The Brönsted Memorial Lecture.

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IT is a difficult task to commemorate and appraise a great man like Brönsted, especially for one thirty years his junior in age, and so much his junior in science. This difficulty is increased by a difference in nationality, and I feel therefore that I ought to begin by acknowledging my debt to the many friends in Denmark who have helped me in the preparation of this lecture. I must mention especially Mrs. Brönsted, who has provided me with much material, especially about Brönsted's early life, and Professor Christiansen, who has made available to me the manuscript of his own memorial lecture to Brönsted. What I have to say owes a very great deal to their willing co-operation.

I shall begin by giving an outline of Brönsted's life and career, followed by some account of his scientific work, and finally I shall try to give a general picture of him as a scientist and as a man.

Johannes Nicolaus Brönsted was born on February 22nd, 1879, in Varde, a small town in West Jutland. His father was a civil engineer employed by "Hedeselskabet," a corporation founded to reclaim moorland by draining, irrigation, and planting. His mother died shortly after his birth, but his father remarried shortly afterwards, and the family moved to a farm in the heart of Jutland, where the young Brönsted and his elder sister spent most of their childhood. This period laid the foundation for the love of country things and country people which played such a great part in his later life. When he was twelve years old his family moved to Aarhus, the second largest city in Denmark, but still an essentially rural environment. He went to school there and seems to have been an apt pupil, particularly in mathematics. There was, of course, no school instruction in chemistry at that time, but Brönsted's interest in the subject was a very early one, his first source of information being an agricultural dictionary which he found in the attic. He did primitive experiments at home in the usual fashion, and the spirit lamp and balance which he used are still in existence.

His father died, in 1893, leaving the family in straitened circumstances. Several friends of the family felt that the young Brönsted ought to begin to earn his living, but his mother recognised his promise and was determined to give him and his sister a good education even if it meant considerable sacrifices. The family moved to Copenhagen, and Brönsted attended the Metropolitan School there, where he found not only a high educational standard, but also a remarkably stimulating set of school-fellows. Of the twenty boys in his class, two became bishops, two distinguished physicians, and five professors. One of the latter was Niels Bjerrum, his closest friend for many years, and his chief rival in making Danish physical chemistry world-famous. Brönsted matriculated in 1897, and went to study at the Polytechnic Institute in Copenhagen, where he met Charlotte Louise Warberg, whom he married in 1903. His studies seem to have sat lightly on his shoulders, and he found plenty of leisure to cultivate other interests such as philosophy, art, poetry, and music. It was at first intended that he should become an engineer like his father, but after taking his first degree in that subject in 1899 he changed over to pure science, and took his "Magister" degree in chemistry in 1902. At that date this degree was something of a rarity, especially in chemistry, and Brönsted's friends used "Magister" as a nickname for many years afterwards.

There was no academic position immediately available, and Brönsted worked for a short time in an electro-technical concern. However, he soon returned to the University Chemical Laboratory, and was made an assistant there in 1905. He worked there on his affinity measurements, and in May 1908 presented the third paper in this series (on mixtures of sulphuric acid and water) for his doctorate degree. In the same year a new chair of chemistry was instituted in Copenhagen which combined the duties of teaching physical chemistry to the University students, and inorganic chemistry to students at the Polytechnic Institute. The two competitors for this chair were Brönsted and Niels Bjerrum, who had been Brönsted's class-mate at school, and had taken his doctorate degree in the same year. It must have been a very difficult decision for the judges to make, but their choice finally fell on Brönsted, who was appointed at the early age of 29. The news reached the Brönsted family in a dramatic way: one day just before Christmas a goods train stopped at the bottom of their garden in the country, and a railway official descended bearing a telegram of congratulation from Bjerrum.

This appointment fixed the whole of Brönsted's subsequent career, as he held the chair until

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his death 39 years later. His laboratory was at first in the Polytechnic Institute, and for a time facilities were very limited, as physical chemistry was a new subject and the laboratory had to be equipped from scratch. However, conditions gradually improved, and in 1919 he was relieved from the onerous task of teaching elementary inorganic chemistry. The greatest change in his working conditions resulted from his visit to the United States in 1926—27, when he was able to discuss the possibility of financing a new physicochemical laboratory in Copenhagen. The International Education Board finally met the cost of a new University Physicochemical Institute, which was completed in 1930. Here Brönsted had not only ideal working conditions, but also a delightful official residence where he and his family could exercise their hospitality and charm.

