THE ELECTROLYTIC DISSOCIATION THEORY

BY

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AUTHORIZED TRANSLATION FROM THE GERMAN

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To My Dear Teacher and Friend

Svante Arrhenius

The Founder of the Dissociation Theory

TRANSLATOR'S PREFACE.

It seemed worth while to give English readers the benefit of this account of the electrolytic dissociation theory at the hand of a master of its details and applications.

I gladly acknowledge my indebtedness, in so many ways, to my wife in preparing this translation, and also to Dr. Frederic Bonnet, Jr., of Worcester Polytechnic Institute, for helpful criticisms and suggestions.

C. L. v. E.

IOWA CITY, IOWA.

AUTHOR'S PREFACE.

As reasons for acting in place of the founder in presenting the dissociation theory, I may be permitted to mention the request of the publisher of this collection[1] to undertake the task, and to this I would add the enthusiasm which must seize upon every one who has taken the opportunity to study thoroughly this beautiful theory and learn how many old problems have been solved by it at one stroke, and how many new ones have come into view and been mastered.

Quite recently, Roloff set himself the same task for a similar class of readers, and it offered some difficulty to keep this presentation from becoming merely competitive. I have for that reason touched but briefly upon the historical development, which is so adequately given by Roloff, and have endeavored to confine myself more to the detailed account of the chemical side, particularly to the development of the equilibrium relations among electrolytes. While I believed that Ostwald's exposition in his "Foundations of Analytical Chemistry," which showed

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[1] "Sammlung chemischer und chemisch-technischer Vorträge," edited by Prof. Dr. Felix B. Ahrens (Ferd. Enke, Stuttgart).

so clearly the usefulness of the ion theory for every-day chemical purposes, was sufficient for the initiated, yet for a deeper insight into this attractive field a fuller account was desirable. In particular I have laid great stress on developing the formulæ as simply and clearly as possible, and therefore the proofs have not infrequently been given in a form differing more or less from those in the original papers. These modifications have also seemed desirable as a result of my teaching experience.

There is, of course, no intention of laying claim to new scientific achievements. We are justified, on the whole, in considering that Arrhenius himself has so thoroughly worked over the material that important advances of a general nature are scarcely to be expected; hence the nitiated will meet with new ideas and developments in only a few instances.

R. A.

BRESLAU, April, 1903.

CONTENTS.

THE THEORY OF
ELECTROLYTIC DISSOCIATION.

FUNDAMENTAL CONCEPTIONS OF THE THEORY.[1]

In the year 1887, when the Swedish physicist Svante Arrhenius propounded the theory of electrolytic dissociation (ionization), physical chemistry was passing from a kind of attractive side issue to a more central position of interest among chemists. Very interesting physical properties had been studied for some time and although the general laws were discovered, which with Ostwald we at present summarize under the caption Additive Properties, yet none of these furthered to any marked extent the constitution problems then prominent in the minds of organic chemists. The eyes of chemists were drawn again to the field of physical chemistry by the methods (discovered in 1883 by the recently deceased

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[1] The sign $^{\cdot}$ = positive ionic charge per equivalent, and the sign $'$ = negative ionic charge per equivalent. Chemical formulæ in parenthesis, for example ($H^{\cdot}$), indicate concentration of the kind of molecule inclosed, in this instance hydrogen ion.

Frenchman Raoult) for determining molecular weights by means of freezing- and boiling-points of solutions. This determination of the molecular weights of substances in solution was an exceedingly useful aid in all kinds of chemical investigations. It was only natural, therefore, that van't Hoff's [1] epoch-making theory of solutions, which appeared in the transactions of the Swedish Academy in 1885, and gave at once the theoretical explanation for the laws found by Raoult, should attract more attention in the chemical world than would have been possible under other circumstances, especially as it dealt with nothing less than judging the certainty of the conclusions based on the molecular-weight determinations of Raoult. General attention was further attracted to physical chemistry by the founding of the "Zeitschrift für physikalische Chemie" by Ostwald, at the beginning of his activities as a teacher at Leipzig, and by the completion, shortly before that, of his well-known "Lehrbuch der Allgemeinen Chemie," in which he brought together and formulated as a whole all physical chemical knowledge.

Through extended studies of his own on the conductivity of electrolytic solutions, and through the theory of van't Hoff as to the state of substances [2] dissolved in water, Arrhenius was led to look upon the so-called electrolytes, i.e., the acids, bases, and salts belonging especially to the field of inorganic chemistry, as broken up to a definite and usually large extent into their con-

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[1] See "Sammlung chemischer und chemisch-technischer Vorträge," Vol. V.

[2] Ibid.

stituents, the ions. These ions, provided with electric charges, conduct the current by moving through the solution to the electrodes.

This conception of free-existing parts of chemical molecules was nothing new among physicists. Davy (1808) and Faraday (1833), in their famous investigations on the electrolysis of fused and dissolved salts, and Hittorf, in his studies on the concentration changes caused by electrolytic conduction, had assumed and made probable such a molecular decomposition, even if such decomposition were not of very definite extent.

These conceptions gained in significance through the experimental verifications of Buff (1855) and the theoretical proofs of Clausius (1857) and Helmholtz (1880), which showed that during electrolysis the components of the chemical molecules, though moving in opposite directions, do so *without the least consumption of energy.* The seemingly necessary assumption, on the part of chemists, of an affinity between the part-molecules was thus disproved, and there was no physical reason, therefore, for not considering the ions as independent of one another, that is, the molecules split up into such ions. We do not intend at this place to enter farther into the very interesting history of the subject, a detailed account of which, it may be well to mention, is to be found in the readable article of Roloff,[1] but rather to occupy ourselves with a presentation of the substance of the theory and its successes in the field of chemistry.

As the name "electrolytic dissociation" indicates, the

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[1] Zeitschr. f. angew. Chem., **15**, Heft 22–24 (1902).

theory of Arrhenius includes all those substances which we term electrolytes, i.e., the substances which conduct the galvanic current in such a way that a movement of material masses takes place simultaneously in the directions of the positive and negative currents. As has long been known, this peculiar kind of electric conduction is a property of salts, acids, and bases, and through them of almost all substances belonging to the field of inorganic chemistry. As Hittorf showed, we can formulate directly the statement that electric conduction is the essential characteristic of those substances known as "salts" in the broader sense, and accordingly acids are looked upon as salts of hydrogen, and bases as salts of hydroxyl. Hereby a clear conception of "salt" was formulated for the first time, about which long experience had given us a practical but nevertheless inexact notion.

In many cases the ions are determined by the nature of the products which separate at the electrodes during electrolysis; thus, for example, the ions of the salt $CuCl_2$ are on the one hand the positive component Cu, separating at the cathode, and on the other the negative Cl. Hittorf in his classical researches showed how one can in general determine the nature of the ions, that is, the components wandering in opposite directions, by the shifting of the concentrations which take place during electrolysis. That a salt, such as K_2SO_4, does not break up into K_2O and SO_3, but into K_2 and SO_4, is shown by comparison with KCl, in which Cl is the negative and therefore K the positive ion; and since both salts behave alike as to their positive component, having the K ion in common, the negative component of K_2SO_4

must be essentially SO_4, or the residue after taking away the K.

On this conception as a basis one readily arrives at the long and vainly sought exact definitions of acids and bases. While it was sufficiently well known that their characteristic constituents were H and OH respectively, nevertheless it had not been possible to define under what circumstances these components showed acid or basic properties; for there are numerous compounds containing H or OH which are not necessarily acids or bases. The dissociation theory, however, defines these substances for us as such which contain H or OH in the form of ions as the result of electrolytic dissociation, and makes clear at once the way of informing ourselves as to the degree of the acid or basic properties of a compound, by determining the concentration of these characteristic $H^{\cdot}$ or OH' ions. This will be discussed later.

Let us here summarize a few of the more characteristic reactions peculiar to these two most important kinds of ions.

The $H^{\cdot}$ ions

1. Change the color of "indicators"; for example, color blue litmus red, methyl orange red, decolorize red phenolphthalein solution and yellow nitrophenol solution, etc.;
2. Hasten catalytically the decomposition of esters by water into alcohol and acid, the inversion of cane-sugar, also the hydrolysis of maltose;
3. Act as a solvent on many metals, marble, etc.;
4. Cause "acid" taste;

5. Neutralize all characteristic properties of OH' ions.

The OH' ions

1. Change the color of indicators in the reverse sense of the $H^{\cdot}$ ions;
2. Act as saponifiers of esters;
3. Accelerate catalytically the condensation of acetone to diacetone alcohol (also the reverse reaction), the conversion of hyoscyamine into atropine, and the disappearance of multirotation;
4. Neutralize all characteristic properties of $H^{\cdot}$ ions.

Other ions have their specific reactions as well, but it is certain that, for reasons as yet unknown, we have to consider catalytic action as especially belonging to $H^{\cdot}$ ions and OH' ions, even if it is true that occasionally other substances can act catalytically.

According to the theory of Arrhenius, these salts must, to a certain extent, be broken up into their ions, and the most convincing evidence for this conclusion was his discovery that all these salts were at the same time such substances as gave in aqueous solutions, according to the investigations of Raoult, freezing-point depressions which did not correspond to the molecular weights assumed from chemical considerations. While many substances dissolved in water depress the freezing-point of the water by 1.85° for each mole per liter, Raoult found that a considerable number of substances, particularly when dissolved in water, gave greater depressions; or, according to the above-mentioned rule, they seemed to contain in a liter more than one mole, in spite of the fact that only one gram-molecule of the substance had been used for solution. Similarly the boiling-points of the same solutions showed too great a rise, thus urging the same conclusion. One was thereby brought to face the alternative, either to doubt on the chemical assumptions the general tenability of Raoult's law, or to admit on the basis of its validity that out of every molecule of these deviating substances several independent parts are formed. In assuming the latter the dissociation theory followed the same line of thought that was so successfully applied by Cannizzaro, Kopp, and Kekulé in explaining the abnormal vapor densities of such substances as ammonium chloride, phosphorus pentachloride, and others. For, according to the van't Hoff solution theory, the changes in the freezing- and boiling-points are the measures of the osmotic pressure of the dissolved substances, and this osmotic pressure is entirely analogous to gas pressure.

It is customary to speak of Raoult's methods as methods for the determination of molecular weights; it would seem clearer, however, to call them methods for determining molecule number or normal concentration, for the changes in freezing-point and boiling-point give directly only the number of moles of whatever kind contained in a definite volume of the solvent. Not until we consider the amount by weight contained in the solution do we arrive at the apparent molecular weight, which only represents a real molecular weight when we can leave out of consideration the grouping together or splitting up of individual molecules. Since in so many cases this is not permissible, it is more rational to speak of the theoretically unobjectionable molecular concentration given by the osmotic pressure or the methods of Raoult. The establishment of the qualitative agreement between the substances which conduct electrolytically and those which, according to the methods of determining normal concentration, suffer a molecular splitting up was of very great immediate significance and was evidence supporting the idea of Arrhenius, for it was only natural to identify this molecular decomposition with the production of electrolytically conducting ions. The next consideration was the finding of a quantitative measure of proof. This was gained through Arrhenius, who considered that the degree of the conductivity must represent a measure of the ionic decomposition, in that the conductivity is essentially carried on by the ions and must take place the more readily the more ions are present, or the farther the electrically inactive molecules are split up into electricity-transporting particles. Again, the molecular-number methods (on condition that we look upon the ions as well as the undissociated molecules as independent individuals) give a direct measure of the degree of ionic decomposition, so that the full molecular concentration of such a salt solution consists of that of its undissociated molecules increased by that of its ions. van't Hoff had introduced a factor i into his theory of solutions, which indicates the number of times the molecular concentration given by the osmotic methods is greater than that to be expected from the chemical formula.

Indicating by α the fraction of a mole[1] of a salt which is split up into ions, and by $(1-\alpha)$ the undecomposed portion, we can calculate the factor i if we know n the number of ions into which one molecule can break up. We have then, for 1 mole, the part $(1-\alpha)$ left undissociated and $(n \cdot \alpha)$ ionic molecules formed from the rest; the sum total of undissociated and ionic molecules is therefore $(1-\alpha+n\alpha)$ individuals, so that $i=1-\alpha+n\alpha=1+(n-1)\alpha$.

A first proof of the theory is given by the fact that α, the degree of dissociation, can be derived from the measurement of the conductivity. Under the assumption, which, as we shall find later, holds for neutral salts, that at very great dilutions the breaking up of the salt into ions becomes practically complete, the comparison of the conductivities produced by one mole of the salt when dissolved in a definite volume of water with the conductivity it assumes at very great dilution gives the degree of ionic decomposition. While we shall later consider in detail the more exact determination of the degree of dissociation of different substances, let us here anticipate to the extent of saying that Arrhenius, in the year 1888,[2] in testing on an extended scale the relationship between i and α, as derived above, found an excellent substantiation of the theory.

A very important question, the solution of which had occupied chemists in vain for a long time, was this, What is formed in a mixture of salts? For instance, to what

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[1] Mole = gram-molecule.

[2] Zeitschr. physik. Chem., **2**, 491 (1888).

extent, if at all, does a reaction take place to form K_2CO_3 and Na_2SO_4 when one mole of K_2SO_4 and one mole of Na_2CO_3 are brought together in solution? It is surprising to note that it is by no means generally known that the solution of the two salts named is identical with the one obtained by mixing a mole each of K_2CO_3 and Na_2SO_4. The author has repeatedly met chemists who to this day in all seriousness discuss how the metal and acid constituents of such a mixture are mutually combined.

The dissociation theory, however, gives for this an entirely convincing explanation that can readily be tested at the hand of experience. Since, according to this theory, K_2SO_4 and Na_2CO_3 as well as K_2CO_3 and Na_2SO_4 are to a large extent split up into the ions K, Na, SO_4, and CO_3, it is clear that it can make no difference from what solid substances these ions take their origin, for in the solution they have become independent of the constituent originally combined with them. This consideration is of practical significance, for example, in the artificial preparation of mineral-water salts which shall give solutions identical with those of the natural springs.[1] Suppose analysis shows that a certain well-water contains for 1 equivalent of sulphate 2 equivalents of chlorine, $\frac{1}{2}$ equivalent of potassium, and $2\frac{1}{2}$ equivalents of sodium, it is absolutely immaterial and leads to exactly the same solution if we mix $\frac{1}{2}$ equivalent K_2SO_4, $\frac{1}{2}$ equivalent Na_2SO_4, and 2 equivalents NaCl, or 1 equivalent Na_2SO_4, $1\frac{1}{2}$ equivalents NaCl, and $\frac{1}{2}$ equivalent KCl, or in general any quantities of the four salts made up of the four

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[1] Zeitschr. f. Elektrochem., **9**, 185 (1903).

components, provided we meet the condition that the total amount of K, Na, SO_4, and Cl equals that of the analysis. This experimental fact may be summed up in the statement that salts are such substances as are in a high degree subject to a so-called mutual decomposition, which, and this is of importance, takes place with immeasurable velocity.

An exceedingly important fact of chemistry and one in very close relationship with the above is the striking phenomenon that in practically all salts the basic and acid components show exactly the same reactions no matter in what combination these components happen to be. Thus it is a well-known fact that all soluble barium salts give with all soluble sulphates one and the same reaction, that is, form barium sulphate. Similarly copper is precipitated as copper sulphide by hydrogen sulphide from all of its salt solutions quite independent of the acid component with which it is combined; chlorine gives the same precipitate with silver nitrate no matter whether it is contained in KCl, NaCl, $CuCl_2$, etc., etc. On the other hand, in the case of organic compounds, the same radical at times shows greatly varying reactions, depending on the nature of the other elements combined with it. Now it seems highly improbable and directly contradictory to the character of chemical compounds that different compounds should give an identical reaction with the same substance; yet in the case of salts, as we saw above, we cannot avoid this very conclusion. But here again the dissociation theory offers the solution of the dilemma, for, according to its concept, the same radical in the different salts, in consequence of electrolytic dissociation, appears as a free and, in all cases, equal ion and therefore gives the same reaction. The entire structure of analytical chemistry is built up on this fact, and the especial feature of the system of inorganic analysis is its relative convenience and simplicity, which is conditioned essentially on the identity of a substance being maintained in spite of its manifold combinations. On the contrary, an organic system of analysis must be, to all intents and purposes, counted with the impossibilities on account of the infinite diversity of the reactions.

A further peculiarity of a salt solution is the additive nature of its physical properties, such as color, density, refractivity, conductivity, and so on. By this we understand that these properties can be made up of two quantities, one of which can be assigned to the base alone, the other to the acid alone, so that if we know these separate values for a certain number of radicals, we can calculate the properties of each combination by simply adding the corresponding quantities. As a type of the additive properties of electrolytes we can take that of the chemical reactions just discussed.

Thus Ostwald[1] established the fact that the characteristic absorption spectra of equivalent solutions of permanganates, for instance, are the same, independent of the (colorless) cathion with which the MnO_4 was combined, that is to say, each ion imparts to the solution its own peculiar color. For this reason all dilute solutions containing copper ions are blue, all ferrous salt solutions greenish, all rosaniline salts red, etc. We may further

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[1] Zeitschr. physik. Chem., 9, 579 (1892)

conclude that all ions present in a colorless solution have no color of their own: as $H^{\cdot}$, $K^{\cdot}$, $Na^{\cdot}$, $Li^{\cdot}$, $Ba^{\cdot\cdot}$, $Sr^{\cdot\cdot}$, $Ca^{\cdot\cdot}$, $Mg^{\cdot\cdot}$, $Be^{\cdot\cdot}$, OH', F', Cl', Br', I', SO_4'', NO_3', ClO_3'.

Frequently the color can also give interesting information as to the constitution of inorganic salts. Thus neither potassium ferrocyanide nor potassium ferro-oxalate possesses the green color of the $Fe^{\cdot\cdot}$ ion, but they are yellow and red respectively, and hence must contain the Fe in some other form, that is, as the complex ions $Fe(CN)_6''''$ and $Fe(C_2O_4)_2''$ respectively, as was demonstrated by Hittorf. Likewise the change in color of $Cu^{\cdot\cdot}$ ions by ammonia, or their decolorization by potassium cyanide, discloses the fact that complex ions are formed in which the copper is no longer present as $Cu^{\cdot\cdot}$. All such conclusions have found their remarkable confirmation experimentally.

Buckingham found[1] that fluorescence is often essentially the property of an ion and is wanting in the undissociated substance, as in the case of eosine, β-naphthylamine disulphonic acid (1 : 2 : 5), and quinine. Here the ions retain their entirely independent properties.

Further, Valson found that equivalent solutions of KCl and NaCl show a difference in specific gravity, which remains unchanged when we substitute for Cl any other acid residue, thus indicating that the difference is independent of the nature of the acid. In the same way any two acids give a constant difference independent of the basic constituent. At every hand, then, we have

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[1] Zeitschr. physik. Chem., **14**, 129 (1894).

evidence that the components of electrolytes do not mutually influence each other.

All these phenomena are to be looked upon as necessary consequences of the ionic dissociation, for the properties of the ions must be constant as long as the ions remain the same. If therefore the combination of the ions does not affect their nature, that is, leaves them independent and free, the additive nature of the properties follows as a necessity.

