$^+NH_3.R.COOH \quad \text{and} \quad NH_2.R.COOH.$$

We might, of course, just as well have considered the *basic function* of the compounds:

$$NH_2.R.COOH \quad \text{and} \quad NH_2.R.COO^-.$$

As we must arrive at the same result either way, we can conclude that the transition of the carboxyl group to the charged form will increase the basic function of the amino group to exactly the same degree as the acidic function of the carboxyl group is increased by the transition of the amino group to the charged form.

11. The behaviour of *aromatic* amino acids differs somewhat from that of the aliphatic amino acids. In table 3 the dissociation constants of some aromatic amino acids are collected. The k_a- and k_b-values of the *amino-benzoic acids* are of rather plausible magnitudes, which favour the formula $NH_2.C_6H_4.COOH$. For benzoic acid itself the dissociation constant is $10^{-4.22}$, and as the amino group acts in a positive direction, somewhat smaller constants are to be expected for carboxyl groups in the molecules $NH_2.C_6H_4COOH$. The k_a-values are from

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* As will be shown in a following paper it is, however, only the decrease of K_2 below $1/4\ K_1$ which can be explained by the influence of charge.

Table 3. Dissociation Constants of Aromatic Amino Acids at 25° C.

	k_a	k_b	K_S	K_B
o-amino-benzoic acid	$10^{-4.98}$	$10^{-11.86}$	$10^{-2.04}$	$10^{-8.92}$
m- – – –	$10^{-4.92}$	$10^{-10.63}$	$10^{-3.27}$	$10^{-8.98}$
p- – – –	$10^{-4.80}$	$10^{-11.92}$	$10^{-1.98}$	$10^{-9.10}$
o-benz-betaine	$<10^{-14}$	$10^{-12.55}$	$10^{-1.35}$	$10^{0.1}$
m- – –	$<10^{-14}$	$10^{-10.47}$	$10^{-3.43}$	$10^{0.1}$
p- – –	abt. 10^{-14}	$10^{-10.49}$	$10^{-3.41}$	abt. $10^{0.1}$
o-amino-benzene sulphonic acid	$10^{-2.48}$	—	—	$10^{-12.42}$
m- – – – –	$10^{-3.73}$	—	—	$10^{-10.17}$
p- – – – –	$10^{-3.24}$	—	—	$10^{-10.64}$

$10^{-4.80}$ to $10^{-4.98}$, i.e. about 5 times smaller in actual fact. On the other hand the dissociation constant of aniline is $10^{-9.34}$, and as a carboxyl groups acts in a negative direction, the constants for the amino groups in the molecules $NH_2.C_6H_4.COOH$ must be smaller than $10^{-9.34}$. Actually the k_b-values are from 5 to 400 times smaller.

Not only k_a and k_b, but also K_S and K_B have, however, satisfactory values for these ampholytes. Consequently we cannot exclude the ampho-ion formula $^+NH_3.C_6H_4.\ COO^-$. K_S is from 10 to 200 times greater for all three amino-benzoic acids than for benzoic acid in accordance with the fact that the positively charged amino group increases the acidic function of the carboxyl group. Furthermore K_B for these compounds is about twice as great as for aniline. This agrees with the view that the negatively charged radical —COO^- increases the basic function of the amino group.

The preceding considerations lead to the result that amino-benzoic acids in aqueous solution probably occur in discernible quantities both as $NH_2.C_6H_4.COOH$ and as $^+NH_3.C_6H_4.COO^-$. If we calculate the ratio between the two forms according to equation 14, the same result is obtained. In this case $K_{H_2O}/(K_S \cdot K_B)$ has values between 1/45 and 1/910. If we write $n = 10$ to 100, we obtain about 0.1 to 0.9 for x. As n is not known with any accuracy x cannot be calculated more exactly. But it is fairly certain that the free amino-benzoic acids in aqueous solution consist of mixtures of $NH_2.C_6H_4.COOH$ and $^+NH_3.C_6H_4.COO^-$ with not less than 10 per cent of the smaller quantity.

It would be interesting to check this result by comparative investigations on the behaviour of the amino-benzoic acids and the aliphatic amino acids towards mustard oils and aldehydes.

With regard to the amino-benzoic acids it should moreover be pointed out that the maximum values for n can be obtained from equation 14, as $x(1—x)$ cannot exceed 1/4; n must consequently be smaller than:

$4 \cdot 10^{-2.94} = 1/294$ for *o*-amino-benzoic acid
$4 \cdot 10^{-1.65} = 1/11$ - *m*- - - -
$4 \cdot 10^{-2.82} = 1/166$ - *p*- - - -

The increasing influence of the transition from —NH_2 to —NH_3^+ on the acidic character of the carboxyl group (respectively the increasing influence of the transformation from —COOH into —COO^- on the basic character of the amino group) is thus able to raise the value of the dissociation constants at most 11 times in the meta-compound, but in the para-compound 166 times, and in the ortho-compound 294 times. According to the current ideas of structure the greater effect is to be expected in the latter cases.

Table 3 shows that k_a and k_b for the *benz-betaines*:

$$^+(CH_3)_3N.C_6H_4.COO^-$$

are too small to permit of the conception that they contain free carboxyl groups and are quaternary ammonium bases. On the other hand the values of $K_S(10^{-1.35}$ to $10^{-3.43})$ appear to go well with a carboxylic acid, the acidity of which has been increased through a positively charged ammonium group. Likewise the K_B-values, which are all greater than 1, agree well with the alkali-like character of quaternary ammonium bases. This leads to the constitution: $^+(CH_3)_3N.C_6H_4.COO^-$. Here the other possible constitution: $(CH_3)_2N.C_6H_4.COOCH_3$ can be excluded by chemical evidence, too. k_a and k_b or K_S and K_B could be used equally well for the amino-benzoic acids. For the benz-betaines, however, only K_S and K_B have values which agree with the structure of these substances.

In the same way only K_S and K_B are suited to represent the acidic and basic functions of the *amino-benzene sulphonic acids* quoted last in table 3. k_b has certainly not yet been measured, but we may assume that it is smaller than 10^{-14}, and consequently $K_S > 1$. The k_a-values are of the order of magnitude 10^{-3}, and as sulphonic acids are generally strong acids, it is improbable that these figures can characterize the acidity of a sulphonic acid group. On the other hand K_B (of the order of magnitude 10^{-11}) computed from these k_a-values may very well characterize the basicity of an aromatic amine. According to the above, the amino sulphonic acids occur exclusively in the ampho-ion form $^+NH_3.C_6H_4.SO_3^-$.

12. For all ampholytes considered so far K_S and K_B agree better with the structural formula than k_a and k_b, or at least as well. There are, however, ampholytes for which k_a and k_b are better suited to characterize their acidic and basic properties, e.g. *amino-phenols* with aromatic amino groups. In these substances the acidic and basic properties are only slightly pronounced with dissociation constants of the order of magnitude 10^{-10}. They will mainly exist in the undissociated state as $HO.R.NH_2$, and the acidity of the phenol group will be correctly represented by k_a, and the basicity of the amino group by k_b.

13. Now we are in a position to understand what K_S and K_B really express about the acidic and basic groups of an ampholyte. By transformation of equations 9 and 10 we get:

$$K_S = \frac{A^{+-} \cdot H^+}{A^+} + \frac{A \cdot H^+}{A^+}; \qquad K_B = \frac{A^{+-} \cdot OH^-}{A^-} + \frac{A \cdot OH^-}{A^-}.$$

We see that K_S is the sum of *a dissociation constant* of the acid $^+NH_3.R.COOH$ and *a hydrolysis constant* of the salt of the amine $NH_2.R.COOH$. Analogously K_B is the sum of the dissociation constant of the amine $NH_2.R.COO^-$ and the hydrolysis constant of the salt of the acid $^+NH_3.R.COOH$. If the dissociation constants are much greater than the hydrolysis constants, K_S will be a dissociation constant of the carboxyl group, and K_B one of the amino group. This holds for the aliphatic amino acids. When, conversely, the hydrolysis constants are much greater than the dissociation constants, the latter may be ignored in the sums. In this case (e.g. in the amino-phenols) K_S becomes a hydrolysis constant characteristic of the amino group, and K_B one characteristic of the phenol group. In the aromatic amino acids the dissociation constants and the hydrolysis constants are of the same order of magnitude. So here we cannot decipher the acidic nature of the carboxyl group and the basic nature of the amino group separately from K_S and K_B.

Similar considerations can be made on k_a and k_b, only that it is here the reciprocal values: $1/k_a$ and $1/k_b$ which must be taken as sums of reciprocal dissociation and hydrolysis constants.

14. Now the question arises whether it is possible to determine the ratio A^{+-}/A in any other way, too, so as to check and extend the result obtained. This question must be answered in the affirmative, and in the following I shall outline some courses possible for this purpose.

If the ionisation of the basic or the acidic group in a coloured ampholyte is connected with a colour change, there is the possibility of a quantitative colorimetric determination. When for instance in the case of an amino acid the formation of the $^+NH_3$-group causes a colour change, while the dissociation of the carboxyl group does not change the colour, the two forms of the undissociated ampholytes will have different colours. The *ampho-ion* form will have the same colour as the cation $^+NH_3.R.COOH$, and the *amino acid form proper* $NH_2.R.COOH$ will have the same colour as the *anion* $NH_2.R.COO^-$. The light absorption of the *cation* is measurable in a strongly acid solution, and that of the *anion* in a strongly basic solution. The light absorption of the *undissociated ampholytes* can be ascertained by an absorption measurement at a hydrogen-ion concentration at which an appreciable fraction of the ampholyte is undissociated. The more the light absorption of the undissociated ampholyte approaches that of the cation, the more predominant is the ampho-ion. On the other hand $NH_2.R.COOH$ is predominant when the absorption approaches that of the anion. If E_K, E_A, and E_U are the extinction coefficients of the cation, the anion, and the undissociated ampholyte at a certain wave-length,

$$\frac{A^{+-}}{A^{+-}+A}=\frac{E_U-E_A}{E_K-E_A}$$

will hold.

We shall apply this method to *methyl red* (*p*-dimethylamino-azo-benzene-*o*-carboxylic acid). In this case we may expect both forms to be present in quantities of the same order of magnitude as in amino-benzoic acids. This is necessary for ascertaining the ratio of their quantities according to the above method.

15. A second possibility for the determination of A^{+-}/A is based on the following consideration. We may expect the solubility of the form of $NH_2.R.COOH$ not to be influenced to a higher degree by the addition of neutral salt than the solubilities of non-electrolytes in general. But it is different with the form of $^+NH_2.R.COOH^-$. On account of its electrical charges an *addition of neutral salt must be expected to decrease its activity and increase its solubility* as it is always the case with salts without common ions. When the two charges are very far from each other, the increase should be twice that of an ordinary univalent salt. The closer the charges are to each other, the smaller must be the effect, the charges mutually weakening each other.

Provisional solubility determinations of *methyl orange* in potassium chloride solutions made in this laboratory by Max Møller have given an effect which is $^1/_3$ of that estimated from the assumption that the distance between the charges is great. According to these experiments the solubility of methyl orange in 0.01 normal hydrochloric acid is increased by potassium chloride in the following way:

Table 4

Solvent	Solubility at 25° C.	c	k
0.01 normal HCl	$0.379 \cdot 10^{-4}$ molar	0.01	—
0.01 normal HCl, 0.05 normal KCl	$0.408 \cdot 10^{-4}$ –	0.06	0.108
0.01 normal HCl, 0.5 normal KCl	$0.501 \cdot 10^{-4}$ –	0.51	0.105
0.01 normal HCl, 1.75 normal KCl	$0.520 \cdot 10^{-4}$ –	1.76	0.068

The solubilities were determined colorimetrically.

In 0.01 normal HCl methyl orange exists in the red ampho-ion form except for a few per cent. The solid substance was a form of the free deeply red-violet methyl orange crystallizing in needles into which the freshly precipitated form was transformed spontaneously when shaken with water.

For the activity coefficient f of a univalent ion in an aqueous solution of univalent ions of the normality c we may write approximatively[12]:

$$-\log f = k \sqrt[3]{c}$$

and then find values for k *(the activity constant)* near 0.3. For methyl orange we shall write:

$$-\log f = 2 \cdot k \sqrt[3]{c}\,.$$

When s_1 and s_2 are the solubilities at the ion normalities c_1 and c_2, and f_1 and f_2 are the corresponding activity coefficients, we have:

$$\log s_2 - \log s_1 = \log f_1 - \log f_2 = 2k\,(\sqrt[3]{c_2} - \sqrt[3]{c_1})$$

and hence:

$$k = \frac{\log s_2 - \log s_1}{2(\sqrt[3]{c_2} - \sqrt[3]{c_1})}$$

In table 4, c stands for the ionic concentration (i.e. the concentration of ionised electrolyte) and k for the activity constants calculated by means of the above equation. Excluding the value in 1.75 normal KCl, because the cube root formula cannot be expected to hold even approximately in this case, we find the mean $k = 0.107$, that is somewhat more than $^1/_3$ of 0.3, the mean value for univalent ions.

The ampho-ion of an ampholyte must also, like all ions, decrease the activity of other ions present although less strongly because the charges partly neutralize each other.

In order to ascertain this, Carl Faurholt has at my request measured the solubility of croceo cobaltic nitrate $(NO_2)_2Co(NH_3)_4 . NO_3$ in different salts and in *glycine* at 18° C and found:

in water	0.0118	moles per litre
in 0.1 normal sodium chlorate	0.0145	- - - *
in 0.1 normal sodium formate	0.0142	- - -
in 0.1 normal glycine	0.0127	- - -

The solubilities were determined by decomposition of the croceo complex with sodium hydroxide and titration of the ammonia distilled off. It appears from the measurements that the effect of glycine is 9/25 of the effect of ordinary univalent salts.

Also for the *activity decreasing* effect in glycine we thus find somewhat over 1/3 of the effect to be expected when it is assumed that the distance between the charges is great.

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* The solution was supersaturated with croceo cobaltic chlorate.

Mixtures of amino acids are much more easily soluble in water than might be expected from the solubilities of the individual acids. Not only do the acids crystallize with greater difficulty, but they are actually more soluble. This increase in solubility which is unexpected in view of the slight solubility of these substances can be explained by their ampho-ionic nature, viz. by the attractive forces between the electrical charges.

It will be of interest to determine the decrease of activity and increase of solubility of the various *amino-benzoic acids* and *amino-benzene sulphonic acids*, respectively, by addition of neutral salts. In this way we can in the first place estimate the distances between the ortho, meta and para-positions. The already well known action of the radicals in *o*, *m*, and *p*-position on each other, e.g. the intensifying effect of a nitro group on the acidic character of benzoic acid is presumably rather due to the length of the atom chain than to the distance in space. Secondly we shall be able to calculate the quantity of the ampho-ion form in *o*-(respectively *m*, *p*) amino-benzoic acid by comparing this acid with *o*-(respectively *m*, *p*) amino-benzene sulphonic acid, because the neutral salt effect must be approximately the same for the ampho-ion form of the two acids, and we know that the amino sulphonic acids exist exclusively in the ampho-ion form. From the experimentally accessible and undoubtedly smaller salt effect in solutions of amino-benzoic acids we may, therefore, draw conclusions as to the quantity of the form $NH_2.C_6H_4.COOH$.

16. It is probable that ampholytes which mainly occur in solution as ampho-ions also have this constitution in the solid state. The molecules must then be held together in their crystal lattices by strong electrical forces, being situated according to something like the following scheme:

$$\begin{array}{lll}
{}^{+}NH_3.R.COO^{-} & {}^{+}NH_3.R.COO^{-} & {}^{+}NH_3.R.COO^{-} \\
{}^{-}OOC.R.NH_3{}^{+} & {}^{-}OOC.R.NH_3{}^{+} & {}^{-}OOC.R.NH_3{}^{+} \\
{}^{+}NH_3.R.COO^{-} & {}^{+}NH_3.R.COO^{-} & {}^{+}NH_3.R.COO^{-}
\end{array}$$

Besides the usual cohesion forces we have in this case strong electrical forces. We must expect such substances to be slightly soluble, particularly in organic solvents which do not, owing to great dielectric constants, facilitate the dissociation of the electrically charged molecules from each other. In accordance with this the ordinary amino acids are actually almost insoluble in ether and alcohol, and only soluble to some extent in water, which has a large dielectric constant. Also the comparatively high melting point of many amino acids can be explained by the firm binding of the molecules in the crystals.

In Meyer and Jacobson's textbook of organic chemistry[13] these physical properties are quoted as arguments for the cyclic formula with quinquevalent nitrogen.

A crystal structure, like the one described above, will probably *tend towards* *the formation of electrically charged particles when pulverized*, the molecules being fissured occasionally, thereby causing particles with positive and negative charges to arise. In amino acids with neighbouring positive and negative charges such a fission is not, however, very probable. All the same it is known that occasionally amino acids may become strongly electrical when pulverized. In polypeptides a fission may occur more easily. Actually the observation has been made by N. Troensegaard[14] that, in certain derivatives from albumins, the substance became so strongly electrical when pulverized that the loose powder could hardly be removed from mortar and pestle. Perhaps we may regard this as evidence in favour of an ampho-ion constitution. In the ordinary ion lattices such phenomena will not be expected, because an electrical charge may easily be neutralised by transition of ions, and moreover the electrical conductivity is not sufficiently small.

Many amino acids may be sublimed, i.e. they may exist in vapour form. According to Willstätter's[15] investigations they evaporate in the form of $NH_2.R.COOH$. At any rate Willstätter has shown that by heating above the boiling point in a closed tube *betaines* turn into amino esters, e.g. $(CH_3)_2N.CH_2.COO.CH_3$.

SUMMARY

1. In their undissociated state the *aliphatic amino acids* exist almost exclusively (to the extent of more than 99.5 per cent) as salt-like *ampho-ions* $^{+}NH_3.R.COO^{-}$. Thus they are not amino acids proper, but *ammonium salts*. A content of hydrogen or hydroxyl ions in their solutions does not mean that they are acids or bases, but only that they are hydrolysed as salts.

The constants k_a and k_b by means of which the acidic and basic properties of the amino acids have hitherto been indicated are not dissociation constants, they are *hydrolysis constants*. The true *dissociation constants* which indicate the strengths of the neutralized acidic and basic groups in the amino acid molecule are:

$$K_S = K_{H_2O}/k_b \text{ and } K_B = K_{H_2O}/k_a$$

(K_{H_2O} is the dissociation constant of water). K_S and K_B have values for the amino acids which agree with their structural formulae. The values of K_S and K_B may be estimated from the nature of the acidic and basic group, when we take into account the influence of the other substituents in the usual way.

Various chemical reactions confirm that these substances contain *no free amino group*. Their physical properties agree with their salt-like nature. Their behaviour is also salt-like in that they increase the solubility of other salts and are themselves more easily soluble in salt solutions than in water.

2. In the aromatic amino acids *ampho-ions*, $^{+}NH_3.R.COO^{-}$, as well as *amino acid molecules proper*, $NH_2.R.COOH$, with a free amino group and carboxyl group are present (in quantities of from 10 to 90 per cent).

3. In the aromatic amino phenols the ampho-ion form is completely suppressed.

4. From the magnitude of the dissociation constant of an *ampholyte* it is possible to estimate the ratio between the quantities of the salt-like ampho-ion and the amino acid proper.

5. It is shown theoretically that probably K_S K_B for an *ampholyte* can never be smaller than 4 K_{H_2O} (k_a k_b never greater than $^1/_4 K_{H_2O}$). It follows from this that the proportion of an ampholyte existing as cation and anion can never amount to more than 50 per cent.

6. It is suggested how the results obtained may be checked by investigations of colours and solubilities. Preliminary experiments of this kind are quoted.

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Dissociation Constants of Multibasic Acids and Their Application to the Calculation of Molecular Dimensions

NIELS BJERRUM

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1. It is the aim of the present work to develop a theory of the ratio between the dissociation constants of multibasic acids.

Firstly, it will be shown in which way it is possible from this ratio to calculate *the effect exerted by the ionization of one hydrogen atom on the state of the other hydrogen atoms.*

Subsequently, a theoretical explanation of this effect will be given and it is assumed that this effect is due to the attraction of the hydrogen atoms by the free charge produced through ionization. In the case of multibasic acids with carboxyl groups which are *not too close to each other*, this electrostatic theory can explain the total effect. However, the latter becomes greater than expected from the theory when the ionizable hydrogen atoms are situated *very closely to each other*. In these cases we must assume a special effect through the *atom chain.*

2. Dissociation of a *dibasic acid* follows the equations

$$H_2S = HS^- + H^+ \qquad \text{and} \qquad HS^- = S^{--} + H^+ .$$

In the corresponding expressions of the law of mass action

$$\frac{[HS^-]\cdot[H^+]}{[H_2S]} = K_1 \text{ and } \frac{[S^{--}]\cdot[H^+]}{[HS^-]} = K_2$$

the symbols in brackets represent concentrations (more exactly: activities) of the respective substances. K_1 and K_2 are the first and the second dissociation constant of the acid.

As a measure for the strength of the acid it is advantageous in many cases to use instead of the dissociation constants rather their negative logarithms[1], which we will call *dissociation exponents* or *dissociation numbers of the acid* (p):

$$p_1 = -\log K_1 \qquad \text{and} \qquad p_2 = -\log K_2 .$$

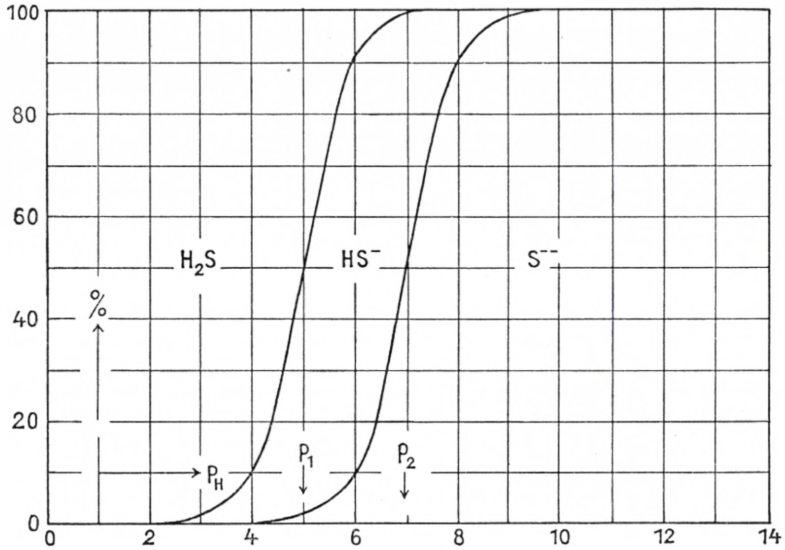


Fig. 1.

The latter denotation is in agreement with the name "Reaktionstal" *(reaction number)* proposed by Hasselbalch[2] for the hydrogen-ion exponent ($pH = -\log [H^+]$).

In equimolar mixtures of a free acid and the corresponding acid salt, or of an acid salt and the corresponding neutral salt, the dissociation numbers and the reaction numbers are almost identical. However, this does not hold when the dissociation numbers fall closely together. Exactly speaking, dissociation numbers mean those reaction numbers where the concentrations (activities) of H_2S and HS^-, or HS^- and S^{--}, respectively, are equal.

The state of a dibasic acid at different reaction numbers may be illustrated very clearly in the following graphical way (fig. 1).

As the abscissa are plotted the reaction numbers increasing, as is well known, from zero to 14 from strongly acid to strongly alkaline solutions. The ordinate at each different reaction number is divided into parts, one over the other, which indicate in per cent how much of the acid is present as S^{--}, HS^-, and H_2S, respectively. The areas between the curves of fig. 1 thus correspond to the forms S^{--}, HS^-, and H_2S. The pieces of the ordinate situated in the different areas show the quantity of the respective form of the acid in per cent at the hydrogen-ion concentration in question. The points of inflection of the two S-shaped curves fall approximately at those points of the reaction scale which correspond to the dissociation numbers p_1 and p_2.

The graphical method described here deviates from the usual one (*cf.* for example[3]). It illustrates much better the relative amounts of the three forms, but it shows less clearly the maximum of the form HS^-.

3. Table 1 given below comprises the first and second dissociation numbers of the normal homologues of oxalic acid. If not otherwise indicated, the values were calculated from those given by Chandler[4] for the dissociation constants at 25° C. Larsson's figures are valid at 18° C. Since for the dissociation of a carboxyl group the heat of ionization Q is rather small (varying from -1600 to $+1100$ calories according to the heats of neutralization found by Jul. Thomsen), the dissociation numbers change at the most by 0.03 between 18 and 25° C according to the formula

Table 1. Normal Dicarboxylic Acids

		p_1	p_2	$p_2 - p_1$	n
Oxalic acid	C_2	1.42	4.35	2.93	2.33
Maleic acid	C_3	2.80	5.69[a])	2.89	2.29
Succinic acid	C_4	4.20[a])	5.62[b])	1.42	0.82
Glutaric acid	C_5	4.32	5.50	1.18	0.58
Pimelic acid	C_7	4.49	(5.36)[c])	(0.87)	(0.27)
Suberic acid	C_8	4.52	5.55	1.03	0.43
Azelaic acid	C_9	4.60	5.56	0.96	0.36
Sebacic acid	C_{10}	4.62	5.60	1.02	0.42

[a]) 18° C. Larsson, E. private communication.

[b]) 18° C. Larsson, E. *Z. anorg. Chem.* **125** (1922) 281.

[c]) Determined only by shaking out. For the homologous acids, this method gives lower values than does the conductivity measurement on the acid salt also applied by Chandler.

$$\frac{d \ln K}{dt} = -\frac{Q}{RT^2}.$$

For all acids given in the table, the second dissociation number is larger than the first, the difference being the more significant, the closer the carboxyl groups are to each other.

The dissociation number of acetic acid and its unibasic homologues is approximately 4.8. The first dissociation number of the acids given in the table is always smaller, the second one larger than this value. It follows from this that the strength of a fatty acid is increased by introduction of a carboxyl group, and is reduced by introduction of an ionized carboxyl group.

This difference between $-COOH$ and $-COO^-$ has already been observed by Ostwald[5], who interpreted it as the effect of attraction of the negative charge on the hydrogen ion. Ostwald has emphasized that this hypothesis also explains why the second hydrogen atom of a dibasic acid is the more difficult to split off, the closer the two charges of the divalent ions are to each other.

4. *A difference between p_1 and p_2* may be caused in different ways.

In an *unsymmetrical* acid, such as malic acid, the more acid carboxyl group will start dissociating, so that we already for this reason must expect $p_2 > p_1$. In a *symmetric* acid, such as succinic acid, this point is lacking, but even though, and owing to the *Ostwald electrostatic action*, p_2 will be greater than p_1.

However, even if the ionizable hydrogen atoms of a dibasic symmetrical acid are so far apart that electrostatic forces no longer play a part, we must expect for statistical reasons that K_1 will exceed the value of K_2 by a factor of 4, i.e. that

$$p_2 - p_1 = \log 4\,.$$

Let us consider the following dissociation processes:

$$\mathrm{R}\Big\langle\begin{matrix}\mathrm{COOH}\\ \mathrm{COOH}\end{matrix} \rightarrow \mathrm{R}\Big\langle\begin{matrix}\mathrm{COO^-}\\ \mathrm{COOH}\end{matrix} + \mathrm{H^+}\,, \qquad (1)$$

$$\mathrm{R}\Big\langle\begin{matrix}\mathrm{COOH}\\ \mathrm{COOCH_3}\end{matrix} \rightarrow \mathrm{R}\Big\langle\begin{matrix}\mathrm{COO^-}\\ \mathrm{COOCH_3}\end{matrix} + \mathrm{H^+}\,, \qquad (2)$$

$$\mathrm{R}\Big\langle\begin{matrix}\mathrm{COOH}\\ \mathrm{COO^-}\end{matrix} \rightarrow \mathrm{R}\Big\langle\begin{matrix}\mathrm{COO^-}\\ \mathrm{COO^-}\end{matrix} + \mathrm{H^+}\,. \qquad (3)$$

Assuming the carboxyl groups so far apart that their ionizations do not affect each other, their dissociation according to scheme 1 will occur just as easily as will the dissociation of the acid methyl ester according to scheme 2. Since, however, in the latter only one and in the former two carboxyl groups dissociate, K_1 must, for statistical reasons, be twice the dissociation constant $K_{\mathrm{CH_3}}$ of the acid ester.

These considerations originate from Wegscheider[6], who found them confirmed by Walden's and Walker's measurements of the dissociation constants of acid methyl- and ethyl esters of those dibasic acids whose carboxyl groups are not closer together than those of succinic acid.

Comparing, furthermore, the dissociation of the acid methyl ester according to scheme 2 with that of the acid ion according to scheme 3, and taking into account that the carboxyl groups far apart from each other do not influence each other we come to the result that, for statistical reasons, K_2 must be the half of $K_{\mathrm{CH_3}}$. In the doubly charged anion formed according to scheme 3, there are two places for the re-entrance of hydrogen ions, while the singly charged ion formed according to scheme 2 has only one.