I shall now give some account of Brönsted's contributions to physical chemistry, not in strictly chronological order, but under their main headings.

The most important general interest in Brönsted's scientific work was undoubtedly thermodynamics. His earlier work dealt entirely with this topic, and even his later work on reaction kinetics has a strong thermodynamic flavour. His series of thirteen experimental papers on " Affinity " appeared during the years 1906—18, and constitute a veritable text-book of thermodynamics. Although Brönsted is well known for his later work on the thermodynamics of dilute electrolyte solutions, it is probably not generally realised how much he contributed to the fundamentals of chemical thermodynamics, where he can be ranked with Nernst and G. N. Lewis. At that time, although it was generally accepted that the affinity of a chemical process was measured by the maximum work and not by the heat of reaction, there were very few accurate or systematic measurements of affinity, and it was this gap which Brönsted set out to fill. In 1906 he showed how the heat and free energy changes in the interconversion of rhombic and monoclinic sulphur could be measured over a range of temperature, and he also speculated as to how affinity changes could be calculated from purely thermal quantities. It was of course Nernst, and not Brönsted, who first solved this last problem successfully, but Nernst himself acknowledged the importance of Brönsted's work in pointing the way. In a later paper in the same series (1910) Brönsted dealt with the thermodynamics of water–sulphuric acid mixtures, and gave one of the first correct treatments of the relations between the various differential and integral thermodynamic quantities in a mixture. In this paper he showed great ingenuity in combining vapour pressure, E.M.F., and calorimetric measurements, and (as in all these early papers) in obtaining accurate results with very modest resources.

Brönsted was always skilled at devising applications of E.M.F. measurements, and one example of this was his measurement of the free energy of formation of naphthalene picrate from its solid constituents, not at first sight a promising system for study by E.M.F. methods. Brönsted pointed out in 1911 that the free energy of this change was measured by the E.M.F. of the cell:

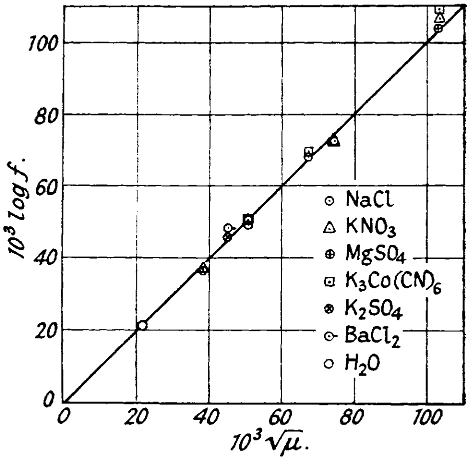
$$\text{Picrate electrode}|\text{solution I}|\mathrm{H_2Pt},\ \mathrm{PtH_2}|\text{solution II}|\text{Picrate electrode}$$

where solution I is saturated with picric acid, and solution II with naphthalene + naphthalene picrate. Brönsted suggested using mercury–mercurous picrate for the picrate electrode, but was unable to make measurements on the above cell because the picrate solutions were reduced at the hydrogen electrodes. He was therefore compelled to use a very ingenious but laborious indirect method of measurement. It is interesting to note that in Oxford we have recently been able to measure the E.M.F. of the cell originally proposed by Brönsted by replacing the hydrogen electrodes by glass ones (which of course were not available to him): the value obtained for the free energy of formation is exactly the same as that obtained in 1911 by the indirect method (Bell and Fendley, *Trans. Faraday Soc.*, 1949, **45**, 121).