A great number of objections have been raised to the conception that the constituents of " salts " in the broader sense lead a chemical existence independent of one another. Above all, the opinion had always been held that the foremost salt-formers, the alkalis on the one hand and the halogens on the other, were bound one to the other by extraordinary affinity forces, since they react with very great affinity manifestations, such as intense heat liberation and even light. And now would these components be separated again by simple solution in water? In asking this, the fact was entirely overlooked that the dissociation theory does not assume that the electrolytes split up into the atoms or molecules from which they were formed, but that these decomposition products are essentially different from those atoms or molecules, in that they are electrically charged. These charges are of enormous magnitude, since, according to Faraday's law, each ion carries for its formula weight, in grams, 96580 coulombs per equivalent.

It is also claimed that the abnormal osmotic pressures of the electrolytes can be explained by a hydrolytic decomposition—for instance, $NaCl + H_2O = NaOH + HCl$, This assumption, however, leads *ad absurdum*, since, in the first place, the assumed decomposition products, NaOH and HCl, which in their turn cannot undergo further hydrolysis, also show, like the salt, too high an osmotic pressure. And secondly, as has long been known, solutions of acids and bases, which according to the assumption of opponents would have to exist alongside without reacting, on the contrary, do react with one another very energetically. The theory of neutralization here involved will be further discussed later on in the light of electrolytic dissociation.

Another criticism has been the impossibility of applying to ionic decomposition the crucial experimental test of separating the decomposition products of the split-up body, as in the case of the gaseous dissociation of ammonium chloride. In this it was overlooked that the separating of the oppositely charged ions cannot take place to a measurable extent by reason of these very charges, since it would require the setting free of enormous quantities of electricity. For should we wish to isolate from each other only one milligram equivalent of cathion and anion, it would be necessary to have appear, at different points of the system in space in which this separation was to take place, electrostatic charges of 96 coulombs. This means charges of a magnitude sufficient to give to a large flask provided with a condenser covering, such as was employed by Ostwald and Nernst,[1] a potential of about 8000 volts! Nernst,[2] however, showed, in his epoch-making theory

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[1] Zeitschr. physik. Chem., **3**, 120 (1889).

[2] Ibid., **2**, 613 (1888); **4**, 129 (1889).

of the diffusion of electrolytes and the so-called diffusion chains, how these local separations of cathions and anions, even though immeasurably small, do take place, and can be employed for a quantitative calculation of these changes. Again, together with Ostwald[1] he demonstrated, by using two vessels connected with a siphon filled with an electrolytic acid solution, that it is possible by means of most powerful electrostatic influences to transfer a sufficient excess of ions with positive charges into the one capillary vessel, and negatively charged ions into the other, so that upon conducting away the excess of electricity in the former the discharged hydrogen ions are made visible as bubbles of hydrogen gas. Hence this objection can also be considered as being in every particular effectively refuted.

Likewise another theory, known as the hydrate theory, attempted to meet the phenomena explained by the theory of Arrhenius, and in particular to explain the important phenomenon of the increased osmotic pressure. This theory states that the molecules of the dissolved substances combine with considerable quantities of the water solvent to form hydrates, whereby the molecular concentration of the dissolved substance, i.e., the ratio of the number of dissolved molecules to that of the free uncombined solvent molecules, may appear greatly increased in that the molecules of solvent consumed for hydration no longer act as solvent. There is nothing to be said against the fundamental conception of this theory of a chemical union between the two components of a

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[1] Zeitschr. physik. Chem., 3, 120 (1889).

solution; on the contrary, the results of recent and varied physico-chemical research make it appear more and more probable. In spite of this the hydrate theory is incapable of competing from a quantitative standpoint with the dissociation theory. Since the abnormally high osmotic pressures also appear in extremely dilute solutions, in fact are most evident there, the hydrate theory would have to assume, in case of a $\frac{1}{1000}$ normal solution which gives double the normal freezing-point depression, that, of the approximately 55 moles of water contained in one liter, about one half, or 27 moles of water at least, are bound to $\frac{1}{1000}$ mole of the dissolved substance, giving as a formula for this hydrate 1 mole salt + 27000 H_2O. Further, it is evident that, in spite of the varying concentration of the solute, the number of bound water molecules would always have to remain approximately constant, provided the abnormality factor i of the osmotic pressure, as is often actually the case, scarcely varies with the concentration. This conclusion is altogether contrary to the law of mass action, according to which the hydrated portion of the salt must be proportional to the product of the anhydrous portion and the active mass of the water, expressed by the equation:

$$\text{Hydrate} = k \cdot (\text{Anhydride}) \cdot (\text{Water}).$$

Now on account of thermodynamical reasons (Nernst) the active mass of water is proportional to its vapor pressure, and this, according to Raoult's measurements, is only about 2% smaller for a normal solution than for pure water, i.e., for dilute solutions it may be considered practically identical with that of water, so that the active mass of the water in the above equation is constant; which means that the quantity of hydrate in such solutions is proportional to the quantity of anhydride. It follows that the quantity of water bound as hydrate would have to become less and less with increased dilution of the solute, and so the abnormalities of the osmotic pressure noted at greater concentrations would also continually decrease, which is directly contrary to the observed facts. But leaving all of this out of the question, the dissociation theory is capable of giving in an extremely convincing manner orientation as to the magnitude of the abnormality factor *i* according to the number of ions into which an electrolytic molecule splits up, in that binary salts of the type of KCl can give rise to twice the normal value of the osmotic pressure, ternary salts such as K_2SO_4 or $MgCl_2$ to three times, and so on. Thus, for instance, we can read directly from the formula $K_4Fe(CN)_6$ that in consequence of the decomposition into five ions, 4K and the anion of the tetrabasic hydroferrocyanic acid, the maximum molecular osmotic pressure (at greatest dilution) must be five times the normal; for sodium mellitate, which can split up into seven ions, Taylor[1] attained nearly the maximum value (see table, p. 25). On the other hand, from the value of the factor *i*, the hydrate theory would have to set up an hypothesis as to the degree of hydration for each particular salt concerned, but this hypothesis would be encumbered by the previously mentioned defect. So we can hardly be in doubt as to which theory to prefer, especially when we consider that

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[1] Ostwald's Zeitschr., **27**, 361 (1898).

the hydrate formulæ, which it would be necessary to employ in order to explain the osmotic pressures, do not in the remotest agree with the known water of crystallization formulæ, making them seem altogether arbitrary. Even if we can herewith consider this theory as disposed of, so far as explaining the fundamental facts of dissociation is concerned, we shall nevertheless meet the same again later on (p. 127), where for certain anomalies of electrolytes it offers a possible explanation.

The most prominent problem which the dissociation theory had to solve—its fundamental concept once accepted—was the determination of the degree of dissociation of the different electrolytes. It has been mentioned that this may be done by means of the abnormality of the osmotic pressure, by introducing into the calculation the increase in the number of molecules produced by the ions formed in extremely dilute solutions, where we may consider the ionization as complete and the abnormality factor i must reach its maximum limiting value. This value at the same time indicates the number of ions that are formed from the salt molecule.

Another way to get at the degree of dissociation Arrhenius found in the study of electric conductivity. The specific conductivity κ of an electrolyte is the current strength which flows when the same is placed between two electrodes of 1 square centimeter area, 1 centimeter apart, with a potential difference of 1 volt.

For one and the same electrolyte this specific conductivity is naturally very much dependent on the concentration, since as it varies, the amount of the electrolyte, contained in the 1 centimeter cubed between the electrodes, must vary. The study of the specific conductivity can therefore give directly no means for finding out in what way the molecule of the substance changes its capacity for conducting electricity with varying dilution. Such a means is gained, however, from the specific conductivity, if we reduce the same by calculation to one and the same concentration—for instance, to one equivalent in a cubic centimeter; or if we imagine (Ostwald) the use of electrodes, which remain at a fixed distance apart of 1 centimeter, but which with increasing dilution of the electrolyte always increase in area, so that the volume of liquid included between the electrodes always contains just one equivalent of the electrolyte. The conductivity of one equivalent in its varying dilutions, thus observed, is evidently a magnitude capable of giving information as to the change of the molecular condition, in so far as this influences the conductivity. Indicating the equivalent conductivity by Λ, and the concentration, in equivalents per c.c., by η,[1] then $\Lambda = \frac{\kappa}{\eta}$.

Now Kohlrausch had found that the equivalent conductivity Λ increased with increased dilution for all electrolytes and in many cases approached a limit value Λ_0 for very great dilution. This best attainable conductivity Λ_0 the theory of Arrhenius conceives as belonging to that molecular condition which consists essentially of ions, so that it can devote itself entirely to the transportation of current, while at higher concentrations the

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[1] Concentration in normals c = equivalent/liter stands to this in the ratio $\frac{c}{\eta} = 1000$.

values for Λ ($< \Lambda_0$) are characteristic of the extent to which the molecule is ionized.

If this conception is correct, there must exist a very simple law for the Λ_0 values of different electrolytes when we consider the manner in which these are dependent on the nature of the ions. Suppose we indicate by u the velocity given to any cathion by the potential fall of 1 volt per centimeter, by v the corresponding value for an anion, and recall the fact that, according to Faraday's law, the charge of F coulombs carried by each equivalent of any ion is always equal, then in one second there will be moved between the electrodes mentioned above $u \cdot F$ coulombs by the cathions in the positive direction, and simultaneously $v \cdot (-F)$ coulombs by the anions in the negative direction, that is, the total current flowing will be

$$\Lambda_0 = u \cdot F - v \cdot (-F) = u \cdot F + v \cdot F = (u+v) \cdot F \ \frac{\text{coul.}}{\text{sec.}}$$

or ampères. Since u and v depend entirely on the nature of the ions, it follows that the Λ_0 values of different electrolytes must be purely additive, i.e., composed of factors characteristic of the two ions, so that, for instance, the differences for K and Na salts should be exactly the same whether derived from the chlorides, nitrates, etc., for

$$\begin{aligned}(u_{\mathrm{K}} + v_{\mathrm{Cl}})F - (u_{\mathrm{Na}} + v_{\mathrm{Cl}})F &= (u_{\mathrm{K}} + v_{\mathrm{NO_3}})F - (u_{\mathrm{Na}} + v_{\mathrm{NO_3}})F \\ &= (u_{\mathrm{K}} - u_{\mathrm{Na}})F.\end{aligned}$$

This relationship was in fact discovered by F. Kohlrausch in 1876, and is called the law of the independent migration of the ions. This law, which, as the formula shows, does not directly give individual specific ionic velocities but only the differences of two such, may be illustrated by the following small table, which includes the figures of those K and Na salts whose acid radicals are given in the first column:

$\Lambda = \frac{\kappa}{\eta}$ FOR 1000 $\eta = c = 0.0001$ EQUIV./LITER.

(Kohlrausch, 1900 and 1885)

	K	Na	$(u_K - u_{Na})F$
Cl	129.1	108.1	21.0
NO_3	125.5	104.6	20.9
IO_3	97.6	76.7	20.9
$(SO_4)\frac{1}{2}$	133.5	110.5	23.0
$F\,(v_{Cl} - v_{IO_3})$	31.5	31.4	
$F\,(v_{SO_4} - v_{IO_3})$	35.9	33.8	
$F\,(v_{NO_3} - v_{IO_3})$	27.6	27.9	

For a large class of electrolytes, namely, almost all salts as well as the strong acids and bases, the values of Λ_0 may be obtained by direct measurement, since with increasing dilution the values of Λ show clearly a convergence toward a limiting value, as can be seen from the following series for KCl (18°) (Kohlrausch, 1885).

POTASSIUM CHLORIDE (18°).

$c =$	1	0.1	0.01	0.001	0.0001	0
$\Lambda =$	98.2	111.9	122.5	127.6	129.5	131.2
$\Delta\Lambda =$		13.7	10.6	5.1	1.9	

A similar series for acetic acid

$\Lambda =$	1.32	4.6	14.3	41	107
$\Delta\Lambda =$		3.3	9.7	26.7	66

gives no evidence of such a convergence in dilutions experimentally accessible, as is typical of all weak electrolytes. In such cases, however, Λ_0 can be obtained indirectly by means of Kohlrausch's law, by making use of, for instance in the case of acetic acid (H acet.), the experimentally accessible Λ_0 values for K acet., KCl, and HCl, and calculating as follows:

$$\Lambda_{0\,(\text{K acet.})}+\Lambda_{0\,(\text{HCl})}-\Lambda_{0\,(\text{KCl})}=\Lambda_{0\,(\text{H acet.})};$$

for

$$F[(u_{\text{K}}+v_{\text{acet.}})+(u_{\text{H}}+v_{\text{Cl}})-(u_{\text{K}}+v_{\text{Cl}})]=F(u_{\text{H}}+v_{\text{acet.}});$$

in short,

$$\text{K}+\text{acet.}+\text{H}+\text{Cl}-\text{K}-\text{Cl}=\text{H}+\text{acet.}$$

Or in words, we begin with Λ_0 of a salt of the weak acid and add to it the difference between the Λ_0 values of a strong acid and its salt, which has the same cathion as the salt of the weak acid.

A prime criterion of the correctness of the course of reasoning lies in the conclusion that the equivalent conductivities Λ_0 for "infinite dilution," calculated with the aid of Kohlrausch's law, must under all circumstances be greater than the experimentally determined equivalent conductivities Λ of weak electrolytes; for if Λ differs from Λ_0, this can only be in the direction corresponding to an incomplete ionization, because Λ_0 is necessarily associated with complete ionization.

For concentrations in which all the molecules do not split up into ions, the degree of ionization being less than 1, the equivalent conductivity will also have to be smaller than Λ_0, for if there are present per equivalent only α ions, α indicating the degree of ionization, then for each equivalent only (analogous to our findings for Λ_0, p. 21),

$$\Lambda = \alpha(u+v)F\,\frac{\text{coul.}}{\text{sec.}}$$

can be carried. Substituting from the above equation the value for Λ_0,

$$\alpha = \frac{\Lambda}{\Lambda_0},$$

the sought-for new definition of the degree of ionization (dissociation), determinable by electrical means. The above consideration, that the measured Λ values must always be less than the Λ_0 values calculated by means of Kohlrausch's law, is confirmed without exception by experience. We are therefore justified in building further on this foundation and in looking upon the ratio of the equivalent conductivity Λ, of a particular concentration, to Λ_0 (exterpolated or calculated as above) at infinite dilution, as the direct measure of the degree of decomposition into ions, and in formulating, as did Arrhenius, the equation for the degree of ionization

$$\alpha = \frac{\Lambda}{\Lambda_0}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The dissociation theory withstood the first crucial test in that α, the degree of ionization calculated from the equivalent conductivities, showed such surprising agreement with that given by the deviations of the osmotic pressure according to the formula (p. 9)

$$i = n \cdot \alpha + (1 - \alpha) = 1 + (n - 1) \cdot \alpha$$

or

$$\alpha = \frac{i - 1}{n - 1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

The following figures, taken from freezing-point determinations of Arrhenius and others, show this agreement:

COMPARISON OF THE OSMOTICALLY AND ELECTRICALLY MEASURED ABNORMALITY FACTORS.

(van't Hoff and Reicher, 1889.)

Salt.	Concentration.	i (osmot.).	i (freez.).	i (electr.).
KCl	0.14	1.81	—	1.86
NH_4Cl	0.148	1.82	—	1.89
$Ca(NO_3)_2$	0.18	2.48	2.47	2.46
$K_4Fe(CN)_6$	0.356	3.09	—	3.07
$MgSO_4$	0.38	1.25	1.20	1.35
$LiCl$	0.13	1.92	1.94	1.84
$SrCl_2$	0.18	2.69	2.52	2.51
$MgCl_2$	0.19	2.79	2.68	2.48
$CaCl_2$	0.184	2.78	2.67	2.42
$CuCl_2$	0.188	—	2.56	2.41
$Na_6C_{12}O_{12}$	0.0018	—	5.92	—

With this there were at hand two methods, differing in principle yet giving like results for getting at the dissociation relations of the long list of electrolytes. The results of these investigations, carried out by Arrhenius and the Leipzig School under the leadership of Ostwald may be summarized as follows:

1. *Strong electrolytes* are such salts, acids, and bases which even in considerable concentrations ionize very much more than half and contain as cathions any alkali metal (Cs, Rb, K, Na, Li), or as anions one of the acid residues NO_3, ClO_3, ClO_4; furthermore, combinations of the following cathions and anions in so far as they are soluble:

$$\left.\begin{array}{l} \mathrm{NH_4^{\cdot}, Ba^{\cdot\cdot}, Sr^{\cdot\cdot}, Ca^{\cdot\cdot}, Mg^{\cdot\cdot},} \\ \quad \mathrm{Mn^{\cdot\cdot}, Zn^{\cdot\cdot}, Fe^{\cdot\cdot}, Co^{\cdot\cdot}, Ni^{\cdot\cdot},} \\ \quad \mathrm{Pb^{\cdot\cdot}, H^{\cdot}, Hg_2^{\cdot\cdot}, Ag^{\cdot}} \end{array}\right\} \text{ with } \left\{\begin{array}{l} \mathrm{NO_3'} \\ \mathrm{F', Cl', Br', I'} \\ \mathrm{SO_4'', S_2O_6''} \\ \mathrm{CrO_4'', Cr_2O_7''} \\ \mathrm{CCl_3COO'} \end{array}\right.$$

Accordingly we have belonging here all alkali salts, nitrates, chlorates, perchlorates, as well as the strong acids HCl, HBr, HI, HNO_3, H_2SO_4, H_2F_2 (the last two, it is true, are markedly less ionized than the previous ones) also all sulphonic acids, and practically speaking all soluble neutral salts, the ammonium and substituted ammonium salts inclusive; of the bases, that is, the hydroxyl compounds, we have only the tetra-substituted amine bases, while ammonia and the substituted amines up to the tri-substituted belong to the next class.

2. *Weak electrolytes* include first of all the three large classes of the organic carboxylic acids, phenols, and primary to tertiary substituted amine bases; also ammonia, and the following compounds which form an exception to the other neutral salts:

$$\mathrm{CdCl_2,\ CdBr_2,\ CdI_2,\ HgCl_2,\ Hg(CN)_2,\ Fe(CNS)_3,\ FeF_3,\ Fe(acet.)_3,}$$

and the weak inorganic acids:

H_2S, HCN, H_3BO_3, H_3PO_2, H_3PO_3, H_3PO_4, H_2CO_3, H_2SO_3, H_2SeO_3, HNO_2, $HClO$, HIO_3, HIO_4.

A large number of inorganic salts not included in the above, such as those of the last-named acids, show the phenomenon of hydrolysis and will receive special mention later (p. 92).

Between these two extreme classes of electrolytes we have, of course, all transitions, for the two classes are only gradually differentiated, since, as has been mentioned and as will later be discussed in detail, the degree of ionization is greatly dependent upon the concentration. A kind of transition class, designated as electrolytes of medium strength, might be set up, consisting on the one hand of the salts of the heavy metals, and on the other of the strongest carboxylic acids, such as tartaric, citric, oxalic, and formic, also many halogen and nitro-substituted carboxylic acids.