From

$$K_1 = 2\,K_{\mathrm{CH_3}} \qquad \text{and} \qquad K_2 = {}^1/{}_2\,K_{\mathrm{CH_3}}$$

it follows that

$$K_1 = 4\,K_2 \qquad \text{and} \qquad p_2 = p_1 + \log 4\,.$$

For a dibasic acid with carboxyl groups close to each other, it naturally holds that

$$K_1 > 4\,K_2 \qquad \text{and} \qquad p_2 > p_1 + \log 4\,.$$

This statistical effect on the ratio of the two constants has been discussed by Adams[7]. He considers it a support of his views that in the oxalic acid series always $K_1/K_2 > 4$, even when the carboxyl groups are far apart. The value of 4 has never been reached here. However, *phenolphthalein* is a dibasic acid where the ratio K_1/K_2 is exactly 4.

According to Adams, this is due to the fact that the acid hydroxyl groups are very far apart, namely at the farthest ends of a diphenyl-methane group. However, we shall see that also in phenolphthalein the ratio of the *true* dissociation constants exceeds 4 and that it is only accidental that the found, apparent constants have the ratio 4 to 1.

In an attempt to find *a measure* (*n*) *for the mutual influence* of the ionization processes of the carboxyl groups in a symmetrical, dibasic acid, $\log 4 = 0.60$ must be subtracted from $p_2 - p_1$ in order to eliminate the statistical effect. We then obtain

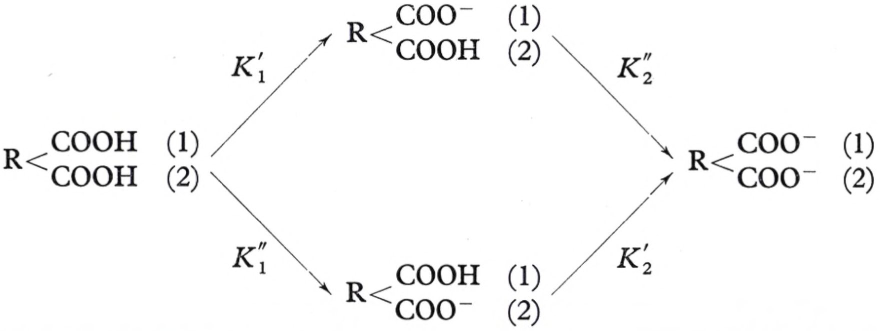
$$n = p_2 - p_1 - 0.60\,. \tag{4}$$

5. In *dibasic, unsymmetrical carboxylic acids* it is less simple to calculate the mentioned mutual influence of the carboxyl groups from the dissociation numbers. However, this can be done with approximation as follows (in close connection with Wegscheider's considerations[8] concerning the dissociation-in-steps of dibasic acids).

On ionization of a dibasic unsymmetrical acid

$$\mathrm{R}\Big\langle\begin{matrix}\mathrm{COOH} & (1)\\ \mathrm{COOH} & (2)\end{matrix}$$

two different singly charged ions and one doubly charged ion are formed



The constants corresponding to these four partial processes be K_1', K_1'' and K_2', K_2'', where the suffices (1 and 2) denote the first and the second dissociation constant, respectively, and the dashes denote the number of the dissociating carboxyl group.

The gross constants of the ionization process found experimentally (for example from conductivity measurements or measurements of the degree of hydrolysis) are related to the mentioned four fundamental constants as expressed in the following equations:

$$K_1 = K'_1 + K''_2$$

and

$$\frac{1}{K_2} = \frac{1}{K'_2} + \frac{1}{K''_2} \, . \tag{5}$$

This appears directly from the respective expressions of the law of mass action.

The ratio to be determined is K'_1/K'_2 or the corresponding logarithm. This fraction actually determines in which way the dissociation of carboxyl group (1) is influenced by that of carboxyl group (2). The analogous ratio K''_1/K''_2, characterizing the effect of ionization of the COOH-group (1) on the state of the other carboxyl group, is of course equally interesting: however, introducing mass action expressions for the constants, it becomes evident that these two ratios are identical.

As a *measure for the inequality of the carboxyl groups* we introduce

$$K'_1/K''_1 = q \, . \tag{6}$$

Taking into account the expressions from the law of mass action, through which the constants are defined, we also get

$$K'_2/K''_2 = q \, . \tag{7}$$

From the equations 5, 6, and 7 follows

$$\frac{K'_1}{K'_2} = \frac{K''_1}{K''_2} = \frac{K_1}{K_2} \cdot \frac{q}{(1+q)^2} \, . \tag{8}$$

For the logarithmic term *n*, representing the measure for the mentioned mutual influence of the carboxyl groups, we obtain

$$n = \log \frac{K'_1}{K'_2} = \log \frac{K''_1}{K''_2} = p_2 - p_1 - \log \frac{(1+q)^2}{q} \, . \tag{9}$$

For a *symmetrically* built acid ($q = 1$), this expression becomes, as was to be expected,

$$n = p_2 - p_1 - \log 4 \, .$$

For an *especially unsymmetrical* acid (q very small or very large), it holds that

$$n = p_2 - p_1 - \log q$$

or

$$n = p_2 - p_1 + \log q \, .$$

Here, the statistical effect can be completely disregarded, and a correction is required only for the different strengths of the acid groups.

Equation 9 takes a more symmetrical form if, as a measure for the inequality of the carboxyl groups, two numbers α' and α'' are used instead of q. These two numbers give the fractions of K_1 falling on K_1' and K_1'', respectively (and also the distribution of the singly charged ion over its two isomeric forms). We have

$$\alpha' = \frac{K_1'}{K_1}, \qquad \alpha'' = \frac{K_1''}{K_1};$$

and

$$\alpha' + \alpha'' = 1 \quad \text{and} \quad \frac{\alpha'}{\alpha''} = q\,. \tag{10}$$

It follows from equations 9 and 10:

$$n = p_2 - p_1 + \log \alpha' \alpha''\,. \tag{11}$$

In order to calculate n, we must find a way of determining q or α' and α''.

Ostwald[9] has shown that introduction of a substituent in a certain position relative to the carboxyl group changes the dissociation constant by a definite factor, rather independent of the presence of other substituents in the acid molecule. This so-called *factor law* was investigated more thoroughly by Wegscheider[10]. He has given a survey of factors which correspond to the substitution with different radicals in different positions. Later, Derick[11] used the factor law in a slightly modified form, without giving any proof of the necessity of this change.

On the basis of the factor law, the ratio K_1'/K_1'' (and thus q) is equal to the ratio of the constants of the two unibasic acids

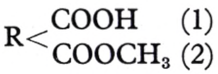
$$\mathrm{R}<\begin{matrix}\mathrm{COOH} & (1)\\ \mathrm{H} & (2)\end{matrix}$$

and

$$\mathrm{R}<\begin{matrix}\mathrm{H} & (1)\\ \mathrm{COOH} & (2)\end{matrix}\,.$$

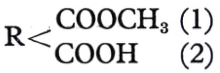
Consequently, we can compute q for malic acid from investigations of α- and β-oxypropionic acid, and q for pyrotartaric acid from investigations of butyric acid and isobutyric acid, etc.

In a similar way, q can also be calculated as the ratio of the constants of two isomeric acid esters, for example



$$\mathrm{R}<\begin{matrix}\mathrm{COOH} & (1)\\ \mathrm{COOCH_3} & (2)\end{matrix}$$

and



$$\mathrm{R}<\begin{matrix}\mathrm{COOCH_3} & (1)\\ \mathrm{COOH} & (2)\end{matrix}\,.$$

6. In tables 1–4 the values of p_1, p_2, and n are given for a number of dibasic acids.

Table 1 shows n decreasing from 2.3 to 0.4 with increasing distance between the carboxyl groups so that the latter are gradually withdrawn from interaction.

Table 2. Glutaric Acids

	p_1	p_2	$p_2 - p_1$	n
Glutaric acid	4.32	5.50	1.18	0.58
Thiodiglycolic acid	3.31 a)	4.46 b)	1.15	0.55
Camphoric acid	4.65 c)	5.8 a)	1.15	0.55
m-phthalic acid	3.54	4.60	1.06	0.46

Table 3. Symmetric Succinic Acids

	p_1	p_2	$p_2 - p_1$	n
Succinic acid	4.20 a)	5.62 b)	1.42	0.82
d-tartaric acid	3.02 a)	4.39 b)	1.37	0.77
Dibromosuccinic acid	1.47	2.80	1.33	0.73
Fumaric acid	3.03	4.47 b)	1.44	0.84
Phthalic acid	2.92	5.45 a)	2.53	1.93
Maleic acid	1.93	6.29 a)	4.36	3.76

Table 4. Unsymmetric Succinic Acids

	p_1	p_2	$p_2 - p_1$	q	n
Pyrotartaric acid	4.13 a)	5.63 b)	1.50	1.07	0.90
l-malic acid	3.48 a)	5.11 b)	1.63	4.45	0.80
Monobromosuccinic acid	2.56	4.50	1.94	11.0	0.82
Aspartic acid	1.98 d)	3.82 d)	1.84	(14.8)	(0.61)

a) 18° C. Larsson, E. private communication.
b) 18° C. Larsson, E. *Z. anorg. Chem.* **125** (1922) 281.
c) 18° C. Ostwald, W. *Z. physik. Chem.* **3** (1889) 369.
d) 25° C. Bjerrum, N. *Z. physik. Chem.* **104** (1923) 152.

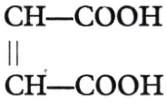
It appears from tables 2–4 that the value of n actually depends on the distance between the carboxyl groups, as indicated in "glutaric acids" and "succinic acids" (with 3 and 2 atoms, respectively, between the carboxyl groups).

Thiodiglycolic acid (table 2), where one methylene group of the glutaric acids is replaced by sulfur, and also *camphoric acid* behave like glutaric acid. However, n is somewhat smaller for m-*phthalic acid* (by 0.14), the carbocyl groups of the latter influencing each other to a less extent, maybe because the stiff benzene ring keeps them further apart.

Among the *symmetric succinic acids* (table 3), tartaric acid, dibromosuccinic acid, and fumaric acid are very much like succinic acid. However, the value for *phthalic acid* deviates considerably (by 1.11) from these *n*-values, and still more does that for *maleic acid* (by 2.94). It is tempting in this connection to think of the *stereochemical* effect causing that here the carboxyl groups come still closer to each other than in succinic acid. In the case of phthalic acid, the deviation can be explained completely in this manner. In the case of maleic acid, this explanation may be insufficient, since the high value of $n = 3.76$ even markedly exceeds the values for malonic and oxalic acid, although the charges of the divalent ions of oxalic acid and malonic acid are just as close to each other as in maleic acid.

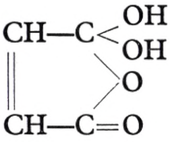
Possibly, for maleic acid, apart from the usual symbol (I) also the old Anschütz formula (II) may be taken into consideration, and we may assume that solutions of the acid contain both forms.

(I)



$$\begin{array}{l} \mathrm{CH{-}COOH} \\ \| \\ \mathrm{CH{-}COOH} \end{array}$$

(II)



If 50–100 per cent of the undissociated acid and the doubly charged ion were present as (I), and 90 per cent of the singly charged ions as (II), the anomalous value of *n* would be understandable. However, this hypothesis claims a higher strength of the Anschütz acid than ordinarily expected.

Among the *unsymmetrically* built succinic acids, *pyrotartaric acid*, *malic acid*, and *monobromosuccinic acid* follow completely succinic acid (mean value $n = 0.84$; for succinic acid $n = 0.82$). *Aspartic acid* has a somewhat deviating value of *n*; however in this case the determination of *q* is rather uncertain because the constants of the β-amino propionic acid are unknown and *q* has to be calculated indirectly.

Already in 1893, Noyes[12] stated that the introduction of new groups into a dibasic acid influences the dissociation constant of the acid and its acid salt "in the same direction". Later Wegscheider[13] showed in greater detail why the factor law leads to this result; moreover, he has shown the approximate validity of the rule on several examples.

7. It is easy *outside the group of carboxylic acids* to find multibasic acids, the ionizable hydrogen atoms of which are still closer to each other than those of oxalic acid. Such atoms are present in carbonic acid, sulphurous acid, and phosphoric acid in the hydroxyl groups, which are bound to the same metalloid atom. In hydrogen sulphide, they are even directly bound to the same metalloid atom.

Owing to anhydride formation, the usual figures for the first dissociation constant of carbonic acid and sulphurous acid are not the true values. According

Table 5. Inorganic Acids

	p_1 (uncorr.)	p_1	p_2	$p_2 - p_1$	n
Carbonic acid	6.51 [a])	abt. 4	10.34 [b])	6.34	5.74
Phosphoric acid		1.96 [f])	7.26 [b])	5.30	4.82
Sulphurous acid	1.77 [c])		5.30 [c])		
Hydrogen sulphide		7.04 [d])	14.92 [e])	7.88	7.28

[a]) 18° C. Warburg, E. J. *Biochem. J.* **16** (1922) 233.
[b]) 18° C. Unmack, A. unpublished.
[c]) 25° C. Jellinek, K. *Z. physik. Chem.* **76** (1911) 257.
[d]) 18° C. Auerbach, F. *Z. physik. Chem.* **49** (1904) 220.
[e]) 25° C. Knox *Trans. Faraday Soc.* (1908) 43. Cited from reference [f]).
[f]) 18° C. Abbot, G. A., and Bray, W. C. *J. Am. Chem. Soc.* **31** (1909) 729.

to Thiel and Strohecker[14] and to Faurholt[15], we must ascribe a p_1 about 4 to the real *carbonic acid.*

In the calculation of n for *phosphoric acid*, log 3 instead of log 4 has been subtracted from $p_2 - p_1$ in view of the tribasic nature of this acid. This point will be discussed later.

The not very different n-values for carbonic acid and phosphoric acid indicate that here the mutual effect of the ionizable hydrogen atoms is of the same order of magnitude and — as was to be expected — even stronger than in any of the dicarboxylic acids.

In the case of *sulphurous acid*, n cannot be calculated because the degree of hydration is still unknown. If we assume that n is the same as in carbonic acid and that the acid is built symmetrically, we obtain — 1.04 as the true value of p_1. This means that in aqueous solution only the fraction $10^{-1.04-1.77} = 0.0016$ of the sulphur dioxide is present as H_2SO_3 (obviously the solution also contains larger quantities of ionized H_2SO_3). The value becomes still smaller if the sulphurous acid has an unsymmetrical structure. Since the value already is very low, it is impossible from the dissociation constants to derive any support for the unsymmetrical structure of H_2SO_3.

The highest value of n, namely 7.28, is found for *hydrogen sulphide*, as was to be expected.

8. If it is assumed that n for *water* is the same as for the analogously built hydrogen sulphide, the *number of doubly charged oxygen ions* O^{--} in water can be calculated. Their existence has frequently been assumed, for example by Nernst[16], in order to explain certain phenomena during electrolysis of water. However, concerning the quantity of such ions not even a rough estimate has been possible so far.

For water we can put $p_1 = 14 + \log 55.5 = 15.7$*. Adding 7.3 to log 4 we find $p_2 = 23.6$. Consequently, we get for the concentration of the oxygen ion

$$[O^{--}] = \frac{[H_2O]}{[H^+]^2} \cdot 10^{-p_1-p_2} = \frac{10^{-37.6}}{[H^+]^2}\,.$$

The concentration of O^{--} thus amounts to

$$\begin{array}{lll} \text{In 1 } N \text{ alkali} & ([H^+] = 10^{-14}) & : 10^{-9.6} \\ \text{At the neutral point} & ([H^+] = 10^{-7}) & : 10^{-23.6} \\ \text{In 1 } N \text{ acid} & ([H^+]) = 1) & : 10^{-37.6}\,. \end{array}$$

The reliability of this calculation suffers from the fact that the dissociation numbers of hydrogen sulphide are not exactly known and, especially, that the equality of n for all acids of the H_2S type is only an approximation. An investigation into the dissociation properties of hydrogen selenide and telluride would be most instructive.

9. It must be assumed that in aqueous solution the hydrogen ion is *hydrated with about 8* H_2O[17]. According to Fajans[18], one water molecule is combined with the ion in a special way, forming the complex H_3O^+; the other 7 molecules must therefore be bound more loosely, similarly as in the hydrated hydroxyl ion and in the associated molecules of water proper. If we disregard these loosely bound H_2O molecules, the following dissociation processes occur in water

$$\begin{array}{lll} H_3O^+ & \rightarrow H_2O & + H^+ \\ H_2O & \rightarrow HO^- & + H^+ \\ HO^- & \rightarrow O^{--} & + H^+. \end{array}$$

The ion H_3O^+ can therefore be considered a *tribasic acid*. Similar considerations hold for the first and second dissociation constants as for the constants of the ordinary tribasic acids. Here, the ratio between the two constants is

$$\frac{K_2}{K_1} = \frac{[H_3O^+][HO^-]}{[H_2O]^2} = \frac{K_{H_2O}}{55.5^2} = 10^{-17.4}\,.$$

Hence, it follows that: $p_2 - p_1 = 17.4$. If H_3O^+ contains three equivalent hydrogen atoms, n becomes $= 16.9$ because we must correct for the statistical effect by subtraction of log 3 (possibly log 3/2, which is unimportant in this connection). The fact that this n-value is so much higher than that for hydrogen sulphide (7.28) seems to indicate that the assumption of equivalency of all three hydrogen atoms in the ion H_3O^+ is far from being justified.

10. Concerning *acids of an basicity higher than 2,* similar considerations can be put forward. We confine ourselves to the discussion of the phenomena in

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* The dissociation constant of water ($[H^+]\cdot[OH^-]$) is, as is well known, about 10^{-14}.

the case of a *tribasic* acid. However, the expressions can be formulated in such a way that generalization for acids of higher basicity becomes directly possible.

The (equivalent or non-equivalent) positions of the three hydrogen atoms in a tribasic acid H_3R be denoted by 1, 2, and 3. In solutions of the acid and its salts the following 8 types of molecules can thus be present:

the undissociated molecule : H_3R;
the three singly charged ions : H_2R^1, H_2R^2, H_2R^3;
the three doubly charged ions : $HR^{1\cdot 2}$, $HR^{1\cdot 3}$, $HR^{2\cdot 3}$;
the triply charged ion : $R^{1\cdot 2\cdot 3}$.

The dissociation constants determined in the usual way are then defined as follows:

$$K_1 = \frac{[H^+]\cdot([H_2R^1]+[H_2R^2]+[H_2R^3])}{[H_3R]}, \tag{12}$$

$$K_2 = \frac{[H^+]\cdot([HR^{1\cdot 2}]+[HR^{1\cdot 3}]+[HR^{2\cdot 3}])}{[H_2R^1]+[H_2R^2]+[H_2R^3]}, \tag{13}$$

$$K_3 = \frac{[H^+]\cdot[R^{1\cdot 2\cdot 3}]}{[HR^{1\cdot 2}]+[HR^{1\cdot 3}]+[HR^{2\cdot 3}]} \tag{14}$$

In additon to these three gross dissociation constants we have 12 partial dissociation constants, viz.

three first dissociation constants:

$$K_1^1 = \frac{[H^+]\cdot[H_2R^1]}{[H_3R]} \text{ and the two analogues } K_1^2 \text{ and } K_1^3; \tag{15}$$

six second dissociation constants:

$$K_2^{2(1)} = \frac{[H^+]\cdot[HR^{1\cdot 2}]}{[H_2R^1]} \text{ and the five analogues } K_2^{a(b)}\ ; \tag{16}$$

three third dissociation constants:

$$K_3^{3(1\cdot 2)} = \frac{[H^+]\cdot[R^{1\cdot 2\cdot 3}]}{[HR^{1\cdot 2}]} \text{ and the two analogues } K_3^{2(1\cdot 3)} \text{ and } K_3^{1(2\cdot 3)}\,. \tag{17}$$

Of these symbols the first upper index number denotes the H atom whose ionization is discussed. The other indices (in brackets) denote those hydrogen atoms which are already ionized. The lower suffices indicate whether the constant is a first, second, or third dissociation constant. *a* and *b* are arbitrarily chosen numbers of 1, 2, and 3.

The 12 elementary constants are not independent of one another. However, it is practical to use a system of independent, if possible symmetrical constants.

This is most suitably done by introducing 7 constants each of which is connected with one of the ions present.

Firstly, the following relations hold:

$$K_1^1 \cdot K_2^{2(1)} = K_1^2 \cdot K_2^{1(2)} \text{ and the two analogous equations.} \qquad (18)$$

This is due to the fact that the concentration of the $HR^{1\cdot 2}$-ion can be expressed by

$$[HR^{1\cdot 2}] = \frac{[H_3R]}{[H^+]^2} \cdot K_1^1 \cdot K_2^{2(1)} \, ,$$

as well as by

$$[HR^{1\cdot 2}] = \frac{[H_3R]}{[H^+]^2} \cdot K_1^2 \cdot K_2^{1(2)} \, .$$

Thus, if three constants are introduced:

$$K_{1\cdot 2}^{1\cdot 2} = K_1^1 \cdot K_2^{2(1)} \text{ and the two analogous } K_{1\cdot 2}^{a\cdot b} , \qquad (19)$$

the six elementary second dissociation constants can be dispensed with, since they can be expressed by

$$K_2^{1(2)} = K_{1\cdot 2}^{1\cdot 2} \,/\, K_1^2 \text{ and the five analogues } K_2^{a(b)} = K_{1\cdot 2}^{a\cdot b} \,/\, K_1^b \, . \qquad (20$$

Moreover, it holds that

$$K_{1\cdot 2}^{1\cdot 2} \cdot K_3^{3(1.2)} = K_{1\cdot 2}^{2\cdot 3} \cdot K_3^{1(2\cdot 3)} = K_{1\cdot 2}^{1\cdot 3} \cdot K_3^{2(1\cdot 3)} \, . \qquad (21)$$

This follows from the fact that the concentration of the $R^{1\cdot 2\cdot 3}$-ion can be formulated as the product of any one of these expressions and $[H_3R] \,/\, [H^+]^3$. Generally, the product

$$K_1^a \cdot K_2^{b(a)} \cdot K_3^{c(a\cdot b)}$$

has always the same value, independent of the order in which the numbers 1, 2, 3 are distributed over a, b, and c. If we therefore introduce a new constant

$$K_{1\cdot 2\cdot 3} = K_{1\cdot 2}^{1\cdot 2} \cdot K_3^{3(1\cdot 2)} = K_{1\cdot 2}^{a\cdot b} \cdot K_3^{c(a\cdot b)} = K_1^a \cdot K_2^{b(a)} \cdot K_3^{c(a\cdot b)} \qquad (22)$$

we can dispense with the three third dissociation constants which can be expressed as follows:

$$K_3^{1(2.3)} = K_{1.2.3} \,/\, K_{1\cdot 2}^{2\cdot 3} , \text{ generalized: } K_3^{a(b\cdot c)} = K_{1\cdot 2\cdot 3} \,/\, K_{1\cdot 2}^{b\cdot c} \, . \qquad (23)$$

By means of the four new constants $K_{1\cdot 2}^{a\cdot b}$ and $K_{1\cdot 2\cdot 3}$, and the three K_1^a, thus altogether seven constants, the three gross constants can be written as follows:

$$K_1 = K_1^1 + K_1^2 + K_1^3 \qquad (24)$$

$$K_1 K_2 = K_{1\cdot 2}^{1\cdot 2} + K_{1\cdot 2}^{2\cdot 3} + K_{1\cdot 2}^{1\cdot 3} \, . \qquad (25)$$

Thus we have

$$K_2 = \frac{K_{1\cdot 2}^{1\cdot 2} + K_{1\cdot 2}^{2\cdot 3} + K_{1\cdot 2}^{1\cdot 3}}{K_1^1 + K_1^2 + K_1^3} \tag{26}$$

$$K_1 \cdot K_2 \cdot K_3 = K_{1\cdot 2\cdot 3}\,, \tag{27}$$

and consequently,

$$K_3 = \frac{K_{1\cdot 2\cdot 3}}{K_{1\cdot 2}^{1\cdot 2} + K_{1\cdot 2}^{2\cdot 3} + K_{1\cdot 2}^{1\cdot 3}} \tag{28}$$

We now wish to express the ratios between K_1, K_2, and K_3 firstly by means of numbers (α) characterizing the difference in the hydrogen atoms of the acid, in other words their unsymmetry, and secondly by means of numbers (β) indicating the effect of ionization of one or several hydrogen ions on the dissociation constants of the others. Putting

$$\alpha_1 = \frac{K_1^1}{K_1}\,; \qquad \alpha_2 = \frac{K_1^2}{K_1}\,; \qquad \alpha_3 = \frac{K_1^3}{K_1}\,; \tag{29}$$

$$\beta_{1\cdot 2} = \frac{K_2^{1(2)}}{K_1^1} = \frac{K_2^{2(1)}}{K_1^2}\,; \text{ generally: } \beta_{a\cdot b} = \frac{K_2^{a(b)}}{K_1^a} = \frac{K_2^{b(a)}}{K_1^b}\,; \tag{30}$$

$$\beta_{1(2\cdot 3)} = \frac{K_3^{1(2\cdot 3)}}{K_1^1}\,, \text{ generally: } \beta_{a(b\cdot c)} = \frac{K_3^{a(b\cdot c)}}{K_1^a}\,; \tag{31}$$

$$\beta_{1\cdot 2\cdot 3} = \beta_{1(2\cdot 3)} \cdot \beta_{2\cdot 3} = \beta_{2(1\cdot 3)} \cdot \beta_{1\cdot 3} = \beta_{3(1\cdot 2)} \cdot \beta_{1\cdot 2}\,. \tag{32}$$

α_1, α_2, and α_3, whose sum equals 1, are proportional to the dissociation constants for the three hydrogen atoms. $\beta_{1\cdot 2}$ and its analogues give the effect of the ionization of the first hydrogen atom on the dissociation constant for the second atom (or the identical counter effect of the second atom on the constant for the first).

$\beta_{1(2\cdot 3)}$ characterizes the influence of the second and third ionized hydrogen atom on the constant for the first. Since, however, $\beta_{a(b\cdot c)} \cdot \beta_{b\cdot c}$ always has the same value, independent of the way in which 1, 2, 3 are substituted for *a*, *b*, c, it is sufficient to use the constant $\beta_{1\cdot 2\cdot 3}$ if the effect of dissociation of two hydrogen atoms on the constant for the third has to be expressed.

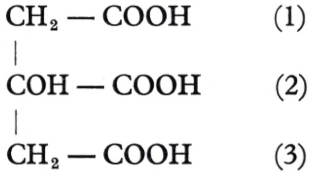
From equations 26, 19, 29, and 30 it follows that

$$\frac{K_2}{K_1} = \alpha_1\alpha_2\beta_{1\cdot 2} + \alpha_1\alpha_3\beta_{1\cdot 3} + \alpha_1\alpha_2\beta_{2\cdot 3}\,. \tag{33}$$

From equations 27, 22, 29, 31, and 32 we obtain

$$\frac{K_3}{K_2} = \frac{\alpha_1\alpha_2\alpha_3 \cdot \beta_{1\cdot 2\cdot 3}}{(\alpha_1\alpha_2\beta_{1\cdot 2} + \alpha_1\alpha_3\beta_{1\cdot 3} + \alpha_2\alpha_3\beta_{2\cdot 3})^2}\,. \tag{34}$$

11. The formulae obtained for K_2/K_1 and K_3/K_1 will now be applied to *citric acid*



$$\begin{array}{ll} \mathrm{CH_2 - COOH} & (1) \\ \quad | & \\ \mathrm{COH - COOH} & (2) \\ \quad | & \\ \mathrm{CH_2 - COOH} & (3) \end{array}$$

The carboxyl groups (1) and (3) are stronger than butyric acid, as 1 β-hydroxyl, 1 β-carboxyl, and 1 γ-carboxyl group have been introduced. Carboxyl group (2) is stronger than isobutyric acid, taking into account the presence of 1 α-hydroxyl and 2 β-carboxyl groups. The factor 4.4 (derived from lactic acid and hydracrylic acid) corresponds to the difference between α- and β-hydroxyl groups, — the factor 1.35 (from succinic acid and glutaric acid) corresponds to the inequality of the β- and γ-carboxyl groups. Butyric and isobutyric acid can be regarded as equally strong.

The carboxyl group (2) of citric acid is thus $4.4 \cdot 1.35 = 6.0$ times as strong as the other carboxyl groups. We therefore have

$$\alpha_1 = \alpha_3 = \frac{1}{8}$$

and

$$\alpha_2 = \frac{6}{8}\,.$$

The carboxyl group (2) is in a β-position to the others, just as the carboxyl groups of succinic acid. We may consequently put

$$-\log \beta_{1 \cdot 2} = -\log \beta_{2 \cdot 3} = n_{\text{succinic acid}} = 0.82\,.$$

The carboxyl groups (1) and (3) are in γ-position to each other, just as in glutaric acid. We may therefore put

$$-\log \beta_{1 \cdot 3} = n_{\text{glutaric acid}} = 0.58\,.$$

It can be calculated from this according to equation 33

$$\log (K_1 / K_2) = 1.49\,.$$

For the *dissociation numbers of citric acid* Miss A. Unmack found by means of electrometric measurements at 18° C (in a yet unpublished work)

$$p_1 = 3.23 \qquad p_2 = 4.85 \qquad p_3 = 6.40\,,$$

from which we obtain

$$\log (K_1 / K_2) = 1.62\,.$$

The calculated value is only 0.13 too high, which is a rather satisfactory result.