Brönsted's thermodynamic studies soon led him into the field of electrolytes, first through E.M.F. measurements, and later through studies of solubility. It was becoming clear, partly through the work of Bjerrum, that very many electrolytes were completely dissociated in solution, and that their deviations from ideal thermodynamic behaviour could not be explained in terms of any association equilibrium. The concept of " activity " had been introduced by G. N. Lewis, and various authors had suggested that electrostatic forces between the ions might be of importance. Brönsted's approach was essentially an experimental one, and his solubility measurements became famous in 1924, when with LaMer he published data on activity coefficients of ions in very dilute salt solutions which provided a most striking confirmation of the theoretical treatment of Debye and Hückel, published while the work was in progress. It should, however, be stressed that this publication with LaMer was really the fifth of a series of papers on solubility, starting in 1919, interspersed with a number of other papers on the properties of ionic solutions. It is in fact remarkable how many important laws Brönsted was able to discover on the basis of his carefully designed and accurate experiments, in most cases before any theoretical basis for these laws was available. Thus he was able to show that the deviations of ionic solutions from ideal behaviour increase greatly with an increase in the charges on the ions present, and that in a solution containing several electrolytes the thermodynamic behaviour of a given ion is mainly a function of the ionic strength μ, defined as $\mu = \frac{1}{2}\Sigma m_i z_i^2$, where m_i is the concentration of an ion of charge z_i, and the summation extends over all the ions in the solution. In more concentrated solutions ions show individual properties not depending only on their charge, and Brönsted's " Principle of the specific interaction of ions " (1921) states that the individual properties of a given ion depend mainly on the ions of opposite charge which are present in solution. Brönsted's investigations on the effect of salts on ionic equilibria will be described under his kinetic work, but one simple principle is worth mentioning here : that even an ionic equilibrium will obey the classical law of mass action in presence of a large excess of non-participating salt. All these principles were later shown to have theoretical bases, and if we add to Brönsted's work the equally important investigations of his countryman Bejerrum, it will be seen that Denmark has had an altogether disproportionate share in the experimental foundations of the modern theory of electrolytes.

Most of Brönsted's solubility determinations, and many of his other researches, were carried out with the cobaltammines. These had been studied in great detail from the preparative point of view by S. M. Jörgensen, Brönsted's teacher, and he therefore had to hand large numbers of specimens and much information about these compounds. This was naturally a piece of good fortune, but Brönsted's genius lay in realising how admirably suited they were for his purposes. By suitable variations in the nature of the six groups co-ordinated to the central atom, ions can be produced with valencies varying from +3 to −3, and by combining these ions with one another or with other anions or cations it is possible to obtain salts of many charge-types and of widely varing solubility. Most of these salts are well-defined and crystalline, and they can be determined accurately even in very dilute solution by the simple process of treatment with sodium hydroxide and distillation of the ammonia into standard acid. These properties made them almost ideal for investigation of solubilities in salt solutions, but there was a great deal of ground-work to be done before the most suitable salts could be chosen : thus in his 1920 paper he measured the solubilities of 90 salts at two temperatures. The salts finally used by Brönsted and LaMer were the following :

FIG. 1.



The relation between the activity coefficient f *and the ionic strength* μ *for a uni-bivalent cobaltammine salt in the presence of solvent salts of various types. The heavy line represents the theoretical equation — log* f $= 1{\cdot}00\ \sqrt{\mu}$.

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$[Co(NH_3)_4C_2O_4]^+[Co(NH_3)_2(NO_2)_2C_2O_4]^-$	$s = 4{\cdot}9 \times 10^{-4}$
$[Co(NH_3)_4(NO_2)(CNS)]^+[Co(NH_3)_2(NO_2)_2C_2O_4]^-$	$s = 3{\cdot}3 \times 10^{-4}$
$[Co(NH_3)_4C_2O_4]_2{}^+[S_2O_6]^=$	$s = 1{\cdot}5 \times 10^{-4}$
$[Co(NH_3)_6]^{+++}[Co(NH_3)_2(NO_2)_2C_2O_4]_3{}^-$	$s = 5{\cdot}0 \times 10^{-5}$

The saturated solutions were obtained by the simple expedient of letting the solvent trickle slowly down a long vertical tube packed with crystals, a method which had been used by Brönsted much earlier in his measurements on rhombic and monoclinic sulphur. In spite of the low solubilities involved, an accuracy of about 0·3% was attained, as may be seen from Figure 1. The line drawn represents the predictions of the Debye–Hückel theory, which are clearly followed very closely.

The cobaltammines also played a considerable part in the development of Brönsted's ideas on acids and bases, and there is one other example of their use which may be mentioned here. On a simple electrostatic picture the solubility of a salt in different solvents should be a smooth function of the dielectric constant, but this is not so in practice, no doubt largely because of the part played by non-electrostatic factors. In a paper given to the 1931 meeting of the British Association Brönsted reported solubility measurements on the two substances $Co(NO_2)_3(NH_3)_3$ and $[Co(NO_2)_2(NH_3)_4]^+[Co(NO_2)_4(NH_3)_2]^-$ which contain exactly the same chemical groupings, but are respectively a non-electrolyte and a uni-univalent salt. By considering the ratio of the solubilities of these two substances, rather than the solubility itself, he hoped to eliminate the non-electrostatic factors, and he did in fact find a fairly regular behaviour for nine solvents with dielectric constants ranging from 21 to 84.