For reasons to be mentioned later, a very special interest attaches to the extremely weak electrolytes, which are transitions from electrolytes to chemical compounds incapable of electrolytic dissociation. These will be discussed in a chapter to follow, and figures given which are characteristic of them; here it will be sufficient to say that they include hydrocyanic acid, hydrogen sulphide, boric acid, carbonic acid, phenol, and above all water; also the bases aniline, pyridine, etc. (see table, p. 53).

In addition to the conductivity method for determining the degree of ionization we have another electrical method, based on the Nernst theory of concentration chains. According to this the electromotive force of such chains, in which the same electrode metal dips into a concentrated and a dilute solution, is proportional to the logarithm of the concentration ratio of the metal ions in the two solutions. Since the mathematical form of this function requires extremely accurate measurements in order to determine small differences of ionic concentrations, this method has not been applied for this purpose until recently by Jahn (see p. 120), though it has been employed with great success in recognizing the extremely small ionic concentrations of very difficultly soluble electrolytes.

MOBILITY OF THE IONS.

THE figures enumerated on p. 22 show that the conductivity differences between alkali salts of the same acid are independent of the nature of the acid, that is, they are evidently dependent only on the difference of the cathion. In a similar way we get equal differences for a change of the acid constituents, no matter from what alkali salts we take the conductivities. It is necessary to take only one step further in order to determine, in the case of any salt, how the conductivity is divided between the anion and cathion, and to calculate from the above table the part each ion takes in the conductivity. This was done in the classical researches of Hittorf on the concentration changes in the vicinity of the electrode during the electrolysis of salts, and permits drawing a conclusion as to the apportionment for the two ions in transporting the current.

Suppose we conduct a definite amount of electricity, say 96580 coulombs, the quantity carried by one ion equivalent, through an electrolytic cell, then

1. At each of the electrodes, according to Faraday's law, one equivalent of the respective ions is separated. This we shall look upon either as remaining in solution, as is actually the case in the electrolysis of salts such as K_2SO_4, or, in case it is precipitated, as belonging

to the solution immediately surrounding the particular electrode.

2. It is necessary for us to gain some insight into the mechanism of the current transport in so far as it takes place within the solution, i.e., between the electrodes. Of our 96580 coulombs one part is carried by the positive ions and the other part by the negative ions in their wandering to the electrodes, so that a certain quantity of anions move away from the cathode and a certain quantity of cathions away from the anode and will be wanting at their former places. It can readily be seen that this reduction of the concentration at the electrodes must give a measure of the nature of the ratio of the rates of migration of the ions wandering in opposite directions. For example, in the case of equal mobility, that is, like rates of wandering for cathions and anions, the reduction in concentration of these ions at the electrodes from which they migrate must be exactly equal; with unequal mobility the reduction in concentration must be greater at the electrode from which the ion of greater velocity moves. The ratio of these ionic concentration reductions at both electrodes, as measured by Hittorf, represents, in other words, the ratio $\frac{u}{v}$, in which the transport of current distributes itself between both ions. Calculating from the shifting of the concentration of one of the ions the coulombs carried by the ionic matter transported away, and comparing this with the total coulombs (measured, for example, by means of a voltameter) which flowed through the electrolyte during the time in which the measured concentration change took place, we obtain the so-called

transference number, which represents the fraction $\frac{u}{u+v}\left(\text{or }\frac{v}{u+v}\right)$ of the total number of coulombs transported by this ion. The transference number 1 for the cathion of a given salt would mean that the entire transportation of current was carried on by the cathion, while the anion had no part in it whatsoever. This, however, could take place only in the extreme and non-existent case of the mobility of the anion being infinitely smaller than that of the cathion, for, as both ions are moved by the same electrical driving force, their velocity must be proportional to their mobility. The transference number 0.5, which, on the other hand, is not infrequently found at least approximately, would indicate that the electric current is carried half by the cathion and half by the anion, or that both ions possess the same mobility. The most exact measurements of transference numbers made are those with potassium chloride, which give for the ion K the value 0.497.

Now we know from Kohlrausch's measurements that for KCl (see p. 22)

$$\Lambda_0=(u+v)96580=130.1,$$

and with the aid of the second equation,

$$\frac{u}{u+v}=0.497,$$

we are in position to calculate separately the values for u and v. In order to avoid too small values, it is better to employ, instead of the "absolute mobilities" u and v, the "electrolytic mobilities" l_K and l_A for cathion and anion, which are 96580 times greater. We may then write

$$\Lambda_0 = l_K + l_A = 96580(u+v) = 130.1$$

and

$$\frac{u}{u+v} = \frac{l_K}{l_K + l_A} = 0.497,$$

from which we get for the potassium ion

$$l_K = 64.67,$$

and for the chlorine ion

$$l_A = 65.44.$$

These values at once enable us to get at the mobility of other ions by using the equivalent conductivities of other potassium salts and other chlorides, and subtracting from these the mobility values of K$^{\cdot}$ and Cl$'$ respectively. What is more, we are also in position to calculate the maximum equivalent conductivity for such electrolytes whose measurements do not show any such maximum conductivity.

For example, in order to obtain the electrolytic mobility of any anion, say F$'$, it is only necessary to know Λ_0 for KF, which Kohlrausch (1902) found to be

$$\Lambda_0 = l_K + l_A = 111.35$$

Subtracting from this $\quad l_K = 64.67$

we have left $\quad l_{\text{Fluorine}} = 46.68$

The mean values of the most accurately known electrolytic mobilities[1] at 18° are given (according to Kohlrausch[2]) along with their temperature coefficients α in the following tables:

	H (3)	Cs	Rb	Tl	K	NH_4	Ag
$l_K=$	318.0	68.2	67.6	66.0	64.67	64.4	54.02
100α	1.53	2.12	2.14	2.15	2.17	2.22	2.29

	Na	Li	½Ba	½Sr	½Ca	½Mg
$l_K=$	43.55	33.44	57.3	54.0	53.0	49.0
100α	2.44	2.65	2.38	—	—	2.56

	OH (3)	Br	I	Cl	ClO_4	NO_3	CNS	ClO_3	MnO_4	IO_4
$l_A=$	174.0	67.63	66.40	65.44	64.7	61.78	56.63	55.03	53.4	47.7
100α	1.80	2.15	2.13	2.16	—	2.05	2.21	2.15	—	—

	HCO_2	F	BrO_3	CH_3CO_2	IO_3
$l_A=$	46.7	46.64	46.2	35.0	33.87
100α	—	2.38	—	2.38	2.34

	$C_2H_5CO_2$	$C_3H_7CO_2$	$C_4H_9CO_2$	$C_5H_{11}CO_2$	½SO_4
$l_A=$	31.0	27.6	25.7	24.3	70.0
100α	—	—	2.44	—	2.27

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[1] The l values give the conductivity of 1 mole of the ion in 1 c.c. (not in 1 l!).

[2] Berl. Akad. Ber., **26**, 586 (1902).

[3] For the $H^{\cdot}$ and OH' ions the electric mobilities are known with a much less degree of certainty, since it is impossible to follow up the Λ values of acids and bases to the very great dilutions where the conductivity of the water and its unavoidable impurities play a part not yet determined.

These numbers enable us to calculate by addition Λ_0, the equivalent conductivity at infinite dilution, for all salts formed by combinations of the above ions. They have been amply confirmed by the fact that the transference numbers $\frac{l}{l_K+l}$ calculated from these values agree admirably with those found.

Evidently an exceptional position is held by the ions of water, $H^{\cdot}$ and OH', of which the former is about five times and the latter about three times as mobile as the most mobile of its kind. In consequence of this, among the strong electrolytes the acids and bases (comparing equivalent solutions) are much better conductors than all neutral salts.

For electrolytes with ions of greater valence the relations are more complex, in that the values for Λ do not converge sufficiently at convenient dilutions to give accurate values for Λ_0. However, as has recently been shown by Steele and Denison,[1] in the case of such electrolytes the transference numbers, which vary considerably with the concentration, converge toward values showing a good agreement with the Λ_0 values measured by Kohlrausch.

A regularity in the magnitude of the mobilities may be formulated for organic anions in the statement that the mobility decreases at first rapidly and then more slowly with increase in molecular weight. For the inorganic ions, however, this rule does not hold; it seems, on the contrary, that some other influence, as in the group of the alkali and alkali-earth cathions, plays a part here which

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[1] Journ. Chem. Soc. Trans., **81**, 466 (1902).

probably must be sought for in hydration. It is notable that the halogens as ions, in spite of their varying weight and varying mobility in the form of diffusing neutral molecules, possess almost equal mobility. Euler[1] offers as an explanation for this the assumption of marked hydration, which might equalize the difference in weight. Possibly this hypothesis finds support in the observation that in the series of the alkalis, as well as the earths, the element of strongest electro-affinity (compare p. 159), which may be assumed to have the least tendency to hydration, forms the most mobile ion.

A very comprehensive research and summarization of the mobilities of all known inorganic as well as organic ions and the accompanying regularities, we owe to Bredig.[2] He found among other things that the mobility of the element ions is a periodic function of the atomic weight; that for compound ions it essentially holds that increasing the number of atoms decreases the mobility; and that constitutional influences also make themselves felt.

The slowest known anion is that of the lactone of *p*-toluido-*β*-*i*-butyric acid with l_A $(25°) = 23.3$; the slowest cathion, that of aconitine with l_K $(25°) = 17.8$.

The influence of temperature on ionic mobility has recently been more carefully investigated by Kohlrausch,[3] with the result that to each ion an independent change of mobility can be attributed, as was to be expected in accordance with the additive law (p. 12).

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[1] Wied. Ann., **64**, 273 (1897).

[2] Zeitschr. physik. Chem., **13**, 191 (1894).

[3] Berl. Akad. Ber., **26**, 574 (1902).

These individual temperature coefficients are to be found under α in the above table of mobilities. They mean that the values for l are to be multiplied by $(1 + [t-18]\alpha)$ in order to obtain the values for l at t°. It is of importance to note that these percentage temperature coefficients are smaller the larger the mobilities; the absolute coefficients, however, show the same order in the series as the mobilities. so that the ions converge in the direction of lower temperatures toward the same mobility.

From the changes in mobility of the ions we can now also calculate the influence of temperature on the conductivity for other concentrations than that of extreme dilution, in so far as we are allowed to assume that essentially the ionic mobility changes and not the degree of dissociation, i.e., the number of ions that take part in the conductivity at the different temperatures. According to the results of investigations on this point, to be discussed later (see pp. 135, 140), this assumption holds approximately for strong electrolytes and also for many weak ones whose heat of dissociation is small, so that their temperature coefficients can be calculated from the above values. The percentage coefficients for salts lie between 0.021 and 0.029, for acids in the neighborhood of 0.015, for bases near 0.020.

EQUILIBRIA AMONG IONS.

Starting with the conception that dissociation is to be considered as a chemical reaction of such a nature that out of the ions, the dissociation products, the undissociated substance is formed by chemical interaction, then we must look upon the law of mass action as the factor determining the equilibrium between the reacting ions and their resulting undissociated product. During the early days of the dissociation theory it was customary to view this reaction from the side of the undissociated molecule, the ions being formed by its decomposition. In principle, however, both mean the same, and it is clearer possibly from a chemical standpoint to consider the reaction in the reverse sense as we did above, and to look upon the ions as primary and their product, the undissociated compound, as secondary. Indeed, the latter seems more natural—though fundamentally a matter of taste—in so far as the presence of ions is an extremely wide-spread property of chemical substances. Yet not incorrectly perhaps and from purely historical reasons, one considers the inappreciably ionized compounds belonging essentially to organic chemistry as the normal, owing to their great number and the intensity of the study that has been concentrated upon them.

If, however, we take as the normal the relations as they prevail with the compounds which show the greatest variation in the elements combining to form them, that is, without favoring carbon compounds, then ionic dissociation is of such a general nature that we may place ionic interaction or the formation of undissociated compounds in the foreground.

It is true, science proceeded in just the opposite way: the undissociated compounds were considered the normal ones. The formation of ions was formerly unknown and in a certain sense did not take place until the introduction of the theory, because not until then was it a conscious change. But however that may be, the compounds which are very little ionized represent such whose components are held together by exceptionally strong forces of atomic affinity, while the chemical relationship between the components (ions) of the strongly dissociated substances must be considerably less, in order to make possible for them the independent existence.

A thing difficult of conception also lies in the assumption that a reaction is to arise out of an undissociated substance without that substance interacting with other substances; this in fact becomes inconceivable when one assumes the hypothesis, to be discussed later, that all reactions are dependent on the presence of ions, and that their velocity is directly determined by the concentration of the ions necessary for the reaction. Suppose we picture to ourselves a molecule, capable of ionization, in an entirely undissociated state, then a dissociation into ions cannot take place at all, because according to our assumption the undissociated substance was to have no ions. We can readily conceive of the reverse, for when ions are once present, undissociated substances form by their reaction. For this it would be necessary, of course, to assume that no chemical element could exist in the state of an absolutely electricity-free non-ion. However, we shall not here continue these speculations, for they are of no consequence as far as the numerical laws of dissociation are concerned.

For the dissociation of substances such as ammonium chloride, phosphorus pentachloride, and others, which in the gaseous state split up into simpler components, the law of mass action has shown that the product of the concentrations (partial pressures) of the reacting constituents is proportional to the product of the concentration of the substances produced by the reaction. Now precisely the same mathematical relation must also hold for dissociation into ions and the reaction of ions to form undissociated molecules. And it was the great service of Ostwald to have recognized this law and confirmed it for a much wider range than that for which it had been established for the then known gas dissociations. This law regulates the concentration of the ions and undissociated molecules with varying total concentration of the solution. In other words, it places us in position to derive from the degree of dissociation of an electrolyte at one concentration the degree of dissociation at any other desired concentration. If, for instance, for the concentration c, the degree of dissociation, or the part per mole split up, is α, then the total concentration of each ion is $\alpha \cdot c$, and the concentration of the undissociated remainder is $(1-\alpha) \cdot c$. Introducing this value into the law of mass action, we get for the product of the concentrations of the reacting substances (the ions), for the simplest case of a binary electrolyte in which two ions unite to form an undissociated molecule,

$$(\alpha \cdot c) \cdot (\alpha \cdot c).$$

This product is to be proportional to the concentration of the undissociated substance, namely $(1-\alpha)\cdot c$. Hence for a binary electrolyte the expression for the law of mass action is

$$\alpha^2 \cdot c^2 = k \cdot (1-\alpha) \cdot c,$$

if k indicates the proportionality constant which is characteristic (at a definite temperature) for this reaction. Now having found the degree of dissociation α for the concentration c, by means of one of the above methods, i.e., conductivity or osmotic pressure measurements (freezing-point, boiling-point, etc.), we can calculate by the given formula the "dissociation constant" k and are then in position to determine the degree of dissociation for other concentrations (c values) with the aid of the transformed equation

$$\frac{\alpha^2}{1-\alpha} = \frac{k}{c} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

or

$$\alpha = \frac{-k + \sqrt{k^2 + 4kc}}{2c},$$

or neglecting k^2 and k as compared with $\sqrt{k}$, which is permissible for small values of k, we have approximately

$$\alpha=\sqrt{\frac{k}{c}}. \qquad (3a)$$

The testing of this important relation, the so-called dilution law of electrolytes discovered by Ostwald,[1] was first undertaken by van't Hoff and Reicher[2] on a series of acids and resulted in an excellent confirmation. The authors close their discussion with these words: "Not a single case of ordinary dissociation has been tested within such wide limits." Some of the figures are given in the following tables:

ACETIC ACID: $k=1.78\times10^{-5}$ (14°).

$v=\frac{1}{c}=$	0.994	2.02	15.9	18.1	1500	3010	7480	15000
100α from conductivity Λ . .	0.40	0.61	1.66	1.78	14.7	20.5	30.1	40.8
100α from k calculated. . . .	0.42	0.60	1.67	1.78	15.0	20.2	30.5	40.1

MONOCHLORACETIC ACID: $k=1.58\times10^{-3}$ (14°).

$v=\frac{1}{c}=$	20	205	408	2060	4080	10100	20700
100α from Λ found	16.6	42.3	54.7	80.6	88.1	94.8	96.3
100α from k calculated. . . .	16.3	43.0	54.3	80.1	88.0	94.4	97.1

Ostwald about the same time, in amassing his extended observations on the organic carboxylic acids, used a

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[1] Zeitschr. physik. Chem., **2**, 36 (1888).

[2] Ibid., **2**, 777 (1888).

method, which since then has remained the customary one, so that usually the law of mass action is tested not by comparing observed and calculated degrees of dissociation, but by testing whether the expression for the characteristic dissociation constant,

$$\frac{\alpha^2}{1-\alpha}\cdot c=k,$$

gives values independent of the dilution. Since in the majority of cases α, the degree of dissociation, is obtained with the aid of conductivity, i.e., from $\frac{\Lambda}{\Lambda_0}$, it is practical to insert this expression directly into the formula, giving it the form

$$\frac{\left(\frac{\Lambda}{\Lambda_0}\right)^2}{1-\frac{\Lambda}{\Lambda_0}}\cdot c=k,$$

or

$$\frac{\Lambda^2\cdot c}{\Lambda_0(\Lambda_0-\Lambda)}=k, \quad . \; . \; . \; . \; . \quad (4)$$

or finally, introducing the specific conductivity $\kappa=\Lambda\cdot c$:

$$\frac{\kappa^2}{\Lambda_0(\Lambda_0\cdot c-\kappa)}=k.$$

For the relatively frequent case of very weakly dissociated electrolytes, in which the degree of dissociation α is only a small fraction (say 1% or less) of the total concentration, the general formula can be conveniently simplified by writing $1 - \alpha = 1$, by reason of the smallness of α, when it becomes

$$\alpha^2 \cdot c = k \quad \text{or} \quad \frac{\Lambda^2 \cdot c}{\Lambda_0^2} = k. \quad . \quad . \quad . \quad . \quad (5)$$

From the latter equation a very simple law for the variation of conductivity may be derived. Since Λ_0 for one and the same electrolyte is constant, being independent of the concentration, we have simply $\Lambda^2 = \frac{\text{Const.}}{c}$ or Λ inversely proportional to $\sqrt{c}$. Finally, the equivalent conductivity being $\Lambda = \frac{\kappa}{c}$, wherein κ is the specific conductivity, we can, by substituting in the last equation, so formulate the relation between the specific conductivity κ and the concentration of the electrolyte that

$$\kappa^2 = \text{Const.} \cdot c \quad \text{or} \quad \kappa = \text{Const.} \cdot \sqrt{c},$$

which means, in other words, that the conductivity of a solution with varying concentration is proportional to the root of this concentration. For example, diluting a solution four times reduces the conductivity only one half, or diluting ten times reduces it only 3.16 times. This is shown by the following small table for acetic acid, taken from measurements of Kohlrausch:

Acetic Acid (18°).

$c = 1.0$	0.5	0.1	0.05	0.01	0.005	0.001	0.0005	0.0001
$\kappa = 1.32$ $\Lambda = 1.32$	1.005 2.01	0.46 4.60	0.324 6.48	0.143 14.3	0.100 20.0	0.041 41.0	0.0285 57.0	0.0107 107.0

The following tabulated figures are taken from the previously mentioned measurements of Ostwald, given for the greater part in Zeitschr. physik. Chem., **3**, 170, 241, 369 (1889), as well as from those of Bredig.[1] Here $\frac{100\Lambda}{\Lambda_0}$ expresses the degree of dissociation in percentages.