For log (K_2 / K_3) these measurements lead to 1.55. From this value and equation 34 together with the mentioned α- and β-values we obtain

$$-\log \beta_{1\cdot 2\cdot 3} = 2.59\,,$$

where $\beta_{1\cdot 2\cdot 3}$ is equal to $\beta_{1\cdot 2} \cdot \beta_{3(1\cdot 2)}$. If it is assumed that the total effect of ionization of the hydrogen atoms (1) and (2) equals the product of the single effects of these ionization processes, it holds that

$$\beta_{3(1\cdot 2)} = \beta_{1\cdot 3} \cdot \beta_{2\cdot 3}\,,$$

thus

$$\beta_{1\cdot 2\cdot 3} = \beta_{1\cdot 2} \cdot \beta_{1\cdot 3} \cdot \beta_{2\cdot 3}\,.$$

In the case of citric acid,

$$-\log \beta_{1\cdot 2\cdot 3} = 2\, n_{\text{succinic acid}} + n_{\text{glutaric acid}} = 2.22$$

and

$$\log (K_2 / K_3) = 1.18\,.$$

The value found directly from the measurements is, however, 0.37 higher. The ionization of both of the two hydrogen atoms has thus a somewhat stronger effect than indicated by the product of the single effects.

It is not improbable that the deviation of the value found for K_2 / K_1 from that calculated can, at least partly, be ascribed to the application of α-values, the incorrectness of which is due to the inaccuracy of the factor law. If we use in the computation of $-\log \beta_{1\cdot 2\cdot 3}$ such α-values ($\alpha_1 = \alpha_3 = 0.087$; $\alpha_2 = 0.826$) that the figures obtained for K_2/K_1 are in agreement with experience, we arrive at $-\log \beta_{1\cdot 2\cdot 3} = 2.50$, a value which is somewhat closer to 2.22 than is the earlier value of 2.59.

The value of K_2/K_1 for citric acid (and other tribasic acids) does not reveal considerably more than can be found out much more easily from a dibasic acid. However, K_3/K_2 gives some additional information. This term tells us how the ionization of two hydrogen atoms affects the dissociation constant for a third hydrogen atom.

12. For a *symmetrical tribasic acid* we have

$$\alpha_1 = \alpha_2 = \alpha_3 = \frac{1}{3}$$

and

$$\beta_{1\cdot 2} = \beta_{1\cdot 3} = \beta_{2\cdot 3} = \beta\,,$$

whereby equations 33 and 34 can be reduced to

$$\frac{K_2}{K_1} = \frac{\beta}{3} \tag{35}$$

and

$$\frac{K_3}{K_2} = \frac{\beta_{1\cdot 2\cdot 3}}{3\,\beta^2}\,. \tag{36}$$

Owing to the statistical effect, K_2 thus becomes three times, and K_3 nine times, smaller than K_1. The term denoted above as n is equal to $-\log \beta$. Taking the logarithms thus leads from equation 35 to

$$n = p_2 - p_1 - \log 3 \tag{37}$$

and from equation 36 to

$$-\log \beta_{1\cdot 2\cdot 3} = p_3 - p_2 - \log 3 + 2\,n\,. \tag{38}$$

In the case of *phosphoric acid* we have[19, 20]

$$p_1 = 1.96 \qquad p_2 = 7.26 \qquad p_3 = 12.44\,.$$

Subsequently, we obtain from equation 37

$$n = 4.82$$

and from equation 38

$$-\log \beta_{1\cdot 2\cdot 3} = 14.34\,.$$

If we have

$$\beta_{1\cdot 2\cdot 3} = \beta_{1\cdot 2} \cdot \beta_{2\cdot 3} \cdot \beta_{1\cdot 3} = \beta^3$$

we must obtain

$$-\log \beta_{1\cdot 2\cdot 3} = 3\,n\,,$$

and consequently $-\log \beta_{1\cdot 2\cdot 3} = 14.46$. The fair agreement with the value found above shows that in the case of phosphoric acid, the effect of ionization of two hydrogen atoms on the dissociation constant for the third must be almost identical with the square of the single effects.

13. The influence of the ionization of one hydrogen atom on that of another may probably arise in two ways.

Firstly, the negative charge liberated through dissociation will attract the hydrogen ions. This *electrostatic* effect will increase the hydrogen-ion concentration in the proximity of that hydrogen atom whose dissociation we consider above that prevailing in the solution. If the value of this deviation is estimated and taken into consideration in the calculation, we arrive at a theory of the electrostatic effect.

Secondly, there must exist an effect *through the atom chain.* During the ionization process intramolecular displacements of electrons take place, which propagate (with decreasing strength) over the chain of linked atoms and cause an increase of those forces which bind the other hydrogen atom. It is impossible to calculate this effect theoretically, but experimental data indicate how far into the atom chain this effect is noticeable.

The *electrostatic effect* can be calculated in the following way. Let r be the distance between the dissociating hydrogen atom and the negative charge already present, and D be the dielectric constant, which we assume does not vary.

In a given place, the concentration of one type of molecules is, according to Boltzmann,

$$c \cdot e^{\frac{\varphi N}{RT}}$$

(φ = the work to be performed in order to move one molecule from the respective place to another place with the concentration c. R is the gas constant, T the absolute temperature, and N Avogadro's constant).

The electric work required to move a hydrogen ion from a negative charge is

$$\varphi = \frac{\varepsilon^2}{Dr}$$

(where ε = the charge of the electron). A negative ion is therefore surrounded by a condensed hydrogen-ion "atmosphere", in which the hydrogen-ion concentration (c_r) depends on the distance r from the charge according to the following formula

$$c_r = c \cdot e^{\frac{\varepsilon^2 N}{DRTr}}.$$

If r is the distance between the charge and the hydrogen atom remaining in the singly charged ion, the dissociation constant (K) must be reduced, owing to electrostatic attraction, by the factor

$$e^{\frac{\varepsilon^2 N}{DRTr}}$$

while the following term must be added to the dissociation number (p)

$$\log_{10} e^{\frac{\varepsilon^2 N}{DRTr}}.$$

Putting $\varepsilon = 4.774 \cdot 10^{-10}$, $N = 6.06 \cdot 10^{23}$, $D = 80$, $R = 8.35 \cdot 10^7$, and $T = 291$, the increase of the dissociation number is found to be

$$\frac{3.1}{r \cdot 10^8}.$$

14. If it is assumed that the value of n (the total effect of ionization on the dissociation number) originates exclusively from the electrostatic effect, we have

$$n = \frac{3.1}{r \cdot 10^8}.$$

Table 6 shows the figures for r calculated according to this formula. In order to estimate their validity, table 7 presents a number of recent data concerning molecular distances, showing that the order of magnitude of the r-values given in the table is rather satisfactory.

Table 6. Distance between Acid Hydrogen Atoms in Some Acids

	n	r	a
Dibasic acids C_8–C_{10}	0.40	$7.8 \cdot 10^{-8}$ cm	$14.0 \cdot 10^{-8}$ cm
Glutaric acid C_5	0.58	5.3	8.0
Succinic acid C_4	0.82	3.8	6.5
Malonic acid C_3	2.29	1.35	5.0
Oxalic acid C_2	2.33	1.33	3.5
Carbonic acid	5.74	0.54	
Phosphoric acid	4.87	0.64	
Hydrogen sulphide	7.28	0.43	

Table 7. Distance between the Centres of:

K^+ and Cl^- in the potassium chloride crystal	$3.1 \cdot 10^{-8}$ cm
C - C - diamond	1.52
C - C - graphite	1.45 3.41
H - Cl in HCl	1.28
N - N - N_2	1.12
O - O - O_2	0.85
H - H - H_2	0.60
Radius of the hydrogen atom according to Bohr	0.55

The values found for succinic acid and higher dicarboxylic acids must be considered very good.

If the charge of the carboxyl group is at a distance of about 10^{-8} cm from the centre of the carbon atom, and the distance between neighbouring links of the carbon chain (as in diamond) is $1.5 \cdot 10^{-8}$ cm, then the distance between the two charges of a dicarboxylic acid (measured through the atom chain) can be calculated (a in table 6).

In succinic acid and the higher acids, the difference between a and r reaches such a value that it can easily be explained by the curved shape of the carbon chain. Here, we thus have none or only a weak effect through the atom chain.

For malonic acid and oxalic acid, and still more for carbonic acid, phosphoric acid, and hydrogen sulphide, the r-values (table 6) are too low (*cf.* table 7). For malonic acid and oxalic acid $r =$ about $1.34 \cdot 10^{-8}$ cm, while at least 3 or 4 times 10^{-8} should be expected. Here, a noticeable effect through the atom chain must be prevailing.

The fact that the atom chain effect is marked only when ionization takes place at an α- or β-carbon atom, is in best agreement with well-known observations concerning the influence of substituents on the dissociation of organic acids. If the strength of an acid is increased by introduction of — OH, — COOH, — Cl, this must be due to an effect through the atom chain. In any case, an electrostatic effect is lacking here. These substituents have a strong effect only in the α- or β-position. If the introduction of a new carboxyl group in a δ-, ε-, or even in a still more remote position reduces the dissociation number of a fatty acid from about 4.9 to about 4.6 (*cf.* p_1 in table 1), this must be ascribed to the statistical effect (presence of *two* carboxyl groups: 0.3) rather than to the effect through the atom chain.

15. The above considerations have shown that removal of a hydrogen ion from a carboxyl group causes electron displacements which propagate from the carboxyl group through the atom chain and which are of a magnitude similar to the displacements due to the introduction of — OH, — COOH, or — Cl in an organic acid. It follows from this that the bonding of the hydrogen ion is far from being exclusively of an electrostatic nature (as suggested by Kossel). This binding must be accompanied by a very considerable *deformation* (*cf.* Fajans[18]) of the carboxyl group; it seems to me that the atom chain effect is so large that it gives the binding of the hydrogen ion in the carboxyl group almost a homopolar character. In favour of this speak also the fundamental optical changes accompanying ionization of carboxylic acids according to Hantzsch and Schäfer.

16. The dibasic nature of *phenolphthalein* is due to the presence of two phenolic hydroxyl groups — in a *p*-position to the same carbon atom — in different benzene rings. Putting the diameter of these rings equal to $3 \cdot 10^{-8}$ cm, the distance between two singly bound carbon atoms to $1.5 \cdot 10^{-8}$ cm, the distance between C and O to $1 \cdot 10^{-8}$ cm, and taking into account the curved shape of the carbon chain, we can estimate the distance between the acid hydrogen atoms to be $8 \cdot 10^{-8}$ cm, that is the same as in dicarboxylic acids with C_9 and C_{10}. From this it follows that

$$n = \text{about } 0.4; \qquad p_2 - p_1 = n + \log 4 = 1.0.$$

Although Rosenstein's[21] measurements are in disagreement with these estimations (he found $p_2 - p_1 = 0.61$), we should not (as Adams[7] did) draw the conclusion of a mutually independent dissociation of the two hydrogen atoms. However, it should be taken into consideration that the doubly charged phenolphthalein ion has suffered a transformation appearing as a red colour of the ion. The approximate quantity of the doubly charged ion transformed into the red coloured form can be calculated from the difference between 1.0 and 0.61. If it is assumed that 60 per cent have been transformed and 40 per cent remained unchanged, the value of p_2 for the untransformed form increases by $-\log 0.4$ (= 0.40) and we have

$$n = 0.61 + 0.40 = 1.01,$$

a value which is in good agreement with expectation (1.0).

17. It follows from our considerations that the effect of ionization of a hydrogen atom on the dissociation of another hydrogen atom can be calculated, using the *ordinary dielectric constant of water*, 80, when it is assumed that the hydrogen atoms are so far apart that no atom chain effect is noticeable. This result is of considerable interest.

A calculation with the ordinary dielectric constant is *theoretically* permissible only when numerous water molecules are present between the charges whose mutual effect has to be derived. The above result shows *empirically*, however, that the procedure is permissible also when the distance between the charges is only of molecular size, i.e. if only a few water molecules find room in the interspace.

In more recent works, a *complete* ionization of strong electrolytes is generally assumed. The effects interpreted in earlier works as being due to incomplete dissociation are now regarded as the consequences of interionic electric forces.

In a work recently[22] concluded, I have found that correct results are obtained when calculating with the ordinary dielectric constant of water, even when the ions touch each other, which means under circumstances where no water is present in the interspace. Under these presuppositions, the diameter of the ions could be calculated from the decrease in osmotic effect of the ions with increasing concentration; it turned out to be in good agreement with the results of X-ray spectroscopy on crystal lattices. The result obtained through the study of multibasic acids offers a valuable support for the validity of this method of calculation.

A theoretical explanation of these conclusions will not be given here, only the following may be pointed out. The decrease in the dielectric constant to be expected for very small distances may be more or less compensated by the fact that the repelling forces that appear when the ions come very close to each other have not been taken into account. If the ions touch each other, these forces become so strong that they completely compensate the electrostatic attraction. Such a consideration certainly makes the admissibility of the mentioned method understandable, indicating at the same time that the method has only the character of a rough approximation.

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Electrometric Measurements with Hydrogen Electrodes in Mixtures of Acids and Bases with Salts

The Dissociation Constants of Water, Phosphoric Acid, Citric Acid, and Glycine.

NIELS BJERRUM and AUGUSTA UNMACK

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I. SURVEY

1. The investigations dealt with in the following report are mostly of an experimental nature. They consist of measurements of electromotive forces in cells which are built up in the following way:

$$\text{Hg} \mid \text{HgCl, 0.1. } M \text{ KCl} \mid 3.5\ M \text{ KCl} \mid \text{acid (or base)} + \text{salt} \mid \text{H}_2 \text{ Pt.}$$

One of us has already previously performed determinations of this kind[1]. A comprehensive investigation was published by S. P. L. Sørensen[2] in 1909, and this investigation has later on been supplemented by a paper by S. P. L. Sørensen and K. Linderstrøm-Lang[3]. Similar measurements have also been carried out by many other investigators. Especially the investigations of Harned[4,5] have yielded important experimental material.

The present study is mainly concerned with acids and bases which have already been investigated by Sørensen and Harned. In this renewed and extended investigation we have attached importance to measurements of the mixtures concerned at varying concentrations and temperatures.

2. In these measurements, hydrogen electrodes were combined with a *calomel electrode*. For this reason, part II of our paper consists of a careful investigation of various calomel electrodes with regard to reproducibility and durability. If

the instructions given here are followed, these electrodes are reproduceable at 18° C within 0.1–0.2 millivolt and will keep for several months. At 25° C and 37° C they were less stable.

We have preferred to perform our measurements with a 0.1 *M* KCl-calomel electrode. In order to correlate measurements with this electrode and with other calomel electrodes, we have compared the differences in potential between calomel electrodes with 0.1 *M*, 1 *M*, 3.5 *M*, and saturated KCl solutions at temperatures of 0°, 18°, 25°, 37° C.

3. In the cells measured, the electromotive force is the sum of the electrode potentials and the liquid-junction potentials. If the liquid-junction potentials are calculated, it is possible from the potentials of the cells to calculate the pure electrode potentials. From the electrode potentials it is further possible to calculate the relative values of the activities of the hydrogen ions in the solutions investigated, by means of Nernst's formula.

The method which we have used in the calculation of the *liquid-junction potentials* is described in details in part III. The formula of Henderson was used in the calculation. It was assumed that the strong electrolytes present were completely dissociated. The interionic forces were taken into account, in as far as the mobilities of the ions in the solution in question were inserted in the equations.

4. The H^+-activities obtained in this way need a more detailed explanation. It is impossible from a purely thermodynamic point of view to determine the individual activities of single ions from measurements of cells with or without liquid-junction potentials. This question is elucidated in the investigations by H. S. Harned[5] and has been especially brought forward and discussed in detail by P. B. Taylor[6] (compare also two papers in press by E. A. Guggenheim[7]). It is not possible to calculate thermodynamically the liquid-junction potentials in a cell without knowledge of the individual activity coefficients of the single ions, and vice versa we cannot calculate the individual coefficients without knowing the liquid-junction potentials.

Only when an assumption, not based in thermodynamics, is introduced is it possible to obtain definite individual ionic activity coefficients and liquid-junction potentials. Such an assumption can to some extent be made arbitrarily. Fundamentally it is permissible to consider the liquid-junction potentials of all other solutions in contact with a certain chosen solution as zero. We could for example stipulate that a 3.5 *M* KCl in water has the potential zero relative to all other solutions, or that the liquid-junction potential can be precisely eliminated by extrapolation from measurements with a 3.5 and a 1.75 *M* KCl solution. One of these assumptions will be sufficient to make possible the calculation of all other liquid-junction potentials and all individual ionic activity coefficients.

The coefficients of ionic activity obtained in this way will, however, be unpractical in one certain respect. The ions of potassium and chlorine in potassium chloride do not migrate at exactly the same rate. For this reason the individual ionic activities obtained will, with increasing dilution, show deviations from proportionality with the ionic concentration. We will not obtain activity coefficients converging towards a certain limiting value with increasing dilution. But if the liquid-junction potentials between 3.5 *M* KCl and the other solutions are calculated according to Henderson's formula in the way outlined above, this difficulty is avoided.*

Thus the activities and activity coefficients for single ions calculated in this paper are intimately connected with the method used in determining the liquid-junction potentials. Together they form a system, which, although arbitrary, is in itself consistent and unobjectionable from a thermodynamic point of view. All the values calculated by means of this system, but without the above mentioned arbitrarily chosen assumption (complete dissociation constants, concentration constants, mean ionic activity coefficients of electrolytes, E_o-values) are quite reliable. The arbitrariness of the system only affects those values, which cannot be subjected to a thermodynamic control (individual ionic activity coefficients, incomplete dissociation constants etc.)

5. The *scale used in measuring the activities* is as a rule defined in such a way that activity and concentration coincide at sufficiently large dilutions. In order to be able to convert our relative H^+-activities to this scale, we have in part IV performed measurements of H^+-activities in dilute hydrochloric acid with and without addition of alkali chlorides. These measurements were extended to very dilute solutions in order to approach as closely as possible the range in which activity and concentration become proportional to each other, so that only a small extrapolation is necessary to define the scale of activity.

In *measurements in very dilute solutions*, however, two difficulties are encountered. Firstly, the *cell potentials* in these solutions cannot be measured quite so accurately as in the more concentrated solutions. Secondly, the calculations of liquid-junction potentials in cells with strongly diluted solutions become to a considerable extent uncertain, since the transference number of the potassium ion in potassium chloride is not sufficiently well known. For these two reasons we have not succeeded in ranging the H^+-activities as accurately within the adopted scale, as we had initially hoped.

In practice, this means that the potential (E_o) of the 0.1 *M* calomel electrode

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* In solutions, in which the mean activity coefficients for the electrolytes present are all of the same magnitude, our individual ionic activity coefficients may, all the same, show deviations from this common value, due to differences in the ionic mobilities (E. A. Guggenheim[7]).

in combination with a normal hydrogen electrode could not be determined with as great a certainty as was originally hoped for.

In the extrapolation to infinite dilution we have assumed that (with increasing dilution) the activity coefficient of the hydrogen ion, $f_{H^+} = A_H/[H^+]$, approaches the limiting value 1 obeying Debye-Hückel's square root law, and in the calculation of the liquid-junction potentials we have reckoned with the transference number 0.497 for the potassium ion in potassium chloride. With these assumptions we obtain the following values for E_o, *the potential of a 0.1 M calomel electrode against a normal hydrogen electrode* (hydrogen pressure 760 mm Hg, hydrogen-ion activity 1):

t	0°	18°	25°	37°
E_o	0.3351	0.3360	0.3360	0.3354

Had we introduced a transference number 0.005 lower, the values would have been about 1 millivolt smaller. Fortunately, this uncertainty, regrettable in itself, plays no important rôle in the subsequent calculation of dissociation constants. Since the measurements, from which these dissociation constants were calculated, are dealt with in the same way as the measurements in hydrochloric acid, the errors, if any, neutralize each other. If the measurements are performed in sufficiently dilute solutions (and with sufficient experimental accuracy) it is possible, in spite of the uncertainty present in the determination of E_0, to obtain determinations of the dissociation constant with any required accuracy.

The H^+-activities calculated on the basis of the values for E_o given above are denoted by A_H and the corresponding H^+-exponents by $-\log A_H$ or pA_H. By the symbol p_H we only denote the H^+-exponents, which are calculated from the conventional values for E_0, established by Sørensen and Clark. At the end of part IV, a survey of the values so far suggested for E_0 is given, and we shall there discuss in further detail the difference between pA_H and p_H.

6. On the basis of our measurements in HCl, in HCl + NaCl and in HCl + KCl we have calculated the expressions for the *individual hydrogen ion activity coefficients* in HCl, NaCl, and KCl. These expressions are valuable in the calculation of H^+-concentrations in solutions with a known H^+-activity or with measured hydrogen-electrode potentials.

7. In order to determine the dissociation constants of water, phosphoric acid, citric acid, and glycine, we have measured cells with alkaline solutions (part V), phosphate mixtures (part VI), with citrate mixtures (part VII), and with glycine mixtures (part VIII).

From these measurements were calculated, firstly the p_H values in the solutions investigated, secondly the dissociation constants, the ionic activity coefficients and heats of dissociation.

8. In the calculation of the dissociation constants, a distinction was made

between three different kinds of constants. Considering the dissociation of an acid HS, the dissociation constant K_0 can be defined as:

$$K_0 = \frac{A_{\mathrm{H}} \cdot A_{\mathrm{S}}}{A_{\mathrm{HS}}} \tag{1}$$

(A_{X} = the activity of the molecules of kind X). According to its definition, the numerical value of this constant must be independent of the composition of the solution. This constant has been called the activity constant or the thermodynamic constant. We shall call it the *complete dissociation constant.*

The *concentration constant* is the quantity K_c defined by:

$$K_c = \frac{[\mathrm{H}^+]\,[\mathrm{S}^-]}{[\mathrm{HS}]} \tag{2}$$

([X] = concentration (in mole per litre) of the molecules of kind X).

Finally, the *incomplete dissociation constant* K is defined by:

$$K = \frac{A_{\mathrm{H}} \cdot [\mathrm{S}^-]}{[\mathrm{HS}]} \tag{3}$$

Hence, in the definition of the incomplete constant, the activity of the hydrogen ions and the molar concentrations of the other participants in the reaction are taken into account.

The concentration constant and the incomplete constant both change with the composition of the solution. By introducing the activity coefficient (f_{X})

$$f_{\mathrm{X}} = \frac{A_{\mathrm{X}}}{[\mathrm{X}]} \tag{4}$$

we get:

$$K_0 = K\frac{f_{\mathrm{S}^-}}{f_{\mathrm{HS}}} = K_c\frac{f_{\mathrm{H}^+} f_{\mathrm{S}^-}}{f_{\mathrm{HS}}} \tag{5}$$

Since the activity coefficients, in accordance with the normally accepted definition of the activity scale, approach unity with increasing dilution, both K and K_c, according to equations 5, will approach K_0 with increasing dilution.

For the dissociation of water we define a complete dissociation constant by the equation:

$$K_0\ (\mathrm{H_2O}) = \frac{A_{\mathrm{H}} \cdot A_{\mathrm{OH}^-}}{A_{\mathrm{H_2O}}} \tag{6}$$

($A_{\mathrm{H_2O}}$ = the activity of water in a scale, in which the activity of pure water is 1), a concentration constant by:

$$K_c(\mathrm{H_2O}) = [\mathrm{H}^+]\,[\mathrm{OH}^-] \tag{7}$$

and an incomplete dissociation constant by:

$$K(\mathrm{H_2O}) = A_{\mathrm{H}}[\mathrm{OH}^-] \tag{8}$$

9. Table 1 comprises our values for the *complete dissociation constants*. As regards the expressions for the incomplete constants and for the concentration constants, we refer to the later chapters, in which we also give a comparison between our values and the results of other investigators.

Table 1. Values of $pK_0 = -\log K_0$. (K_0 = complete dissociation constant)

		0°	18°	25°	37°
Water		14.926	14.222	13.980	13.590
Phosphoric acid	1	—	2.120	2.161	2.232
—	2	—	7.227	7.207	7.165
—	3	—	12.465	12.325	12.180
Citric acid	1	—	3.087	3.057	3.042
—	2	—	4.769	4.759	4.747
—	3	—	6.398	6.400	6.424
Glycinium ion	1	2.420	2.347	2.332	2.276
(Amino acetic acid)	2	10.478	9.965	9.779	9.466

On the basis of these calculations, one obtains the following expressions for the dependence of pK_0 values upon temperature:

Water	$pK_0 = 14.926 - 0.0420t + 0.00016t^2$	(0° — 37°)
Phosphoric acid	$pK_0' = 2.120 + 0.0059(t - 18)$	(18° — 37°)
	$pK_0'' = 7.228 - 0.0033(t - 18)$	—
	$pK_0''' = 12.45 - 0.015\,(t - 18)$	—
Citric acid	$pK_0' = 3.081 - 0.0024(t - 18)$	—
	$pK_0'' = 4.769 - 0.0012(t - 18)$	—
	$pK_0''' = 6.395 + 0.0014(t - 18)$	—
Glycinium ion	$pK_0' = 2.420 - 0.0039t$	(0° — 37°)
(Amino acetic acid)	$pK_0'' = 10.478 - 0.0295t + 0.00006t^2$	—

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11. The dependence of a dissociation constant upon the temperature permits the calculation of the corresponding *heat of dissociation* by means of the following equation:

$$Q = -RT^2\frac{d\ln K}{dT} = 4.57\,T^2\frac{dpK}{dT} \qquad (16)$$

If pK_0 values are inserted in this formula, one obtains heats of dissociation valid for infinitely dilute solutions. In this way the following values were found:

Table 4. Heats of dissociation in (infinitely) dilute solutions

Water	— 14.22 kcal	0° to 18°
—	— 13.73 -	18° to 37°
H_3PO_4 1. H+	2.43 -	18° to 37°
— 2. H+	— 1.35 -	-
— 3. H+	— 6.20 -	-
Citric acid 1. H+	— 1.02 -	18° to 37°
— 2. H+	— 0.52 -	-
— 3. H+	0.60 -	-
Glycinium ion 1. H+	— 1.51 -	0° to 37°
— 2. H+	— 10.57 -	-

If, however, the concentration constants are inserted in equations 16, one obtains the heats of dissociation for the salt solutions in question. In the case of water and phosphoric acid, the values calculated in this way can be compared with some figures obtained calorimetrically (comp. tables 5 and 6). It is, however, not permissible to identify the calculated and the experimental values, since the former represent differential, the latter integral values. On the other hand, these values can hardly be expected to deviate considerably from each other as long as both of them show only small deviations from the value which is valid for infinite dilution.

Table 5. Heats of neutralization in about 1/4 normal solution

	Observed by Wörmann	Calculated by Bj. and U.
9° NaOH + HCl	14.20 kcal	14.17 kcal
KOH + HCl	14.33 –	14.27 –
27.5° NaOH + HCl	13.19 –	13.58 –
KOH + HCl	13.41 –	13.53 –

Table 6. The three heats of dissociation of phosphoric acid in about 0.1 normal sodium phosphate buffer

	Calculated by Bj. and U. (18°—37°)	Thomsen's measurements (18°)
Q'	1.46 kcal	1.55 kcal
Q''	—1.11 –	—1.47 –
Q'''	—5.15 –	—4.27 –

12. Our measurements were completed a long time ago. The publication of the material has, however, been delayed by difficulties encountered in the theoretical treatment of the extensive material. During the period in which the measurements were performed, our knowledge of the properties of ionic activity has been greatly increased. Therefore, we have several times altered the form in which we wished to publish the experimental material, and at the present moment the circumstances are still such that we prefer to stress the experimental side of the investigation rather than the form of the theoretical interpretation of the results.

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Acids, Salts, and Bases

NIELS BJERRUM

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It is not the purpose of this article to present a complete account of the way in which the concepts of acid, salt, and base have been developed in the course of time. Rather it is its purpose to give a description of the developments these concepts have undergone during the last twenty years, developments to which J. N. Brønsted[8] in particular has made important contributions. In the presentation an effort is made to emphasize the continuity between the old and the new conceptions, and to show how it is possible to use what is good in the new development without giving up the good in the old. It is my hope to help to bring about the more common use and recognition of the new ideas, not only in scientific work, but also in elementary teaching.

ACIDS

Let us begin with the concept of an acid. About 1900, in elementary teaching an acid was described as a hydrogen compound which tasted sour and in aqueous solution colored litmus red (reacted acid). In somewhat more advanced teaching, this description was elaborated by defining an acid as a hydrogen compound which could split off hydrogen ions. By and large, I believe that this presentation is still valid.

Just after the coming out of the ionic theory, there was an inclination to stipulate that the hydrogen compound should be separated into ions before it could be called an acid. Thus it was said that hydrogen chloride was not an acid until it was dissolved in water. From my student days I remember how Biilmann, then an assistant, came up to a group of young students one day and raised the question as to whether hydrogen sulfide was really an acid. At that time it was a little puzzling, the question of whether the hydrogen compound itself should be called an acid, or whether only the part separated into hydrogen ions and anions should have that name. The point was soon cleared up, however, at least among the better informed. The power to split off hydrogen ions became the official criterion for an acid. It is quite another matter that the quantity of hydrogen ions in the aqueous solution of the substance in question tells whether the substance is a stronger or a weaker acid.