Apart from electrolytes, a particular thermodynamic problem which interested Brönsted from 1930 onwards is the effect of molecular size on thermodynamic properties. He carried out experiments on the solubilities and distribution between phases of molecules (or colloidal particles) which were chemically very similar, and differed mainly in size. These led him to the concept of an "isochemical series," and he established several laws governing the solubilities and other properties of such a series. Although he did not realise that large entropy effects might be present in mixtures of molecules of different sizes, Brönsted's laws are essentially the same as those developed recently for high polymers such as rubber. Some of Brönsted's last published work was on the vapour pressures of mixtures of the normal paraffins, for which he obtained experimental results of very high accuracy, and established some new regularities which have not yet been explained theoretically. This work contains some very neat experimental devices: for example, in order to weigh a vessel containing liquid and vapour without detaching it from the rest of the apparatus, he suspended it from an ordinary balance and used as a connecting tube such a fine glass capillary that it had little effect within the sensitivity of the balance.

Brönsted's work on isochemical series is of particular interest, because it represents one of the few cases in which he gave a molecular interpretation for the laws which he had established experimentally. In general he was curiously reluctant to consider any detailed molecular picture, preferring to derive from experiment empirical regularities which should be independent of any particular features of the molecules concerned. For example, one sometimes felt that he regretted the mechanistic explanation given by the Debye–Hückel theory for the laws which he had established experimentally, and other examples of a similar attitude will be given later. I well remember his indignation when I suggested to him, shortly before his death, that a statistical approach was helpful in explaining the laws of thermodynamics to students.

Certainly there was no suggestion of any molecular interpretation in his writings on the fundamental bases of thermodynamics, which occupied him to an increasing extent during the last ten years of his life. Although he criticised severely the conventional approach to the Second Law, his treatment remained a strictly phenomenological one. It is difficult to give an estimate of the value of this work, and I shall not attempt to summarise its content here. It roused violent controversy in Denmark, but has received little attention elsewhere: it is usually regarded as formally correct, but rather sterile. It is true that a similar view was at one time held about Brönsted's acid–base definition, which proved to have such a widespread importance, and it would indeed be interesting if his concepts of heat and entropy should eventually prove equally fruitful. They may perhaps be helpful in treating processes in which a steady state is set up by the irreversible flow of energy or matter through the system, a field which Brönsted had begun to study experimentally shortly before his death.

The second main field of Brönsted's activities was reaction kinetics, and in particular catalysis by acids and bases. This interest arose comparatively later in Brönsted's scientific development, but is probably the work for which he is best known, especially outside Denmark. It was closely connected with his work on electrolytes, and it is difficult to trace the exact order in which the various interwoven ideas arose, since papers on both kinetic and thermodynamic topics followed one another with bewildering rapidity in the nineteen-twenties.

Brönsted first used kinetic measurements in 1921 in connection with the effect of salts on acid–base equilibria. He was particularly concerned to show that the effect of salt concentrantion on hydrogen-ion concentration depends on the nature of the equilibrium involved: for example, in the system

$$CH_3{\cdot}CO{\cdot}OH \rightleftharpoons CH_3{\cdot}CO{\cdot}O^- + H^+$$

the hydrogen-ion concentration will be increased by added salt, while the equilibrium

$$NH_4^+ \rightleftharpoons NH_3 + H^+$$

will be little affected by salt additions, and in the system

$$[Fe(H_2O)_6]^{+++} \rightleftharpoons [Fe(H_2O)_5OH]^{++} + H^+$$

the hydrogen-ion concentration will be decreased by addition of salt. These results follow directly from the Debye–Hückel expression for activity coefficients, but were derived by Brönsted from the experimental evidence on the activity coefficients of ions of different charges. In order to test his conclusions it was necessary to measure the hydrogen-ion concentrations in these solutions, and for this purpose he used the rate of reaction of diazoacetic ester with water to give glycollic ester and nitrogen, a well-known example of hydrogen-ion catalysis. This at once raised questions of fundamental importance, for it was held in many quarters that the reaction velocity in such a system was proportional to the activity rather than to the concentration of hydrogen ions. Brönsted showed definitely that the concentration was the appropriate quantity: for example, when only a strong acid is present, the effect of added salt on the reaction velocity is much less than its effect on the hydrogen-ion activity. This justified the use of the diazoacetic ester reaction for measuring hydrogen-ion concentrations, and the salt effects observed with solutions of weak electrolytes agree with those predicted from activity data. This type of kinetic salt effect, depending on the displacement of an equilibrium, was termed by Brönsted a " secondary salt effect."