$v=\frac{1}{c}$	Acetic Acid: $\Lambda_0=388$			Monochloracetic Acid: $\Lambda_0=386$			Dichloracetic Acid: $\Lambda_0=385$		
	Λ	$\frac{100\Lambda}{\Lambda_0}$	10^5k	Λ	$\frac{100\Lambda}{\Lambda_0}$	10^5k	Λ	$\frac{100\Lambda}{\Lambda_0}$	10^5k
16	6.5	1.67	1.79	56.6	14.6	155	—	—	—
32	9.2	2.38	1.82	77.2	19.9	155	269.8	70.2	5170
64	12.9	3.33	1.79	103.2	26.7	152	309.9	80.5	5200
128	18.1	4.68	1.79	136.1	35.2	150	338.4	88.0	5040
256	25.4	6.56	1.80	174.8	45.2	146	359.2	93.4	5160
512	34.3	9.14	1.80	219.4	56.8	146	375.4	97.6	—
1024	49.0	12.66	1.77	265.7	68.7	147	383.8	99.7	—

$v=\frac{1}{c}$	Ammonia: $\Lambda_0=253$			Methylamine: $\Lambda_0=240$			Piperidine: $\Lambda_0=216$		
	Λ	$\frac{100\Lambda}{\Lambda_0}$	10^5k	Λ	$\frac{100\Lambda}{\Lambda_0}$	10^5k	Λ	$\frac{100\Lambda}{\Lambda_0}$	10^5k
8	3.4	1.35	2.3	15.1	6.3	52	23.0	10.6	157
16	4.8	1.88	2.3	21.0	8.7	52	32.3	14.9	163
32	6.7	2.65	2.3	28.9	12.0	51	44.2	20.3	162
64	9.5	3.76	2.3	39.3	16.3	50	59.2	27.2	159
128	13.5	5.33	2.3	53.0	22.0	49	77.8	35.8	156
256	18.2	7.54	2.4	70.0	29.1	47	99.7	45.9	152

That the measurements of the degree of dissociation from determinations of the freezing-points lead to the same results is shown by the following series of observa-

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[1] Zeitschr. physik. Chem., **13**, 289 (1894).

tions: Δ indicates the depression of the freezing-point, 1.85 the depression in water of each mole of undissociated substance.

TARTARIC ACID.

(Abegg, 1896.)

c	$\frac{\Delta}{c}$	$i = \frac{\frac{\Delta}{1.85}}{c}$	$\alpha = i - 1$	$\alpha = \frac{\Delta}{\Delta_0}$
0.00516	2.45°	1.32	0.32	0.35
0.0103	2.29	1.24	0.24	0.26
0.0154	2.24	1.21	0.21	0.22
0.0204	2.23	1.205	0.205	0.20
0.0254	2.18	1.18	0.18	0.18
0.0303	2.15	1.16	0.16	0.16
0.0353	2.08	1.12	0.12	0.15

The extent of the observations confirming the dilution law—in other words, showing the validity of the law of mass action—may be seen by a glance at the comprehensive tables to be found very systematically arranged in the excellent book of Kohlrausch and Holborn,[1] "Leitvermögen der Elektrolyte," pp. 176 to 194.

Of this material the greater part relates to weak organic acids and is taken from the researches of Ostwald and his pupils,[2] among whom Walden is to be especially mentioned. A smaller part consists of the measurements of Bredig [3] on bases, among which especially the weak amine bases confirm the dilution law.

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[1] Teubner, Leipzig, 1898.

[2] The complete literature is to be found in the mentioned work of Kohlrausch and Holborn.

[3] Zeitschr. physik. Chem., **13**, 289 (1894).

THE DISSOCIATION CONSTANT.

THIS great mass of material naturally offered not only a confirmation of the mathematical formulation of the relation between the degree of dissociation and the concentration of the electrolyte, but also enabled us to gain important chemical knowledge from the measure of the dissociation constant. This constant is indeed an expression of the chemical nature of substances, in that it gives a numerical measure of the tendency to split into ions. If we do not apply the above form of the dissociation constant given by Ostwald, but rather its reciprocal value $\frac{1}{k}$, then this would constitute an analogous numerical expression for what we have previously termed the atomic affinity, which exists between ions and tends to produce undissociated molecules out of them.

The physical significance of the constant k can also be expressed, with Ostwald, as indicating one half of that concentration at which the various electrolytes possess exactly the degree of dissociation equal to $\frac{1}{2}$. For example, taking for comparison the constant of acetic acid (0.000018), of monochloracetic acid (0.00155), of dichloracetic acid (0.051), and also let us say of malonic acid (0.00158) and maleic acid (0.012), it means that these acids are dissociated 50% in solutions which for acetic acid have the normal concentration 0.000036, for monochloracetic acid 0.0031, for dichloracetic acid 0.12, for malonic acid 0.00316, and for maleic acid 0.024. The definition for $\sqrt{k}$ taken from the formula (3*a*), p. 41, is possibly clearer, $\sqrt{k}$ being the ionic concentration present in the 1-normal solution of the electrolyte. Since the action of acids is determined by the concentration of the hydrogen ion, that of bases by the hydroxyl ion, it is easy to see the great value of knowing this dissociation constant in comparing chemical nature, and it was to be expected from the very first that this characteristic constant should bear a marked relationship to the chemical constitution of these substances. This has in fact been found to be true, and as it is our desire to trace at least the bolder outlines of this relationship between chemical nature and the dissociation constant, we shall bring together in the following tables the dissociation constants of some interesting acids.

SUBSTITUTION OF CH_3.

Formic acid, $HCOOH$	$k = 127.0 \times 10^{-5}$
Acetic acid, CH_3COOH	1.8×10^{-5}
Propionic acid, C_2H_5COOH	1.3×10^{-5}
Butyric acid, C_3H_7COOH	1.5×10^{-5}
Isobutyric acid	1.45×10^{-5}
Valeric acid, C_4H_9COOH	1.6×10^{-5}
Caproic acid, $C_5H_{11}COOH$	1.45×10^{-5}

While the first substitutions without doubt produce a weakening of the acid, the very first as much as seventy times, the subsequent ones are occasionally accompanied by a slight strengthening.

SUBSTITUTION OF HALOGENS.

Acetic acid	$10^5 \times k =$	1.8
Chloracetic acid		155
Dichloracetic acid		5100
Trichloracetic acid		about 120000
Bromacetic acid		138
Cyanacetic acid		370
Sulpho-cyanacetic acid		260
Lactic acid	$k =$	1.4×10^{-4}
Trichlorlactic acid		46.0×10^{-4}
Propionic acid		1.3×10^{-5}
β-Iodpropionic acid		9.0×10^{-5}
Benzoic acid		6.0×10^{-5}
m-Fluorbenzoic acid		14.0×10^{-5}

Here one sees that all these substitutions bring about a very marked strengthening, and again that with several successive ones—as in general—the first step is the most effective; furthermore, that the proximity of the substituting groups is of great influence, as will later be pointed out more fully.

SUBSTITUTION OF OH.

Acetic acid, CH_3COOH	$10^5 \times k =$	1.8
Glycollic acid, $CH_2OHCOOH$		15.0
Propionic acid, CH_3CH_2COOH		1.3
Lactic acid, $CH_3CH(OH)COOH$		14.0
β-Oxypropionic acid, $CH_2(OH)CH_2COOH$		3.1
Benzoic acid, C_6H_5COOH		6.0
Salicylic acid, $C_6H_4(OH)COOH$ (1 : 2)		102.0
m-Oxybenzoic acid, $C_6H_4(OH)COOH$ (1 : 3)		8.7
p-Oxybenzoic acid, $C_6H_4(OH)COOH$ (1 : 4)		2.9

The nearer to the COOH group the OH is introduced, the more it increases the dissociation of acids; the same is true of NO_2 and COOH:

Substitution of NO_2.

Benzoic acid	$10^5 \times k = 6.0$
o-Nitrobenzoic acid	620.0
m-Nitrobenzoic acid	35.0
p-Nitrobenzoic acid	40.0
Phenol	$k = 1.3 \times 10^{-10}$
o-Nitrophenol	4.2×10^{-8}
2,6-Dinitrophenol	1.7×10^{-4}
Trinitrophenol	1.64×10^{-1} (1)
Salicylic acid	$10^3 \times k = 1.02$
o-Nitrosalicylic acid	115.7
p-Nitrosalicylic acid	9.0

Substitution of COOH.

Acetic acid, CH_3COOH	$10^5 \times k = 1.8$
Malonic acid, $COOHCH_2COOH$	158.0
Propionic acid, C_2H_5COOH	1.3
Succinic acid, $COOHC_2H_4COOH$	6.6
Benzoic acid, C_6H_5COOH	6.0
o-Phthalic acid, $COOHC_6H_4COOH$	121.0
m-Phthalic acid, $COOHC_6H_4COOH$	29.0

Substitution of NH_2

exceptionally weakens the acid character, so that on the one hand the very strong sulpho-acids, whose constants, for reasons to be given later (see p. 121), lie beyond those capable of measurement, are brought by substitution within the scope of those measurable, while on the other hand the acids of the average strength of the above are decidedly weakened. A constant for these is not to be

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[1] Rothmund and Drucker, Zeitschr. physik. Chem., **46**, 827 (1903).

obtained directly by conductivity measurements, on account of their capacity for amphoteric (acid and basic) dissociation; however, Bredig and Winkelblech[1] showed how both the acid and basic dissociation constants may be obtained (see table, p. 55).

INFLUENCE OF THE POSITION OF THE SUBSTITUTING GROUPS.

In addition to the preceding characteristic examples, the series of dicarboxylic acids may be given:

Oxalic acid, COOH.COOH........	$10^5 \times k =$ about	10000
Malonic acid, $COOH.CH_2.COOH$..		158
Succinic acid, $COOH.C_2H_4.COOH$..		6.65
Glutaric acid, $COOH.C_3H_6.COOH$..		4.75
Adipic acid, $COOH.C_4H_8.COOH$...		3.7
Pimelic acid, $COOH.C_5H_{10}.COOH$..		3.6
Suberic acid, $COOH.C_6H_{12}.COOH$..		2.6
Sebacic acid, $COOH.C_8H_{16}.COOH$..		2.3
Methylmalonic acid, $COOH.CH(CH_3).COOH$......		87
Pyrotartaric acid, $COOH.C_2H_3(CH_3).COOH$......		8.6
Fumaric acid, $\begin{array}{l}\text{COOH.CH}\\ \qquad\ddot{\text{C}}\text{H.COOH}\end{array}$...	$10^3 \times k =$	0.93
Maleic acid, $\begin{array}{l}\text{CH.COOH}\\ \ddot{\text{C}}\text{H.COOH}\end{array}$............		11.70

In these instances the essential relation coming into play is the distance apart of the two COOH groups: the more carbon atoms between them the weaker the acid becomes—here again the first steps are decidedly the most effective. Upon attaining a certain separation a further increase of the distance makes less and less impression.

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[1] Zeitschr. physik. Chem., **36**, 546 (1901).

Comparing fumaric and maleic acids, the action of the proximity of the two carboxyl groups is especially apparent.

In the case of organic compounds one condition for the production of $H^{\cdot}$ ions is evidently the direct union of H and O; for that reason the alcohols show a distinct, even if extremely slight, acid function (the alcoholates). Another important condition is the proximity of carbonyl groups, which, for example, in the case of malonic-acid ester, acetic-acid ester, and also in acetylacetone makes the hydrogens in the neighborhood of the CH_2 groups capable of dissociation and salt formation.[1] The carboxyl compounds undoubtedly owe their marked acid property to the combination of both conditions. In the representatives of the first two groups of compounds the dissociation is scarcely detectable by physical means; therefore the decomposition of their salts by water (see Hydrolysis, p. 76) is almost complete.

In the case of bases, all substituting groups have just the reverse action of that on acids; the halogens, the carboxyl group, and the NO_2 group have an especially weakening effect on the basic character. A detailed investigation of Bredig[2] gives a fuller account of this. Because of the great influence of constitution a quantitative determination of the effect of substitution has up to the present not been possible.

Another phenomenon deserves special mention, which was likewise first noted and made clear by Ostwald, namely, the dissociation of the dibasic organic acids. As these contain two COOH groups, there is a possibility

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[1] Ehrenfeld, Zeitschr. f. Elektrochem., **9**, 335 (1903).

[2] Zeitschr. physik. Chem., **13**, 289 (1894).

of a hydrogen ion dissociation taking place at both of these, the more so as we have just seen that the presence of a second carboxyl group in the molecule markedly increases the dissociating tendency of the first. Now, strange to say, a calculation of the constant by equation (3), $\frac{\alpha^2 \cdot c}{(1-\alpha)} = k$, which holds only for binary electrolytes (those splitting into two ions), shows that this is not the case. For if both carboxyl groups split off $\dot{H}$ ions, such an acid would have ternary dissociation, that is, would have to obey another dissociation formula. One is forced, therefore, to the view that the dissociation at the second carboxyl group takes place with considerably greater difficulty than at the first, so that an influence of such a nature must be present that the first step of the dissociation prevents the second from taking place. That a second stage sets in at all, can be recognized by the fact that in general the binary dissociation formula ceases to apply when the degree of dissociation of the first stage has reached about $\frac{1}{2}$, for here the constancy of the expression $\frac{\alpha^2 \cdot c}{1-\alpha}$ ceases (compare table on opposite page). The physical significance of this phenomenon Ostwald finds in that the presence of a negative charge on a univalent acid anion makes more difficult the placing upon it of a second ionic charge, for the electrostatic reason that like charges repel one another. This second ionic charge would be necessitated by a dissociation at the second carboxyl group. One consequence of this view may be empirically tested: the appearance of the second stage of dissociation would have to be influenced by the relative

SECOND DISSOCIATION OF DIBASIC ACIDS.

(Ostwald, 1889.)

$\frac{1}{c}=v=$	16	32	64	128	256	512	1024	2048	
	$k=$								α
Malonic acid, $CH_2(COOH)_2$	1.59	1.5[illegible]	1.58	1.57	1.57†	1.62	1.68	1.87×10^{-3}	0.46—0.58
Tartronic acid, $CH(OH)(COOH)_2$	—	1.07	1.07	1.07	1.07†	1.10	1.22	1.55×10^{-3}	0.40—0.52
Malic acid, $C_2H_3(OH)(COOH)_2$	—	—	3.99	3.99	4.01	4.00	4.02†	4.32×10^{-4}	0.47—0.60
Tartaric acid, $C_2H_2(OH)_2(COOH)_2$	9.6	9.8	9.8	9.9†	10.3	10.9	12.7	17.9×10^{-4}	0.30—0.40
o-Phthalic acid, $C_6H_5(COOH)_2$	—	—	1.21	1.21	1.20	1.20	1.22†	1.31×10^{-3}	0.66—0.78
m-Phthalic acid, $C_6H_4(COOH)_2$	—	—	—	—	—	2.87	2.88†	3.03×10^{-4}	0.42—0.54
α-Nitrophthalic acid, $C_6H_3NO_2(COOH)_2$	1.22	1.27	1.22	1.22	1.25†	1.44	—	$- \times 10^{-2}$	0.80—0.89
Maleic acid, $C_2H_2(COOH)_2$	—	1.3	1.2	1.16	1.14	1.15	1.17	$- \times 10^{-2}$	>0.93
Fumaric acid, $COOH.C_2H_2\,COOH$	—	9.3	9.4	9.5	9.7 †	9.9	11.0	14.0×10^{-4}	0.40—0.50

position of the two carboxyl groups in the molecule, for it is evident that the electrostatic interaction must be greater the nearer the negatively charged carboxyls are to each other. This surmise is fully confirmed. In dibasic acids whose constitution shows a close proximity of the two carboxyls, the second dissociation sets in with considerably greater difficulty than in acids where the carboxyls are farther apart. In the enumeration on p. 53 are given the constants *k* of different dibasic acids calculated according to the dilution law for binary dissociation. At the dilution marked † the binary constants increase, showing the beginning of the second, the ternary stage of dissociation. Under α the two degrees of dissociation are given, between which the ternary dissociation begins. The most marked evidence of the influence of the proximity of the carboxyls is given by fumaric and maleic acids and the phthalic acids with the adjacent position of the two COOH groups.

As is to be seen, when the two COOH groups are near together, in spite of far-reaching primary dissociation, the secondary does not set in until very late (α-nitrophthalic acid) or not at all (maleic acid), while in most cases it begins with α equal to about 0.5.

Of especial interest are the extremely weak electrolytes, previously mentioned, a list of which is appended here[1] (for 25°):

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[1] From Walker and Cormack, Journ. Chem. Soc., **77**, 5 (1900); Zeitschr. physik. Chem., **22**, 137 (1900).—Walker, ibid., **4**, 332 (1889), and **32**, 137 (1900).—Bredig, ibid., **13**, 322 (1894).—Winkelblech, ibid., **36**, 587 (1901).—Löwenherz, ibid., **25**, 385 (1898).—Morse, ibid., **41**, 709 (1902).—Bader, ibid., **6**, 289 (1890).—Walker and Wood, Proc. Chem. Soc., **19**, 67 (1903).

EXTREMELY WEAK ELECTROLYTES.