It has no doubt always been considered self-evident that not only neutral molecules (like hydrogen chloride and acetic acid), but also anions (like the bicarbonate ion, HCO_3^-, and the primary and secondary phosphate ions, $H_2PO_4^-$ and HPO_4^{--}) should be regarded as acids. In the acid salts which contain these acids one has to do with substances which are at the same time acids and salts.

On the other hand, it is only recently that cations which can split off hydrogen ions have been regarded as acids. Of course many people have long realized that the so-called hydrolysis of ammonium salts results from the reaction

$$NH_4^+ = NH_3 + H^+$$

and that accordingly the weakly acid character of aqueous solutions of ammonium salts is due to the power of the ammonium ion to split off a hydrogen ion[14, 18], but to Brønsted[8] belongs the honor of having drawn from that fact the conclusion that we should regard the ammonium ion as an acid.

Brønsted designates uncharged acids (HCl, CH_3COOH) as neutral acids, negatively charged acids (HCO_3^-) as anion acids, and positively charged acids (NH_4^+) as cation acids.

Using Brønsted's extension of the name "acid" we must reckon as acids not only the ammonium ion and the alkyl substituted ammonium ions in the salts of the amines, but also the hydrated metal ions (aquo ions) which many salts form in aqueous solution, for example, $Cr(H_2O)_6^{+++}$, $Al(H_2O)_6^{+++}$, $Cu(H_2O)_4^{++}$, and so on. As Pfeiffer[18] pointed out in 1906, these aquo ions can split off hydrogen ions, forming the so-called hydroxo compounds. Thus by the splitting-off of hydrogen ions from the hexaaquochromic ion there can be formed the monohydroxo ion, $Cr(H_2O)_5(OH)^{++}$, the dihydroxo ion, $Cr(H_2O)_4(OH)_2^+$, chromic hydroxide, $Cr(H_2O)_3(OH)_3$, and the chromite ion, $Cr(H_2O)_2(OH)_4^-$. The basic compounds which are formed upon the hydrolysis of salts of metals are very often (but by no means always) such hydroxo compounds, formed by the simple splitting-off of hydrogen ions from aquo ions. By regarding the hydrated metal ions as acids, as Brönsted does, one obtains a pedagogically useful, simple explanation of the acid reaction of these salts (their hydrolysis).

The advantage of Brønsted's extended use of the name "acid" is easy to see. Our mode of expression is thereby brought into closer agreement with the definition of an acid, and is in many cases made simpler and more comprehensible. The extension does not seem to have encountered much opposition. On the contrary, with hindsight it appears so obvious that one involuntarily asks one's self, "How is it that chemists didn't hit upon it sooner?" The extension cannot be explained as the result of new, previously unknown facts. No, the thing which prevented chemists from applying their own definition of an acid to the cation acids is certainly the fact that they have unconsciously required that an acid combine with metal hydroxides to form a salt and water. This requirement the cation acids do not meet. Thus ammonium chloride and sodium hydroxide form not only salt and water, but also ammonia. This requirement is certainly not contained in the official definition of an acid, but has existed and still exists, more or less unrecognized, in chemists' ideas of an acid. It possesses the rights of age. In calling the ammonium ion and ammonium salts acids, one must refuse to recognize this requirement.

My early work with aquo salts and their hydrolysis[2], and with the constitution of the amino acids[3], made it especially easy for me to see the usefulness of Brønsted's extension of the acid concept. And I believe that I may take credit for having seen, even earlier than the originator, the applicability of the new use of the word to the hydrogen ion in aqueous solution. By that time it had become a commonly accepted idea that the hydrogen ion, H^+, is not found free in its solutions, but is always present in solvated form, for example, as H_3O^+ (hydroxonium ion) in aqueous solution. This idea, which can be traced back to the work of Franklin[12], Goldschmidt[15], and Fitzgerald and Lapworth[11] received strong support shortly before 1923 in a paper by Fajans[10]. In my work on polybasic acids[4] I start out from the supposition that the hydrogen ion exists in aqueous solution as hydroxonium ion, and in agreement with Brønsted's concept, I regard the hydroxonium ion as a tribasic acid and discuss the values of its three dissociation constants.

While the hydrogen ion is present in water as H_3O^+ (hydroxonium ion), in methyl alcohol it is present as $CH_3OH_2^+$ (methyloxonium ion), in liquid ammonia as NH_4^+ (ammonium ion), and so on. Chemists speaking of hydrogen ions in daily conversation practically always have in mind these solvated hydrogen ions. This is a somewhat dangerous use of words, — especially dangerous when it is necessary to distinguish between free and solvated hydrogen ions. If it is decided to call the free hydrogen ion a hydrogen kernel or proton, the term "hydrogen ion" can still be used for the solvated hydrogen kernel. But I regard it as distinctly more practical to introduce a special common name for these solvated hydrogen ions, and I propose to call them "lyonium" ions (the Greek word "lyo," to dissolve, is used in the prefix of the terms "lyophilic" and "lyophobic" colloids).

When an acid ionizes in a medium, its hydrogen ion is given to the solvent with formation of a lyonium ion. For example,

$$HCl + CH_3OH = Cl^- + CH_3OH_2^+$$

In this reaction the original acid (hydrogen chloride) disappears, but there is formed in its stead a new acid, i.e., the lyonium ion (in our example, the methyloxonium ion). In solutions of strongly dissociated acids we have in fact no longer the original acid, but only the lyonium-ion acid.

Summarizing, it can be said that the new Brønsted phase in the development of the concept of an acid does not bring any change in the commonly used definition of an acid. It merely requires that the definition be taken quite literally, just as it is stated.

SALTS

While the concept of an acid may now be said to have found rational demarcation, the salt concept still suffers from an irrational ambiguity.

We have all been brought up to regard as salts those substances which are formed upon neutralization of acids by bases, and whose formulas can be derived from those of acids (neutral acids) upon replacing the hydrogen atoms of the acid with metal atoms, or with certain compound radicals which behave like metal atoms.

By the side of this official concept, as it might be called, another use of the word "salt" has quietly appeared. Thus it is often said that mercuric chloride and mercuric cyanide are not salt-like substances, there is doubt as to the salt-like nature of anhydrous aluminium chloride, etc. Behind these statements lies the thought that only ionized substances should be spoken of as salt-like. In the same way an effort is made to avoid calling the alkyl derivatives of acids alkyl salts. The term "ester" furnishes an excellent, noncommittal name for them.

It is easy to see the danger of using the word "salt" simultaneously with two different meanings, one which lays emphasis upon the *composition*, metal plus acid residue, and another which lays emphasis upon the *properties* which result from ionization. We should try to agree to use the word "salt" for one of these meanings only. This is surely most easily accomplished if at the same time we introduce a new name for the other meaning.

I believe that it will be most practical to keep the word "salt" for the substances which possess ionic structure, i.e., which are built up from and still contain ions. As the new name for the derivatives of neutral acids in general, without consideration of their ionization, I propose the term "acidate". This word seems to me to serve excellently as a common name for ionized salts, complex metal compounds, and organic esters, in the same way that the word "sulfate" (chloride, etc.) serves as a common name for substances of all these types derived from sulfuric acid (hydrochloric acid, etc.). If this differentiation between salts and acidates is adopted, it can be said that mercuric cyanide and ethyl acetate are acidates, but not salts. Dry hydrogen chloride is not a salt, but upon dissolving in water it forms a salt solution, since chloride and hydroxonium ions (i.e., a lyonium salt) are formed. Other strong acids behave in the same way. In aqueous solution a weak acid like acetic acid is a mixture of a small amount of ions (a lyonium salt) and a great quantity of undissociated nonsalt. Alum is both a double acidate and a double salt. On the other hand, potassium ferrocyanide is a double acidate but not a double salt.

Salt and acidate. Since all anions can combine with the hydrogen ion to form acids, every salt is of necessity an acidate. The salts form a subdivision of the larger class of acidates. The term "salt" is therefore more restrictive than the term "acidate", and it is generally easier to decide whether or not a substance is an acidate, than it is to decide whether or not it is a salt. A knowledge of composition alone as a rule enables one to decide whether a substance is an acidate of a given acid or not. On the other hand, it is frequently difficult to establish the fact that a substance is composed of ions, i.e., that it has the nature of a salt. If the substance is soluble, we have in the power to conduct electricity an excellent criterion for ions. But in the solid state we have no such reliable test, and at the present time doubt exists in many cases. At ordinary temperatures, are the silver halides salts as defined above, or not? Opinion on this point is divided.

Salt and ion. The term "salt" plays in the nomenclature of substances a part similar to that which the term "ion" plays in the nomenclature of molecules. An ion cannot be obtained in the pure state as a substance. If one wishes an ion in the form of a substance which can be collected and weighed, bought and sold, one must take another ion at the same time, i.e., one must deal with a salt.

Salt and electrolyte. The introduction of the new usage does not mean that salt and electrolyte become two names for one and the same thing. An electrolyte is a substance which is dissociated into ions to a demonstrable, but to any arbitrarily small, degree. A salt on the other hand is a substance which is entirely composed of ions.

Acidate and derivative. The term "derivative" is closely related to the term "acidate". Derivatives are frequently understood to be substances derived from hydrogen compounds upon replacement of hydrogen by something else, and since formally all hydrogen compounds may be regarded as acids (although sometimes extremely weak), all such derivatives are acidates. The term "derivative" is, however, also used in a more inclusive way. Thus acetamide may be derived from acetic acid upon replacement of the *hydroxyl* group by the amino group. It is a derivative of acetic acid, but not an acidate of it.

Salt and acid. That a substance is an acid has nothing to do with the fact that it is possibly a salt as well. A substance which is an acid is not necessarily a salt, but it may be a salt in the same way that a substance which is an acid may also be an alcohol (an oxy acid). Thus the ammonium salts and the so-called acid salts are at the same time acids and salts. Nevertheless, there is always a certain relationship between acid and salt in that those acids which are not themselves ions become ions upon neutralization (i.e., upon splitting off hydrogen ions).

For the understanding of the significance of the new concept of a salt it is very helpful to recall that our chemical substances can be divided quite naturally into three large groups, for each of which there are characteristic criteria: (1) metals, which consist of positive ions together with negative electrons. (2) Salts, which consist of positive and negative ions. (3) The remaining nonmetallic and nonsalt-like substances, which consist of neutral molecules.

Summary. In order to obtain a clear and unambiguous nomenclature, it is proposed to call all substances which can be derived from neutral acids by replacement of hydrogen with metal atoms, or with other radicals, acidates. Many of the acidates, but by no means all, belong to the great class of substances which are characterized by being constructed of ions. It is proposed to restrict the use of the term "salt" to these ionized substances.

BASES

The use of the word "base" is at the present time particularly vague and ambiguous. We have all been brought up to think of a base as a hydroxyl compound which splits off hydroxyl ions in aqueous solution. Back of this definition lies the idea that a base shall be a substance which, in the first place, can neutralize an acid solution, i.e., rob it of its acid properties, and in the second place, upon neutralization combine with the acid to form a salt (or more generally an acidate) and water. But whether we consider the matter logically or empirically, the power to neutralize and the power to form an acidate and water are not inseparably linked. Since in general there has been a more or less instinctive tendency to regard the power to neutralize an acid as the more important, there have been constant efforts to extend the concept of a base so as to include, in addition to the hydroxyl compounds, other substances which can neutralize acids.

Thus many chemists have continued to call ammonia and the amines bases, as was done long ago. I can mention Goldschmidt[14] and Fitzgerald and Lapworth[11], for example. Even water and other solvents which can combine with the hydrogen ion to form lyonium ions are called bases by Fitzgerald and Lapworth. Pfeiffer[18] was the first to notice that many metal hydroxides—the hydroxo compounds—can add acids and thereby form aquo salts without splitting off water; he decided for this reason to call the hydroxo compounds pseudo bases.

At almost the same time Werner[20] made a distinction between anhydro bases and aquo bases, according as the salt formation takes place without or with the formation of water.

The concept of a base was extended in another way by Franklin[13]. Through his work with the solvent liquid ammonia he was led to call metal amides like $NaNH_2$ ammono bases. For in liquid ammonia the metal amides react with acids to form salt plus solvent according to the equation

$$NaNH_2 + HS = NaS + NH_3$$

i.e., in a way quite analogous to the formation of a salt from a metal hydroxide and acid in aqueous solution

$$NaOH + HS = NaS + H_2O$$

If one generalizes Franklin's idea, in alcoholic solution the alcoholates or alkylates, as I prefer to call them, are to be regarded as bases

$$NaOC_2H_5 + HS = NaS + C_2H_5OH$$

and similarly in glacial acetic acid the acetates should be regarded as bases

$$CH_3COONa + HS = NaS + CH_3COOH$$

This generalization, however, leads very easily to the masking of what is the essential property of a base. For example, continuing as before one is easily brought to look upon sodium chloride dissolved in dry hydrogen chloride as just as good a base as sodium hydroxide in water.

In 1923 Brønsted[8] attempted to extend the concept of a base in a different way. He advocated the use of the term "base" for molecules which can neutralize acids, and entirely disregarded what is formed in the neutralization. When an acid is neutralized, its hydrogen ion is removed, and so Brønsted arrived at the simple conclusion that a base should be defined as a molecule which can combine with the hydrogen ion. Through this extended definition Brønsted evaded a number of difficulties. Among the bases he included all the molecules which in any way have previously been counted as bases.

The list in table 1 gives some idea of the molecules which are bases according to Brønsted's definition. Many of them are ions. All the salt-like substances which contain these ions are to be regarded as bases, and are accordingly included in the table.

Brønsted's definition, like Franklin's generalization, causes every anion (and so every salt) to be classed as a base. For we know no anion which cannot form undissociated acid molecules with the hydrogen ion. The perchlorate ion possesses this power to the smallest extent, and is therefore the weakest known anion base.

Table 1. Bases according to J. N. Brønsted

Molecules or ions	Salt-like substances
NH_3 and the amines	
H_2O and the alcohols	
Hydroxo compounds (nonsalt-like metal hydroxides)	
$C_2H_5O^-$ ($C_nH_{2n+1}O^-$)	Ethylates (alkylates)
OH^-, O^{--}	Hydroxides and oxides
HCO_3^-, CO_3^{--}	Bicarbonates and carbonates
CH_3COO^-	Acetates
ClO_4^-	Perchlorates

The useful feature of Brønsted's definition is that it points out the basic nature of the substance in question without reference to a solvent, and at once indicates a way to measure basic strength by measuring the power of the base to combine with the hydrogen ion.

Quite rightly Brønsted is much pleased with his new and elegant definition of a base. In his easily understood enthusiasm, however, he has been hardly sufficiently aware of the unique position which the hydroxides occupy among bases, and which is the reason that the name "base" was previously reserved for these substances. If we follow Brønsted and use the name "base" not only for sodium hydroxide but also for sodium carbonate and sodium acetate, substances which all of us have actually employed to neutralize acid solutions, we shall need a new term for the substances which, like hydroxides and oxides in aqueous solution, alkylates in alcoholic solution, and acetates in glacial acetic acid, unite with acids to form acidates (salts) plus solvent. In preparative chemistry this is a very important property. In distinction to these bases, other bases (bases in the extended sense) form upon neutralization an acidate (salt) and an acid different from the solvent. Thus carbonates in aqueous solution give carbonic acid (carbon dioxide), acetates in aqueous solution give acetic acid, and so on.

The bases to which we are thinking of giving a special name are the solvents' own acidates. I propose to call them "lyates." The ion base characteristic of these substances, which consists of the solvent minus the hydrogen ion, may very well be called "the lyate ion." Just as the concentration of the lyonium ion is customarily written c_H, the concentration of the lyate ion may well be written c_{-H}.

The special character of the lyates and the lyate ions among bases is evident not only in preparative work, where the lyates react with acids to form pure acidate solutions, but is also important in applications of the mass action equations to ionic equilibria in dilute solution. This last is due to the fact that the lyates, as acidates of the solvent, are derived from an acid which in dilute solution acts at nearly constant concentration and active mass.

One more property may be mentioned as a characteristic of lyate ions. In a solvent of acid nature any strong base will react with the solvent to form lyate ion. For example,

$$NH_2^- + H_2O = NH_3 + OH^-$$

$$C_2H_5O^- + H_2O = C_2H_5OH + OH^-$$

$$PO_4^{---} + H_2O = HPO_4^{--} + OH^-$$

$$NH_3 + H_2O = NH_4^+ + OH^-$$

If the base is sufficiently strong the reaction will be practically complete. So in an acid solvent bases which are appreciably stronger than the solvent's lyate ion cannot exist. Similarly, in a basic medium which is capable of forming lyonium ions, acid molecules which are appreciably stronger acids than the lyonium ion do not exist, for these acids will react with the solvent to form lyonium ion.

The adoption of Brønsted's extended definition of a base means that the old classical equation

$$\text{acid} + \text{base} = \text{salt} + \text{water}$$

must be abandoned. Nor can the somewhat modernized version of this equation

$$\text{neutral acid} + \text{base} = \text{acidate} + \text{solvent}$$

be kept. It is, however, not necessary to give up the equation altogether. We can keep the equation if for *base* we substitute *metal hydroxide*

$$\text{neutral acid} + \text{metal hydroxide} = \text{acidate} + \text{water}$$

or more generally,

$$\text{neutral acid} + \text{lyate} = \text{acidate} + \text{solvent}$$

When a neutral acid is dissolved in a basic medium, as already mentioned, there is formed a smaller or greater amount of lyonium salt. For example,

$$H_3PO_4 + H_2O = H_3O^+ + H_2PO_4^-$$

The lyonium salt formed is neutralized by lyates, just as the original acid is, with formation of acidate and solvent. It does not as a rule do any harm, therefore to use the word "acid" to represent the sum of the actual neutral acid (HS) and its lyonium salt (in aqueous solution $H_3O^+ + S^-$) present in the solution. On the contrary, this nomenclature is to be recommended as suitable and convenient in many instances.

If a solution of a strong base (the base being completely transformed to lyate salt) neutralizes a solution of a strong acid (the acid being present wholly as lyonium salt), the process of neutralization is of an especially simple character. When the equation

$$\text{acid} + \text{lyate} = \text{salt} + \text{solvent}$$

is rewritten in ionic form and simplified, we get for the process of neutralization

$$\text{lyonium ion} + \text{lyate ion} = \text{solvent}$$

This takes on for aqueous solutions the well-known form

$$H_3O^+ + OH^- = 2H_2O$$

It follows from these equations that dilute solutions of all strong acids and strong bases have the same heat of neutralization in the same amphoteric solvent.

The trouble with the old concept of a base comes from the fact that we have tried to kill two birds with one stone, and combine the concepts of base and lyate. By separating the two concepts we succeed in preserving the good in them both. The lyates are a subdivision of the bases. They occupy a unique position in synthetic and formal chemistry.

I regard it as an advantage that the name "lyate" as defined here includes both oxides and hydroxides without reference to the greater or smaller water content of these compounds. I have always felt it pedagogically unwise to emphasize the hydroxyl compounds, which are often known only on paper (for example, $Fe(OH)_3$), at the expense of their partial or complete anhydrides ($Fe_2O_3 \cdot H_2O$, Fe_2O_3).

As a matter of fact, the lyate concept is more closely related to the old official concept of a base than is Brønsted's extended concept. There is therefore some reason for continuing to use the word "base" for the substances which in this paper are called lyates. In that event it would be necessary to coin a new word for Brønsted's bases in the extended sense. The term "antiacid" might be suggested. But after long hesitation I have finally come to the conclusion that it is best to try to push through the use of the term "base" for the extended concept, and introduce the new name "lyate" for the acidates of the solvent.

Summary. It is probably satisfactory, in preparatory school, to describe bases as substances which impart a basic reaction (taste, litmus) to water, and which can neutralize (quench) the acid properties of acid solutions. Among the bases should be reckoned, besides the hydroxides of the alkalis and other metals, the oxides of the metals, and ammonia, and the carbonates. In addition it should be pointed out that the hydroxides and oxides are remarkable in that they combine with an acid to give an acidate and water, and that ammonia combines with an acid to give an acidate with no formation of water. To the more advanced student Brønsted's definition of a base should be taught, and the lyate concept should be formulated to cover nonaqueous solutions.

ACID, NEUTRAL, AND BASIC REACTION

In aqueous solution distinction is made between acid, basic, and neutral reaction according as the hydrogen ions (more exactly expressed, the hydroxonium ions) or the hydroxyl ions, or neither, preponderate to a marked degree. The new extension of the concepts of acid and base causes no change here. The reaction of the solution can still be stated quantitatively in terms of the hydrogen-ion concentration, or, to use the system devised in 1909 by Sørensen[19], in terms of the hydrogen-ion exponent, defined as the negative logarithm of the hydrogen-ion concentration, $\mathrm{pH} = -\log c_{\mathrm{H}}$. Since 1909 the only important changes which have taken place in stating the reaction of aqueous solutions have been: first, to define the hydrogen-ion exponent pH in a new way, according to which it is not exactly equal to $-\log c_{\mathrm{H}}$, but is more easily calculated from electrometric determinations[9], and secondly, to introduce as a measure of the reaction of a solution the hydrogen-ion activity a_{H}, measured on a scale which for every dilute solutions coincides (or almost coincides) with hydrogen-ion concentration[5,7]. This requires furthermore the use of $\mathrm{p}_a\mathrm{H} = -\log a_{\mathrm{H}}$ in place of pH.

The rational use of the concepts of acid, basic, and neutral reaction in a nonaqueous solution is dependent upon the ability of the medium to take up and give off hydrogen ions.

In amphoteric media which, like water, can form both lyonium and lyate ions, it is possible to use the concentration of these ions to distinguish between acid, basic, and neutral solutions, just as in water. On the other hand, if the medium lacks acid character and so cannot form lyate ions, one cannot speak of basic solutions in the same sense as in water. If the medium lacks basic character and consequently cannot form lyonium ions, one cannot speak of acid solutions in the same sense as in water. And finally if the medium is neither acid nor basic, and so can form neither lyate nor lyonium ions, one can speak of neither acid nor basic solutions in the same sense as in water.

The hydrogen-ion exponent pH, defined as $-\log c_{\mathrm{H}}$ (and $\mathrm{p}_a\mathrm{H}$ defined as $-\log a_{\mathrm{H}}$, where a_{H} is the hydrogen-ion activity, measured on a scale which at infinite dilution coincides with lyonium-ion concentration), has a definite value only in basic media which can form lyonium ions. There is, to be sure, nothing to prevent the determination of *relative* hydrogen-ion activities in nonbasic media. But the hydrogen-ion activity cannot be given on a lyonium-ion scale. It must be given on the scale of hydrogen-ion activity established for aqueous solutions. The hydrogen-ion activity A defined in this manner, or rather its negative logarithm pA, was proposed by Michaelis and Mizutani[17] as a measure of the degree of acidity of all nonaqueous solutions. Linderstrøm-Lang[16] has agreed to this proposal. Brønsted[8] has suggested calling the hydrogen-ion activity measured on

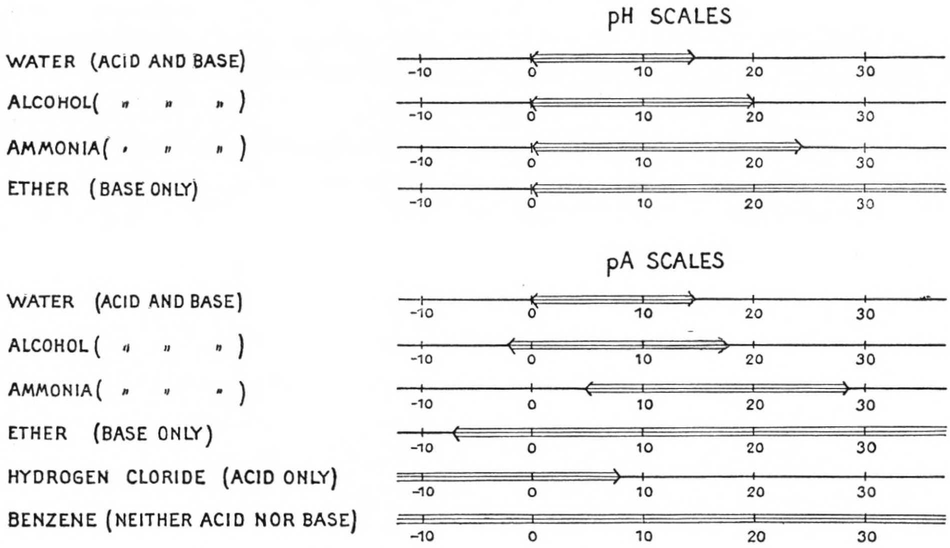

Fig. 1. Position of the reaction scales in typical solvents.

the water scale (*A*) the acidity of the solution. Correspondingly pA might be called the acidity exponent.

For nonaqueous solutions which can form lyonium ions it is possible to use both c_H and *A*, both pH and pA, as a measure of the degree of acidity. A great deal can be advanced in support of the use of the different quantities, and probably fields will be found in which each is most convenient. I shall not go into this question at the present time, however.

The extent and position of the scale of reaction. Where only dilute solutions (at the most 1 normal) are concerned, the pH scale in water has a rather definite length. The hydrogen-ion concentration in even the most acid solution (1 normal in acid) cannot be greater than 1, and the pH accordingly not less than 0. On the other hand, the hydrogen-ion concentration in the most strongly basic solution (1 normal in base) cannot be less than the dissociation constant of water, about 10^{-14}, and consequently the pH cannot be greater than $- \log K = 14$, approximately. There is naturally a close connection between the limited extent of the reaction scale in water and the fact that acids and bases whose strength exceeds certain limits do not exist as such in aqueous solution. Acids like hydrochloric acid, whose strength exceeds that of the hydroxonium ion, will form hydroxonium ion upon dissolving in water. And bases like sodium amide, whose strength exceeds that of the hydroxyl ion, will form hydroxyl ions in water. Since the substances are thereby transformed, and are present only in the transformed state, their greater strength is not manifest in the reaction of the solution.

Since ethyl alcohol is both an acid and a basic medium, and its dissociation constant is of the order of magnitude of 10^{-20}, the pH reaction scale in ethyl alcohol goes from 0 to 20. On the pA scale the most strongly acid solutions in alcohol do not lie at pA = 0, but at pA = — 2.5, and since the pA scale has the same extent as the pH scale, the most strongly basic solutions lie at pA = 17.5 in ethyl alcohol. The pA scale therefore extends from — 2.5 to 17.5. The value of pA for the most strongly acid solutions (the end of the pA scale on the acid side) is determined primarily, although not exclusively, by the basic strength of the medium. If the medium is a stronger base than water, the pA scale usually begins at positive values. If on the other hand the medium is a weaker base than water, the pA scale usually begins at negative values. In alcohol the pA scale begins on the negative side, and in liquid ammonia on the positive (see figure 1).

In the case of a medium which can take up but cannot give off hydrogen ions (for example, ether $(C_2H_5)_2O$), both the pH and pA scales are without a limit on the basic side.

In the case of a medium which cannot take up hydrogen ions, only the pA scale can be used, and this is unlimited on the acid side. In a medium which cannot take up but can give off hydrogen ions the pA scale is without a limit on the acid side, but limited on the basic. As an example of such a medium hydrogen chloride may be mentioned. If hydrogen chloride should be found upon closer examination to possess some slight power to take up hydrogen ions, the pA scale for this solvent would not be infinitely long on the acid side, but would merely extend far out on this side.

If the medium can neither take up nor give off hydrogen ions (for example, benzene), the pA scale is unlimited on both sides.

In figure 1 is given a diagrammatic representation of the scale of reaction in a number of typical solvents.

THE MEASURE OF ACID AND BASIC STRENGTH

The commonly used measure of the strength of an acid is its dissociation constant. As is well known, the dissociation constant is equal to the hydrogen-ion concentration (lyonium-ion concentration) in a half-neutralized acid solution. (By a half-neutralized acid solution is meant a solution which contains just as many molecules of the acid itself as of the acid minus hydrogen ion). As a measure of the acid strength one can use, in place of the hydrogen-ion concentration, any other of the numbers which may be employed to give the reaction of the half-neutralized solution (*A*, pH, pA). Using pH one obtains the pK value of the acid (its dissociation exponent). In general it is most practical to use the same number as that selected for stating the reaction of a solution.

When an acid molecule (S) splits off its hydrogen ion, there is formed an acid residue (B). The acid residue, as Brønsted quite rightly emphasizes, must always be a base, in that it can combine with hydrogen ion to form an acid

$$S \rightleftarrows B + H^+$$

Brønsted calls acids and bases which stand in this mutual relationship to each other "corresponding". It is easy to understand why chemists in the past have not been aware of the correspondence between acids and bases. In the first place, correspondence appears only when Brønsted's extended concept of acids and bases is used. Moreover, the base corresponding to a fairly strong acid is a very weak base, and conversely the acid corresponding to a fairly strong base is a very weak acid. Only when one understands by *acids* and *bases* not only the substances which give to water a decidedly acid or basic reaction, but rather all substances which have the power to split off or take up hydrogen ions, does the correspondence emerge clearly.