There existed at the time a mass of unco-ordinated data on the effect of added salts on reaction velocities, including many reactions involving only strong electrolytes, where no secondary salt effect could be involved. In this latter class of reaction it is customary to speak of " primary salt effects." Brönsted next showed in 1922 that all the existing data for primary salt effects could be summarised by the following simple statement: reactions between ions of like charge exhibit a large positive salt effect, reactions between ions of unlike charge a large negative salt effect, and reactions between an ion and a neutral molecule a small salt effect which may be either positive or negative. This classification was in itself a great step forward, but Brönsted gave it a further interpretation in terms of his famous expression for the effect of environment on the rate of a chemical reaction. For a reaction between two species A and B the expression for the reaction velocity v is

$$v = k[\mathrm{A}][\mathrm{B}]\frac{f_{\mathrm{A}}f_{\mathrm{B}}}{f_{\mathrm{X}}} \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (1)$$

where k is independent of environment, f is an activity coefficient, and X represents the " critical complex " of A and B through which they must pass in order to react. It now seems obvious to us that the correct expression must involve the activity coefficient of some intermediate complex, as well as those of the reacting species, but Brönsted was the first to realise this, though the concept of a critical complex had previously been employed by Marcellin. We know very little about the nature of X, but we do know that its charge is the algebraic sum of the charges on A and B, and this is sufficient to predict approximately how its activity coefficient will vary with salt concentration. Nowadays this prediction would be made on the basis of the Debye–Hückel theory, but Brönsted again had to use the experimental data available for ionic activity coefficients, and was able to show that equation (1) corresponds to the rules for the salt effect given above, and agrees approximately with the magnitude of the observed effects. In particular it shows that in a reaction involving an ion and a neutral molecule (such as the decomposition of diazoacetic ester ion in presence of hydrogen ions) the activity coefficient factor will be near to unity, and hence the reaction velocity will be proportional to the concentrations of ester and hydrogen ions, and not to their activities. After the advent of the Debye–Hückel theory Brönsted made more measurements on salt effects in very dilute solutions, and found a complete confirmation of equation (1). It is interesting to note that Brönsted did not attempt to give any detailed molecular explanation of this equation, and the semi-thermodynamic derivation which he gave in 1922 was not made much clearer by a more detailed treatment in 1925. Brönsted's equation is now of course regarded as a special case of the transition-state expression for reaction velocity, but Brönsted himself showed little interest in later developments in this field.

The second major advance which served to clarify a large mass of kinetic work was Brönsted's extended definition of acids and bases, first published in 1923. Identically the same definition was put forward almost simultaneously by Lowry in this country. This definition is now generally accepted: it states that *an acid is a species which has a tendency to split off a proton, and a base is a species which has a tendency to add on a proton.* All acids and bases can therefore be arranged in conjugate or corresponding pairs according to the scheme

$$\mathrm{A} \rightleftharpoons \mathrm{B} + \mathrm{H}^+$$

This definition of acids includes not only uncharged molecules such as $CH_3{\cdot}CO_2H$, but also anions like HSO_4^-, $HPO_4^{=}$ and cations like NH_4^+, $[Fe(H_2O)_6]^{+++}$. The new definition of bases was even more fruitful, since there had previously been great confusion, for example as to whether the ammonia molecule or the hypothetical ammonium hydroxide should be regarded as a true base. The Brönsted–Lowry definition includes uncharged bases like NH_3, NMe_3 and anion bases such as $CH_3{\cdot}CO{\cdot}O^-$, OH^-, $CO_3^{=}$. It was not so easy to find an example of a cation base, but once again the cobaltammines and similar compounds came to the rescue : for example the ion $[Co(NH_3)_3(H_2O)_2OH]^{++}$ is a base in virtue of the reaction

$$\underset{\text{Base.}}{[Co(NH_3)_3(H_2O)_2OH]^{++}} + H^+ \longrightarrow \underset{\text{Acid.}}{[Co(NH_3)_3(H_2O)_3]^{+++}}$$

It is immediately clear that the hydroxyl ion is not in any way unique, since it is only one member of a whole class of anion bases. On the other hand the hydrogen ion does appear to occupy a privileged position as long as we write it as H^+, *i.e.*, a bare proton. However, following Fajans and others, Brönsted realised that the free proton could not exist in any significant concentration in the presence of other molecules, and that in aqueous solution it existed as the hydroxonium ion, H_3O^+, entirely analogous to the ammonium ion, NH_4^+. In fact, the " hydrogen ion " is a different entity in each solvent, in each case being only one of a class of cation bases.