Acids:	
Meta-arsenious acid, $H^{\cdot}$, AsO_2'	2.1×10^{-8}
m-Amidobenzoic acid, $H^{\cdot}$, $C_6H_4(NH_2)COO'$	9.6×10^{-6}
Carbonic acid, $H^{\cdot}$, HCO_3'	3.04×10^{-7}
p-Nitrophenol, $H^{\cdot}$, $C_6H_4(NO_2)O'$	1.2×10^{-7}
Hydrogen sulphide, $H^{\cdot}$, SH'	5.7×10^{-8}
Boric acid, $H^{\cdot}$, H_2BO_3'	1.7×10^{-9}
Hydrocyanic acid, $H^{\cdot}$, CN'	1.3×10^{-9}
Alanine, $H^{\cdot}$, $C_2H_5(NH_2)COO'$	9.0×10^{-10}
Phenol, $H^{\cdot}$, C_6H_5O'	1.3×10^{-10}
Water (25°), $H^{\cdot}$, OH'	1.2×10^{-14} (ionic product)
Cacodylic acid, $H^{\cdot}$, $(CH_3)_2AsOO'$	4.2×10^{-7}
Bases:	
ψ-Cumidine, OH', $C_6H_2(CH_3)_3NH_3^{\cdot}$	1.7×10^{-9}
p-Toluidine, OH', $C_7H_7NH_3^{\cdot}$	1.6×10^{-9}
Aniline, OH', $C_6H_5NH_3^{\cdot}$	4.9×10^{-10}
m-Amidobenzoic acid, OH', $C_6H_4(COOH)NH_3^{\cdot}$	1.9×10^{-11}
m-Nitraniline, OH', $C_6H_4(NO_2)NH_3^{\cdot}$	4.0×10^{-12}
Alanine, OH', $C_2H_5(COOH)NH_3^{\cdot}$	3.8×10^{-12}
Thiazole, OH', $C_3H_3SNH^{\cdot}$	3.3×10^{-12}
Glycocoll, OH', $CH_2(CO_2H)NH_3^{\cdot}$	2.9×10^{-12}
Asparagine, OH', $C_2H_3(CO_2H)(CONH_2)NH_3^{\cdot}$	1.5×10^{-12}
p-Nitraniline, OH', $C_6H_4(NO)_2NH_3^{\cdot}$	1.0×10^{-12}
Thiohydantoin, OH', $C_3H_5N_2SO^{\cdot}$	9.5×10^{-13}
Aspartic acid, OH', $C_2H_3(CO_2H)_2NH_3^{\cdot}$	8.7×10^{-13}
Betaine, OH', $CH_2(CO_2H)N(CH_3)_3^{\cdot}$	7.6×10^{-13}
Acetoxime, OH', $(CH_3)_2CNHOH^{\cdot}$	6.1×10^{-13} (25°); 1.8×10^{-12} (40°)
Urea, OH', $CON_2H_5^{\cdot}$	1.5×10^{-14} (25°); 3.7×10^{-14} (40°)
o-Nitraniline, OH', $C_6H_4(NO_2)NH_3^{\cdot}$	1.0×10^{-14}
Water (25°), OH', $H^{\cdot}$	1.2×10^{-14} (ionic product)
Acetamide, OH', $CH_3CONH_3^{\cdot}$	3.0×10^{-15} (25°); 3.3×10^{-14} (40°)
Propionitrile, OH', $C_2H_5CNH^{\cdot}$	1.8×10^{-15}
Thio-urea, OH', $CSN_2H_5^{\cdot}$	1.1×10^{-15}
Cacodylic acid, OH', $(CH_3)_2AsO^{\cdot}$	2.5×10^{-13} (25°); 3.8×10^{-13} (0°)
Salts:	
Mercuric chloride, $HgCl_2$	1×10^{-14}
Mercuric bromide, $HgBr_2$	2×10^{-18}
Mercuric iodide, HgI_2	1×10^{-25}

Among these, the dissociation of pure water into H˙ and OH′ ions is of particular importance. This constant at room temperature is equal to about 10^{-14}, i.e., the product of the hydrogen and hydroxyl ion concentrations has the above value, or in pure water each kind of ion is present in the concentration 10^{-7}. In other words, pure water is one ten-millionth normal with reference to the hydrogen and hydroxyl ions.[1]

This value has been arrived at in four entirely independent ways, and the different results show excellent agreement. Kohlrausch and Heydweiller[2] determined the conductivity of water purified with extreme care, after they had discovered that the conductivity of the common distilled water is for the most part due to such substances as carbonic acid, ammonium salts, glass, etc., dissolved from the atmosphere and the walls of the vessel. By repeated distillation in vacuo in specially prepared vessels of most sparingly soluble glass, they succeeded in obtaining a conductivity,

$$\kappa = 0.04 \times 10^{-6} \ (18°),$$

which in conjunction with the mobility of the H˙ and OH′ ions gives the named ionic concentration; since 1 mole

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[1] The constant 10^{-14} is in the true sense not a dissociation constant, but merely represents the ionic product, that is, $(H^\cdot)\cdot(OH')$ or $k\cdot(H_2O)$; since, however, on the one hand the concentration of the H_2O molecules in water is unknown (on account of polymerization), and on the other hand practically does not vary to any extent in dilute solutions, it is to no purpose to introduce for the ionic equilibria in which water takes part any other constant than the ionic product, namely, $k\cdot(H_2O)$, which in the future shall be designated by k_w or the "water constant."

[2] Wied. Ann., **53**, 209; Zeitschr. physik. Chem., **14**, 317 (1894).

$H^{\cdot}+OH'$ ions in 1 c.c. would produce (see p. 33) the conductivity $318+174=492$, therefore there are only $\frac{0.04\times10^{-6}}{492}$ mole ions in 1 c.c. $=0.8\times10^{-7}$ mole per liter.

Ostwald followed a second method requiring much less precision. He measured the electromotive force of two hydrogen electrodes opposed to each other, the one dipping into an acid, the other into an alkali, of known $H^{\cdot}$ and OH' concentration respectively. This galvanic combination can be looked upon as a concentration chain of hydrogen ions, whose force, according to Nernst's theory, serves to determine the $H^{\cdot}$ ion concentration in the hydroxide solution employed, and in consequence permits the calculation of the product of $H^{\cdot}$ and OH' ion concentrations. This product represents the dissociation constant of water. The result was the same as above. (We shall learn later how in such cases as this, where the concentration of the two ions is very different, the law of mass action is applied.)

A third way, that led to the same result, was the measurement of the rate of saponification of esters by water, as carried out by Wijs according to a theory of van't Hoff.[1]

Finally, Shields,[2] at the suggestion of Arrhenius, studied the hydrolysis of salts, which, as we shall have to consider later, allows the calculation of the dissociation constant of water. This constant proves to be the same as given above.

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[1] Zeitschr. physik. Chem., **12**, 514 (1893).

[2] Ibid., **12**, 167 (1893).

Let us now discuss one of the most interesting conclusions from this extremely small water dissociation, namely, the process of neutralization of acids by bases. The slight dissociation of water is nothing more than the expression of the fact that $H^{\cdot}$ and OH' ions possess a very strong affinity for each other, so that the extent to which they unite to form undissociated water is so complete that only the repeatedly mentioned very small number of $H^{\cdot}$ and OH' ions is left. If therefore these ions meet in any solution in higher concentrations, they cannot be in equilibrium with one another, but must continue to unite to form undissociated water until the product of their concentrations remaining has reached the value 10^{-14}. Therefore upon mixing equivalent solutions of $H^{\cdot}$ ions (acids) and OH' ions (alkalis) the union of these ions to form undissociated water will set in above all other things, aside from any further reactions. Whether the anions of the acid and the cathions of the alkali undergo further chemical action with one another is of course a question by itself. For ordinary cases this question is, however, to be answered in the negative, since, as alluded to above, salts, which would have to be formed by the combination of these two kinds of ions, are for the most part strongly dissociated, i.e., consist of ions, so that these ions find no occasion to form any marked quantities of undissociated salts. We see then that the essential change taking place upon mixing acids and bases is the formation of undissociated water by the $H^{\cdot}$ and OH' ions. One conclusion from this conception has been known for a very long time, ever since the investigations of the Russian thermochemist Hess,[1] who made the most startling discovery, and one at that time inconceivable, that the heat effect of neutralization of dissolved acids and bases in equivalent amounts always gave the same value, 13700 cal. per gram-equivalent. On the basis of the dissociation theory this fact could have been predicted, for in all these neutralizations no other reaction takes place than the one expressed by the equation

$$H^{\cdot}+OH'=H_2O,$$

which results when we take into consideration the ionization of the participating substances; thus, for example,

$$KOH+HCl=KCl+H_2O$$

in the ionic sense becomes

$$K^{\cdot}+OH'+H^{\cdot}+Cl'=K^{\cdot}+Cl'+H_2O,$$

and leaving out the unchanged substances on the right and left sides, the ions $K^{\cdot}$ and Cl', we arrive, as you see, at the above simple equation $H^{\cdot}+OH'=H_2O$ for the process of neutralization. A test of the question whether this heat effect really has the significance of a heat of dissociation of water, as the simple neutralization equation represents it, has been possible in another way, namely, by the investigation of the variation of the water dissociation α with the temperature T. Thermodynamical considerations give the following mathematical relation of α and T to the heat of dissociation W (p. 137):

$$\frac{1}{\alpha}\cdot\frac{d\alpha}{dT}=\frac{W}{2RT^2}.$$

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[1] Ostwald's Klassiker, Nr. 9, 1839–1842.

Kohlrausch and Heydweiller experimentally tested this variation of the dissociation of water with the temperature by means of the conductivity of pure water, and found that the heat of dissociation, calculated by the van't Hoff equation given above, gave results in complete agreement with the heat of neutralization as determined by Hess and Thomsen. (In reality the reverse, which in principle means the same thing, was done; that is to say, the variation of the degree of dissociation with the temperature was calculated by van't Hoff's equation, on the assumption that the heat of neutralization really represents the heat of dissociation of water.)

Another thermochemical result of Hess is explained very nicely by the dissociation theory, namely, the thermoneutrality of salt solutions, or the fact that moderately dilute salt solutions when mixed together give no heat effect—in other words, show no signs of reaction. This in spite of the fact that, according to our old views in such a process of mixing, at least a partial mutual decomposition of both salts with the formation of new salts ought to take place. According to the dissociation theory, however, the ions are for the most part free before and after the mixing, and therefore no reaction takes place; for it is extremely improbable that in all these various cases the heat effects of the reactions taking place would just compensate each other, making the total effect equal to zero.

EQUILIBRIA AMONG SEVERAL ELECTROLYTES.

THE dilution formula for binary electrolytes in the form given above, $\frac{\alpha^2 c}{(1-\alpha)}=$Const., evidently holds only on the assumption that both ions of the electrolyte are present in equivalent amounts, which is necessarily correct as long as no second electrolyte is present in solution at the same time. It is frequently the case, however, that in a solution two electrolytes are present which have one of their ions in common, as, for instance, two acids or two bases, each of which forms $H^{\cdot}$ and OH' ions respectively; or a salt and an acid, as sodium acetate and acetic acid; or a salt and a base, as ammonium chloride and ammonia. In the last case the ammonium cathion, in the preceding the acetate anion, are the ions in common. Now in the same manner as the gaseous dissociation of PCl_5, for example, is affected by the addition of chlorine or PCl_3, just so the addition of a "like-ioned" electrolyte must influence the dissociation of a co-solute, and indeed the law of mass action gives here, as above, the quantitative relations. Suppose the two electrolytes to be binary, and k_1 and k_2 the constants which regulate the equilibrium between the ions and the undissociated portion of the electrolytes 1 and 2; then in the common solution the conditions of the equilibrium for each electrolyte,

$$\frac{\text{Product of the ionic concentrations}}{\text{Concentration of the undissociated portion}}=k,$$

must be fulfilled.

If we indicate by c_1 and c_2, respectively, the total concentrations of the two electrolytes and by α_1 and α_2 their degrees of dissociation, then the concentrations of the ions not mutual, that is, those which are produced by one of the electrolytes alone, are equal to $\alpha_1 \cdot c_1$ and $\alpha_2 \cdot c_2$, respectively; while the concentration of the mutual ions is made up of those formed from each of the two electrolytes, and hence is represented by the expression

$$\alpha_1 \cdot c_1 + \alpha_2 \cdot c_2.$$

Therefore in the common solution we have the following relations:

$$\left.\begin{aligned} k_1 &= \frac{\alpha_1 \cdot c_1 \cdot (\alpha_1 \cdot c_1 + \alpha_2 \cdot c_2)}{(1-\alpha_1) \cdot c_1} = \frac{\alpha_1}{1-\alpha_1}(\alpha_1 c_1 + \alpha_2 c_2), \\ \text{and} \qquad & \\ k_2 &= \frac{\alpha_2 \cdot c_2 \cdot (\alpha_1 \cdot c_1 + \alpha_2 \cdot c_2)}{(1-\alpha_2) \cdot c_2} = \frac{\alpha_2}{1-\alpha_2}(\alpha_1 c_1 + \alpha_2 c_2). \end{aligned}\right\} \quad (6)$$

The most important application of this double formula was made by Arrhenius in his theory of isohydric solutions,[1] which says that upon mixing the solutions of two electrolytes having a common ion no change in the degree of

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[1] Zeitschr. physik. Chem., 2, 284 (1888).

dissociation of either takes place, if the concentrations of the common ion are the same in both solutions before mixing.

The correctness of this statement becomes evident at once when we consider the following example. Assuming that we have a weak acid HA at any concentration *c*, then we may write

$$k_1 = \frac{(H^\cdot)(A')}{(HA)}.$$

Now if we dilute this acid HA by the addition of such a solution of a second acid in which the concentration of the $H^\cdot$ ions is just as great as in HA, or, as Arrhenius puts it, an acid of isohydric concentration, it has no influence on the concentration of the $H^\cdot$ ions, while the anions A' as well as the undissociated molecules HA are both diluted to the same extent. The effect, therefore, of this dilution disappears in the expression

$$(H^\cdot)\frac{(A')}{(HA)} = k_1,$$

or in such a case the condition of dissociation remains unchanged and independent of the mixing ratio; for with unchanged $H^\cdot$ concentration the $H^\cdot$, A' equilibrium requires that the concentration ratio of anion to undissociated portion be kept the same as in the pure solution of the acid.

It is clear that we can look upon any mixture of two acids as composed of such quantities of each pure acid solution as are isohydric with one another. These isohydric concentrations may be arrived at through the following consideration. In the mixture suppose c_1 to be the concentration of the acid HA_1, c_2 that of HA_2, $(H^\cdot)$ the total concentration of $H^\cdot$ ions, determined by conductivity, catalysis, inversion, or in some other way, and finally α_1 and α_2 the respective degrees of dissociation; then

$$k_1 = \frac{(H^\cdot)(A'_1)}{(HA_1)} = (H^\cdot)\frac{\alpha_1 c_1}{(1-\alpha_1)c_1} = (H^\cdot)\frac{\alpha_1}{1-\alpha_1},$$

$$k_2 = \frac{(H^\cdot)\,(A'_2)}{(HA_2)} = (H^\cdot)\frac{\alpha_2 c_2}{(1-\alpha_2)c_2} = (H^\cdot)\frac{\alpha_2}{1-\alpha_2},$$

from which

$$\frac{1}{\alpha_1} = 1 + \frac{(H^\cdot)}{k_1}, \quad \frac{1}{\alpha_2} = 1 + \frac{(H^\cdot)}{k_2}.$$

The sought-for concentrations x_1 and x_2 of the pure solutions, whose degrees of dissociation are also α_1 and α_2, are given by the relations:

$$k_1 = \frac{\alpha_1^2 x_1}{1-\alpha_1}, \quad x_1 = k_1\frac{1-\alpha_1}{\alpha_1^2};$$

$$k_2 = \frac{\alpha_2^2 x_2}{1-\alpha_2}, \quad x_2 = k_2\frac{1-\alpha_2}{\alpha_2^2};$$

or by substituting for α_1 and α_2 the values for k_1 and k_2, respectively, found above:

$$x_1 = (H^\cdot)\frac{\alpha_1}{1-\alpha_1}\cdot\frac{1-\alpha_1}{\alpha_1^2} = (H^\cdot)\frac{1}{\alpha_1} \quad \text{and} \quad x_2 = (H^\cdot)\frac{1}{\alpha_2},$$

or by replacing α with k:

$$x_1=(\mathrm{H}^\cdot)\left(1+\frac{(\mathrm{H}^\cdot)}{k_1}\right)=(\mathrm{H}^\cdot)+\frac{(\mathrm{H}^\cdot)^2}{k_1} \quad \text{and} \quad x_2=(\mathrm{H}^\cdot)+\frac{(\mathrm{H}^\cdot)^2}{k_2},$$

in place of which, for small k values, the approximation usually suffices:

$$x_1=\frac{(\mathrm{H}^\cdot)^2}{k_1} \quad \text{and} \quad x_2=\frac{(\mathrm{H}^\cdot)^2}{k_2},$$

$$\frac{x_1}{x_2}=\frac{k_2}{k_1}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (7)$$

That is, two acids upon mixing do not influence each other's dissociation when their concentrations are very nearly inversely proportional to their dissociation constants, or the ratio of their concentrations is equal to the reciprocal ratio of their dissociation constants. Let us suppose we wish to prepare 1 liter of a mixture containing $\frac{1}{10}$ mole acetic acid ($k_1=1.8\times10^{-5}$) and $\frac{1}{10}$ mole glycollic acid ($k_2=15\times10^{-5}$). This can be done, without influencing the dissociation, by combining solutions of acetic and glycollic acids having their concentrations in the ratio $x_1:x_2=15:1.8=8.3:1$. Hence we must mix 8.3 volumes of glycollic acid with one of acetic acid of isohydric concentration (giving 9.3 volumes), and to fulfill at the same time the above conditions of concentration $\frac{8.3}{9.3}$ liter of glycollic acid must contain $\frac{1}{10}$ mole, i.e., be $\frac{9.3}{8.3}\times0.1=0.112$ normal, and $\frac{1}{9.3}$ liter of acetic acid must contain $\frac{1}{10}$ mole, that is, be 0.93 normal.

The knowledge of isohydric concentrations is important for the reason that from the conductivities κ_1 and κ_2, and the mixing volumes V_1 and V_2, the conductivity κ of the mixture may be very simply calculated thus (by the rule of three):

$$\kappa = \frac{\kappa_1 V_1 + \kappa_2 V_2}{V_1 + V_2}.$$

Or, as Arrhenius expresses this: when two acids are present in a common solution, the conductivity may be calculated by introducing into the calculation for each resulting conductivity the concentrations based on the assumption that the acids distribute themselves in the aqueous solvent in the inverse ratio to their dissociation constants. The agreement of this statement with experimental results has been proved by Wakeman [1] as well as by Arrhenius. And it deserves to be mentioned that in case of a mixture of acids the expression $\frac{\Lambda^2 c}{\Lambda_0(\Lambda_0 - \Lambda)}$ derived from the conductivity is not constant, as in the case of pure acids, but varies with c, so that the study of the conductivity becomes a valuable criterion of the purity of such electrolytes.

In order to determine how strongly the presence of a second acid diminishes the degree of dissociation α_1 of the first acid below the value β_1 of the pure solution of the same concentration, we combine our two equations (6) (p. 62) into the expression:

$$\frac{k_1}{k_2} = \frac{\dfrac{\alpha_1}{(1 - \alpha_1)}}{\dfrac{\alpha_2}{(1 - \alpha_2)}},$$

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[1] Zeitschr. physik. Chem., **15**, 159 (1894).

in which for weak electrolytes it is permissible to write $1-\alpha_1=1-\alpha_2=1$, so that we may arrive at the convenient but nevertheless good approximation formulæ:

$$\alpha_1=\frac{k_1}{k_2}\cdot\alpha_2 \quad \text{or} \quad \alpha_2=\frac{k_2}{k_1}\cdot\alpha_1. \quad . \quad . \quad . \quad (8)$$

Now if we are interested in the acid 1, we employ the equations for the law of mass action, both for the pure and the mixed acid 1:

$$k_1=\frac{\beta_1{}^2\cdot c_1}{1-\beta_1}=\frac{\alpha_1}{1-\alpha_1}(\alpha_1 c_1+\alpha_2 c_2)=\frac{\alpha_1{}^2}{1-\alpha_1}\left(c_1+\frac{k_2}{k_1}c_2\right)$$
$$=\frac{\alpha_1{}^2\cdot c_1}{1-\alpha_1}\left(1+\frac{k_2}{k_1}\cdot\frac{c_2}{c_1}\right).$$

Substituting again as above $1-\alpha_1=1-\beta_1=1$, we obtain:

$$\beta_1{}^2 c_1=\alpha_1{}^2\cdot c_1\left(1+\frac{k_2}{k_1}\cdot\frac{c_2}{c_1}\right),$$

or

$$\frac{\beta_1}{\alpha_1}=\sqrt{1+\frac{k_2}{k_1}\cdot\frac{c_2}{c_1}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

This then is the ratio in which the degree of dissociation of the acid 1, at the concentration c_1, is depressed by the addition of c_2 moles per liter of an acid having the dissociation constant k_2. For the latter acid the analogous expression holds with interchanged indices.