As a measure of the strength of bases Brønsted[8] has proposed to use the reciprocal of the dissociation constant of the corresponding acid. It is surely more practical, however, to use the same value for an acid and for its corresponding base, i.e., to use as a measure of strength for both acids and bases the reaction of the half-neutralized solution. Both the strength of the ammonium ion as an acid and the strength of ammonia as a base can be measured by the number which gives the reaction of a solution in which the ammonium ion and ammonia are present at the same concentration. Using the reciprocals for bases merely increases the number of quantities to be remembered and tabulated, and makes more difficult the grasp of the relationship between the reaction and the extent of neutralization in the case of bases. I grant that people are going to be reluctant to express basic strength by a number which increases with decreasing basic strength. But just as we have become accustomed to expressing the degree of acidity in pH values, which undeniably increase with decreasing acidity, we can surely become accustomed to expressing basic strength by a number which increases as basic properties decrease.

In aqueous solution one can use as a measure of the reaction of the half-neutralized solution the lyonium-ion concentration (c_H) or the hydrogen-ion exponent (pH). In nonaqueous, basic media one can use, in addition to these quantities, the acidity A or its negative logarithm, the acidity exponent pA. On the other hand, in nonaqueous, nonbasic media one can use only the last two, the acidity and the acidity exponent (A and pA).

Whether the one or the other of these possible measures is used, care must be taken that the same measure is employed throughout the work in a given solvent. The value of the strength of an acid depends on the medium, whatever scale of reaction is used. It is not even to be expected that the same sequence of acid strength (except very approximately) will be found upon comparing acids in different media. In a paper on the distribution coefficients of ions between different media, Larsson and I[6] have tried to work out the theory of the variation of acid strength with medium, but I shall not go into the matter at this time.

Since free hydrogen ions (hydrogen kernels, protons) are not found at finite, determinable concentrations in any of our solutions, it is not possible to determine the absolute dissociation constants or absolute strengths of acids and bases. The strength of the acid (base) is given in relation to the strength of the lyonium ion (the medium itself) when the strength is stated in terms of the lyonium-ion concentration of the half-neutralized solution. And when the acidity scale is employed, the strength of the acid (base) is compared with the strength of the hydroxonium ion (water). It must not be forgotten, however, that the specific properties of the medium, especially the dielectric constant, have a marked and very varied effect upon the strength of acids (bases), so that even in the case where the strength is always compared with that of the hydroxonium ion (water), different values may be obtained in different media.

Summary. As a measure of the strength of an acid and the strength of the corresponding base in a given medium, one of the quantities which may be employed to give the reaction of their half-neutralized solution should be used. The choice lies between the lyonium-ion concentration c_{H}, the acidity A, the hydrogen-ion exponent pH, and the acidity exponent pA. The worker should always select the same quantity which he employs in stating the reaction of his solutions. None of these quantities gives numerical values of acid and basic strength which are independent of the medium, or even proportional to one another in different media (or which in the case of the logarithmic quantities yield the same difference in different media).

THE THEORY OF TITRATION

The theory of titration is not changed by the introduction of the new concepts of acid and base from the form in which I gave it many years ago[1], but because of its close relation to the problems discussed in this paper, I shall make a few remarks about it here, especially about its application to nonaqueous solutions.

The theory of titration furnishes a means of calculating the error made in titrating a solution of one or several acids or bases to the change point of some given indicator. For aqueous solutions the procedure is as follows: The position of the change point of the indicator (p_T) is marked on the scale of reaction, as are the points which give the strengths of the acids and bases present ($p_1, p_2, p_3 \ldots$). The errors which arise depend altogether upon the position of p_T relative to the points $p_1, p_2, p_3 \ldots$, and relative to the ends of the scale of reaction (0 and 14). Sharp change of color and consequent accurate titration result when p_T lies far from all these points. If p_T is kept at a distance of at least three units from a p, the error arising from the presence of the acid (base) is less than 0.1 per cent of the amount of the acid (base) in question. If d is the distance between p_T and p, the error is less than 10^{-d} of the amount of the acid (base) corresponding to the p. If the distance between p_T and the ends of the scale is at least four units, the so-called hydrogen- and hydroxyl-ion errors are at most 0.01 cc. of 1 normal titration liquid when the final volume of solution is 100 cc. Generally speaking, this error is at most $v \times 10^{-d}$ cc. of normal titration liquid (v is the final volume and d the distance between p_T and the nearer end of the scale (0 or 14)).

When the procedure is to be transferred to nonaqueous solutions, the only thing to be changed is the ends of the scale, which no longer lie at 0 and 14, but at the numbers which give the reaction of solutions 1 normal in lyonium ion and 1 normal in lyate ion respectively. If the medium does not form lyonium ions, or does not form lyate ions, the scale is unlimited on the corresponding side, and the error arising from too close approach to the end of the scale on this side disappears. In benzene and other media where the scale of reaction is unlimited on both sides, one has to prevent only the too close approach of the titration exponent p_T to the p's corresponding to the acids and bases present.

I hope that I have succeeded in describing the manner in which the recent extension of the concepts of acid, base, and salt, primarily through Brønsted's useful and clarifying work, has progressed to a point where it will be desirable to introduce the new viewpoint and the new definitions into the elementary teaching of chemistry.

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Investigations on the Solubility of Calcium Phosphates

NIELS BJERRUM

Paper read at the *Nordic (19th Scandinavian) Scientist Meeting* in Helsingfors 11th August, 1936.
Translated from the report of the meeting, pp. 344–48

For some time past, together with P. Damsgaard-Sørensen and A. Tovborg Jensen, I have been studying the solubility of calcium phosphates, a very complicated problem. Our investigations are not yet terminated, but certain facts have been proved, and it is of these I shall speak in the following.

The difficulties of the work were considerable. The *concentrations* of phosphate and calcium to be measured were *small.* The solutions have the tendency to remain *supersaturated* and *saturation equilibria are but slowly established*, even in the presence of the solid calcium phosphates. Great difficulties arose because, as shown by A. Rindell, *solid calcium phosphates decompose in the presence of water.* We have finally succeeded in overcoming all these difficulties by using X-ray analysis (Debye-Scherrer diagrams) in a constant control of the nature of the precipitates.

Theoretically, a troublesome complication arises, because in calcium phosphate solutions, to a certain degree, complexes are formed between calcium and phosphate. This plainly manifests itself in the fact that calcium phosphate solutions show a more acid reaction than corresponding sodium phosphate solutions with the same degree of neutralization with respect to phosphoric acid. A complex, such as $Ca(HPO_4^-)_2$ seems to have nearly the same acid strength as the ion $H_2PO_4^-$ and is consequently much more acid than the ion HPO_4^{--}. The strength with which the hydrogen ions are bound is determined more by the free electric charge of the PO_4-group, than by the number of hydrogen atoms tied up to it. We have not yet succeeded in determining the composition and amount of the complexes. Fortunately the degree of complex formation is usually less than 10 per cent, and since it is impossible to determine the composition of the dilute solutions of calcium phosphates with great accuracy, this complex formation is not taken into account in the following calculations of solubility products.

Besides the *primary calcium phosphate* $Ca(H_2PO_4)_2, H_2O$, with degree of neutralization 1 and 1 molecule of water of crystallization (we shall call it (1,1)-phosphate) we have until now studied the two *secondary calcium phosphates*, the di-hydrate (2,2) and the "anhydrous" salt, which, however, always contains about $^1/_6\,H_2O$, and which is therefore designated the $(2,{}^1/_6)$-phosphate. According to Trömel's excellent investigations, with which we perfectly agree, tertiary calcium phosphates are never precipitated from aqueous solutions. Precipitates of that composition are always mixtures of the *hydroxyl apatite* $Ca_5(PO_4)_3OH$, with a degree of neutralization $3^1/_3$ and calcium phosphates with a degree of neutralization below 3. We have studied especially the solubility of the hydroxyl apatite, which is precipitated from boiling aqueous solutions showing incipient red colour with phenolphthalein. In air-dry condition this contains a little water, about 1 H_2O when the formula is written as above. I shall call it $(3^1/_3,1)$-phosphate. Its particles are so small that the substance has colloidal properties, yet it shows the same Debye-Scherrer lines as ignited hydroxyl apatite.

Finally we determined the solubility of a *new crystalline calcium phosphate*, which we encountered by chance. It has the formula $Ca_4(PO_4)_3\,H, 3H_2O$, that is to say, with a degree of neutralization $2^2/_3$, and 3 molecules crystal water, $(2^2/_3,3)$-phosphate.

For the calcium phosphates mentioned we use as "solubility products" in saturated solutions the following expressions:

$$pL_{1,1} = -\log([Ca]\cdot[H_2PO_4]^2) = p\,[Ca] + 2\,p\,[H_2PO_4],$$

$$pL_{2,{}^1/_6} = -\log([Ca]\cdot[HPO_4]) = p\,[Ca] + p\,[HPO_4],$$

$$pL_{2,2} = -\log([Ca]\cdot[HPO_4]) = p\,[Ca] + p\,[HPO_4],$$

$$pL_{2^2/_3,3} = -\log\left(\frac{[Ca]^4\cdot[HPO_4]^3}{A_H{}^2}\right) = 4\,p\,[Ca] + 3\,p\,[HPO_4] - 2\,pA_H,$$

$$pL_{3^1/_3,1} = -\log\left(\frac{[Ca]^5\cdot[HPO_4]^3}{A_H{}^4}\right) = 5\,p\,[Ca] + 3\,p\,[HPO_4] - 4\,pA_H.$$

[Ca], $[H_2PO_4]$ and $[HPO_4]$ designate the molar concentrations of the calcium and hydrogen-phosphate ions, A_H the hydrogen ion activity, and pL the negative logarithm of L.

In the following table the values of these solubility products at 18° C and 37° C are collected.

$$pL_{1,1} \qquad < -1^{\star}$$

$$pL_{2,2} \quad (18^\circ) = 6.57 - 3.99\sqrt{\mu}$$

$$pL_{2,2} \quad (37^\circ) = 6.62 - 4.12\sqrt{\mu}$$

$$pL_{2,{}^1/_6} \quad (18^\circ) = 6.81 - 3.99\sqrt{\mu}$$

$$pL_{2,{}^1/_6} \quad (37^\circ) = 7.01 - 4.12\sqrt{\mu}$$

$$pL^{\text{diss.}}_{2^2/_3,\;3} \; (18^\circ) = 11.8 - 14.0\sqrt{\mu}$$

$$pL^{\text{prec.}}_{2^2/_3,\;3} \; (18^\circ) = 9.3 - 14.0\sqrt{\mu}$$

$$pL^{\text{diss.}}_{2^2/_3,\;3} \; (37^\circ) = 12.1 - 14.4\sqrt{\mu}$$

$$pL^{\text{prec.}}_{2^2/_3,\;3} \; (37^\circ) = 10.7 - 14.4\sqrt{\mu}$$

$$pL^{\text{diss.}}_{3^1/_3,\;1} \; (37^\circ) = 7.5 - 16.5\sqrt{\mu}$$

$$pL^{\text{prec.}}_{3^1/_3,\;1} \; (37^\circ) = 6.5 - 16.5\sqrt{\mu}$$

In the formulae μ indicates the ionic strength.

With $2^2/_3$- and $3^1/_3$-phosphates, it has been necessary to introduce two pL values, corresponding to dissolution ($pL^{\text{diss.}}$) and precipitation ($pL^{\text{prec.}}$), because in the times of rotation used, it was not possible from both sides to attain saturated solutions of the same compostion. As a rule, in the course of twenty-four hours, it is possible, from unsaturated and supersaturated sides, by rotation with the solid phase, to obtain solutions, whose composition will then remain unchanged for weeks, and which are yet quite far removed from each other.

The pL values, quoted above, permit a computation of the solubilities and transformations of the phosphates examined, under very different conditions. A graph gives the most perspicuous survey of these conditions. In fig. 1, curves are drawn for a series of round pA_H-values, which show the connection between $p\,[\text{Ca}]$ and $p[\text{P}]$ in saturated solutions. [P] the total concentration of phosphoric acid may, for pA_H-values between 4 and 10 be computed from $[\text{HPO}_4]$ according to the formula

$$[\text{P}] = [\text{HPO}_4] \cdot \frac{K'' + A_H}{K''}$$

in which K'' is the 2nd (incomplete) dissociation constant of the phosphoric acid.

It is our intention to study further the solubility of ignited, anhydrous, hydroxyl apatite, and eventually, other hydroxyl apatites. After that, the solubility of the important fluor apatite will be determined. For this, some preparatory work has

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$\star$ The primary calcium phosphate (1,1) is so soluble that it is misplaced to compute its solubility product. According to Bassett's solubility determinations, L at 25° C must be considerably larger than 15.

already been done. Finally, a series of typical, natural phosphates (raw phosphates, bone phosphates) will be studied, to determine whether their solubilities are in agreement with observations made in studying pure, artificially prepared phosphates.

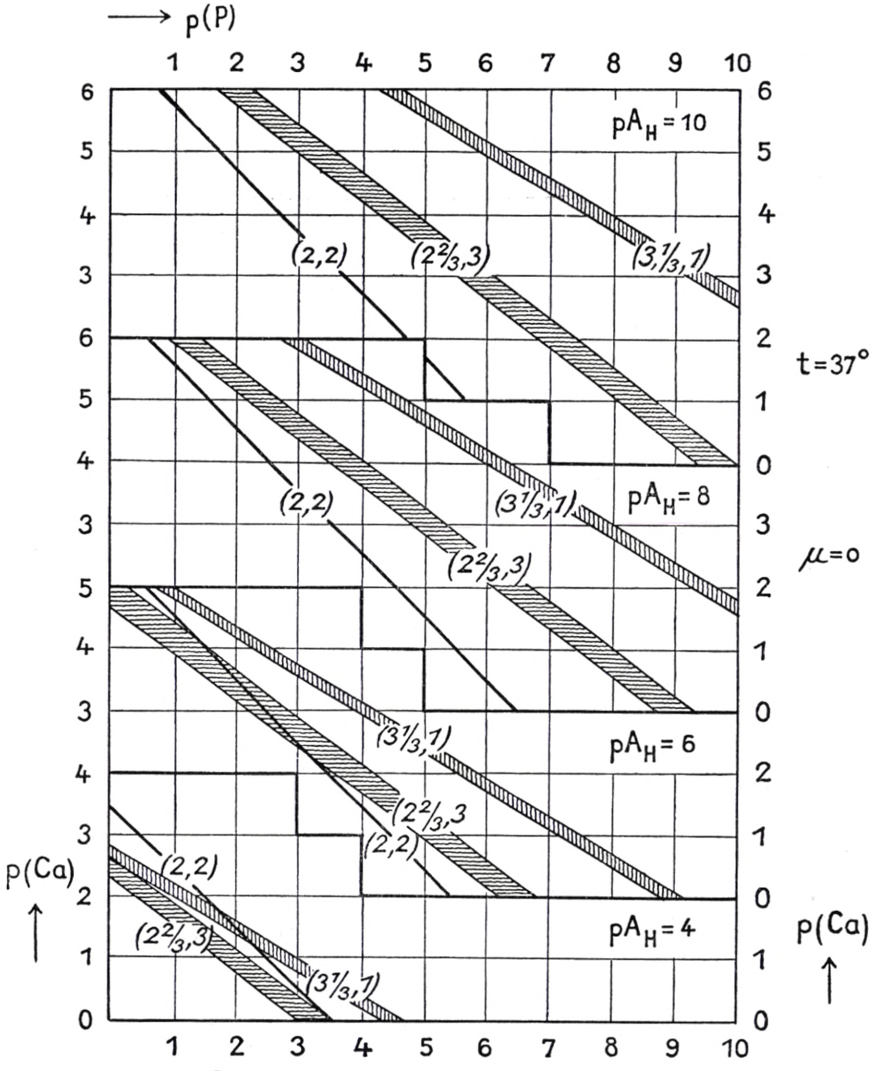


Fig. 1.

Some Comments on Chromium Chloride-Sulphates

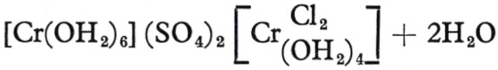
Preliminary communication

NIELS BJERRUM

Translated from *Ber.* **39** (1906) 1597–1602. The paper was received by the journal 12th April, 1906.

Recently, papers have been published by A. Werner and R. Huber[1] and also by R. F. Weinland and R. Krebs[2] on chromium chloride-sulphates. I have been occupied for some time with work on the chlorides of chromium and shall soon report these results in detail. In the course of this work, I have also carried out investigations on chromium chloride-sulphates, and since I have arrived at conclusions about the constitution of these compounds different from those of the above mentioned authors, I shall here briefly state my conclusions and the most important facts upon which I base them. Furthermore, I also hope to be able to show that the basis for the opinions which are described in the above mentioned papers is insufficient, or allows of another explanation.

A new chloro-sulphate has been prepared by Werner and Huber by adding sulphuric acid to a mixture of violet chromium sulphate and green chromium chloride; it is isomeric with Recoura's[3] compound $CrClSO_4,6H_2O$ and has similar properties, as regards the solubility and precipitation of the sulphate radical. I have already some time ago prepared this isomeric salt and can in all respects confirm the data given for the new salt. From the method of preparation of the salt, Werner and Huber conclude that it is apparently a di-molecular compound of which the constitutional formula can be written as follows:



$$[Cr(OH_2)_6]\,(SO_4)_2\left[Cr^{Cl_2}_{(OH_2)_4}\right] + 2H_2O$$

Further support is gained for this constitutional formula by the preparation of an analogous compound, in which they have substituted aluminium sulphate for the chromium sulphate grouping. That this interpretation, to which I also subscribe, is correct, I was able to prove in another way. A solution (1:10) of the salt in dilute hydrochloric acid gave on saturation with hydrogen chloride a precipitate of blue chromium chloride, which contained almost half of the chromium (calculated 0.48 g, found 0.45 g). Since a solution of blue chromium chloride is nearly quantitatively precipitated by hydrogen chloride, (at 10° C only 0.05 per cent remains in solution) this experiment shows that half the chromium is present as blue chromium ion, quite as is to be expected from Werner's formula.

Werner and Huber ascribed the same formula to Recoura's salt. Their reason for this seems to me rather unconvincing.

They succeeded in preparing a little blue chromium chloride from Recoura's chloro-sulphate, but only by repeated precipitation with hydrogen chloride and storing the precipitate on a clay disc in open air. By this procedure a part with green colour goes into the clay disc while the violet chromium chloride hydrate remains. From this experiment the authors conclude "dass die Entstehung von violettem Chromchloridhydrat aus dem Chlorosulfat unter den beschriebenen Bedingungen sich nur dann erklären lässt, wenn man annimmt, dass sich das Radical $[Cr(OH_2)_6]$ im Chlorosulfat schon vorfindet".

Firstly, it should be pointed out that the reactions of chromium chlorides are not so well known that one can entirely exclude formation of $[Cr(OH_2)_6]$ even if it is improbable. Secondly, it is possible that a small amount of $[Cr(OH_2)_6]$, in the form of the new chloro-sulphate, has been present as an impurity in the chloro-sulphate used (no data are given on the amount of violet chromium chloride prepared). When I tried to prepare Recoura's compound from heated solutions of green chromium chloride, I always obtained such impure preparations. If, however, I prepared the salt according to Recoura's method, it was always pure. (No precipitation occurred when a solution (1:10) in hydrochloric acid was saturated with hydrogen chloride). It seemed to me, however, quite possible that the small alteration in Recoura's method of preparation which Werner and Huber had introduced (drying of the boiled hydrochloric-acid solution of violet chromium sulphate in the vacuum desiccator instead of simple storing), may have resulted in a greater yield, but a less pure salt.

That the chloro-sulphate, in a damp atmosphere, lying on a clay disc, partly deliquesces and leaves behind a little violet chromium sulphate, appears to me unconvincing as a proof of the constitution suggested by Werner.

On the other hand, I think it can be concluded from the following experiments that a fresh solution of Recoura's chloro-sulphate can contain no $[Cr(OH_2)_6]$. A solution of 1 g of Recoura's chloro-sulphate in 10 cc of hydrochloric acid gives no precipitation with hydrogen chloride during the first hours. If but a few centigrams (that is the quantity of blue chromium chloride which can be precipitated with hydrogen chloride from 10 cc of water) of blue chromium chloride had been present in the solution, precipitation would have occurred.

From this fact I concluded that Recoura's chloro-sulphate cannot be a dichlorochromium-chromium sulphate. That it really is a monochlorochromium sulphate I think I can demonstrate in the following way.

First of all, I should mention that I was able to prepare a new chromium chloride $CrCl_3,6H_2O$, the properties of which revealed it as being the *monochlorochromium chloride*, which has so far been unsuccessfully sought. It is prepared from a concentrated, boiled solution of green chromium chloride, by precipitating by hydrogen chloride the blue chromium chloride formed, and transferring the filtrate to a large amount of ether saturated with hydrogen chloride. By this procedure the new chloride separates out, while the dichlorochromium chloride contained in the solution is transformed into compounds giving a red colour when dissolved. The monochloro compound may be recrystallized by dissolving in a mixture of ether and fuming hydrochloric acid (1:1), in which the two other chromium chlorides are insoluble, and then pouring into ether saturated with hydrogen chloride. If the chloride is freshly prepared — it is unfortunately rather unstable — exactly 2/3 of the chlorine is precipitated by silver nitrate in nitric acid solution. From this it can be concluded that the new salt must be a monochlorochromium chloride or an equi-molecular compound of blue and green chromium chlorides. Since, however, the aqueous solution of the salt has properties differing from those of a mixed solution of blue and green chromium chlorides, for example in the presence of hydrogen chloride or concentrated sulphuric acid, the first supposition is the more probable. This new chloride can now be obtained with good yield (about 75 per cent) from Recoura's chloride-sulphate by dissolving in hydrochloric acid and pouring into a large excess of ether saturated with hydrogen chloride. Similarly a solution of the new chloride gives Recoura's chlorosulphate on treatment with concentrated sulphuric acid. From these observations it follows with great probability that Recoura's chlorosulphate is really a monochlorochromium sulphate $[CrCl]SO_4$.

The electrical conductivity and the changes in electrical conductivity of solutions of both chloride-sulphates agree well with this type of constitution for the salts.

The paper by Weinland and Krebs is concerned with two isomeric chromium chloride-sulphates with the formula $CrClSO_4,8H_2O$. One is green and is prepared by evaporating to dryness a solution of the green chromium chloride after adding sulphuric acid. Except for the water content, the authors found that their salt was identical with Recoura's. The second is violet. They prepare it by the addition of an equi-molecular amount of sulphuric acid to a solution of blue chromium chloride. If the solution is sufficiently concentrated, precipitation occurs immediately, otherwise it must first be evaporated.

From the properties of these salts it doubtless follows that the chlorine in the green salt is bound complexly and in the violet in the ionic state. However, when Weinland and Krebs conclude from their experiments that all SO_4 in both salts is bound complexly, I cannot agree with them. They conclude this from the fact that barium chloride does not precipitate the SO_4 immediately from a dilute solution (less than 0.01 *M*) when a certain amount of nitric acid is present.

It appeared very improbable to me that the SO_4 in these salts should be complexly bound. The instantaneous precipitation of the violet chloride-sulphate from a blue-violet solution of chromium chloride makes a complex bond highly improbable, since chromium and sulphuric acid only slowly form complex linkages with one another. I sought, therefore, another explanation of Weinland and Krebs's experimental results; and I think that I have found this explanation in the fact that precipitation of barium sulphate always takes place slowly in dilute solution. It is generally known that many sulphates e.g. calcium sulphate, show the phenomenon of supersaturation to a great extent. Therefore, it is also necessary, when estimating sulphuric acid, to wait a certain time before filtering. That this phenomenon of supersaturation is sufficient to account for the slow precipitation of SO_4 in chromium chloride-sulphate, I have demonstrated by the fact that potassium sulphate shows exactly the same behaviour.

To 10 cc of 0.01 *M* solution of potassium sulphate, I added varying amounts of 1 *N* nitric acid, and after cooling in ice to about 1° C, 1 cc of 0.1 *M* barium chloride solution (equi-molecular amounts) was added; the following results were obtained:

Moles HNO_3 per mole K_2SO_4	Time, before the appearance of a precipitate
0	0
10	less than 1 sec.
20	about 2 sec.
50	5—10 sec.
150 (1 cc 15 *N* nitric acid added)	2—10 min.

Especially at higher acid concentrations, the time before the appearance of a precipitate, varied from experiment to experiment. In another experiment the same amount of nitric acid was added to 10 cc of water instead of potassium sulphate solution. After cooling in ice, about 0.03 g of chromium chloride-sulphate was dissolved which took $\frac{1}{4}$ min. 1 cc of 0.1 *M* barium chloride was added, and it was found that the same times elapsed before the appearance of the precipitates. These time intervals are of course somewhat irregular, as is to be expected in such phenomena, and I was not able by parallel experiments to discover whether potassium sulphate or the different chloride-sulphates (the two prepared by Weinland and Krebs, as well as the salt prepared by Recoura) were precipitated more slowly. Sometimes potassium sulphate produced a precipitate more quickly and sometimes it produced a precipitate more slowly than the chloride-sulphates. In a solution of 0.01 *M* K_2SO_4 and 150 moles HNO_3 per mole K_2SO_4 to which an equivalent amount of $BaCl_2$ had been added, a precipitate appeared after 2 minutes, but only about half of the sulphuric acid had been precipitated after 10 minutes. The clear filtrate gave a copious precipitation after it had been heated and allowed to stand.

Weinland and Krebs[2] write: "Die Bestimmung des Molekulargewichtes bezw. des Dissociationsgrades der Verbindungen auf kryoskopischem Wege steht mit dem angegebenen Befund der Fällbarkeit des Chlors bezw. der Schwefelsäure im Einklang". They find namely for the violet chloride-sulphate a molecular depression of the freezing point which is approximately twice as great as is to be expected for an undissociated compound. "Beim violetten Salz stimmt die gefundene Depression mit der für ein in zwei Ionen gespaltenes Salz berechneten völlig überein". For the green chloride-sulphate, they find a somewhat greater molecular depression, than was calculated for the undissociated compound. Nevertheless, the depression is not so great as is required for a compound split into two ions. The figures increase with the time; hence they attribute the too great figures to the rather rapid hydration of the compound.

In order to show that this type of conclusion is not necessary, nor even permissible, I have compared in the following table, the molecular depressions, calculated from the results of Weinland and Krebs, for the green chloride-sulphate (concentrations in moles per 1000 g water), with those found for other sulphates of divalent metals[4] (concentrations in moles per liter).

	Molar concentration	Molar depression
Green $CrClSO_4, 8H_2O$	0.0769	2.99
—	0.1044	2.80
Green $CrClSO_4, 5H_2O$	0.0499	2.10
$MgSO_4, 7H_2O$	0.0638	2.59
$ZnSO_4, 7H_2O$	0.0689	2.45
$CuSO_4, 5H_2O$	0.112	2.17
$CdSO_4, {}^8/_3H_2O$	0.0417	2.59
—	0.104	2.28

The values found for the green chromium chloride-sulphate, $CrClSO_4,8H_2O$, are not smaller, but on the contrary somewhat larger than those given for the other sulphates. That the figures are all considerably smaller than would be expected (3.70) for a salt completely dissociated into two ions, is of course explained by the incomplete electrolytic dissociation of the compound. The fact that the anions are linked to the cations, need not imply that they are in complex combination. By analogy, the sulphate radical is not complexly bound in undissociated magnesium sulphate; and since green chromium chloride-sulphate, $CrClSO_4,8H_2O$, behaves similarly to this compound, it is as little justifiable to assume such a combination in this case. The depression of the freezing point of the green $CrClSO_4,5H_2O$, appears, however, to be rather small, but in this compound a part of the sulphuric acid is without doubt complexly bound.

Similar considerations can be applied to the depression of the freezing point of the violet chloride-sulphate. Just because the depression of the freezing point of this salt in 0.0822 *M* solution is approximately as great (3.98), as that calculated for a compound completely dissociated into two parts (3.70), it must be concluded that the salt is tri-ionic, and not that it is di-ionic as Weinland and Krebs believe. At the dilution used, it will certainly not be fully dissociated, and in this case it is not possible to use, as an explanation for the somewhat too large figures, the fact that the depression increases with time.

Hence the statement that the sulphuric acid in the chromium chloride-sulphate is complexly bound, must be considered as unwarranted, since Weinland and Krebs have given no other reasons for their conclusions, than the two discussed here.

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Studies on Chromic Chloride

NIELS BJERRUM

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SUMMARY

1. It is shown that if blue chromic chloride is dissolved in water, it instantaneously undergoes, to a greater or lesser extent, hydrolysis according to the equation $CrCl_3 + H_2O = CrCl_2OH + HCl$. This hydrolysis takes place according to the law of mass action, and changes with temperature, as it is to be expected from the heat evolved in the process.

2. The product of hydrolysis, $CrCl_2OH$, is also formed, when one equivalent of sodium hydroxide is added to a solution of chromic chloride, $CrCl_3 + NaOH = CrCl_2OH + NaCl$. It is soluble in water, green, and is slowly transformed on standing. When more sodium hydroxide is added a corresponding amount of the "normal" chromic hydroxide is precipitated, $CrCl_2OH + 2\,NaOH = Cr(OH)_3 + 2\,NaCl$.