Once the claim of hydrogen and hydroxyl ions to uniqueness has been abandoned, it becomes possible to write all the reactions of acids and bases (variously described as dissociations, neutralisations, hydrolyses, buffer systems, etc.) in the symmetrical form :

$$\text{Acid (1)} + \text{Base (2)} \rightleftharpoons \text{Base (1)} + \text{Acid (2)}$$

Some examples of this are given in the following table, and a similar set could be given for non-aqueous solvents.

A_1	+ B_2	⇌ A_2	+ B_1	Description.
$CH_3{\cdot}CO_2H$	H_2O	H_3O^+	$CH_3{\cdot}CO{\cdot}O^-$	Dissociation in water *or* buffer action in acetic acid + acetate.
$CH_3{\cdot}CO_2H$	NH_3	NH_4^+	$CH_3{\cdot}CO{\cdot}O^-$	Dissociation of acetic acid in liquid ammonia, *or* dissociation of ammonia in glacial acetic acid, *or* neutralisation of $CH_3{\cdot}CO_2H$ by NH_3, with or without solvent.
H_2O	$CH_3{\cdot}CO{\cdot}O^-$	$CH_3{\cdot}CO_2H$	OH^-	Hydrolysis of acetate solutions.
NH_4^+	H_2O	H_3O^+	NH_3	Hydrolysis of ammonium salts, *or* buffer action in NH_3 + NH_4Cl.
H_2O	$HPO_4^{=}$	$H_2PO_4^-$	OH^-	Hydrolysis of secondary phosphates.
H_2O	NH_3	NH_4^+	OH^-	Dissociation of ammonia in water.
$H_2PO_4^-$	H_2O	H_3O^+	$HPO_4^{=}$	Dissociation of primary phosphate *or* buffer action in mixtures of primary and secondary phosphate.

Since the hydrogen and hydroxyl ions are not unique among acids and bases, there is no reason why they should have the monopoly of catalytic cation in chemical reactions, and Brönsted's next important contribution was the experimental demonstration of *general acid–base catalysis* in a number of reactions. Brönsted and Pedersen's paper on the nitroamide decomposition, published in 1924, showed that the reaction was catalysed by the following classes of base :

(1) Anion bases like acetate ion, oxalate ion, etc.
(2) Uncharged bases like aniline and pyridine.
(3) Cation bases like $[Co(NH_3)_5OH]^{++}$.

Brönsted and Pedersen made a detailed study of catalysis by anion bases, and later papers (1925—34) extended this to the other types of base and also to non-aqueous solvents. The mutarotation of glucose offered rather more complications, since it is catalysed by both acids and bases. Thus in an acetate buffer solution the full expression for the reaction velocity is

$$v = k_0 + k_1[H_3O^+] + k_2[OH^-] + k_3[HOAc] + k_4[OAc^-]$$

However, by carefully designed experiments it was possible to separate out the effects of different species, and the 1927 paper by Brönsted and Guggenheim demonstrated the catalytic effect of anion bases, uncharged bases, cation bases, uncharged acids like acetic acid, and cation acids like the ammonium ion. Very similar conclusions were published by Lowry in the same year, though his investigations were less complete.

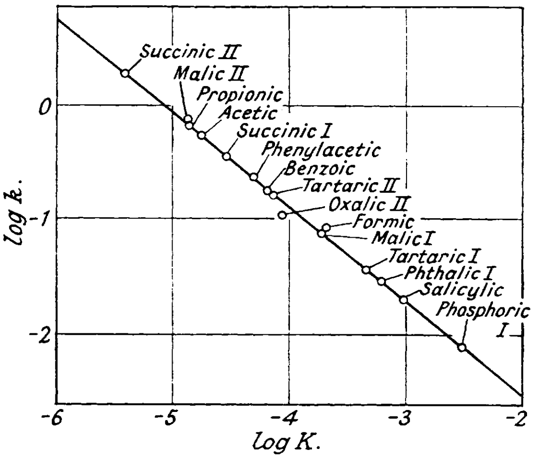
The idea of catalysis by species other than hydrogen and hydroxyl ions was not altogether a new one, and in particular the " dual theory," suggested by Acree, Snethlage, and H. S. Taylor, had assumed catalysis by undissociated acid molecules. However, most of their deductions were based upon incorrect values for the degree of dissociation of electrolytes, and did not allow for primary and secondary salt effects. In his monograph on " acid–base catalysis " (published in Danish in 1926, English translation in 1928) Brönsted devoted a good deal of space to a severe criticism of this earlier work, and was in fact able to show that in almost all cases the supposed catalytic effect of acid molecules was based on a misinterpretation of the data, or could reasonably be attributed to a salt-effect. The only notable exception to this statement was Dawson's work on the acetone–iodine reaction, and here Brönsted's strictures were rather less than just. It is true that Dawson did not take into account recent views on electrolytes and that his experiments were planned in such a way as to involve complicated salt-effects. Nevertheless, there is no doubt that his work definitely establishes catalysis by carboxylic acid molecules, and in fact still provides the most extensive set of data for this type of catalyst, although his numerical values need some revision in the light of modern developments.