In order to form an idea of the magnitude of the values involved, let us consider the case of a mixture of 1 mole of acetic acid ($k_1=1.8\times10^{-5}$) and 1 mole of cyanacetic acid ($k_2=370\times10^{-5}$) per liter. In pure acetic acid we should have $\beta_1=\sqrt{1.8\times10^{-5}}=0.00425$; since $\frac{k_2}{k_1}=205$ and $\frac{c_2}{c_1}=1$, we get

$$\beta_1:\alpha_1=\sqrt{1+205}=14.4;$$

that is, the degree of dissociation is reduced to $\frac{1}{14.4}$ part, or from 0.00425 to 0.0003, or from 0.4% to 0.03%. In general we can see from the equation that the reduction of β_1 is greater the stronger the acid (k_2) and the higher its concentration (c_2) is.

To learn the counteraction of the acetic acid on the dissociation of the cyanacetic acid, we make use of the analogous expression

$$\beta_2:\alpha_2=\sqrt{1+\frac{k_1}{k_2}\cdot\frac{c_1}{c_2}}. \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Here we see the factor under the radical becomes equal to $1+\frac{1}{205}=1.0049$ (instead of, as before, 206!), or the going back of the dissociation $\frac{\beta_2}{\alpha_2}$ is only about 0.25% (instead of 1440% as before!); the general comparison is given by the equation:

$$\frac{\beta_1:\alpha_1}{\beta_2:\alpha_2}=\sqrt{\frac{1+\frac{k_2}{k_1}\cdot\frac{c_2}{c_1}}{1+\frac{k_1}{k_2}\cdot\frac{c_1}{c_2}}}=\sqrt{\frac{k_2c_2}{k_1c_1}}.$$

The general result may be summed up in the statement that in a mixture of acids the acids mutually reduce their degree of dissociation, but the weaker acid is influenced very much more strongly. What has been said here about acids is, by analogy, absolutely true of all other weak electrolytes, in particular of bases.

From the above it also follows that the farther two electrolytic solutions are removed from being isohydric the more also the conductivity of their mixture must be reduced as compared with that of the unmixed solutions; for the minimum o of the mutual influence corresponds to the isohydric state. So having a solution *a* of an electrolyte, it is possible to determine the isohydric condition of another solution *b* having ions in common with it, by adding the solution *a* to different concentrations of *b*. That concentration of *b* is isohydric with the given solution *a*, which by the addition of the latter brings about the maximum increase in conductivity. This deduction may under circumstances be useful for determining the degree of dissociation of *a*, when that of *b* is known and *a* is not directly determinable.[1]

In a precisely similar manner the mass-action formulæ for any more complex mixtures of electrolytes may be derived, as Arrhenius has made clear in his studies of the equilibrium relations between electrolytes.[2] Let the discussion of a simple special case suffice here, a case of extreme importance to analytical chemistry, namely, that of two electrolytes, one very strong, the other very weak,

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[1] Compare W. Bonsdorff, Ber. d. deutsch. chem. Ges., **36**, 2322 (1903); Zeitschr. anorg. Chem., **41**, 132 (1904).

[2] Zeitschr. physik. Chem., **5**, 1 (1890).

so that by their mixture the dissociation of the strong electrolyte is only slightly influenced, while that of the weak is affected all the more.

This case is realized in general whenever we mix a weak acid or a weak base with one of its neutral salts (strongly dissociated according to the rule, p. 26) or with a strong acid or base respectively. Then by equation (6) (p. 62), designating the weak electrolyte by 1 and the strong by 2,

$$k_1 = \frac{\alpha_1 \cdot c_1 \cdot (\alpha_1 \cdot c_1 + \alpha_2 \cdot c_2)}{(1 - \alpha_1) \cdot c_1} = \frac{\alpha_1}{1 - \alpha_1}(\alpha_1 c_1 + \alpha_2 c_2),$$

the degree of dissociation α_1 is greatly reduced according to the measure of the concentration c_2.

In order to obtain an approximation for this reduction, let us, as before, but with even greater exactness, write $1 - \alpha_1 = 1$, for the degree of dissociation of our weak electrolyte 1 in unmixed solution. This degree of dissociation, small by assumption, is made even smaller by the mixing. Further, for the sake of simplicity we shall assume that $\alpha_2 = 1$, or that the dissociation of the strong electrolyte is practically complete. Then we may also write our equation:

$$k_1 = \alpha_1(\alpha_1 c_1 + c_2) = \alpha_1^2 c_1 + \alpha_1 c_2.$$

Again, if the concentrations c_1 and c_2 are of the same order of magnitude, i.e., the concentration of the strong electrolyte is not very much smaller than that of the weak, we may in the latter expression drop the first summation as compared with the second without introducing any great error, because α_1, the degree of dissociation of the weak electrolyte in the mixture, is a small magnitude, hence its second power represents a magnitude of the second order. It follows then that approximately

$$k_1 = \alpha_1 \cdot c_2, \quad \text{i.e.,} \quad \alpha_1 = \frac{k_1}{c_2},$$

and the concentration $\alpha_1 c_1$ of the non-mutual ion is

$$\alpha_1 c_1 = k_1 \frac{c_1}{c_2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

or in words: the degree of dissociation α_1 of the weak electrolyte in the common solution of both electrolytes is directly proportional to the concentration of the strong electrolyte and inversely proportional to its dissociation constant. In order to point out the significance of these relations by way of several examples, let us consider the cases mentioned above of equivalent mixtures of acetic acid and alkali-acetate or of ammonia and ammonium salts; then for α_1 we must introduce the degree of dissociation of acetic acid and ammonia respectively, for the constant k_1 the value 1.8×10^{-5} and 2.3×10^{-5} respectively. We find thus that in pure 1-normal solutions of acetic acid and ammonia the degree of dissociation is respectively 0.4% and 0.5%, while the same upon addition of 1-normal acetate and ammonium salt is depressed to 0.0018% and 0.0023% respectively. These degrees of dissociation in the mixtures express at the same time, in the case of the acetic acid, the concentration of the $H^{\cdot}$ ions, in the case of the ammonia, that of the OH' ions, and give us a measure of how very greatly the acid and basic properties, based on the concentration of these ions, are diminished. In the case of ammonia this fact was made use of long before its theoretical explanation was known, namely, in reducing by the addition of ammonium salts the power of ammonia to precipitate magnesium ions as magnesium hydroxide, or, practically speaking, counteracting it altogether. Likewise the reduction of the concentration of the sulphur ions in hydrogen sulphide, by increasing the concentration of $H^{\cdot}$ ions through the addition of strong acids, is made use of in analysis to counteract the power of H_2S to precipitate zinc. The equilibria appearing in connection with precipitating reactions will be further discussed later on. This driving back of dissociation, Arrhenius also proved experimentally for formic acid and acetic acid. As previously alluded to (p. 5), the inversion of cane-sugar is catalytically accelerated by acids, in proportion to the $H^{\cdot}$ ion concentration of these acids, which is shown by a comparison of the catalytic action of varying acid concentrations. The following table gives the value of this catalyzing constant for several such acids and the influence upon it of additions of neutral salts.

ρ indicates the reaction-velocity constant, i.e., the quantity of sugar inverted per minute, when the sugar possesses during the minute the concentration 1. The measurements were carried out at 54°, at which temperature k (acetic acid) $= 1.615 \times 10^{-5}$ and k (formic acid) $= 1.83 \times 10^{-4}$, for calculating the $H^{\cdot}$ concentration.

For $\frac{1}{80}$-normal HCl it was found that $\rho = 4.69 \times 10^{-3}$; this velocity of inversion is therefore brought about by an H˙ concentration $=\frac{1}{80}=0.0125$ normal, since HCl in $\frac{1}{80}$-N solution practically may be considered as completely ionized.

A 0.25-N acetic acid has, since $k=1.615\times10^{-5}$, the H˙ concentration $(\mathrm{H}^{\cdot})^2=k\times0.25$ or $(\mathrm{H}^{\cdot})=\sqrt{0.25\times1.615\times10^{-5}}=0.002$ normal, hence we should have $\rho=4.69\times10^{-3}\frac{0.002}{0.0125}=0.74\times10^{-3}$; the value observed was $\rho=0.75\times10^{-3}$; likewise for 0.25-N formic acid we calculate $(\mathrm{H}^{\cdot})=\sqrt{0.25\times1.83\times10^{-4}}=0.00678$ and $\rho=4.69\times10^{-3}\frac{0.00678}{0.0125}=2.54\times10^{-3}$, while 2.55×10^{-3} was the value found. In exactly the same manner the (H˙) values, and from these the $\rho_{\text{calc.}}$ values, have been derived for the following mixtures, and the good agreement of $\rho_{\text{calc.}}$ and $\rho_{\text{obs.}}$ proves that the basis of the (H˙) calculation in the above equation agrees with the facts.

0.25-N ACETIC ACID + c-NORMAL SODIUM ACETATE.
(Arrhenius, 1889.)

$c=0$	0.0125	0.025	0.05	0.125	0.25
$10^3\rho_{\text{obs.}}=0.75$	0.122	0.070	0.040	0.019	0.0105
$10^3\rho_{\text{calc.}}=0.74$	0.129	0.070	0.038	0.017	0.0100

0.25-N FORMIC ACID + c-NORMAL SODIUM FORMATE.

$c=0$	0.025	0.1	0.25
$10^3\rho_{\text{obs.}}=2.55$	0.72	0.24	0.118
$10^3\rho_{\text{calc.}}=2.54$	0.75	0.24	0.117

Another special case of electrolytic equilibria is that of a mixture of two electrolytes with common ions, having equal strengths ($k_1 = k_2$), as seems to be approximately the case with analogous salts. Then by equation (6) (p. 62)

$$k_1 = k_2 = k = \frac{(\alpha_1 c_1 + \alpha_2 c_2)\alpha_1 c_1}{(1 - \alpha_1)c_1} = \frac{(\alpha_1 c_1 + \alpha_2 c_2)\alpha_2 c_2}{(1 - \alpha_2)c_2},$$

that is,

$$\frac{\alpha_1}{1 - \alpha_1} = \frac{\alpha_2}{1 - \alpha_2} = \frac{k}{\alpha_1 c_1 + \alpha_2 c_2},$$

from which it follows $\alpha_1 = \alpha_2 = \alpha$ and $\frac{\alpha^2}{1 - \alpha} = \frac{k}{c_1 + c_2}$, or in words: the degree of dissociation in mixtures of electrolytes of like strength is equal to and of the same value as that which would correspond to each alone for the concentration $(c_1 + c_2)$.

From the theory of the electrolytic equilibria relations we can derive the explanation of a whole series of well-known manifestations. Theoretically in every case in which two electrolytes, that is their four ions, are present in the same solution, there must be formed by the interaction of these ions some certain quantities of the four possible undissociated substances. So, for example, upon mixing KCl and NaBr, there are present in the solution, in addition to these two undissociated salts, certain amounts of NaCl and KBr, resulting from the reciprocal interaction of their ions. Since, however, the tendency of all these four substances to dissociate is great, there cannot be formed any appreciable quantities of the new undissociated substances. It is a very different situation if it so happens that one of the four possible substances possesses a very slight tendency to dissociate, or the reverse as we had probably better say here, in case exceptionally strong atomic affinities are in action between any two of the ions participating in the equilibrium. This is, for instance, the case when we bring together the strongly dissociated substances HCl and Na-acetate. The possibility is then at hand that NaCl and H-acetate will be formed simultaneously; however, while NaCl is strongly dissociated, there exists a marked tendency to combine between the ions $H^{\cdot}$ and acetate$'$, which causes almost all of these ions to unite to form undissociated acetic acid, and results in a disappearance from solution of the particular ions as such. As one sees, this view contains the theory of the general experience that strong acids "liberate" the weak acid from the salts of weak acids, and likewise of course strong bases liberate the weak base from the salts of weak bases, or, in the language of the dissociation theory, transform their ions into the undissociated state. Wherever, then, an $H^{\cdot}$ ion meets the anion of a weak acid, or an OH' ion the cathion of a weak base, the opportunity is made use of for both these ions to pass from the ionic state into undissociated substances. When we, for example, "set free" ammonia ($k=2.3\times10^{-5}$) from the strongly dissociated ammonium salt by the addition of strongly dissociated alkali-hydroxide, or carbonic acid ($k=3.04\times10^{-7}$) from strongly dissociated sodium carbonate by strongly dissociated HCl, or hydrocyanic acid ($k=1.3\times10^{-9}$) from strongly dissociated potassium cyanide by strongly dissociated acid, etc., we are doing nothing else than giving the ions of these weakly dissociated electrolytes the opportunity to unite and form undissociated electrolytes. Writing the equation for any such reaction, for example:

$$K^{\cdot}+CN'+H^{\cdot}+Cl'=K^{\cdot}+Cl'+HCN,$$

we see that, similar to the case of neutralization, the unchanged ions remaining on both sides may be omitted, and the formula for the reaction becomes:

$$H^{\cdot}+CN'=HCN.$$

We have here evinced, then, a very striking analogy to neutralization, or, as we must express it in the sense of the ionic theory, the analogy of the formation of undissociated water from its ions to the formation of a weakly dissociated electrolyte (HCN, H_2CO_3, NH_4OH, H_2S, etc., etc.) from its ions, or, put in the old way, to the liberation of weak acids or bases from their salts.

The old formulation, still employing the last example, that potassium chloride is produced from potassium cyanide by the action of hydrochloric acid, is, strictly speaking, a distorted mode of expression, inasmuch as the constituents of potassium chloride continue in the same condition (ionic) after the reaction as before. The really essential part of the change is the formation of the undissociated weak electrolytes, precisely as it is the formation of water in neutralization.

HYDROLYSIS.

In the cases of aqueous solutions discussed thus far, we have left out of consideration altogether that there is peculiar to the solvent, water, as we saw above, a very small but nevertheless measurable and exactly known dissociation into the ions $H^{\cdot}$ and OH'. We have, then, still to discuss how far and in what cases we are justified in assuming a participation of the water in the equilibrium between the electrolytes, and what may occur under those circumstances. For instance, in the simplest case, the solution of a strong salt such as NaCl, there is the possibility of the $Na^{\cdot}$ ions combining with the OH' ions of the water to form undissociated NaOH, and the Cl' ions with the $H^{\cdot}$ ions of the water to form undissociated HCl. We know, however, from the conductivities, freezing-points, etc., that neither of these two new compounds possesses to any sensible degree the tendency to assume the undissociated state, but that, on the contrary, they split up to a far-reaching extent into their ions. In consequence of this, neither of the ions of water is to any appreciable extent taken into custody by the ions of such a salt. The matter takes on a different aspect when, for example, the strongly dissociated salt of a very weak acid or base is involved; in such cases the ion of the weak acid or base present in the salt in large concentration finds an opportunity to unite with the ion of water necessary to form the weak acid or base. What is more, we are in position to determine, on the basis of the law of mass action, the extent to which this can take place. Taking under consideration a 1-normal solution of potassium cyanide in water, we must have in this, in addition to the equilibrium between $K^{\cdot}$ and CN' ions and undissociated KCN, the following three equilibria:

1. $K^{\cdot}$ ions and OH' ions (of water) with undissociated KOH;
2. CN' ions and $H^{\cdot}$ ions (of water) with undissociated HCN;
3. $H^{\cdot}$ ions (of water and the HCN formed) and OH' ions (of water and the KOH formed) with undissociated water.

The $K^{\cdot}$, OH' equilibrium, as well as the $K^{\cdot}$, CN', corresponds to strongly dissociated substances, while for the $H^{\cdot}$, CN' equilibrium we have the equation (see pp. 63 and 55)

$$k_s = \frac{(H^{\cdot})\cdot(CN')}{(HCN)} = 1.3\times 10^{-9},$$

and for the $H^{\cdot}$, OH' equilibrium

$$k_w = (H^{\cdot})\cdot(OH') = 1.2\times 10^{-14}.$$

Suppose this action of the water, the so-called hydrolysis, the result of which consists in the splitting up of part of a neutral salt into acid and base according to the equation

$$KCN + H_2O = KOH + HCN,$$

has taken place to the extent x, so that x represents the fraction of each mole of neutral salt which has been split up in this way into base and acid. If c stands for the total concentration employed, then, according to the statements made, there would be present in the "hydrolytic" equilibrium

$$xc\text{KOH} + xc\text{HCN} + (1-x)c\text{KCN}.$$

Applying to these quantities the equilibrium equations of hydrocyanic acid and of water,

1. We may practically identify the concentration of the undissociated HCN with the total concentration of the same equal to $x \cdot c$, for hydrocyanic acid is an exceedingly weakly dissociated acid, whose degree of dissociation in addition is reduced by the presence of the many cyanogen ions of the strongly dissociated KCN.

2. The concentration of the CN′ ions we may without marked error place equal to the concentration $(1-x)c$ of the undecomposed KCN, since, for the reasons named, the cyanogen ions arising from HCN must be exceedingly few.

3. The H˙ ion concentration, which is here required for the H˙, CN′ equilibrium, we obtain with the aid of the water equilibrium, since we know the concentration of the OH′ ions. This is practically equal to the total concentration of the (strongly dissociated) KOH, that is $= x \cdot c$. Now since

$$(\mathrm{H}^{\cdot}) \cdot (\mathrm{OH}') = k_w \quad \text{or} \quad (\mathrm{H}^{\cdot}) = \frac{k_w}{(\mathrm{OH}')} = \frac{k_w}{x \cdot c},$$

we can introduce all the values into the H˙, CN′ equilibrium equation and get

$$k_s = \frac{(\mathrm{H}^{\cdot}) \cdot (\mathrm{CN}')}{(\mathrm{HCN})} = \frac{\frac{k_w}{x \cdot c} \cdot (1-x)c}{x \cdot c} = k_w \cdot \frac{1-x}{x^2 \cdot c}.$$

In the form

$$\frac{k_w}{k_s} = \frac{x^2 \cdot c}{1-x} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

the analogy with the dilution law is very evident, and this hydrolytic dilution law can also be formulated in the words:

$$\frac{(\text{Conc. Acid})\cdot(\text{Conc. Base})}{(\text{Conc. non-hydrolyzed Salt})}=\text{Hydrolytic Constant},$$

just as we have

$$\frac{(\text{Conc. Cathions})\cdot(\text{Conc. Anions})}{(\text{Conc. undissoc. Salt})}=\text{Dissociation Constant}.$$

Herewith we have an expression consisting entirely of known factors, namely, the known total concentration c and the constants of hydrocyanic acid ($k_s=1.3\times10^{-9}$) and of water ($k_w=1.2\times10^{-14}$), which enables us to calculate the degree of hydrolysis (x).