3. Dilute chromic chloride solutions become green immediately on warming or on addition of sodium acetate. This is due to the formation of the same product of hydrolysis, $CrCl_2OH$. The blue chromic chloride is re-formed by rapid cooling or addition of hydrochloric acid, provided that this is done immediately, before the unstable $CrCl_2OH$ has been transformed.

4. The constant of hydrolysis of the green dichlorochromic chloride is about $4 \cdot 10^{-6}$ at 25° C.

5. In dilute solution, the rate of the green dichlorochromic chloride's conversion to the blue chromic chloride (estimated by conductivity measurements) can only be explained theoretically, when it is assumed that monochlorochromic chloride is first formed, and then converted into blue chromic chloride, and that acids retard the process.

On the basis of measurements of the rate of transformation in hydrochloric acids of different strengths, expressions have been obtained for the influence of acids on the two velocity constants of the process. The transformation of chromic chloride in aqueous solution is in agreement with these expressions, if the amount of acid, which is present in the solution owing to the hydrolysis of the chlorides, is inserted in the expressions.

6. The experimentally found expressions for the negative catalysis by acids ($k_1 = a + \frac{b}{s}$ and $k_2 = \frac{c}{s} + \frac{d}{s^2}$, where s denotes the amount of free acid and a, b, c, and d are constants) can be theoretically deduced, when it is assumed that the products of hydrolysis are transformed much more quickly than the chromic chlorides themselves. This assumption also explains the large temperature coefficient which is characteristic for the rate of transformation (10° C giving a fourfold increase); not only the rate of transformation of the products of hydrolysis increases at higher temperature, but also their amount.

7. In explaining the analytical findings in concentrated chromic chloride solutions, which have been standing until equilibrium has been reached, it is necessary to assume that the solution contains, besides green and blue chromic chlorides, a third substance. This substance I have prepared. It has the formula $CrCl_3,6H_2O$, is green, crystalline and extremely hygroscopic. It contains only one chlorine atom with a complex bond, and hence is a monochlorochromic chloride. On standing, it is transformed into dichlorochromic chloride. It can be separated from the other two chromic chlorides by its solubility in a mixture of equal volumes of ether and fuming hydrochloric acid. It is the same substance, the formation of which as an intermediate product was necessary for the explanation of the transformation of the green chromic chloride in dilute solution.

8. Some estimations have been carried out of the amounts of the three chromic chlorides present in the solutions which had been allowed to stand until equilibrium between the chromic chlorides was reached. It has been shown that the equilibrium is altered, as the theory requires, by changes in either the concentration or the temperature.

The displacement of the equilibrium by the addition of various salts and hydrochloric acid, is also in qualitative agreement with the law of mass action.

9. A chloro-sulphate, which turns out to be identical with the chlorochromic sulphate prepared by Recoura, can be prepared from the monochlorochromic chloride with sulphuric acid. Since, conversely, monochlorochromic chloride can be prepared from Recoura's sulphate in good yield, Recoura's salt must be the sulphate which corresponds to the monochlorochromic chloride.

10. From a solution of equal parts of green chromic chloride and blue chromic

chloride, sulphuric acid precipitates a compound which is isomeric with Recoura's chloro-sulphate. In agreement with Werner, who has recently prepared the same substance, I find that this compound is dichlorochromic-chromic sulphate, $CrCl_2 — SO_4 — Cr = SO_4$.

11. By dehydration of the green $CrCl_3,4H_2O$ over phosphoric anhydride in a vacuum of less than 1 mm mercury, I have prepared a red chromic chloride, the composition of which corresponds most nearly to the formula $CrCl_3,1\frac{1}{2}H_2O$, but which could not be prepared with a completely constant composition. It is extremely hygroscopic; its aqueous solution is green.

Some Investigations on Basic Chromic Compounds

NIELS BJERRUM and CARL FAURHOLT

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1. If chromic salt solutions are heated with or without addition of bases, part of the chromium is transferred to "*latently basic*" compounds. In these compounds the chromic hydroxide will bind less than three equivalents of acid, even in the presence of an excess of acid. Consequently part of the hydroxyl of the chromic hydroxide is masked. These latently basic compounds may be sharply discerned from the "*true basic*" compounds, which immediately combine with acids even at low temperatures[1a,2].

Formerly[1a,2] the quantity of masked hydroxyl was determined by means of hydrogen-ion concentration measurements in the cooled solutions. But in the present investigations on the formation of latently basic chromic compounds we have used another method, viz. determination of the quantity of chromium which still after heating existed in the original form of the hexaquochromic cation, $Cr(H_2O)_6{}^{+++}$, or which could quickly be converted into this form at normal temperature by means of an acid (true basic compounds). As nitrate solutions were used, and the nitrate ion forms no complexes with chromium under the experimental conditions employed, we may assume that the remaining part of chromium existed as latently basic compounds.

2. In the present investigations, the hexaquochromic ion had to be determined in rather dilute solutions (down to 0.01 molar). Consequently precipitation of the chloride[1b,3] by hydrogen chloride or the sulphate[1c,4] by sulphuric acid and alcohol could not be used. And precipitation of the potassium alum[4] required such large quantities of alcohol that new difficulties arose. We found, however, that it is possible to precipitate hexaquochromic salt quantitatively as caesium alum in the following manner:

3. *Determination of the Hexaquochromic Ion by Precipitation as Caesium Alum.* 20 cc. about 0.01 molar chromium solution is mixed with 0.2 to 0.3 cc. about 2 normal sulphuric acid and 1 g. caesium sulphate. After 25 minutes 10 cc. 96 per cent alcohol is added, and after standing another 5 minutes the precipitate

of caesium alum is filtered off on a small filter and washed four times, each time with 8 cc. dilute alcohol (2 volumes of water + 5 volumes of 96 per cent alcohol). The amount of chromium left on the filter was then determined according to R. Weinland[5] by oxidation in alkaline solution by hydrogen peroxide, addition of hydrochloric acid and potassium iodide, and finally titration with thiosulphate.

Control experiments showed that by this procedure the amount of hexaquochromic salt remaining in the mother-liquor and in the washings only corresponded to some 0.0002 molar chromium in the original solution. A corresponding small correction is consequently introduced for this amount. To obtain as complete a precipitation in the form of potassium alum, 8 volumes of alcohol instead of $^1/_2$ volume would have been necessary.

In a number of cases we encountered the particular difficulty at the alum precipitation that a green basic compound was precipitated besides the alum. This green precipitate may best be described as colloidal chromic hydroxide. It occurred already on addition of sulphuric acid and was somewhat increased by addition of caesium sulphate and alcohol. Some analyses of precipitates obtained by sulphuric acid and sulphuric acid + alcohol, respectively, showed that they were basic chromic sulphates with only from 0.28 to 0.47 equivalents SO_4^{--} per Cr.

To overcome this difficulty the alum precipitate was treated with 50 cc. of water, and the alum precipitation was repeated in 20 cc. of the latter solution. The precipitate from the second alum precipitation was dissolved in 50 cc. of water, and the electrical *conductivity* of this solution was determined. From the result obtained the hexaquochromic ion content was calculated. For now we could assume that the conductivity was exclusively due to alum. Beforehand, freshly prepared chromic nitrate solutions (which contained chromium exclusively as hexaquochromic salt) had been subjected to the same treatment so as to determine the relation between the conductivity of the solution of the second alum precipitate and the hexaquochromic salt content of the original solution. All hexaquochromic ion contents of table 1 are obtained conductometrically in this way.

4. Besides determining hexaquochromic salt by alum precipitation we determined the amount of "colloidal chromic hydroxide" which was precipitated in 20 cc. of chromium solution by 0.2 cc. 2 normal sulphuric acid and 10 cc. 96 per cent alcohol. In that way it became possible to differentiate between two kinds of latently basic chromium: the typically colloidal form which is precipitated by sulphuric acid and alcohol, and the slightly colloidal or non-colloidal form which is not precipitated by sulphuric acid and alcohol.

5. In table 1 we have collected the results obtained from the investigation of chromic nitrate solutions heated to 75°C, with or without addition of sodium

hydroxide. The chromic nitrate used was prepared from chromium trioxide, which was reduced by means of 3 per cent hydrogen peroxide in the presence of a small excess of nitric acid, evaporated until crystallization and twice recrystallized from water.

The percentage distribution of chromium on 1) hexaquochromic salt, 2) latently basic chromium not precipitable by sulphuric acid and alcohol, 3) latently basic chromium precipitable by sulphuric acid and alcohol, is shown in the table. But no greater accuracy than a few per cent can be reckoned with in these figures.

It can be seen from the figures that in a short time, one day or a few days, at 75° C an equilibrium seems to be established between the hexaquochromic ion and the latently basic chromium which is not precipitable by sulphuric acid and alcohol. On the other hand the formation of the latently basic chromium which is precipitable by sulphuric acid and alcohol sets in very slowly; it cannot be seen from the data of the table whether equilibrium has been attained with regard to this formation in the experimental period of three or four months.

It is interesting to observe how the equilibrium between the hexaquochromic ion and chromium not precipitable by sulphuric acid is shifting towards an increase of the hexaquochromic ion content when there is an increasing formation of chromium precipitable by sulphuric acid. No doubt there is a relation between this fact and the increasing acidity of the solution.

6. The following two experiments are instructive with regard to the behaviour of chromic salt solutions at heating over a long period. In these experiments the solutions were refluxed for a long time, the small quantity of evaporated water being replaced.

A 0.1 molar chromic nitrate solution was still clear after 74 days' boiling; but after another 30 days' boiling the solution was quite turbid, and after standing deposited a greyish white precipitate which was easily filtered off. An analysis of the filtrate showed that 91 per cent of the chromium had deposited. Out of the remaining 9 per cent, 8 per cent was hexaquochromic salt and 1 per cent latently basic chromium which was not precipitable by sulphuric acid. A titration with sodium hydroxide and phenolphthalein showed that the solution was still 0.3 normal with regard to nitric acid, free or bound to chromium. This fact can be taken as a proof that during the long period of boiling the solution has not to any perceptible degree absorbed any bases from the Jena glass flask used.

After desiccation over sulphuric acid the greyish white precipitate was to a rather close approximation of the composition $Cr_2O_3,2H_2O$ (determined by ignition loss).

After eight days' boiling a 0.1 molar solution of $Cr(NO_3)_3 + 2NaOH$ contained 83 per cent basic chromium which could be precipitated by sulphuric acid. After 38 days the solution was still clear. After a total boiling time of 68 days an

Table 1. Chromic Nitrate Solutions Heated to 75° C without or with Addition of Sodium Hydroxide

Composition of the solution	Time of heating in days	Distribution of chromium on		
		Hexaquo-chromic ion %	Latently basic chromium	
			Not precipitable by H_2SO_4 + alcohol %	Precipitable by H_2SO_4 + alcohol %
0.1 molar $Cr(NO_3)_3$	1.5	81.8	18.2	0
	4.4	82.4	17.6	0
	72	83.3	16.7	0
	98	80.0	20.0	0
0.05 molar $Cr(NO_3)_3$	4.4	78.4	21.6	0
	6.4	79.9	20.1	0
	81	77.7	22.3	0
0.01 molar $Cr(NO_3)_3$	1.5	70.0	30.0	0
	4.4	68.6	31.4	0
	28	69.1	30.9	0
0.1 molar $[Cr(NO_3)_3 + 0.5NaOH]$	1.6	54.0	46.0	0
	4.6	54.5	45.5	0
	97	51.8	48.2	0
0.05 molar $[Cr(NO_3)_3 + 0.5NaOH]$	4.7	52.7	47.3	0
	9.5	50.4	49.6	0
	107	51.7	48.3	0
0.01 molar $[Cr(NO_3)_3 + 0.5NaOH]$	1.7	49.7	50.3	0
	4.7	50.0	50.0	0
	9.5	47.0	53.0	0
	107	48.3	30.4	20.7
0.1 molar $[Cr(NO_3)_3 + 1NaOH]$	2.8	30.5	69.5	0
	105	37.0	47.7	15.3
0.05 molar $[Cr(NO_3)_3 + 1NaOH]$	9.5	33.0	59.9	7.1
	114	41.4	34.0	24.6
0.01 molar $[Cr(NO_3)_3 + 1NaOH]$	3	35.9	55.9	8.2
	7.5	32.1	53.4	14.5
	21	36.8	33	30
	42	38.4	28.5	33.1
	92	39.2	18.6	42.2
	133	41.5	10.5	48
0.05 molar $[Cr(NO_3)_3 + 2NaOH]$	2.8	10.9	30	59
	105	18.9	4.8	76.3
0.01 molar $[Cr(NO_3)_3 + 2NaOH]$	2.9	10.7	25.0	64.3
	11	13.4	15.3	71.3
	31	14.9	7.1	78.0
	82	13.3	3.8	82.9
	133	9.1	3	88

ample amount of green precipitate had appeared. After filtration the filtrate only contained 10 per cent of the chromium, and out of this 8.5 per cent was hexaquochromic salt and 1.5 per cent latently basic chromium which could be precipitated by sulphuric acid and alcohol. Titration of the solution and the precipitate deposited in it with sodium hydroxide and phenolphthalein showed that the system was always 0.1 normal with regard to nitric acid, free or bound to chromium, and consequently that no perceptible error due to corrosion of the glass flask was introduced. On the other hand the solution by itself contained only 0.091 normal nitric acid, consequently the precipitate has bound 9 per cent of the nitric acid.

On dialysis in a collodion bag against pure water an opalescent greenish colloidal solution was obtained from the precipitate. But the solution was so unstable that flocculation of a sample was brought about by shaking. When dried up and desiccated over calcium chloride to a constant weight, the colloidal solution gave a chromium hydroxide which according to its ignition loss was of the approximate composition Cr_2O_3, $2H_2O$.

These experiments show that the latently basic chromium which is precipitable by sulphuric acid is formed very slowly even at 100° C. Everything indicates that the formation observed at 75° C of basic chromium which is precipitable by sulphuric acid has not reached its maximum in the experimental period of three or four months.

7. To determine the total amount of chromium in the solutions, we used in most cases oxydation by hydrogen peroxide in alkaline solution and titration of the chromic acid formed with thiosulphate after addition of hydrochloric acid and potassium iodide. However, this method proved impracticable in the presence of colloidal basic chromium precipitable by sulphuric acid, because hydrogen peroxide in alkaline solution was not able to oxidize this chromium completely. In these cases the chromium was precipitated by ammonia and filtered off, the filter was burnt in a platinum crucible, and the remainder melted with a mixture of sodium and potassium carbonate over an intense blow-pipe flame until dissolved, and then another 10 minutes, after which the chromate formed was titrated as usual.

In table 2 the behaviour of various chromic solutions towards alkaline hydrogen peroxide is set out.

Solutions 1 and 2, which only contained hexaquochromic salt or basic chromium not precipitable by sulphuric acid, were oxidized even at ordinary temperature. If hydrogen peroxide is added to the solutions which have been made alkaline, they turn yellow at once. This is not the case with the four other solutions. In solution 3 oxidation may, however, still be accomplished satisfactorily by boiling. If the solution contains larger quantities of non-oxidizable chromium,

Table 2. Behaviour of Some Chromic Solutions towards Alkaline Peroxide

No	Composition	Heated	Hexaquochromic ion %	Latently basic chromium		Oxidizable by $KOH+H_2O_2$ %
				not precipitable by H_2SO_4 %	precipitable by H_2SO_4 %	
1	0.01 molar $Cr(NO_3)_3$	0 days (fresh)	100	0	0	100
2	0.1 molar $[Cr(NO_3)_3 + NaOH]$	2.8 days at 75°	30	70	0	100
3	0.05 molar $[Cr(NO_3)_3 + 2NaOH]$	2.8 days at 75°	11	30	59	99—100
4	0.01 molar $[Cr(NO_3)_3 + 0.5NaOH]$	107 days at 75°	48	30	21	96
5	0.01 molar $[Cr(NO_3)_3 + 1.5NaOH]$	160 days at 75°	20	10	70	95
6	0.1 molar $[Cr(NO_3)_3 + 2NaOH]$	38 days at 100°	—	—	80	85

it becomes quite turbid when boiled with alkaline hydrogen peroxide. In solutions 4 and 5, where some 95 per cent of the chromium was oxidized, it was contrived to carry out the oxidation quantitatively after a preceding evaporation with strong hydrochloric acid. This procedure was, however, useless in the case of the most resistant solution: no. 6, in which only 85 per cent of the chromium was oxidized. Here the chromium seemed to be even less oxidizable after the treatment with hydrochloric acid.

8. By means of electrometric hydrogen-ion determinations the quantity of masked hydroxyl in heated chromic salt solutions has previously[1a] been determined. Those investigations were made on the system of chromic chloride + barium hydroxide. We consider it, however, permissible to apply the results obtained to the system of chromic nitrate + sodium hydroxide investigated in this paper.

In table 3 the results are collected for the cases where the same concentrations have been investigated according to both methods. In all cases the solutions have only been heated to 75° C for a few days.

In column 4 the total quantity of latently basic chromium is stated as a percentage of the total quantity of chromium. In column 5 the number of masked hydroxyl groups per 100 chromium atoms is calculated. Finally the number of masked hydroxyl groups occurring in the latently basic compounds per chromium atom is presented in column 6. With a decreasing content of latently basic chromium this figure is approaching 1. The primarily formed latently basic compound thus seems to contain *one* masked hydroxyl group per chromium atom.

Table 3

Molarity of the chromic salt	Equivalents of base added per Cr-atom	Heated to 75° in days	Latently basic chromium in per cent	Number of masked OH per 100 Cr	Number of masked OH per Cr-atom in latently basic chromium
0.1	—	3 resp. 4	17.6	20	1.14
0.05	—	7	20.1	25	1.24
0.01	—	5	31.4	40	1.27
0.05	0.5	1 resp. 5	47.3	57	1.21
0.05	1	2 resp. 9	67.0	103	1.54
0.05	2	2 resp. 3	89	179	2.01

But in the solutions with much latently basic chromium, large quantities of latently basic compounds with more than one masked hydroxyl group per chromium atom are present.

SUMMARY

1. A method for the determination of the hexaquochromic ion: $Cr(H_2O)_6^{+++}$ by precipitation as caesium alum is described.

2. This method is used to determine the quantity of latently basic compounds in chromic nitrate solutions which are heated to 75° C, with or without addition of base.

3. Further, the quantity of colloidal latently basic chromium precipitable by sulphuric acid (and alcohol) in these chromic nitrate solutions is determined.

4. Equilibrium with regard to slightly colloidal or non-colloidal latently basic compounds appears to be attained at 75° C in a few days. On the other hand, the formation of colloidal latently basic compounds at this temperature is not yet complete after three or four months.

5. By application of previous determinations of the quantity of masked hydroxyl in heated chromic salt solutions, the ratio between chromium and masked hydroxyl in the latently basic compounds is calculated.

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Studies on Chromic Chloride. III.

Hydroxoaquochromic Chlorides

NIELS BJERRUM

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THE HYDROLYSIS OF HEXAQUOCHROMIC CHLORIDE

During the work it proved necessary to undertake some electrometric determinations of the degree of hydrolysis of chromic chloride in potassium chloride solutions. The results, recorded in table 1, show that the hydrolysis constant in this case is considerably smaller than in pure water. μ is the decimillimolar concentration of chromic chloride, i.e. the number of moles in 10000 litres. The constant of hydrolysis in these units, $k_h = [CrOH^{++}][H^+]/[Cr^{+++}]$, is 10^4 times as great as when molar concentrations are used.

Table 1. The hydrolysis constant of hexaquochromic chloride

μ	t	without KCl	0.1 *N* KCl	0.2 *N* KCl
100	18°C	0.65	0.48	
33.33	18	0.88	0.51	0.32
6.25	18	1.05	0.44	
33.33	0	0.27	0.156	

Of course, the great influence of potassium chloride on the hydrolysis constant makes it necessary in calculations of hydrolysis to employ a value corresponding to the actual quantity of potassium chloride present.

Without entering upon a discussion of the theory of this effect of potassium chloride, I wish to make the following remark. One might conceive that the decrease of the hydrolysis constant with increasing concentrations of chromic chloride is an effect similar to the decrease of the hydrolysis constant with increasing concentrations of potassium chloride, and that it is an Arrhenius neutral salt effect. In 0.1 *N* potassium chloride the neutral salt effect of chromic chloride is negligible compared with that of potassium chloride and consequently the hydrolysis constant is only slightly dependent on the concentration of chromic chloride.

THE CONSTITUTION OF MANIFESTLY BASIC CHROMIC CHLORIDES

Hitherto we have not been quite justified in calling the manifestly basic hydrolysis products of chromic chloride hydroxo compounds, for we have estimated only the numbers of acid equivalents and of chromium atoms per molecule of each compound.

In order to form a well-founded opinion regarding the constitution of these unstable basic aquochromic compounds we must go a circuitous way (compare[1a,2,3]). Among the more stable basic chromammines we seek out analogous compounds of established constitution; and from the constitution of these ammines we draw inferences regarding the constitution of the corresponding aquo compounds. The *basic* chromammines may be classified into three groups. The first group comprises the latently basic compounds. To this group belong the rhodo-, erythro-, and rhodoso-compounds found by Jørgensen, and two series of basic ethylenediamine-containing compounds prepared by Pfeiffer. In a second group we may collect the numerous manifestly basic salts of a weakly basic nature similar to that of ammonia. Such compounds have been prepared by Jørgensen, by Pfeiffer, and by Werner. Finally, to the last group belong some strongly alkaline compounds known only in solution. Jørgensen has prepared such strongly alkaline solutions from purpureo chloride and from rhodo and erythro chlorides with silver oxide, and Christensen from nitropentamminechromic chloride with silver oxide.

There can hardly be any doubt that the constitution of the manifestly basic aquo compounds mentioned in the present paper is analogous to that of the likewise manifestly basic compounds belonging to the second group of ammines. This view is supported not only by their analogous behaviour towards acids but even more by the fact that both these groups contain only one chromium atom in their nucleus while the latently basic chromammines and, as I shall show later on, also the latently basic aquochromic salts are polynuclear, "condensed" compounds.

With respect to the constitution of the manifestly basic chromammines resembling ammonia, the present state of knowledge is as follows: In 1902 Pfeiffer[4] advanced the opinion that in certain dipyridinechromic compounds the basic hydroxyl must be attached directly to the chromium atom and must occupy the same place as the complexly bound anions in chloro, bromo, and nitro compounds. Consequently, these basic compounds were hydroxylo salts or, using an abbreviated term introduced by Werner, *hydroxo salts*. Pfeiffer supported his view by the observation that the basic dipyridinechromic compounds contained one molecule of water less than the corresponding normal salts. In 1906 Pfeiffer[5] defined these concepts more precisely and after that he wrote: "If one accepts the opinion of Werner that aqueous solutions of salts of heavy metals contain no metal ions but exclusively hydrated metal ions and that, consequently, constitutional formulae of the salt hydrates should be written $[Me(OH_2)_n]\,X_n$, then I consider it justified to infer that, generally speaking, in the case of heavy metal hydroxides having hydroxyl groups attached directly to the heavy metal atom, salt formation is primarily an addition reaction. However, in most cases it will be difficult to furnish experimental proof of this assumption".

Even before Pfeiffer had written this, I[1b] had arrived at the conclusion that all bases and basic salts of chromium and of chrom- and cobaltammines hitherto prepared, apart from basic salts of a complexly basic nature, were to be regarded as hydroxo compounds. This opinion I supported not merely on the water content of these compounds but also on their colours which are different from those of the normal salts and on their slight electrolytic dissociation. I made it probable that direct addition compounds of ions — and only such — always possess the colour of their ions and show a normal degree of dissociation just as common strong electrolytes. "On dissolution in water they (the basic chromic salts) to a slight extent are converted into *real bases* containing hydroxyl ions and the unchanged cation of the series of salts in question combined to each other. The fraction of the basic salt transformed in this manner, by its normal electrolytic dissociation, proceeding in accordance with Ostwald-Walden's law, controls the hydroxyl-ion concentration of the solution, i.e. the strength of the base".

Werner in 1907 accepted this notion of many basic compounds being hydroxo compounds. He has furnished a copious experimental material demonstrating that basic salts, apart from polynuclear compounds, always contain one molecule of water less than the corresponding normal salts. And he claims to have found further evidence in support of this view in the fact that the basic salts regarded as hydroxo salts yield carbonato salts with carbon dioxide and acetato salts with acetic anhydride[6].

This new proof, however, does not seem very convincing to me; for we have no reason to believe that hydroxo compounds should form acido compounds with acid anhydrides with special ease. —

Immediately it may seem strange that just the manifestly basic salts are regarded as hydroxo compounds. We know that other radicals attached directly to the chromium atom are bound so firmly or rather so inertly that they cannot be exchanged instantaneously. It must be borne in mind, however, that when a hydroxo ion is transformed by acid into an aquo ion this process need not consist in an exchange of hydroxyl against water; we must imagine that a hydrogen ion combines with the hydroxyl group. So if we assume that hydroxo groups capable of adding a hydrogen ion do this almost instantaneously we have an explanation of the manifestly basic nature of the hydroxo compounds. —

These considerations lead us to the conclusion that our manifestly basic aquochromic compounds are to be regarded as hydroxo compounds. Their ions are derived from the hexaquochromic ion by exchange of water for hydroxyl and must be constituted in the following way:

$$\mathrm{Craq_6}^{+++}, \mathrm{Craq_5(OH)}^{++}, \mathrm{Craq_4(OH)_2}^{+}, \mathrm{Craq_3(OH)_3}.$$

And the corresponding chlorides are:

$$\mathrm{Craq_6Cl_3}, \mathrm{Craq_5(OH)Cl_2}, \mathrm{Craq_4(OH)_2Cl}.$$

Even if the compounds probably do contain the quantities of water indicated in these formulae I generally prefer to omit the water both in the formulae and in the names. For the direct experimental determination of the quantities of water has not yet been accomplished*. And that this determination is not superfluous may be inferred e.g. from the existence of compounds (bisaquo compounds[7]) in which for no obvious reason two molecules of water appear in a place where in analogous compounds only one is present.

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* In the hydroxide three molecules of water have been found (Fremy and Prudhomme); but it is beyond doubt that the hydroxide is changed on drying.

Physico-chemical Studies on Chlorochromic Sulphates

NIELS BJERRUM

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In 1906 I published a preliminary report on chromic chloride-sulphates[1]. The present paper supplements the information presented there, and further contains the results of some new investigations.

Two isomeric chlorochromic sulphates of the composition $CrClSO_4,6H_2O$ are known in which all chlorine is in complex and all sulphuric acid in ionogenic linkage. One of them has first been prepared by Recoura[2], and more recently Weinland in collaboration with Krebs[3] and with Schumann[4] has given new and better methods of preparation. The other has been found by Werner and Huber[5], and almost simultaneously by me[1]. In my first report, I concluded from the genetic relations between these compounds and the three chromic chlorides, that Recoura's chloro sulphate was to be regarded as monochlorochromic sulphate, while Werner and Huber's compound was dichlorochromic chromic sulphate. When we indicate the distribution of water molecules, so far as we know it, we get the formulae:

$(CrCl\,aq_5):SO_4,H_2O$	$(CrCl_2\,aq_4)\,(Cr\,aq_6)\,(SO_4)_2,2H_2O$
Recoura's salt	Werner and Huber's salt.

It is interesting to see that the electrical conductivity, the velocity of transformation, and the colour of these compounds agree with these formulae as shown in the following.

The agreement proves the usefulness of these physical methods and enables one to use them with more confidence in cases where the constitution cannot be established by simple chemical means.

1. ESTABLISHMENT OF CONSTITUTION BY MEASUREMENT OF CONDUCTIVITY

Tables 1 and 2 show the electrical conductivity of the salts. t denotes the time having passed since dissolution of the salt, and λ_t is the molar conductivity calculated in accordance with the formula $CrClSO_4.6H_2O$, in reciprocal ohms.

Table 1. Recoura's salt in 0.0100 M solution, 25° C.

t, min.	λ_t	k
0	140.0	0.0080
10	145.8	62
20	150.0	47
40	156.0	39
60	160.5	
80	164.3	
120	170.0	
210	178.1	
340	183.7	
660	187.0	
1400	184.1	
3170	180.6	
4220	180.1	

Table 2. Werner and Huber's salt in 0.0098 M solution, 25° C.

t, min.	λ_t	k
0	125.0	0.0137
10	137.2	127
20	147.1	0.0095
40	159.6	65
60	166.9	
80	171.4	
360	188.7	
1420	188.6	
2080	186.2	
2720	184.9	
4180	183.5	
5830	183.6	
7400	183.6	

Note: λ_t ($t = 0$) has been extrapolated from the values during the first five minutes.

In fig. 1 the variation of conductivity with time is shown graphically. The conductivities at first increase rapidly, then pass through maxima and begin to decrease, and finally they asymptotically approach limiting values*. The initial rapid increase is explained by rapid liberation of the chlorine in the form of chloride ion[6c] while the subsequent slow decrease may be explained by the formation of sulphato complexes.

It must be possible to calculate approximately the conductivity of a monochlorochromic sulphate from the conductivity of monochlorochromic chloride by subtraction of the usual difference between the molar conductivities of chlorides and sulphates of a common divalent cation. The molar conductivity of monochlorochromic chloride at 25° C in 0.01 molar solution has formerly been found by me[6j] to be 208.5; and the difference between the conductivities of chloride and sulphate in the case of magnesium is 64.4; in the case of nickel and cobalt it is 74 (calculated for the same conditions[7]); hence, the mean value is about 70.