If we consider a series of similar acids and bases, it is natural to expect that their catalytic power for a given reaction will depend on their acidic or basic strength. In his first paper on the nitroamide decomposition Brönsted gave a quantitative form for this dependence which has been found to be generally valid, and which is commonly known as the " Brönsted relation." For basic catalysis it can be written in the form :

$$k_b = GK_b^{\alpha}$$

where k_b is the catalytic coefficient of a base of dissociation constant k_b, and G and α are constants characteristic of the reaction, the temperature, and the solvent, α being less than unity. Figure 2 shows how well this relation is obeyed for the anion-catalysed decomposition of nitroamide : for most other reactions the agreement is rather less good. As in many other cases Brönsted arrived at the form of this relation primarily by considering the experimental data. The only theoretical basis which he gave for it was a vague and unsatisfactory one, and he was not particularly interested in later attempts to interpret the relation in terms of molecular potential-energy curves.

FIG. 2.



The relation between catalytic effect and acid–base strength for the anion-catalysed decomposition of nitramide.

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I must now attempt some kind of summing up of Brönsted as a scientist and as a man. His skill as an experimentalist was not immediately apparent because of the simple nature of many of his methods, and it took some time to realise how much skill and discrimination lay behind an apparently simple piece of experimental work. His great strength lay in the choice of the most suitable substance or reaction, and in the planning of a series of experiments to attain the desired end with the greatest certainty and economy. For this reason his researches always had a much wider application than the immediate purpose in hand, and one of the greatest benefits of working with him was the opportunity of sharing his insight into general methods and planning of research. Many of his pupils have modelled their subsequent work on Brönsted's prototypes : for example, most later work on activity coefficients from solubility measurements and on general acid–base catalysis follows closely on some lead originally given by Brönsted.

It is more difficult to place Brönsted as a theoretical physical chemist in relation to the main developments of his time. We have already seen several examples of his absorption in thermodynamics and his love of an experimental approach, and the adjective " classical " seems an appropriate one to describe his contributions to physical chemistry. In the field of solutions his work has had a clarifying effect to which it is difficult to find a parallel. Although his mind was a most agile one, several of the major trends in modern physical chemistry failed to rouse his interest : for example, the experimental and theoretical study of molecular structure, and the theoretical treatment of reaction velocities. Looking back, it seems strange that one of the greatest investigators of reaction kinetics in solution should never have deliberately measured an activation energy. On the other hand, there is no doubt that this limitation of interest enabled him to attack his chosen field with greater intensity and singleness of vision.

Brönsted was an individualist in his work, and owed little to the influence of other scientists, though the tradition of Julius Thomsen fostered his early interest in thermodynamics, and his training under S. M. Jörgensen introduced him to the cobaltammines and gave him high standards of preparative and quantitative work. There is only one instance where he collaborated with another scientist outside his own field, and that was in his famous work with Hevesy on the separation of the isotopes of mercury and chlorine by ideal distillation at low pressures. In his earlier days he had few junior collaborators, but in the period 1922—37 many chemists from other countries, particularly England and the United States, went to work with him. I myself spent four years in his laboratory, and I remember very clearly the impression of integrity and intensity of scientific endeavour which I received. One guest worker described his laboratory as a place of " high chemical potential," and the phrase does give something of the tense and personal feeling which Brönsted inspired. He showed great kindness and consideration to his collaborators from overseas, and the subsequent work done by many of them shows the lasting effect of his influence. On first acquaintance he seemed rather reserved, but one soon realised that this arose from an unwillingness to talk carelessly or lightly on scientific matters. When he had once embarked on a discussion his acuteness and remorseless logic were remarkable, and there can be very few occasions on which he was worsted in a scientific argument. He did in fact very much enjoy a keen polemical discussion, and never hesitated to express his criticisms in an edged and sometimes personal manner. This involved him in a number of controversies, beginning in 1908 with his criticism of Nernst's concept of " ideal concentrated solutions," and ending with a lengthy argument with Danish physicists about the foundations of thermodynamics.