Solving this equation for x, we get

$$x=\frac{-1}{2c}\cdot\frac{k_w}{k_s}+\sqrt{\frac{1}{4c^2}\left(\frac{k_w}{k_s}\right)^2+\frac{1}{c}\frac{k_w}{k_s}}.$$

For the cases in which the ratio $k_w : k_s$ is small as compared with 1, i.e., the constant of the weak acid is much greater than the water constant, this equation may be simplified without great error to the approximation equation:

$$x=\sqrt{\frac{1}{c}\frac{k_w}{k_s}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

The equation teaches us that the degree of hydrolysis is dependent on the ratio of the dissociation constants of the weak acid, whose salt we are considering, and that of the water. Hydrolysis increases, therefore, the weaker the weak acid or base contained in the salt is. In a qualitative way one can get a very good picture of the relations by the following considerations.

The $H^{\cdot}$ ions of the water act upon the weak anions of the salt with the formation of free undissociated acid; the place of the acid anions thus consumed is taken in equivalent amount by the OH' ions of the water that were formerly bound to the $H^{\cdot}$ ions, producing a definite OH' ion titer of the solution. Thereby, however, the concentration of the $H^{\cdot}$ ions (on account of the $H^{\cdot}, OH'$ equilibrium, that must always be maintained) is reduced to such a small amount that no further free acid can be formed by their action. By the production, then, of the OH' ions or the free base the continuation of the hydrolysis is retarded (in that these ions suppress the hydrolytic action of the $H^{\cdot}$ ions) and is finally brought to a standstill, this standstill setting in the later the less $H^{\cdot}$ ions the acid anions require for the formation of undissociated acid, i.e., the weaker the acid is.

The same is true of course, *mutatis mutandis*, for the salts of very weak bases, in which case the OH' ions of the water are the hydrolyzing and the $H^{\cdot}$ ions the retarding ones.

Starting with a salt hydrolyzed to the amount x, then, the concentrations (acid and base) are equal and equivalent, and the above equation holds, as Shields[1] demonstrated for KCN:

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[1] Zeitschr. physik. Chem., **12**, 167 (1893).

POTASSIUM CYANIDE.

(Shields, 1893.)

c	$100x$	$\frac{x^2 \cdot c}{(1-x)}$
0.947	0.31%	0.9×10^{-5}
0.235	0.72	1.22×10^{-5}
0.095	1.12	1.16×10^{-5}
0.024	2.34	1.3×10^{-5}
		Mean: 1.1×10^{-5}

The hydrolytic constant, which for immediate purposes we can derive on the basis of the law of mass action without any knowledge of the dissociation theory, nevertheless represents the ratio $k_w : k_s$ according to this theory, and therewith makes it possible to obtain the constant k_s of the weak acid, by means of (12), from the water constant $k_w = 1.2 \times 10^{-14}$ by dividing the same by the hydrolytic constant. Accordingly, for HCN the same becomes $\frac{1.2 \times 10^{-14}}{1.1 \times 10^{-5}} = 1.1 \times 10^{-9}$, while Walker found by direct measurement and in close agreement with it the value 1.3×10^{-9}. Similar to the significance given to the dissociation constant (p. 46), we may formulate the physical sense of the hydrolytic constant so that it signifies the half of that concentration at which the salt is just hydrolytically decomposed one half, or (in case the degree of hydrolysis is small) the root of the hydrolytic constant of the concentrations of the products of hydrolysis in the 1-N salt solution (when the salt contains only one very weak ion).

It is possible, then, to obtain inversely from the table

(p. 55) the hydrolytic constant by dividing the water constant 1.2×10^{-14} by the dissociation constant given, that is, the degree of hydrolysis of the 1-N salt solution according to (13) by dividing 1.1×10^{-7} by the root of the dissociation constant.

The constant $\frac{(\text{Acid}) \cdot (\text{Base})}{(\text{Salt})}$ Walker[1] determined experimentally on mixtures of the very weak base urea with hydrochloric acid, by measuring the velocity of inversion ρ produced on the one hand by the pure acid (ρ_0) and on the other by the urea to which acid had been added. Then $\frac{\rho}{\rho_0}$ represents the fraction still having inverting action, and $1 - \frac{\rho}{\rho_0}$ the part of the acid bound as a salt of urea, as well as the urea itself thus bound, so that $c - \left(1 - \frac{\rho}{\rho_0}\right)$ gives the free urea which, for the concentration c employed, is left after the formation of salt; consequently we should have

$$\frac{\frac{\rho}{\rho_0}\left(c - 1 + \frac{\rho}{\rho_0}\right)}{1 - \frac{\rho}{\rho_0}} = \text{Hydrolytic Constant.}$$

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[1] Zeitschr. physik. Chem., **4**, 319 (1889).

NORMAL HYDROCHLORIC ACID + c-NORMAL UREA.
(Calculated after Walker, 1889.)

c	ρ	$\frac{\rho}{\rho_0}=$ Conc. of Free HCl.	$1-\frac{\rho}{\rho_0}=$ Conc. of Salt Formed.	$c-1+\frac{\rho}{\rho_0}=$ Conc. of Free Urea.	Hydrol. Const.
0	$0.00315=\rho_0$	1	—	—	—
0.5	0.00237	0.753	0.247	0.253	0.77
1	0.00184	0.585	0.415	0.585	0.82
2	0.00114	0.36	0.64	1.36	0.77
3	0.00082	0.26	0.74	2.26	0.80
4	0.0006	0.19	0.81	3.19	0.75
					Mean: 0.78

In a similar manner Walker's measurements (recalculated) give the following hydrolytic constants:

Thiazole	0.00367
Glycocoll	0.00425
Asparagine	0.0079
Thiohydantoin	0.0127
Aspartic acid	0.0137
Acetoxime	0.0196
Acetamide	4.0
Propionitrile	6.7
Thio-urea	10.5

from which the dissociation constants given on p. 55 for these basic-acting substances were calculated.

Hydrolysis is outwardly recognized by the fact that a salt of neutral composition reacts in aqueous solution either acid or alkaline and not neutral, i.e., that the formation of $H^\cdot$ or OH' ions from the water is induced. In this particular the reaction of hydrolysis may possibly be most clearly represented thus, that the particular salt by means of its one weak ion acquires the opposite ion of the water for the formation of the undissociated compound and thereby disturbs the $H^{\cdot}$, OH' equilibrium. Since this equilibrium, in consequence of the presence of water, must be maintained, there appears in place of the water ion which disappeared a quantity of the other water ion, to be calculated according to the equation

$$(H^{\cdot}) = \frac{k_w}{(OH')} \quad \text{and} \quad (OH') = \frac{k_w}{(H^{\cdot})} \quad \text{respectively.}$$

As a result the salt of a weak base reacts acid, and that of a weak acid alkaline.

From the fact of this reaction it follows, on the basis of the law of mass action, that hydrolysis in the case of a weak base is reduced by the addition of $H^{\cdot}$ ions, in the case of a weak acid by the addition of OH' ions, for both these kinds of ions are reaction products of hydrolysis, and the increasing of the concentration of reaction products always acts against the progress of the reaction. We may also picture this to ourselves thus: start with the consideration of the $H^{\cdot}$, OH' equilibrium and look upon the addition of OH' ions (in the form of any strong base) as a forcing back of the $H^{\cdot}$ ion concentration of the water. This works against the reaction of these $H^{\cdot}$ ions with the weak anion of the electrolyte, because the quantity of the undissociated weak electrolyte produced by the hydrolysis is proportional to the concentration of the hydrogen ions which come into consideration for this equilibrium. The same is true also, *mutatis mutandis*, of the hydrolysis of a salt of a weak base upon the addition of $H^{\cdot}$ ions. These deductions from the law of mass action may likewise easily be confirmed at the hand of experience. If, for example, we add strong caustic alkali, i.e., increase in this way very considerably the concentration of the OH' ions in a solution of potassium cyanide or ammonium sulphide, both of which reveal their hydrolysis not only by their alkaline reaction but also by the odor of undissociated hydrocyanic acid and hydrogen sulphide respectively, then the forcing back of the hydrolysis manifests itself in the disappearance of the odor of hydrocyanic acid and hydrogen sulphide respectively. Again, if we add strong acid to a solution of ferric chloride or iron alum, which react acid in consequence of hydrolysis and at the same time show the brown color of the undissociated ferric hydroxide (in colloidal solution), the brown color of the undissociated ferric hydroxide disappears more and more, giving place to the colorless condition belonging to the ferric ions. Generally speaking, by forcing back hydrolysis by means of OH' ions or $H^{\cdot}$ ions, those properties of a hydrolyzed solution that belong to the undissociated component disappear.

As the equilibrium equation of hydrolysis shows, the hydrolytic decomposition can not only be forced backward by the addition of either $H^{\cdot}$ or OH', but also by the addition of the undissociated product of hydrolysis. Thus, for instance, the acid reaction of a solution of aniline hydrochloride is destroyed by an excess of aniline, and Bredig[1] was enabled by this device to measure the ionic mobilities of salts subject to hydrolytic decomposition.

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[1] Zeitschr. physik. Chem., **13**, 214 (1894).

In reality, according to the theory, all salts should be subject to hydrolytic decomposition, and the equation (13) (see p. 80) for hydrolysis enables us to determine quantitatively the degree of decomposition as soon as we are in possession of the dissociation constant of the weak constituent of the salt. It turns out that the degree of hydrolysis of weak electrolytes, whose dissociation constant is of the order of magnitude of that of acetic acid, is still exceedingly slight, so that a 0.1-normal solution of sodium acetate is hydrolyzed only 0.008%,[1] as shown by the investigation of Shields.[2] He measured a reaction velocity which is proportional to the concentration of the OH′ ions, namely, the saponification of ethyl acetate, whereby he determined the OH′ ion concentration and therewith the hydrolysis of salts of weak acids. His results are contained in the table, p. 91, as well as Walker's [3] calculated degrees of hydrolysis, which he obtained by means of the dissociation constant of the weak acid, this constant having been determined by conductivity measurements.

As can be seen, noteworthy degrees of hydrolysis are to be expected only in the case of salts of extremely weak electrolytes, such as those enumerated in the table on p. 55. All the salts of the acids and bases mentioned there

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[1] According to equation (13):

$$\sqrt{\frac{1}{10}\ \frac{1.2\times10^{-14}}{1.8\times10^{-5}}}=\sqrt{0.067\times10^{-9}}=0.8\times10^{-5}.$$

[2] Zeitschr. physik. Chem., **12**, 167 (1893).

[3] Ibid., **32**, 137 (1900), and Journ. Chem. Soc., **77**, 5 (1900).

are hydrolyzed to such an extent that one can demonstrate by indicator reactions the presence of measurable quantities of OH' or $H^{\cdot}$ ions. One frequently meets with the view that the determination of this OH' or $H^{\cdot}$ concentration, or, what is the same thing, the alkali or acid titer, is possible by means of alkalimetric or acidimetric titrations respectively. But this is impossible, for the reason that the ionic reactions take place with an immeasurable velocity, and in consequence, as the $H^{\cdot}$ or OH' titer in the hydrolyzed solution changes, new equilibria of the various ionic concentrations establish themselves at once. An illustration, at the same time of great importance to the chemistry of our daily life, will help to make the case clear. Consider a solution of borax, which on account of the weakness of boric acid (see p. 55) is hydrolyzed and hence gives an alkaline reaction; in this for the moment we may attempt to convert these hydroxyl ions into water by the addition of hydrogen ions. This would at once raise the $H^{\cdot}$ ion concentration to a greater value than is in keeping with the equilibrium $H^{\cdot}$, H_2BO_3' of boric acid. The excess of $H^{\cdot}$ ions would then be taken up again by the borate ions forming undissociated boric acid, whereupon a fresh quantity of hydroxyl ions would again have to be formed, owing to the $H^{\cdot}$, OH' equilibrium, or, in other words, the alkaline reaction, that we attempted to destroy by the addition of acid, persists in spite of it. In fact, this continues as long as appreciable quantities of borate ions are present in the solution, sufficient to take possession of the $H^{\cdot}$ ions added with the acid. On this behavior is based the possibility of choosing borax for neutralization, as is not infrequently done in alkalimetry, instead of alkali-hydroxides. Likewise potassium cyanide might be used, but for other reasons it is not feasible.

The application of soap, soda, and borax in the household is also essentially based on the fact that these Na salts of very weak acids, as a result of hydrolysis, give solutions of appreciable but yet of such small OH' concentration that their caustic action is not annoying, though still sufficient to make their swelling and fat-solvent action effective.

It is evident that salts composed of two weak ions must be still more strongly hydrolyzed, without therefore the concentration of the $H^{\cdot}$ or OH' ions becoming greater than in the previously discussed case. The mass-action equation for the hydrolysis of such a salt can likewise be very simply derived. Take a salt such as ammonium cyanide or aniline acetate of the concentration c, and indicate, as before, the degree of hydrolysis by x, that is, the quantity of free acid and base formed by the water per mole of salt, then in the hydrolytic equilibrium we have:

$$x \cdot c \text{ free base} + x \cdot c \text{ free acid} + (1 - x)c \text{ non-hydrolyzed salt.}$$

Indicating further the dissociation constant of the base by k_b, of the acid by k_s, and the ionic product of water by k_w (at ordinary temperature 10^{-14}), then the following conditions of equilibrium must be fulfilled at the same time:

$$\text{1. For the base: } \frac{(\text{Cathions}) \cdot (\text{OH}')}{(\text{Undissoc. Base})} = k_b,$$

$$2.\ \text{For the acid: } \frac{(\text{Anions})\cdot(\text{H}^{\cdot})}{(\text{Undissoc. Acid})}=k_s\ ,$$

$$3.\ \text{For the water: } (\text{H}^{\cdot})\cdot(\text{OH}')=k_w.$$

On the strength of similar considerations as above (p. 79), we may place the concentrations of the undissociated base as well as the undissociated acid equal to their total concentration $(x\cdot c)$, and further, as experience has shown (of the four electrolytes here present only the neutral salt is to be considered as strongly dissociated), we may with useful approximation assume the concentration of the basic cathions as well as of the acid anions as equal to the concentration of the salt $(1-x)$. We obtain then

$$\left.\begin{aligned} 1.\ k_b &= \frac{(\text{OH}')\cdot(1-x)\cdot c}{x\cdot c} \\ 2.\ k_s &= \frac{(\text{H}^{\cdot})\cdot(1-x)\cdot c}{x\cdot c} \end{aligned}\right\}, \quad . \ . \ . \quad (14)$$

and by multiplying these two values, the relation

$$k_b\cdot k_s=(\text{H}^{\cdot})\cdot(\text{OH}')\cdot\left(\frac{(1-x)\cdot c}{x\cdot c}\right)^2=k_w\left(\frac{1-x}{x}\right)^2,$$

or (compare pp. 79, 80)

$$\frac{k_w}{k_b\cdot k_s}=\frac{(\text{Conc. Acid})\cdot(\text{Conc. Base})}{(\text{Conc. Salt})^2}, \ . \ . \quad (15)$$

after having introduced for the product $(\text{H}^{\cdot})\cdot(\text{OH}')$ its value k_w. We get for the hydrolysis of such a salt, consisting of two weak components, the interesting result that the hydrolyzed portion is entirely independent of the concentration of the salt, since this concentration falls out of the final equation. The correctness of this relation has been experimentally confirmed by Walker at the instigation of Arrhenius. The accompanying table on hydrolysis contains these results taken from the fundamental research of Arrhenius.[1]

DEGREES OF HYDROLYSIS.
(Shields, 1893, and Walker, 1900.)
Salts of Weak Acids.

	Shields, Found.	Walker, Calc.
0.1-N. Sodium acetate..................	0.008%	0.008%
0.1-N. Sodium bicarbonate..............	—	0.06
0.1-N. Sodium hydrosulphide............	—	0.14
0.1-N. Sodium metaborate.......... ...	—	0.84
0.1-N. Borax$=2NaBO_2+B_2O_3$.........	about 0.5	0.3
0.1-N. Sodium cyanide 0.1-N. Potassium cyanide }	1.1	0.96
0.1-N. Sodium phenolate 0.1-N. Potassium phenolate }	3.0	3.0

Salts of Weak Bases.

$^1/_{32}$-N. Aniline chlorhydrate........	2.6%
$^1/_{32}$-N. *p*-Toluidine chlorhydrate....	1.5
$^1/_{32}$-N. *o*-Toluidine chlorhydrate. ...	3.1
$^1/_{32}$-N. Chlorhydrate of urea.......	95.0

ANILINE CHLORHYDRATE.
(Bredig, 1894.)

$v=\frac{1}{c}$	$100x$	$\frac{1}{c}\cdot\frac{1-x}{x^2}=\frac{k\text{Aniline}}{k_w}$
32	2.63	45×10^3
64	3.90	40×10^3
128	5.47	40×10^3
256	7.68	40×10^3
512	10.4	42×10^3
1024	14.4	42×10^3

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[1] Zeitschr. physik. Chem., **5**, 18 (1890).

ANILINE ACETATE.
(Arrhenius and Walker, 1890.)

v	$100x$
12.5	54.6
25	55.8
50	56.4
100	55.1
200	55.6
400	55.4
800	56.9
	Mean: 55.7[1]

Of inorganic salts those of the following weak cathions show hydrolysis with acid reaction[2] when associated with strong anions:

$$Be^{\cdot\cdot},\ Hg_2^{\cdot\cdot},\ Hg^{\cdot\cdot},\ Cu^{\cdot\cdot},\ Al^{\cdot\cdot\cdot},\ Cr^{\cdot\cdot\cdot},\ Fe^{\cdot\cdot\cdot},\ Mn^{\cdot\cdot\cdot},\ Sn^{\cdot\cdot},\ Sn^{\cdot\cdot\cdot\cdot},\ Sb^{\cdot\cdot\cdot},\ Bi^{\cdot\cdot\cdot},\ U^{::::}.$$

With weak anions we usually have great insolubility, the formation of basic salts, or inappreciable dissociation ($Hg^{\cdot\cdot}$). Alkaline reaction is shown by the weak anions,

$$H_2BO_3',\ PO_4''',\ HPO_4'',\ HS',\ S'',\ CO_3'',\ HCO_3',\ CrO_4'',\ SiO_3'',\ SO_3'',\ ClO',\ NO_2',$$

when associated with strong (alkali) cathions; with weak cathions we have in all cases insolubility.

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[1] $\left(\frac{x}{1-x}\right)^2 = \left(\frac{0.557}{0.443}\right)^2 = 1.6;\qquad \frac{k_w}{k_b \cdot k_s} = \frac{1.2\times 10^{-14}}{4.9\times 10^{-10}\times 1.8\times 10^{-5}} = 1.4.$ Compare equation (15), p. 90.

[2] Concerning the quantitative relations, compare the thorough and comprehensive study of H. Ley, Zeitschr. physik. Chem., **30**, 193 (1899).