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* These limiting values, however, seem not to be absolute, since the conductivities begin to increase again if the observations are extended over periods of months. After 10 months λ_t was found to be 203 in the case of Recoura's salt. Probably an extremely slow hydrolysis takes place.

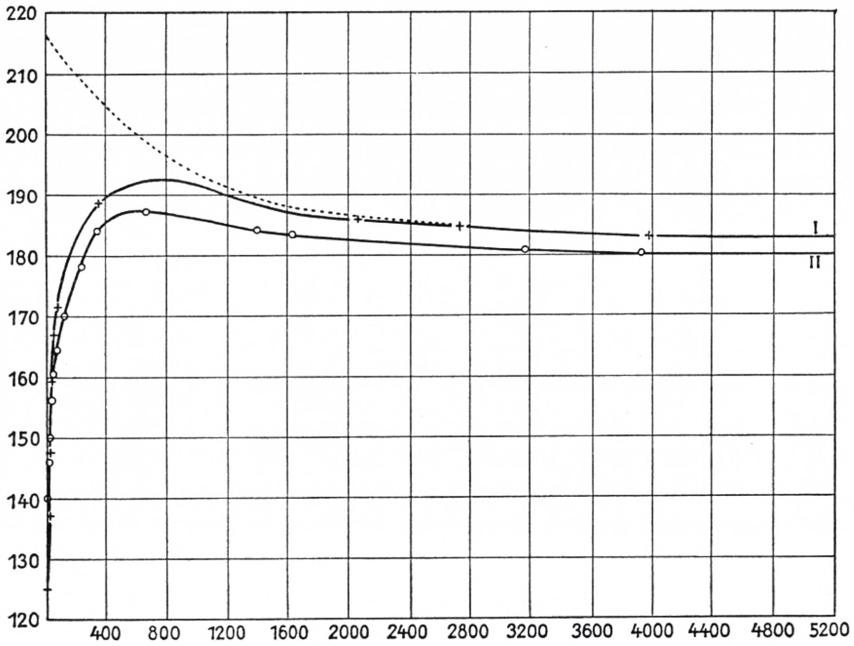

Fig. 1. Molar conductivity of: I. Werner and Huber's chlorochromic sulphate. II. Recoura's chlorochromic sulphate.

According to this the conductivity of monochlorochromic sulphate in 0.01 molar solution at 25° C should be 208.5 — 70 = 138.5 while, in agreement herewith, the value found with Recoura's chlorosulphate was 140.

The molar conductivity of a dichlorochromic chromic sulphate may be calculated in the following manner. It must be equal to the molar conductivity of potassium chromic sulphate[8] minus the difference between the molar conductivities of potassium chloride[7] and of dichlorochromic chloride[6d]. The result of this calculation is: 283.4 — (141 — 98) = 240.4. One half of this value has to be compared with the molar conductivities of the chloro sulphates found when assuming their molecular formula to be $CrClSO_4$. Half the value is 120.2 which agrees satisfactorily with the value 125 found for Werner and Huber's chloro sulphate.

2. ESTABLISHMENT OF CONSTITUTION FROM VELOCITY OF TRANSFORMATION

Since the reaction in which sulphate is bound as a complex is very much slower than the liberation of chloride ions, it is possible with good approximation to calculate a velocity constant for the liberation of chloride ions from the observations during the first hour. For this purpose it is only necessary to know the value the conductivity would have reached if the sulphate had not been complexly bound. We are able to calculate this value in the following manner. It must be equal to $^1/_3\, a + {}^1/_3\, b$ where a is the molar conductivity of hexaquochromic chloride and b that of hexaquochromic sulphate, both in solutions 0.01 molar with respect to the blue chromic ion. a is equal to 343.5[6a] and b is 306.4[8]. Consequently $^1/_3\, a + {}^1/_3\, b$ is 216.6. This value agrees with the curvature of the conductivity curve after completion of the liberation of chloride ions. In the figure the dotted line represents the conductivity the solution would probably have had if the chloride ions had been in a free state all the time. From this curve may be seen that the decrease of conductivity due to the sulphate during the first hour is insignificant (about two units) in comparison with the increase due to the liberation of chloride ions (20—40).

Under the heading k in tables 1 and 2 are entered the values of the velocity constants of the liberation of chloride ion calculated in accordance with the equation of a first-order reaction:

$$k = \frac{\log(216.6 - \lambda_{t1}) - \log(216.6 - \lambda_{t2})}{0.4343\,(t_2 - t_1)}$$

Let us try how far these values agree with the assumed constitutions of the salts. In an investigation of the conversion of green dichlorochromic chloride in about 0.01074 molar solution[6d], the values found for the velocity constant of the liberation of chloride ion from monochlorochromic chloride were 0.0057—0.0036. These values agree well with those found for Recoura's salt, viz. 0.0080 — 0.0039. The high values found in the beginning with Recoura's salt originate from a period when the solution does not contain so much hexaquochromic salt and consequently not so much free acid as the chromic chloride solution in the period when the values 0.0057 — 0.0036 were found.

That the increase in the conductivity of Werner's chloro sulphate agrees with its assumed constitution may be shown in the following manner.

The transformation of dichlorochromic chromic sulphate must proceed at the same rate as the transformation of dichlorochromic chloride in a solution of the same acid content as the solution of the double salt. For the rate of change of the dichlorochromic ion depends solely on the content of free acid in the solution[6i]. From the value of the hydrolysis constant of hexaquochromic salts at 25° C ($0.9 . 10^{-4}$), the concentration of acid in the solution of the double salt is computed to be 0.00061 initially and 0.00091 after liberation of the chloride ion[6b]. Since in 0.01 molar solutions of dichlorochromic chloride in approximately 0.0004 N and 0.001 N hydrochloric acid, the concentration of free acid varies with time from 0.0004 to 0.0011 and from 0.001 to 0.0015, respectively,[6g] the rate of transformation of dichlorochromic chromic sulphate must be between those of di-

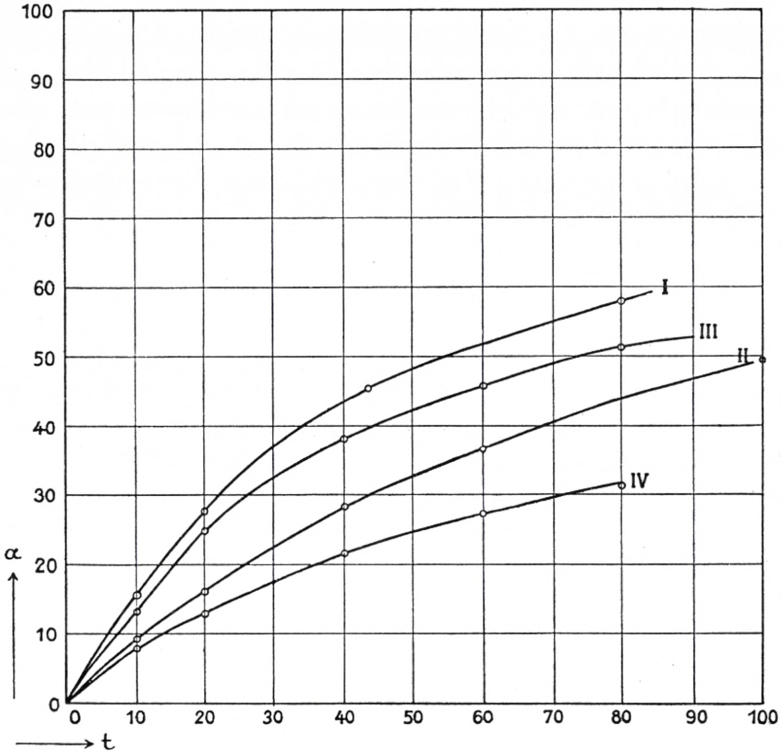

Fig. 2.

chlorochromic chloride in these solutions in hydrochloric acid. In fig. 2 the degree of transformation in per cent as computed from the conductivity data is plotted against time. Curves I and II show the transformation of dichlorochromic chloride in 0.0004 and in 0.001 *N* hydrochloric acid, respectively[6e]; curves III and IV show the transformation of Werner and Huber's and of Recoura's chlorochromic sulphate.

It is seen that the curve of Werner and Huber's double salt is between those of dichlorochromic chloride whereas the curve of Recoura's compound lies under both these curves. From this we may infer that only Werner and Huber's double salt can be dichlorochromic chromic sulphate.

We see then that not only the values of the conductivities in the moment of dissolution but also the changes of conductivity with time are explained by the assumed constitutions; and the differences between the two chloro sulphates are great enough to permit the use of these properties for the establishment of their constitution. The investigation of the colours of these compounds, however, affords a still finer means to this end.

3. ESTABLISHMENT OF CONSTITUTION BY INVESTIGATION OF COLOURS

The colour of a salt in solution is completely and exactly defined (setting aside surface and fluorescence colours) when its molar coefficients of extinction at various wave-lengths of light have been determined. The molar extinction coefficient (mEk) is defined by the formula

$$mEk = \frac{\log I_o / I}{l m}$$

where I_o is the intensity of incident light, I that of transmitted light, l the thickness of the absorbing layer (in cms.), and m the concentration of the coloured substance in moles per litre.

For determination of the molar extinction coefficients of my solutions I have used a König-Martens' spectrophotometer fitted out with a Rutherford prism and with an illumination system (maker Schmidt and Haensch in Berlin); the light source was a large Nernst projection lamp (220 volts, 3 amps).

First of all I wish to emphasize that it is permissible to assume that the ions of an electrolyte possess the same colour in the free and in the combined state as long as they do not form a complex compound. As early as the spring of 1906 this assumption was laid down by me as probable[9]. I arrived at it by combination of the available optical measurements with the recent views on the constitution of inorganic salts. In the autumn of 1907 Hantzsch has advanced the same theorem and furnished new experimental support of it. Quite recently some investigations into the colours of chromic salts have provided me with new, very good evidence in favour of the theorem. I intend to enlarge further upon these investigations elsewhere, and here I shall only state the following. According to these investigations all normal hexaquochromic salts have exactly the same colour, namely that of the hexaquochromic ion, even at concentrations where they are only very

Table 3. Molar extinction coefficients at 18° C ± 2°

λ	$Cr(H_2O)_6Cl_3$ in 0.01 N HCl			$Cr(H_2O)_6(NO_3)_3$ in 0.1 N HNO_3			$Cr(H_2O)_6(SO_4)_{3/2}$ in 0.2 N H_2SO_4		
	1 M	0.02 M	0.004 M	1 M	0.1 M	0.01 M	1 M	0.1 M	0.01 M
626 ± 15	7.08	6.87	6.88	7.07	7.10	6.99	7.24	7.11	7.00
524 ± 11	13.09	12.63	12.67	13.22	12.89	12.65	13.14	13.07	13.14
519 ± 8	6.56	6.30	6.42	6.65	6.56	6.36	6.73	6.58	6.65
486 ± 6	3.36	3.22	3.26	3.26	3.32	3.18	3.27	3.24	3.26
462 ± 8	4.63	4.16	4.39	4.36	4.42	4.16	4.47	—	4.19
440 ± 14	9.21	8.61	8.68	8.92	8.71	8.75	—	—	—

slightly dissociated into ions. This is seen clearly from table 3 showing the molar extinction coefficients of various hexaquochromic salts in various concentrations.

Within the error of the experimental method identical molar extinction coefficients have been found for all solutions.

In all the solutions tested, hydrolysis was strongly suppressed by addition of acid. In 0.1 normal acid hydrolysis at 18°C amounts only to about 0.06 per cent and in 0.01 normal acid it is about 0.6 per cent as calculated from a hydrolysis constant[10] of $0.66 \cdot 10^{-4}$.

In table 4 are given the molar extinction coefficients of the two chlorochromic sulphates, as calculated when using the formula $CrClSO_4$. Furthermore, the molar extinction coefficients of the hexaquochromic ion and of the dichlorotetraquochromic ion are listed.

Table 4. Molar extinction coefficients at 18° C ± 2°

λ	Chlorochromic sulphate		$Cr(H_2O)_4Cl_2^+$	$Cr(H_2O)_6^{+++}$	Calcd. for $\frac{1}{2}[CrCl_2(H_2O)_4][Cr(H_2O)_6](SO_4)_2$
	Recoura's salt	Werner and Huber's salt			
693 ± 24	4.26	7.61	14.87*	0.92	7.89
666 ± 19	7.44	11.04	20.86*	2.12	11.49
646 ± 16	11.64	13.88	24.38*	4.07	14.22
626 ± 15	14.80	15.11	23.61	7.07	15.34
608 ± 14	16.25	14.19	18.75	10.05	14.40
591 ± 12	15.40	12.63	13.16	12.35	12.75
564 ± 11	10.72	9.12	5.52	12.96	9.24
539 ± 9	6.24	6.51	2.95	9.75	6.35
519 ± 8	3.98	4.83	3.14	6.55	4.84
501 ± 7	3.48	5.17	6.02	4.15	5.09
486 ± 6	4.92	7.30	11.04*	3.26	7.15
473 ± 5	8.24*	9.81	16.16*	3.18	9.67
462 ± 8	12.03*	12.16	20.39*	4.34	12.36

* In these cases the wave-lenght interval was twice that indicated in the first column.

If Werner and Huber's chloro sulphate is to be regarded as dichlorotetraquochromic hexaquochromic sulphate the molar extinction coefficients of this substance calculated in accordance with the formula $CrClSO_4$ must be mean values of the figures pertaining to dichlorotetraquochromic ion and to hexaquochromic ion, for the molar extinction coefficients are additive properties.

In the sixth column these means are listed and by comparison with the figures in column 3 it is seen that the means agree within experimental error with the

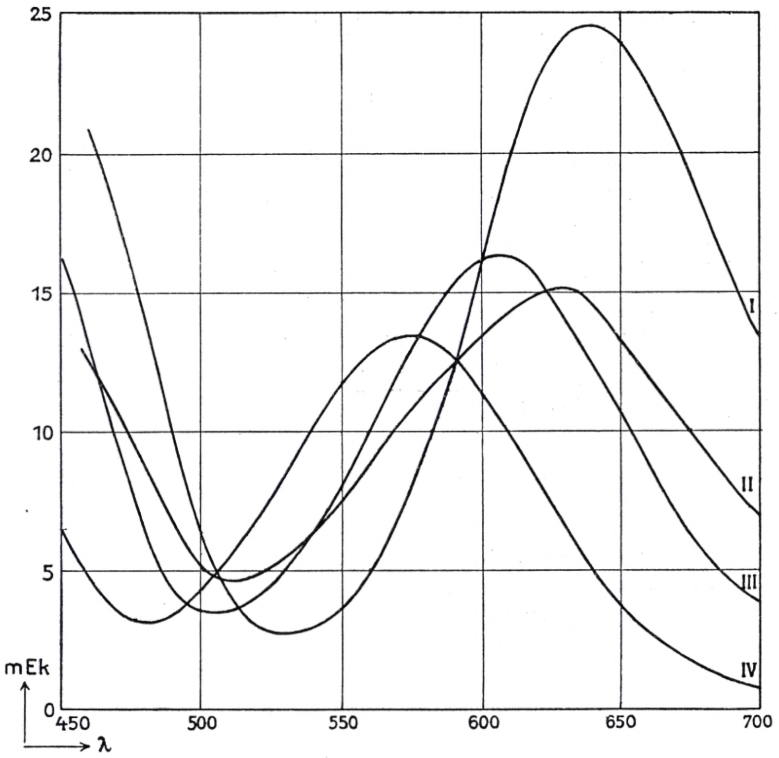

Fig. 3.

values of Werner and Huber's compound*. In contrast the values found with Recoura's chloro sulphate deviate significantly from the means. Thus we may conclude that Werner and Huber's compound actually is dichlorotetraquochromic hexaquochromic sulphate while Recoura's compound must have another constitution.

In fig. 3 the experimental values are represented graphically. Curve I represents the dichlorotetraquo ion, curve IV the hexaquochromic ion. Curve II corresponds to Werner and Huber's and curve III to Recoura's chloro sulphate. It is worth noticing how well curve II goes through the points of intersection of the curves I and IV. Curve III (Recoura's chloro sulphate) in another respect occupies an intermediary position between I and IV. Its maximum is between the maxima of curves I and IV and has an intermediate value. The same applies to the minima. The intermediate values, however, are not exact means.

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* The comparatively great differences found with the two highest wave-lengths (3.5 and 4 per cent, respectively) may perhaps be explained by the fact that in these cases the band widths have not been identical throughout. However, they may just as well be considered due to experimental error.

Table 5. Molar extinction coefficients for 0.05 molar dichlorochromic chloride in 1 normal hydrochloric acid at about 18° C.

λ	t	t min. after dissol.	1 hour later	3 days later	16 days later	extrapol. to the time 0	$[Cr(H_2O)_5Cl]SO_4$
693 ± 24	12	14.75	14.02	5.83	—	14.87	4.26
666 ± 19	16	20.55	19.32	9.22	7.47	20.86	7.44
646 ± 16	20	23.95	22.59	13.13	—	24.38	11.64
626 ± 15	25	23.24	22.35	15.75	14.75	23.61	14.80
608 ± 14	29	18.59	18.26	16.41	—	18.75	16.25
591 ± 12	33	13.26	13.45	15.28	15.31	13.16	15.40
564 ± 11	37	5.84	6.36	9.88	10.60	5.52	10.72
539 ± 9	41	3.13	3.40	5.74	—	2.93	6.24
519 ± 8	45	3.22	3.33	3.83	4.02	3.14	3.98
501 ± 7	49	5.93	5.82	3.97	—	6.02	3.48
486 ± 6	54	11.10	10.78	6.18	5.03	11.40	4.92
473 ± 5	58	16.07	15.98	9.76	—	16.16	8.24
462 ± 8	63	19.99	19.63	14.44	12.48	20.39	12.03

The molar extinction coefficients of chloro compounds given in table 4 were all determined in 1 normal hydrochloric acid because hydrochloric acid makes the chlorochromic compounds much more stable[6c]. In the cases of dichlorotetraquochromic chloride and of Werner and Huber's chloro-sulphate it was necessary to extrapolate the observed values to the time zero; this was easily done by observation of the changes during the following hour. In table 5 my measurements of the time-changes in the molar extinction coefficient of a 0.05 molar solution of dichlorochromic chloride in 1 normal hydrochloric acid are listed. The figures of this table give us a determination of the velocity of transformation of dichlorochromic chloride in 1 normal hydrochloric acid. During one hour about 9 per cent was converted into monochloro chloride. This gives the value 0.0016 of the velocity constant

$$k_1 = \frac{\log 100 - \log 91}{0.4343 \cdot 60}$$

Previous experiments[6h] on solutions not more than 0.01 normal with respect to hydrochloric acid gave the following formula for the same velocity constant at 25° C.

$$k_1 = 0.00272 + \frac{0.0000161}{s}$$

where s is the normality of free hydrochloric acid present. A rather bold extrapolation using this formula leads to the value $k_1 = 0.00274$ in 1 normal hydrochloric acid at 25° C. This value obviously agrees well with the value 0.0016 found above at room temperature (the temperature during the hour when the experimental k_1 was determined, was 21°). After three days about 84 per cent monochloro chloride had been formed, and after 16 days the molar extinction coefficients showed that the solution contained exclusively monochlorochromic chloride (compare the columns 6 and 8). This also agrees well with my earlier investigations in very dilute solutions for, according to the formulae laid down then[6f-g], the conversion of dichlorochromic chloride into monochlorochromic chloride in 1 normal hydrochloric acid should proceed about 1000 times as fast as the conversion of monochlorochromic chloride into the pure hexaquo compound. The first liberation of chloride ions may therefore be practically complete before the second liberation is noticeable. In the weakly acid solutions studied formerly, the situation was quite different.

After these experiments it lies near to prepare monochlorochromic sulphate by the following method, a variant of Weinland's method.

One part of dichlorochromic chloride is dissolved in one part of 1 normal hydrochloric acid, and after two weeks it is precipitated with concentrated sulphuric acid. In this way I have obtained a yield of 30 per cent of pure salt. This is somewhat more than I have obtained using Weinland's method (20—25 per cent); the difference, however, is not great.

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Studies on the Thiocyanates of Chromium

NIELS BJERRUM

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1. The object of the studies, the results of which I am going to summarize here, has been to find satisfactory numerical expressions for the complex formation between two ions, which have a strong tendency to form complexes. With a view hereto a comprehensive examination has been made of the complexes formed by the ion Cr^{+++} and the ion CNS^-, and after having determined the composition and the properties of the complex groups formed, it has been possible to achieve the main object of the work by studying the chemical equilibrium in solutions of thiocyanates of chromium.

2. *Composition of the complexes.* With the ion CNS^- the atom of trivalent chromium forms six different complex groups, the formulae of which can be derived from that of the hexaquochromic ion by substituting the six molecules of water successively by thiocyanate ions.

$Cr(H_2O)_6{}^{+++}$	hexaquo-chromic ion,
$Cr(CNS)(H_2O)_5{}^{++}$	thiocyanato-pentaquo-chromic ion,
$Cr(CNS)_2(H_2O)_4{}^{+}$	dithiocyanato-tetraquo-chromic ion
$Cr(CNS)_3(H_2O)_3$	trithiocyanato-triaquo-chrome,
$Cr(CNS)_4(H_2O)_2{}^{-}$	tetrathiocyanato-diaquo-chromiate ion,
$Cr(CNS)_5(H_2O)^{--}$	pentathiocyanato-monaquo-chromiate ion,
$Cr(CNS)_6{}^{---}$	hexathiocyanato-chromiate ion.

The complexes with one or two thiocyanato groups are cations forming salts with various acids. Trithiocyanato-triaquo-chrome is undissociated, it is a non-electrolyte. The complexes with four or more thiocyanato groups are anions which form salts with various metals.

3. *Preparation and analysis of the complexes.* It has been ascertained that the *monothiocyanato* and *dithiocyanato complexes* exist in solution, but it has not been possible to find acids suitable for separating the complexes and thus obtaining

them in the form of solids, and consequently their content of water has not been determined experimentally. They are insoluble in ether.

Trithiocyanato-triaquo-chrome has been prepared in crystalline form. The crystals were, however, not completely pure. In solution the complex has been obtained in a much purer form. The low electric conductivity of this substance shows that it is not dissociated into ions. For a 0.1 M solution of the crystals at 0° C μ has been found to be 3.87 ($\mu =$ the molecular conductivity); for purified solutions of a strength of 0.015 M at 9° C μ has been found to be 0.61. It should be noticed that trivalent electrolytes in the corresponding condition will exhibit a molecular conductivity between 250 and 300. After dehydration in vacuum above calcium chloride at ordinary temperature the highly hygroscopic crystals only retained 3.2–3.6 molecules of water; it is thus probable that the trithiocyanato complex contains 3 molecules of constitutional water. This complex is easily soluble in ether, by evaporation of the ether solution a residue is obtained which, when heated with water, releases more ether.

The *tetrathiocyanato complex* has been isolated in the form of a dilute solution of the free acid, from which it is possible by neutralisation to prepare the corresponding salts. Neither the acid nor any of the salts have been prepared in the solid state. It has, however, been possible to ascertain that salts of quinine or strychnine precipitate the complex, and that, when a great quantity of a quinoline salt is added, it will precipitate a quinoline salt of the complex in the form of an oil. Tetrathiocyanato-chromiate acid is soluble in ether; in that respect it does not resemble its salts.

From the *pentathiocyanato complex* an insoluble quinoline salt has been obtained. It appears in the form of beautiful crystals; and from the quinoline salt it has been possible to prepare solutions which contained the sodium salt and the free acid. An analysis of the quinoline salt has given the result that it contains two molecules of water, one of which is so closely attached that it is not lost in dry air at ordinary temperature. From this we can conclude that the pentathiocyanato complex, as expected, contains one molecule of constitutional water. Pentathiocyanato-chromiate acid is soluble in ether, while its salts are insoluble.

The *hexathiocyanato complex* is already known, as it constitutes the radical of the well-known complex double-salts of the type $R_3Cr(CNS)_6$. Of this series two new insoluble salts have been prepared: the salts of pyridine and quinoline. Analysis of the quinoline salt shows that it contains one molecule of water; but by dehydration in dry air at ordinary temperature this salt readily loses this molecule of water. As it might be expected, the hexathiocyanato-chromiates thus do not contain constitutional water. By treating a strongly acid solution of a hexathiocyanato-chromiate in water with ether, three liquid layers are obtained: at the bottom a rather acid, slightly coloured, aqueous layer, in the centre a thin, highly coloured layer, consisting of a concentrated solution of hexathiocyanato-chromiate acid in ether, and at the top a thicker, slightly coloured ethereal layer. The behaviour of the complex chromicthiocyanic acid towards ether is thus similar to that of phospho- and silico-tungstic acid.

4. In *aqueous solution* the chromicthiocyanate complexes are of a reddish-violet *colour*. An increase in the content of thiocyanate has the effect of making the colour slightly more reddish, and at the same time the intensity of the colour is increased considerably. In *ethereal solution* the trithiocyanato-chrome complex assumes a greenish colour, and tetrathiocyanato-chromiate acid is of an almost pure green colour. On the other hand, pentathiocyanato-chromiate acid and hexathiocyanato-chromiate acid have almost the same colour in ethereal solution as they have in aqueous solution.

5. The *partition coefficient* for ether and water of the complexes soluble in ether has at ordinary temperature approximately the following values:

$Cr(CNS)_3(H_2O)_3$	$H[Cr(CNS)_4(H_2O)_2]$	$H_2[Cr(CNS)_5(H_2O)]$	$H_3[Cr(CNS)_6]$
about 3.6 (3.3 — 4.7)	about 9.4	about 4	about 0.3

Velocity constants of the decomposition of thiocyanato-chromic complexes at ordinary temperature (16°–18° C)

	In acidified water	In water[6]	In 0.25 M solution of CH_3COONa	In 0.035 M solution of $NaHCO_3$	In 0.01 M solution of NaOH	In ether
$Cr(CNS)(H_2O)_5^{++}$		0.0000054[7]			large	
$Cr(CNS)_2(H_2O)_4^{+}$					large	
$Cr(CNS)_3(H_2O)_3$		0.00002	0.0035		large	<0.000007
$Cr(CNS)_4(H_2O)_2^{-}$	<0.00004	0.00004	0.00025[3]		large	<0.00003
$Cr(CNS)_5(H_2O)^{--}$	<0.00014[5]	0.00014[1]		0.013[4]	large	0.005[4]
$Cr(CNS)_6^{---}$	0.00041	0.00050[2]			0.00060	large

1) In the dark. ($C_H = 0.73 \cdot 10^{-3}$).

2) In the dark. In diffuse daylight: 0.0017–0.0064.

3) A little acetic acid has been added to the solution so as to make the solution 0.002 *M* with regard to acetic acid.

4) In the dark.

5) In the dark. In diffuse daylight: 0.002.

6) Due to hydrolysis the solutions were slightly acid. Probable values of C_H: about 10^{-3} to 10^{-5}.

7) at 25° C.

For the acids, the partition coefficient is defined by the expression:

$$K = \frac{a}{b \cdot C_{\mathrm{H}}{}^{n}}$$

where a is the molar concentration of the acid in the ethereal layer, b the molar concentration of the complex in the aqueous layer, and n the basicity of the acid.

The tri- and tetrathiocyanato complexes have partition coefficients which vary slightly according to the method of preparation. This seems to indicate that the preparations used represent different mixtures of two isomers. In fact *Werner's theory* implies the existence of these complexes in two stereoisomeric forms.

6. The *stability* of the various complexes has been measured by measuring the quantity of CNS-ions formed by the decomposition of the complexes. This measurement has been performed colorimetrically by means of the colour which the solutions assume when ferric nitrate is added. The above table contains the velocity constants of the decomposition of the complexes. In case the velocity constant is low, it will be a direct measurement of the relative amount of complex decomposed in unit of time, i.e., in this case, in one minute.

It appears from the above table that in *aqueous solution* the stability of the hexathiocyanato-chromiate complex is almost independent of the reaction of the solution — whether it is acid, neutral or basic. As regards the other complexes they are more stable in acid solution than the hexathiocyanato complex, and their stability increases with decreasing content of thiocyanate in the complex. In basic solution, on the other hand, the other complexes are less stable than the hexa-complex, and their stability decreases with decreasing content of thiocyanate in the complex.

In *ethereal solution* the trithiocyanato complex is fairly stable, but the stability of the complexes in ethereal solution decreases rapidly with increasing content of thiocyanate, and hexathiocyanato-cromiate acid decomposes almost instantaneously in ethereal solution.

The thiocyanato-chromic complexes are rather *photosensitive*. In diffuse daylight the decomposition of hexa- and penta-complexes proceeds more than ten times faster than in the dark.

7. *Explanation of the decomposing effect of hydroxyl ions*. It seems probable that if the hydroxyl ion decomposes the thiocyanato-chromic complexes, it is because it facilitates the formation of instable hydroxo-compounds. These compounds are formed when in the hydrated ions the water molecules are replaced by, or rather transformed into, hydroxyl radicals. The hexathiocyanato complex is the only one which cannot form hydroxyl derivatives, consequently the decomposition of this complex is not influenced by hydroxyl ions.