Brönsted's duties as a professor involved a considerable amount of elementary teaching, especially in his earlier days, and his lectures were elegant in delivery and content. Their concentrated exactness made them perhaps rather indigestible for the average student, and the same was true of his text-book of physical chemistry. The later editions of this book incorporated his own treatment of thermodynamic principles, and we can sympathise with the polytechnic student who had to use terms like " heat " and " work " in one sense in his physics and engineering, and in another sense in his chemistry. The Danish system involves a large amount of oral examination, and in his earlier days Brönsted gained some reputation for severity as an examiner: his standards were certainly high, and he was not much given to compromise, least of all in scientific matters. There are many anecdotes about these examinations, and I remember one candidate who had rashly professed some knowledge of the occurrence and properties of the silicates, and who was finally driven by Brönsted's remorseless logic into maintaining that a paving-stone would probably dissolve completely if stirred up with a little water! However, as he became older Brönsted became more lenient towards his younger students, though he could still be a formidable opponent to candidates for the doctorate degree.

In private life Brönsted had great personal charm and a wealth of interests outside his science. The chief of those was his love of the countryside and its people, which remained with him all his life. His family holidays were usually spent in some remote part of the country, and he had a very extensive knowledge of Danish wild life, especially of birds. It is interesting to note that his last publication, just before his death, was a note describing some observations on insect behaviour made during his summer holiday. He felt very keenly about the preservation of natural beauty and nature reserves, and took a prominent part in campaigns to this end. Music and painting were also among his accomplishments, and through his marriage he came into close contact with many of Denmark's leading artists and musicians. He had a wide knowledge of literature in several languages and a remarkable gift not only for accuracy but also for elegance in expression in both Danish and English.

Brönsted travelled widely in Europe, and made several visits to the United States. In spite of his strong Danish patriotism he had a great deal of sympathy and understanding for other countries, and especially for England. His early contacts were mostly with German scientists, but after the First World War his sympathies turned decisively towards this country. In 1920 he spent several months in England, mainly with Professor Donnan at University College, and he made at least seven more visits before 1939, including several to attend meetings of the Faraday Society. Among many other honours he was made an honorary member of the Academy of Arts and Sciences in 1929, an honorary Fellow of the Chemical Society in 1935, and an honorary doctor of London University in 1947.

The Second World War served only to strengthen the ties which bound him to English things and English people, and he never had any doubts as to the rightness or the eventual outcome of the struggle. From the first day of the German occupation he spent several hours daily listening to the broadcast news from London, and he also read widely in English history and biography : when I visited him in 1945 he still had on his table a list of English Foreign Secretaries from 1769 onwards. The occupation also turned his attention to public affairs in general, in particular the vexed question of Schleswig and the Danish–German frontier, about which he spoke and wrote in his usual forthright manner. Nevertheless, it was a surprise to many of his friends when in 1947 he accepted nomination as a candidate for the Danish parliament, and a still greater one when on October 28th he was elected. He took this responsibility seriously, and immediately began to study parliamentary procedure, but he was overtaken by his last fatal illness before he could take his seat, and died on December 17th. It is interesting to speculate how he would have fared in Parliament and how his logical and uncompromising mind would have dealt with the half-truths of politics. He himself believed that many of the ills of mankind were due to the lack of logic and precise definition in public affairs, and it is an open question whether the application of this principle would have brought success or frustration.

It is very fortunate that Brönsted was able to visit England again in the summer of 1947, when he attended the Chemical Society Centenary celebrations and the International Congress. He enjoyed this visit to the full : not only the formal scientific occasions, but also the quieter times which he and Mrs. Brönsted spent in the homes of their English friends, and by themselves in a remote corner of the English countryside. It was a great shock to hear of his sudden death so soon afterwards, and many people in many countries will mourn him, not only because of his contributions to science or for his inspiring personal genius, but also as a fine and lovable person. Many of his ideas have passed into the common currency of physical chemistry, and, although one hesitates to predict the future of any scientific subject, it is difficult to imagine a state of affairs in which they would not still be valid and useful. This society has done itself a great honour by numbering him among its Honorary Fellows.

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