8. A method for *quantitative analysis* of the six different thiocyanato-chromic complexes has been evolved. Firstly the hexa- and pentacomplexes are precipitated in the form of *quinoline salts,* and the respective amounts of the two complexes contained in the precipitate are established by quantitative determination of chromium and thiocyanate. The filtrate from the precipitate contains the other complexes. The tri- and tetra-complexes are separated from this liquid by systematic *extraction with ether,* and this ether extraction in itself enables us to separate the tri- and tetra-complexes, the respective quantities being determined by a subsequent determination of the chromium. Finally the amounts of chromium and thiocyanate complexes which remain in the mother liquor from the ether extractions are determined by titration. When these determinations are performed, we only require to know the amount of hexaquo-complex to be able to calculate the amounts of mono- and di-thiocyanato complexes. To obtain this value hexaquo-complex is precipitated *in the form of alum* by means of acid potassium sulphate and alcohol.

9. The thiocyanato-chromic complexes which we have referred to here are formed slowly in solutions containing hexaquo-chromic ions and thiocyanate ions. The *velocity* with which this formation takes place has not been subjected to a systematic study. It may, however, be observed that in aqueous solution the chemical equilibrium of these complexes will be attained at 100° C in about half an hour, at 50° C in 1–2 days, while at ordinary temperature the equilibrium will probably be reached only in the course of some years.

For the formation of the monothiocyanato-chromic complex the velocity constant in aqueous solution has been found to be 0.0018 at 25° C and 0.13 at 50° C.

10. *The chemical equilibrium* which exists between the different complexes and the thiocyanate ion in aqueous solution has been determined for 10 different solutions at 50° C.

These experiments have given the following mean values:

$$K_{\mathrm{CrCNS}} = 328; \quad K_{\mathrm{Cr(CNS)_2}} = 17.5; \quad K_{\mathrm{Cr(CNS)_3}} = 4.56;$$

$$K_{\mathrm{Cr(CNS)_4}} = 1.93; \quad K_{\mathrm{Cr(CNS)_5}} = 0.81; \quad K_{\mathrm{Cr(CNS)_6}} = 0.41;$$

$$K_{\mathrm{Cr(CNS)}_n} = \frac{C_{\mathrm{Cr(CNS)}_n}}{C_{\mathrm{Cr(CNS)}_{n-1}} \cdot C_{\mathrm{CNS}}}$$

The six values stated above represent a quantitative measurement of the tendency to form complexes which the chromium thiocyanates have at 50° C. As the number of complexes formed is six, it is evident that this tendency cannot be expressed by a single figure.

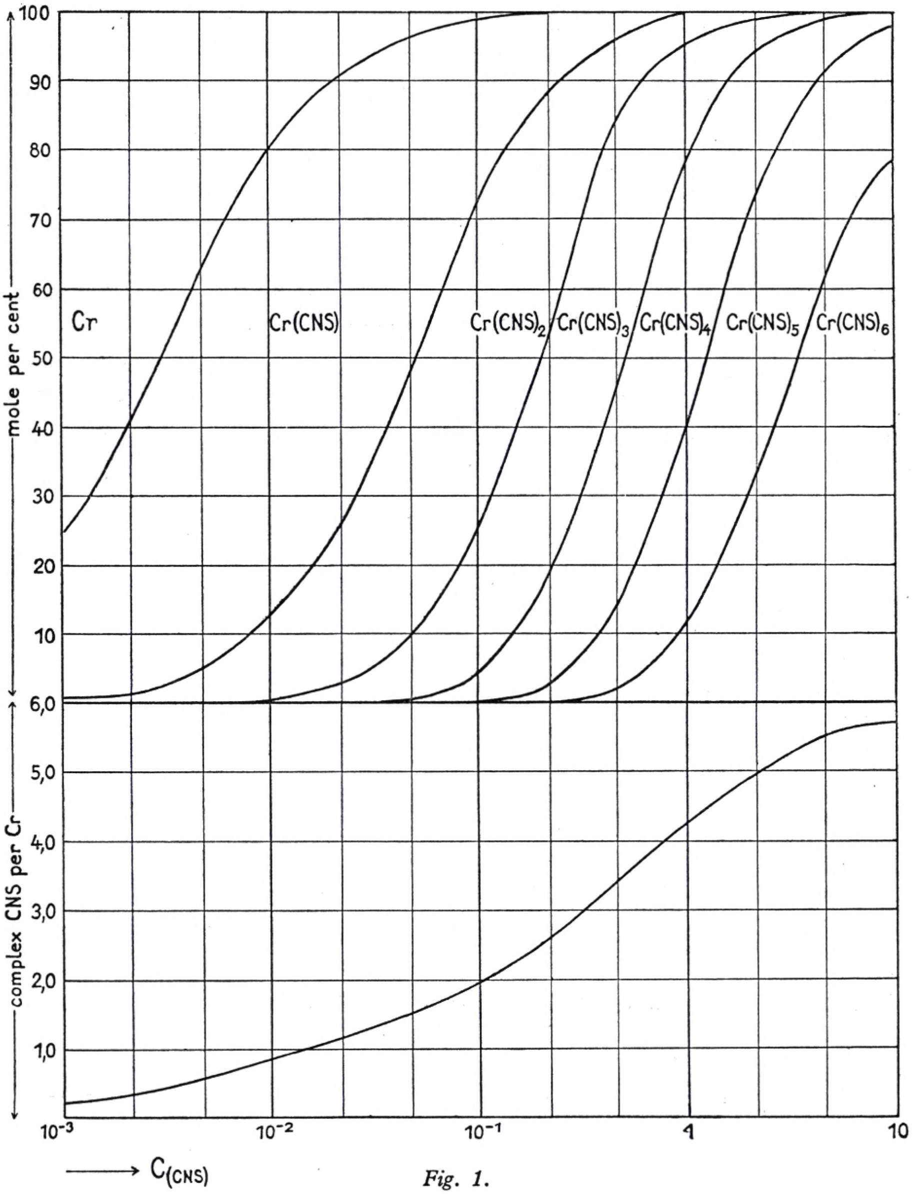

Fig. 1.

Measurements of conductivity have confirmed the results obtained by the chemical analysis of the solutions of chromium thiocyanates.

11. *The affinity* between the thiocyanate ion and the chromium atom in solutions, the molarity of which is 1 as regards all the substances can be calculated from the equilibrium constants and will be as follows:

For	the	first	thiocyanato	group	3710	cals.
–	–	second	—	–	1840	–
–	–	third	—	–	970	–
–	–	fourth	—	–	420	–
–	–	fifth	—	–	—130	–
–	–	sixth	—	–	—570	–

The calculation has been performed by means of the formula $A = RT \log_e K$. An increase of the temperature will produce a slight decrease in the tendency exhibited by chromium to form complexes with the thiocyanate ion.

12. The figure shows the variation of the amounts of the different complexes with the concentration of the thiocyanate ion. Along the axis of abscissa the concentration of the thiocyanate ion has been plotted in logarithmic scale. In the upper part of the diagram the sections of the ordinates delimitated by the curves represent the molecular percentages of the various complexes, the areas contained within the curves each corresponding to the complex stated in that area. The curve in the lower part of the diagram indicates the correlation between the concentration of the thiocyanate ion (C_{CNS}) and the number (n) of complexly bound thiocyanato groups per atom of chromium.

Calculation of the state of equilibrium in a solution with known concentrations of chromium and thiocyanate.

If a and b denote the total concentrations as regards chromium and thiocyanate respectively, we have

$$C_{\mathrm{CNS}} + n \cdot a = b.$$

When taken together with the curve (C_{CNS},n) of the diagram, this equation enables us by the method of trial and error to find the value of C_{CNS}; next we can, from the curves of the upper part of the diagram, find the molecular percentages of the various complexes.

Studies on Basic Chromic Compounds

A Contribution to the Theory of Hydrolysis

NIELS BJERRUM

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SUMMARY

1. There are two distinct classes of *basic chromic compounds* which, owing to their different reactivities toward acids, may be called *manifestly basic* and *latently basic*, respectively.

2. *Manifestly basic compounds* are formed in lesser quantities when chromic salts are dissolved in water, in greater quantities when a base is added to the solution. Typical of these compounds is their *instantaneous* formation even at room temperature.

3. From the bluish-violet hexaquochromic chloride two soluble, green, manifestly basic chromic chlorides, $Cr(OH)Cl_2$ and $Cr(OH)_2Cl$, and the insoluble, grayish-green, manifestly basic chromic hydroxide, $Cr(OH)_3$, are formed. $Cr(OH)_2Cl$, however, never is present in great amounts, and a precipitate of chromic hydroxide is obtained only on addition of base. These compounds are hydroxo compounds, i.e., they contain hydroxyl attached directly to the chromium atom. Their content of constitutional water presumably is that given in the following formulae:

$$[\mathrm{Craq_5(OH)}]\mathrm{Cl_2},\quad [\mathrm{Craq_4(OH)_2}]\mathrm{Cl},\quad \mathrm{Craq_3(OH)_3}$$

4. The quantities formed of these three compounds may be calculated from the following three equations (ξ is the concentration of free acid):

$$\frac{\mathrm{Cr(OH)Cl_2}}{\mathrm{CrCl_3}}\cdot\xi = K_h,\qquad \frac{\mathrm{Cr(OH)_2Cl}}{\mathrm{Cr(OH)Cl_2}}\cdot\xi = K'_h, \qquad (1)\ (2)$$

$$\mathrm{Cr(OH)_3} = 0 \qquad (3)$$

as long as $Cr(OH)Cl_2/\xi^2$ is less than or equal to K_b. But if these equations give a $Cr(OH)Cl_2/\xi^2$ greater than K_b (indicating supersaturation with chromic hydroxide), the state of equilibrium (with a precipitate of chromic hydroxide) is found by replacing equation 3 with

$$\frac{Cr(OH)Cl_2}{\xi^2} = K_b \tag{3a}$$

The constants in these equations have the following values (in decimillimolar units of concentration):

	0° C.	17° C.	25° C.
K_h:	0.22	0.62	0.98
K'_h:	$\leq$0.0025*	0.0059	—
K_b:	36000*	10200*	—

From the changes of these values with temperature are calculated:

1) The evolution of heat in the reaction $Cr(OH)_3 + 3HCl \rightarrow CrCl_3 + 3\,H_2O$: 21200 cals.; Recoura found 20700 cals.

2) The evolution of heat in the reaction $Cr(OH)_2Cl + HCl \rightarrow Cr(OH)Cl_2 + H_2O$: at least 8060 cals.

3) The evolution of heat in the reaction $Cr(OH)\,Cl_2 + HCl \rightarrow CrCl_3 + H_2O$: 9600 cals.; Recoura found 8200 cals.

The constants vary somewhat with the nature and the concentration of electrolytes in the solution. Thus *the presence of potassium chloride and of chromic chloride lowers the value of the hydrolysis constant* K_h.

5. The validity of these formulae shows that *even in rather involved cases the law of mass action in combination with the theory of electrolytic dissociation gives a correct evaluation of the factors governing hydrolysis* when one confines oneself to the investigation of dilute solutions. Furthermore, it should be emphasized that this investigation has shown that freshly precipitated chromic hydroxide is a definite chemical compound of well-defined solubility.

6. *Solutions of nitrates* are hydrolyzed to manifestly basic products to the same extent as dilute solutions of chlorides, but *solutions of sulphates* behave differently. Thus the hydrolysis constant K_h in chrome alum solutions is smaller than in chromic chloride solutions. This may be explained by assuming that sulphates have a stronger decreasing influence on the hydrolysis constant than chlorides. And the precipitate obtained on addition of base to dilute solutions of chrome alum is neither chromic hydroxide nor dihydroxochromic sulphate nor a mechanical mixture of the two, but probably a single phase of varying composition.

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* In 0.1 normal potassium chloride solution.

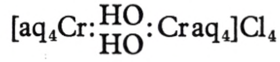
7. In dilute hexaquochromic chloride solutions — with or without added base — basic compounds that cannot instantaneously combine with acids are formed *slowly*.

8. These *latently basic chromic chlorides* are easily soluble in water and are green; their inclination to form complex chloro compounds is as slight as that of normal chromic chloride; and they contain *more than one chromium atom per molecule*. If one assumes that two compounds are formed containing one and two latent hydroxyl groups per chromium atom, respectively, the first compound can be proved to contain two chromium atoms per molecule and the second about six. However, it is not improbable that more compounds are formed besides these two.

The latently basic compounds in analogy to the latently basic ammines presumably are either *oxy compounds* the chromium atoms of which are linked through oxygen, e.g.:

$$Cl_2[aq_5Cr.O.Craq_5]Cl_2,$$

or *ol compounds*, i.e. aquo-chromic chloride whose water molecules to a greater or lesser extent have been replaced by hydroxochromic chlorides, e.g.:



$$[aq_4Cr:\genfrac{}{}{0pt}{}{HO}{HO}:Craq_4]Cl_4$$

9. From the temperature change (from 75 to 100° C) in the equilibrium resulting from formation of latently basic compounds, is calculated that the transformation of monohydroxochromic chloride to a latently basic salt evolves 1890 cals. From two different calorimetric determinations by Recoura the values 1000 and 2900 cals., respectively, are calculated.

10. The latently basic chromic chlorides are hydrolyzed to soluble, manifestly basic products to approximately the same extent as is the normal, bluish-violet chromic chloride.

11. *The velocity of formation of latently basic* compounds at 100° C is so great that the process goes to completion during a couple of hours. At 75° C this requires a couple of days and at room temperature equilibrium is not attained even during several years.

From the decreasing *(negatively catalytic)* influence exerted by free acid on the initial velocity of formation of latently basic chromic chloride it can be inferred that the reaction proceeds via manifestly basic chromic chlorides. The lower the temperature, the more basic the chlorides constituting the main proportion of the intermediate products.

At room temperature the latently basic chromic chlorides are not changed measurably during one day by dilute (0.01 — 0.1 normal) hydrochloric acid. And even in fuming hydrochloric acid only 1.5 to 10 per cent is transformed during fifteen minutes at room temperature.

12. The velocity of transformation of normal, freshly precipitated chromic hydroxide into latently basic compounds has been measured under varying conditions at room temperature. In a distinctly alkaline medium the velocity of transformation increases with the alkalinity of the supernatant and a *hydroxide* is formed *in which one hydroxyl group per chromium atom is latent.* This hydroxide is — at least comparatively — stable. The presence of baryum chloride or of sulphates catalyzes the transformation of the hydroxide to a hydroxide that is insoluble in acid (in which all hydroxyl is latently basic).

13. *Dilute solutions of chromic nitrate* are on boiling transformed into latently basic compounds to the same extent as the chloride solutions; the compounds formed possess a stability resembling that of the latently basic chromic chlorides.

On the other hand, *in chromic sulphate solutions* boiling leads to liberation of more free acid than in chromic chloride solutions (in solutions containing 0.1 — 0.05 g. atoms of chromium per litre, nearly twice as much). The difference between sulphate and chloride solutions decreases when the concentration is lowered.

14. There is reason to believe that all the chromic salts of strong acids that do not form complexes in dilute solution and corresponding to which no sparingly soluble basic salts exist, will behave like chromic chloride with respect to hydrolysis. And with modifications of a quantitative kind the scheme of hydrolysis of chromic chloride will also apply to the hydrolysis of salts of other trivalent metals.

15. *Werner's general theory of hydrolysis and of bases* — for the time being, at least — rests on an insufficient foundation; and, anyway, the current hydrolysis theory of physical chemistry remains unaffected by its correctness or incorrectness.

The Thiocyanates of Gold and Free Thiocyanogen

With an Appendix on Gold Chloride

NIELS BJERRUM and AAGE KIRSCHNER

Kgl. Danske Videnskab. Selskab Skrifter, naturvidenskab. math. Afdel. (8) 5 (1918) 1–77 (in German).
Only the authors' summary was translated for this volume.

SUMMARY

1. *Aurous thiocyanate* in the solid state, as shown already by Cleve, is stable only in the form of double salts. Besides the potassium and silver dithiocyanato-auroates of Cleve we have prepared a new double salt of the same type, viz. *ammonium dithiocyanato-auroate* $NH_4Au(SCN)_2$. The corresponding *dithiocyanato-auroate acid* may be extracted from an aqueous solution by ether; by evaporation of the ethereal solution it remains as a partly decomposed oil.

In aqueous solutions aurous thiocyanate is always present as *dithiocyanato-auroate ion* $Au(SCN)_2^-$. The complexity constant of this complex ion is $10^{22.4}$ times smaller than that of the dicyano-auroate ion.

$$K_{\mathrm{SCN}} = \frac{[\mathrm{Au(SCN)_2{}^-}]}{[\mathrm{Au^+}][\mathrm{SCN^-}]^2}; \quad K_{\mathrm{CN}} = \frac{[\mathrm{Au(CN)_2{}^-}]}{[\mathrm{Au^+}][\mathrm{CN^-}]^2}; \quad \frac{K_{\mathrm{CN}}}{K_{\mathrm{SCN}}} = 10^{22.4}.$$

In a solution rich in thiocyanate ions the dithiocyanato-auroate ion is not perceptibly hydrolyzed at p_{H} 9; in strongly alkaline solution it is decomposed.

The action of ammonia on dithiocyanato-auroates through a reversible reaction leads to formation of Cleve's sparingly soluble, water-susceptible *monammino-aurous thiocyanate* $AuNH_3SCN$. $Au(SCN)_2^- + NH_3 = AuNH_3SCN + SCN^-$.

The dithiocyanato-auroate ion and compounds containing aurous thiocyanate are *colourless*.

2. *Auric thiocyanate.* We are able to corroborate Cleve's statement that auric thiocyanate does not exist in the solid state and we have prepared two new compounds of Cleve's tetrathiocyanato-auriate type, viz. sodium *tetrathiocyanato-auriate* $NaAu(SCN)_4$ and *tetrathiocyanato-auriate acid* $HAu(SCN)_4, 2H_2O$. The latter acid can be extracted from an aqueous solution with ether and after drying

of the ethereal solution with sodium sulphate it is obtained with two molecules of water.

Estimation of auric thiocyanate in the presence of aurous thiocyanate may be accomplished by titration with sulphite till the colour disappears.

In solution auric thiocyanate is present chiefly as tetrathiocyanato-auriate ion $Au(SCN)_4^-$. The complexity constant of this ion is $10^{17.7}$ times as large as that of the tetrachloro-auriate ion.

$$K_{SCN} = \frac{[Au(SCN)_4^-]}{[Au^{+++}][SCN^-]^4}; \quad K_{Cl} = \frac{[AuCl_4^-]}{[Au^{+++}][Cl^-]^4}; \quad \frac{K_{SCN}}{K_{Cl}} = 10^{17.7}.$$

The tetrathiocyanato-auriate ion is strongly reddish-brown. At $\lambda = 578$ mμ its molar coefficient of extinction is 108, at $\lambda = 546$ mμ the coefficient is 2.6 times as great, and at 436 mμ it is nearly 10 times as great.

At thiocyanate ion concentrations exceeding 0.2 *penta-* and *hexathiocyanato-auriate* ions are present in appreciable quantities. The complexity constants of these complex ions are:

$$K_{Au(SCN)_5} = \frac{[Au(SCN)_5^{--}]}{[Au(SCN)_4^-][SCN^-]} = 1.0; \quad K_{Au(SCN)_6} = \frac{[Au(SCN)_6^{---}]}{[Au(SCN)_5^{--}][SCN^-]} = 1.1.$$

The penta- and hexa-complexes are more strongly coloured than the tetra-complexes. At $\lambda = 578$ mμ the molar coefficient of extinction of the penta-complex is about 218 and that of the hexa-complex about 248.

At small thiocyanate-ion concentrations and hydrogen-ion concentrations the tetrathiocyanato-auriate ion seems to undergo *hydrolysis* according to the following scheme:

$$Au(SCN)_4^- + H_2O \rightleftarrows Au(SCN)_3OH^- + H^+ + SCN^-.$$

However, even at $[H^+][SCN^-] = 0.01$, this hydrolysis amounts to hardly more than 20 per cent.

Very important in connection with the properties of auric thiocyanate is the *dissociation* of the tetrathiocyanato-auriate ion to dithiocyanato-auroate ion and free thiocyanogen $(SCN)_2$:

$$Au(SCN)_4^- \rightleftarrows Au(SCN)_2^- + (SCN)_2.$$

At 18° C the dissociation constant has the following value:

$$K = \frac{[Au(SCN)_2^-]\,[(SCN)_2]}{[Au(SCN)_4^-]} = 0.49 \cdot 10^{-4};$$

it increases about 8 per cent per degree.

3. *Free thiocyanogen* $(SCN)_2$ is to be regarded as a colourless pseudo-halogen situated between bromine and iodine. It is instantaneously liberated from thio-

cyanates by bromine, and in its turn it immediately liberates iodine from iodides. It is extremely unstable; in aqueous solution it is hydrolyzed according to the following scheme:

$$3(SCN)_2 + 4H_2O \rightarrow 5H^+ + 5SCN^- + HCN + H_2SO_4.$$

This gross process is the result of the following 4 partial processes:

$$(SCN)_2 + H_2O \rightleftarrows H^+ + SCN^- + HSCNO;$$

$$2\,HSCNO \rightarrow H^+ + SCN^- + HSCNO_2;$$

$$HSCNO + HSCNO_2 \rightarrow H^+ + SCN^- + HSCNO_3;$$

$$HSCNO_3 + H_2O \rightarrow HCN + H_2SO_4.$$

The second of these partial processes controls by its slow rate the reaction velocity for which the following equation has been shown to be valid:

$$\frac{d\,[(SCN)_2]}{dt} = -k'\,[HSCNO]^2 = -\,k\,\frac{[(SCN)_2]^2}{[H^+]^2\,[SCN^-]^2}$$

At 18° C the velocity coefficient k has a numerical value of about 5, and the value increases about 11 per cent per degree.

4. *The auto-reduction.* In solution auric thiocyanate by *auto-reduction* is converted into aurous thiocyanate according to the following equation:

$$3\,Au(SCN)_4^- + 4H_2O \rightarrow 3\,Au(SCN)_2^- + 5H^+ + 5SCN^- + HCN + H_2SO_4$$

The presence of hydrogen ions, of thiocyanate ions and of aurous thiocyanate strongly depresses the velocity of this autoreduction.

The autoreduction is caused by the instability of the free thiocyanogen arising from dissociation of auric thiocyanate. It has been shown that its rate of reaction can be correctly calculated from the dissociation constant of auric thiocyanate and the velocity of decomposition of free thiocyanogen.

5. *The deposition of gold.* A solution of aurous thiocyanate deposits gold with simultaneous formation of auric thiocyanate according to the following equation:

$$3Au(SCN)_2^- \rightleftarrows 2Au + Au(SCN)_4^- + 2SCN^-.$$

This reaction is reversible, auric thiocyanate dissolving gold with formation of aurous thiocyanate. The *equilibrium constant* of this reversible reaction has the following value:

$$K = \frac{[Au(SCN)_4^-][SCN^-]^2}{[Au(SCN)_2^-]^3} = \text{about } 33.$$

The *velocity* of the gold-dissolving effect of auric thiocyanate, we have not investigated more closely. Concerning the velocity of the reciprocal reaction, the separation of gold from aurous thiocyanate, we have found that with decreasing concentration of thiocyanate ions it increases rapidly; with decreasing concentration of hydrogen ions it increases slowly. The velocity is catalytically increased by addition of gold powder. In 0.1 M HCl, 0.5 M NaSCN, 0.1 M Au^{I} at 40° C about half of the gold is deposited during three days.

The joint effect of the autoreduction and the gold deposition is that during a sufficient length of time gold thiocyanate solutions deposit all their gold in metallic form.

6. *The solubility product of sodium auric thiocyanate,* $[Na^+][Au(SCN)_4^-]$ at 18° C was found to be 0.0005 in a solution 2.2 normal with respect to strong electrolytes and 0.0004 in one 0.6 normal with respect to electrolytes. In the calculation of these values, concentrations were used instead of activities. The solubility product of *potassium auric thiocyanate,* $[K^+][Au(SCN)_4^-]$, has the value 0.00006 at an electrolyte concentration of 1.4 normal.

7. *Auric chloride.* In a solution of chlorauric acid *in hydrochloric acid* gold is present chiefly as *tetrachloro-auriate ion* $AuCl_4^-$. This ion in solution is hydrolyzed according to the following equation:

$$AuCl_4^- + H_2O = AuCl_3(OH)^- + H^+ + Cl^-.$$

Its *hydrolysis constant* has the following value:

$$K = \frac{[AuCl_3(OH)^-][H^+][Cl^-]}{[AuCl_4{}^-]} = 0.55 \cdot 10^{-4}.$$

8. The following *standard potentials* have been determined:

Electrode reaction	Standard potential. ${}_0E_h$
$Au + 2SCN^- = Au(SCN)_2^- + e$	0.689 volts
$Au(SCN)_2^- + 2SCN^- = Au(SCN)_4^- + 2e$	0.645 –
$Au + 4SCN^- = Au(SCN)_4^- + 3e$	0.660 –
$Au + 4Cl^- = AuCl_4^- + 3e$	1.001 –
$2SCN^- = (SCN)_2 + 2e$	0.769 –

These values are valid around 18° C. In their calculation ion concentrations were used instead of activities.

9. The value given by *Abegg* and *Campbell* of the *standard potential of gold-aurous ion,* viz. 1.5, is unreliable for in measurements of gold electrode potentials in strong nitric acid saturated with aurous oxide, only the oxidation potential of nitric acid is measured.

Investigations on the Chlorides of Gold

NIELS BJERRUM

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1. *Hydrolysis of the $AuCl_4^-$ Ion* (from experiments by N. H. ARNFRED and G. E. HJORT).

Even in acid solution Cl^- ions are only split off from $AuCl_4^-$ ions when HO^- ions are taken up at the same time. In dilute solution (0.01 molar) the hydroxo complexes: $AuCl_3OH^-$, $AuCl_2(OH)_2^-$, $AuCl(OH)_3^-$, $Au(OH)_4^-$ will be formed on addition of NaOH. The equilibrium constants:

$$K_n = \frac{[AuCl_{4-n}(OH)_n][H^+][Cl^-]}{[AuCl_{4-n+1}(OH)_{n-1}]} \cdot f^2$$

(f being a mean ion-activity coefficient) are determined through measurements of pH with a gold electrode in solutions of $HAuCl_4$ (with or without addition of KCl), to which NaOH is added.

$$pK_1 = 6.07; \quad pK_2 = 7.00; \quad pK_3 = 8.04; \quad pK_4 = 8.51.$$

Equilibrium is set up almost immediately except as regards the tetrahydroxo complex for which it takes about 24 hours.

In concentrated solutions complexes with several gold atoms are formed slowly on addition of NaOH, and subsequently a deposition of impure auric hydroxide will occur.

2. *The Redox Potentials of the Gold Chlorides* (from experiments by G. BJØRLING).

If sulphite is added to a dilute solution of auric chloride, aurous chloride is at once formed in the solution. If the course of the redox potential during this addition is followed by means of a platinum electrode, falling potentials will be observed at the beginning. In this initial period the fall of the potential shows that the process determining the potential is $AuCl_4^- + 2e^- \rightleftarrows AuCl_2^- + 2Cl^-$, and for the corresponding standard potential we calculate:

$${}_0E_{3,1} = E + 0.029 \log \frac{[AuCl_2^-][Cl^-]^2 f^2}{[AuCl_4^-]} = 0.932 \text{ volts}$$

(E is the measured potential, corrected for diffusion potential and converted to the potential of the standard hydrogen electrode). After the addition of a certain small amount of sulphite the potential begins to *rise*, and at the same time gold deposits on the platinum electrode. The gold does not, however, separate out in the liquid, and even the amount deposited on the electrode is small. When one mole Na_2SO_3 has been added per one mole $HAuCl_4$, and the gold has been completely reduced to aurous chloride, the redox potential passes through a flat maximum simultaneously with decoloration of the solution.

In this 2nd period the process determining the potential is $AuCl_2^- + e^- \rightleftarrows Au + 2Cl^-$, and for the standard potential corresponding to this process we calculate:

$$ {}_0E_{1.0} = E + 0.058 \log \frac{[Cl^-]^2 f}{[AuCl_2^-]} = 1.119 \text{ volts.} $$

If substantially more than one mole Na_2SO_3 is added per one mole $HAuCl_4$, gold also begins to separate out in the solution; but not until somewhat more than $1\frac{1}{2}$ mole Na_2SO_3 per 1 mole $HAuCl_4$ has been added, does the reduction potential decrease to the low value characteristic of sulphite.

3. With a knowledge of the above mentioned four hydrolysis constants and the two redox potentials, it is possible to calculate the composition of a pure auric chloride solution as well as that of a dilute auric chloride solution saturated with gold. The chlorine and oxygen tensions corresponding to equilibrium in such solutions can be calculated, and a quantitative determination of the stability of gold chloride towards bases and reducing substances has been obtained.

Errata

Owing to a fault by the printer two of the papers in the book have been interchanged. The following corrections should therefore be made in the Table of Contents:

Page 6, end of the 4th line, *for* 258 *read* 286

Page 6, end of the 8th line, *for* 286 *read* 258

Note also:

Page 5, end of the 2nd line from bottom, *for* 238 *read* 228