The other question, whether such a salt reacts alkaline or acid, may according to the above mathematical relations for k_b and k_s be very easily decided. If we recall that a neutral reaction means the same as the presence of equivalent amounts of $H^{\cdot}$ and OH' ions, or, in the form of equations,

$$(H^{\cdot})=(OH') \quad \text{or} \quad \frac{(H^{\cdot})}{(OH')}=1,$$

then by analogy the basic reaction must be formulated thus:

$$\frac{(H^{\cdot})}{(OH')}<1,$$

and the acid reaction:

$$\frac{(H^{\cdot})}{(OH')}>1;$$

and so we may express the value

$$\frac{(H^{\cdot})}{(OH')}$$

according to equation (14) (p. 90) in terms of the ratio $\frac{k_s}{k_b}$, for, as we see,

$$\frac{k_s}{k_b}=\frac{(H^{\cdot})}{(OH')}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

Hence we obtain acid reaction when, as with aniline acetate,

$$k_s>k_b,$$

basic (alkaline) reaction when, as with $(NH_4)_2CO_3$ or $(NH_4)_2S$,

$$k_s < k_b,$$

and neutral reaction when, as is approximately the case with $(NH_4)_2C_2H_3O_2$,

$$k_s = k_b.$$

The hydrolytic relations of a salt with two weak ions will also establish themselves if we add to a solution of a salt of one-sided weakness a salt that has a second weak ion of opposite nature. To cite an example, consider the hydrolysis of ammonium chloride, which is limited upon reaching a certain (in this case very small) $H^{\cdot}$ ion concentration. If we add another salt with a very weak anion, for example KHS or K_2CO_3, then its anion HS', or CO_3'', will consume the $H^{\cdot}$ ions, formed by the hydrolysis of the ammonium chloride, for the production of the undissociated acid H_2S or H_2CO_3 respectively. Herewith the previously existing check, which interfered with the progress of the NH_4Cl hydrolysis into $NH_3 + HCl$, is removed. The result is that the first NH_3-producing hydrolysis goes on and the newly formed $H^{\cdot}$ ions continue to be bound by the HS' or CO_3'' ions respectively, etc., so that the undissociated products of hydrolysis of a weak pair of ions must reach much higher concentrations. In the case selected this becomes very evident; for while a solution of NH_4Cl is so little hydrolyzed that there is no sign of the odor of ammonia, the odor is in evidence at once on the addition of K_2CO_3 or NaHS solution. In the latter case the odor of H_2S also appears as an indication that the HS′ ions have executed their H˙-binding action.

Such action is also made use of in analysis, for instance in the precipitation of Al˙˙˙ and Fe˙˙˙ by means of an acetate (see p. 142).

The hydrolytic relations may in addition be viewed from another side, by considering the possibility of arriving at and examining the equilibrium of a reaction not only by starting with the reacting substances (salt + water), but also by starting with the products of the reaction (acid + base).

We arrive at the equilibrium in the latter way by adding, we shall assume gradually, an equivalent amount of strong base to, for example, a weak acid (dissociation constant $= k_s$, ionic concentration in pure solution $= \sqrt{k_s}$, equivalent for anions and H˙ ions). Thereby we disturb the equilibrium of the weak acid, for we consume the H˙ ions of the same, which must form undissociated water with the OH′ ions of the added base. In consequence of which, in order to maintain the ionic product k_s, a quantity of acid anions must be produced equivalent to the consumed H˙ ions, and these in turn again reduce more and more the H˙ ion concentration, on account of the dissociation equilibrium of the weak acid, until finally this has become as small as is demanded by the H˙, OH′ equilibrium.

AVIDITY.

The phenomenon of hydrolysis, discussed in the preceding pages, is fundamentally nothing more than an interesting special case of a general and important equilibrium problem. Long before the time of the dissociation theory, this problem had been investigated thermochemically by Thomsen[1] and volume-chemically by Ostwald,[2] as the distribution of a base between two acids and an acid between two bases, and was termed by the former the avidity of acids and bases.

In order to dispose of the theory of the question, let us consider the case of having mixed in a liter of solution

b moles of a strong base (BOH),
c_1 moles of the acid$_1$ (HA_1), and
c_2 moles of the acid$_2$ (HA_2),

and let $b < c_1 + c_2$, i.e., the amount of the base is insufficient to neutralize both acids. If now we call x the fraction of each mole of base which reacts with the acid$_1$, then $(1-x)$ is evidently the fraction remaining for the acid$_2$.

In the resulting equilibrium there will be formed and be remaining:

Salt $BA_1 : bx$; Acid $HA_1 : c_1 - bx$;
Salt $BA_2 : b(1-x)$; Acid $HA_2 : c_2 - b(1-x)$.

If both acids are weak, and both salts, as is usually the case, almost completely dissociated, then the ionic concentration $(A_1') = bx$, $(A_2') = b(1-x)$, and the remaining portions of the acids may, on account of the presence of their salts (see pp. 70, 71), be considered

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[1] Thermochemische Untersuchungen. Leipzig, 1884.

[2] Journ. prakt. Chem. (2), **18**, 328 (1878).

as essentially undissociated; their small hydrogen ion concentration $(\mathrm{H}^{\cdot})$ in the solution has of course the same value. Accordingly, the dissociation constants k_1 and k_2 of the acids are represented by the following expressions:

$$k_1=\frac{(\mathrm{H}^{\cdot})(\mathrm{A}_1{}')}{(\mathrm{HA}_1)}=\frac{(\mathrm{H}^{\cdot})\cdot bx}{c_1-bx},$$

$$k_2=\frac{(\mathrm{H}^{\cdot})(\mathrm{A}_2{}')}{(\mathrm{HA}_2)}=\frac{(\mathrm{H}^{\cdot})b(1-x)}{c_2-b(1-x)},$$

so that the quotient

$$\left.\begin{aligned}
&\frac{k_1}{k_2}=\frac{(\text{Salt BA}_1)}{(\text{Salt BA}_2)}\cdot\frac{(\text{Acid HA}_2)}{(\text{Acid HA}_1)}=\frac{x}{1-x}\cdot\frac{c_2-b(1-x)}{c_1-bx}\\
&\text{or}\\
&\qquad\frac{(\text{Salt BA}_1)}{(\text{Salt BA}_2)}=\frac{k_1}{k_2}\cdot\frac{(\text{Free Acid HA}_1)}{(\text{Free Acid HA}_2)}
\end{aligned}\right\}\qquad(17)$$

represents the equation from which the distribution ratio of the base $\dfrac{x}{1-x}$ may be calculated for any case, as a function of the acid dissociation constants and their quantities (c_1 and c_2). The solution of this general equation leads to the expression

$$x=\frac{\begin{array}{c}(K-1)b+Kc_1+c_2\\ \pm\sqrt{[(K-1)b+Kc_1+c_2]^2-4(K-1)Kbc_1}\end{array}}{2(K-1)b},\qquad(18)$$

and

$$1-x=\frac{(K-1)b-Kc_1-c_2 \pm\sqrt{[(K-1)b+Kc_1+c_2]^2-4(K-1)Kbc_1}}{2(K-1)b},$$

in which

$$K=\frac{k_1}{k_2}.$$

The simplest case, investigated by Ostwald and theoretically calculated by Arrhenius, was the one in which equivalent quantities of a salt and a second acid were mixed, or, since we may look upon the salt as made up of one equivalent each of base and acid, it follows that in our general equation we must write $b=c_1=c_2$. That means that the above quotient (17) becomes

$$\frac{k_1}{k_2}=\frac{x}{1-x}\cdot\frac{b\cdot x}{b(1-x)}=\frac{x^2}{(1-x)^2},$$

or

$$\frac{x}{1-x}=\sqrt{\frac{k_1}{k_2}}. \quad . \quad . \quad . \quad . \quad . \quad . \qquad (19)$$

Since in the case of equal concentration the ionic concentrations of pure (unmixed) acids are to each other as the roots of their dissociation constants (p. 47), we may with Arrhenius also express this equation thus, that both acids divide themselves between the base in the same ratio as their degrees of dissociation would be, if each were present alone in the volume considered. Arrhenius derived this for the case of a strong and a weak acid.

In both cases Arrhenius compared his calculations with Ostwald's measurements, and found an excellent agreement, as the following examples show. They refer to solutions which contain of each of the three substances 0.33 moles per liter, resulting from the mixing of 1 liter of each of the three normal solutions. The figures in the table give the value x, that is, the portion of the first and stronger acid consumed per mole of base.

DISTRIBUTION-RATIO OF TWO ACIDS BETWEEN ONE BASE.
(Observed by Ostwald, 1878; Calculated by Arrhenius, 1889.)

	Observed.	Calculated.
$HNO_3 : Cl_2CH.COOH$	0.76	0.70
$HCl : Cl_2CH.COOH$	0.74	0.70
$CCl_3COOH : Cl_2CH.COOH$	0.71	0.70
$CHCl_2COOH : CH_3CH(OH)COOH$	0.91	0.95
$CCl_3COOH : CH_2ClCOOH$	0.92	0.92
$CCl_3COOH : HCOOH$	0.97	0.96
$HCOOH : CH_3CH(OH)COOH$	0.54	0.55
$HCOOH : CH_3COOH$	0.76	0.77
$HCOOH : C_3H_7COOH$	0.80	0.79
$HCOOH :$ iso-C_3H_7COOH	0.81	0.79
$HCOOH : C_2H_5COOH$	0.79	0.80
$HCOOH : CH_2OHCOOH$	0.44?	0.54
$CH_3COOH : C_3H_7COOH$	0.53	0.53
$CH_3COOH :$ iso-C_3H_7COOH	0.53	0.53

The more complicated case, the interaction of a weak acid with any concentration, not equivalent, of the salt of another weak acid $\left(b = c_1 \lessgtr c_2\right)$, was investigated by Wolf[1] by means of conductivity studies, and was found to agree splendidly with equation (18), easily simplified for this case.

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[1] Zeitschr. physik. Chem., 40, 226 (1902).

INDICATORS.

A number of weak electrolytes possess the peculiarity of having a very different color for the undissociated part and its ions, or of having only one of the two colored.

If the substances possessing a different color in the undissociated and dissociated condition are quite weak electrolytes, they may be employed as "indicators." This prerequisite makes it impossible for anything but bases and acids to be classed here, salts being excluded, since as a rule they are strongly dissociated.

In using indicators the purpose is to recognize whether a solution is neutral, or whether it contains $H^{\cdot}$ or OH' ions in excess. If the indicator is (1) an acid, then $H^{\cdot}$ ions work against its dissociation, that is, make its anions disappear, while OH' ions (by "salt formation" with the same) produce its anions; if on the other hand the indicator is (2) a base, then $H^{\cdot}$ ions react with the same to form salt, that is, produce its cathions, while OH' ions force back its dissociation, or, in other words, transfer the cathions to the undissociated substance.

It is scarcely necessary to add that, as far as the color change is concerned, only the anions of the acid or the cathions of the basic indicators come into question, since neither the $H^{\cdot}$ nor the OH' ion possesses color, as is proved by the existence of colorless acids and bases (see p. 13).

The theory of the action of indicators may be developed by means of the recently derived equations, if we only remember that here also we have the competition of two acids for one base, of which the indicator acid is one, or the competition of two bases for one acid, of which the indicator base is one.

An example will make the matter clear. Suppose we desire to titrate dichloracetic acid ($k_1 = 5.1 \times 10^{-2}$) by means of the indicator acid *p*-nitrophenol ($k_2 = 1.2 \times 10^{-7}$). (We shall see later that in this case it would be better to choose another indicator.) Nitrophenol is a weak acid, which by itself in an aqueous solution is so little dissociated that the intensely yellow color of the nitrophenol anion is scarcely perceptible. Upon the addition of a base, i.e., OH′ ions, it is, however, as good as completely converted into (H_2O and) nitrophenol salt, which means nitrophenol anions, and so gives rise to yellow color.

Let us assume that we are titrating 100 c.c. of a dichloracetic acid solution of the concentration $2c_1$ (per liter), to which a quantity of nitrophenol has been added such as to give the latter the concentration $2c_2$ (per liter), with an equally strong base, say potassium hydroxide, likewise of the concentration $2c_1$. We now add an amount of alkali which is exactly equivalent[1] to the dichloracetic acid, and apply the general avidity equation (see p. 97, equation [18]), in order to determine how much of the alkali goes to the dichloracetic acid (acid$_1$) and how much to the nitrophenol (acid$_2$), since these are the two acids competing for the base.

For the above case $K = \frac{k_1}{k_2} = \frac{5.1 \times 10^{-2}}{1.2 \times 10^{-7}} = 4.25 \times 10^5$, and also $b = c_1$. By introducing these values into equation

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[1] Thereby the original concentrations $2c_1$ and $2c_2$ sink to half the values, c_1 and c_2, on account of the doubling of the volume.

(18) and neglecting 1 as compared with K, then on the assumption that the indicator concentration $c_2=\frac{c_1}{1000}$, which will be about the equivalent of the quantities practically employed, we find in round numbers $\frac{5}{1000000}$ for the portion $1-x$, which is the portion left for the nitrophenol by the added base. That is, 999995 millionths of the dichloracetic acid is neutralized by the concentration c_1 of the base, and $\frac{5c_1}{1000000}$ falls to the concentration c_2 of the nitrophenol, which we assumed to be $=\frac{c_1}{1000}$. Hence $\frac{5}{1000}$ of the nitrophenol is first neutralized, i.e., $0.005c_2$ is the titer of the yellow nitrophenol anions. If now one more drop (=approx. 0.04 c.c.) of the titrating alkali of the concentration $2c_1$ is added, there is brought into the solution $0.04\times 2c_1=0.080c_1$ millimole of base, while there was still left in the approximately 200 c.c. of the titrating mixture $\frac{200\times 5\cdot c_1}{1000000}=0.001c_1$ millimole of free dichloracetic acid. Even if straightway all the dichloracetic acid would now be neutralized, there would still be left $0.079c_1=79c_2$ millimoles of alkali for the neutralization of nitrophenol, of which almost all of the $200c_2$ millimoles in the 200 c.c. are still present unneutralized. There will be formed, then, in our 200 c.c. of titrating liquid (outside of hydrolysis) about $79c_2$ millimoles of nitrophenol salt, which means a titer of $\frac{79c_2}{200}$=approx. $0.04c_2$ normal as to yellow nitrophenol

anions. With one drop of alkali less the titer $= 0.005c_2$; this drop then increased it about 80 times.

The calculation shows that it is of importance to choose an indicator with a somewhat small dissociation constant k_2, so that the same does not take up appreciable quantities of the base before the stronger acid is neutralized; the weaker the acid to be titrated is, the much more weak the indicator must be, since by the avidity equation the ratio of the constants is the determining factor. Likewise the indicator concentration must not be too great, so that the mass action does not compensate for the weakness; on the other hand, it is not advantageous to take the concentration too small, so that the first drop of excess of the titrating solution may be most effectively utilized to form the colored indicator ions. As a rule, then, it is best to take an amount of indicator equivalent to the quantity of acid or base contained in one drop of the titration liquid. This may be accomplished by adding to the reaction mixture one drop of an indicator solution made up equivalent to one of the titration liquids.

The selection of an indicator having a very small dissociation constant, such as phenolphthalein, makes it necessary that the base used in neutralization be strong. Suppose, for example, we titrate our acid with ammonia, using phenolphthalein as indicator, then in the first stages of the titration up nearly to the neutral point we would have formed essentially the ammonium salt of the acid to be neutralized, and so the first traces of excess of ammonia would find themselves in the presence of a large quantity of ammonium ions. These (according to p. 71) can bring only very few OH' ions into the solution and would not be able to dissociate the indicator acid to any marked extent, or, in other words, the ammonium salt of the indicator becomes far-reachingly hydrolyzed, which amounts to a non-formation of its colored ions. In such cases, therefore, it would require a considerable excess of ammonia to gradually form sufficient indicator ammonium salt to show the color change distinctly, that is, the turning-point would not be sharp. It is evident, then, that no very weak indicator acid can be employed in the titration of weak bases, but that we must employ relatively strong ones (always, however, much weaker than the acid taking part in the titration). Such relatively strong indicator acids are, for instance, nitrophenol and methyl orange. On the other hand, a very weak acid (or a strongly basic) indicator such as phenolphthalein is necessary in titrating weak acids, so that the indicator in its competition with the other acid does not successfully interfere (i.e., form anions) before the neutralization of the latter.

From this we may derive the following rule for the selection of the indicator acids (indicator bases are not in use). If we have to titrate:

1. Strong acid and strong base—indicator at random;
2. Strong acid and weak base—indicator strongest (methyl orange, nitrophenol);
3. Weak acid and strong base—indicator weakest (phenolphthalein, litmus);
4. Weak acid and weak base—to be avoided, since the color change with every indicator is not sharp.

The importance of the exact knowledge of the electrolytic equilibria for these relations is shown by the following question: Which indicator is to be chosen in order to titrate hydrochloric acid, containing ammonium chloride, with potassium hydroxide?

Having here case 1, one might think it permissible to choose at random and employ phenolphthalein as indicator, since it gives the sharpest color change, and potassium hydroxide is ordinarily easily titrated with it. In this case, however, we must remember that the $NH_4^{\cdot}$ ions of the ammonium chloride addition destroy the large OH' concentration of the first excess of potassium hydroxide by forming undissociated ammonia, and that phenolphthalein in order to form salt (red coloration) requires much OH'. Therefore, in order to get a sharp end-point it is necessary to use a stronger acid indicator; hence case 1 must be modified thus: if the solution contains a salt with a weak cathion, then the equilibrium relations correspond to those of case 2; if it contains a salt with a weak anion, then they become those of case 3.

HETEROGENEOUS ELECTROLYTIC EQUILIBRIA.

It is scarcely possible to treat here exhaustively every phase of electrolytic equilibria; for that reason let us consider only one more case, one which is of fundamental significance to analytical chemistry, namely, that the concentration of an electrolyte is limited by its solubility. As to form such equilibria become simpler, because the concentration or active mass of the substance, which is present in the state of saturation and is kept in this condition by the presence of the substance in the solid state, becomes constant. We have learned to recognize the electrolyte "water" as a substance of never varying concentration, whose ionic product, the water constant k_w, is unchanging, because the undissociated water always has very nearly the same concentration. Precisely the same holds for the ionic product of any substance whose saturation is maintained, for then, according to Nernst's partition law, the solution contains under all circumstances (at constant temperature) an invariable[1] concentration l of undissociated electrolyte. According to the law of mass action, the product of its ions $M^{\cdot n}$ and A'^{m} is

$$(M^{\cdot})^{n} \cdot (A')^{m} = k \cdot l = L,$$

in which, according to Ostwald, L stands for "solubility product" (or the ionic product). This equation shows us at once what the effect is of the addition of an electrolyte having, for instance, $M^{\cdot}$ in common: we have formed immediately more undissociated substance M_nA_m, but since the solution was previously saturated with the same, it precipitates until the ion A', not in common with the addition, is reduced so far that its concentration, following the above equation, has become

$$(A')^{m} = \frac{L}{(M^{\cdot})^{n}},$$

that is, upon increasing $M^{\cdot}$, A' becomes correspondingly smaller than originally.

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[1] It is true the presence of other electrolytes changes somewhat the solvent medium. Compare Arrhenius, Zeitschr. physik. Chem., **31**, 197 (1899).

This formulation we owe to Nernst,[1] and a thorough experimental testing to Noyes,[2] as well as to Goodwin,[3] who employed an entirely different method from that of Noyes, namely, the measurement of concentration chains. The quantitative agreement between theory and experiment still suffers from the uncertainty with which the ionic concentrations in strong electrolytes (see p. 121) are burdened, but nevertheless the same is sufficient to show the correctness of the law of solubility influence. The following small table taken from Noyes's measurements teaches especially that the equivalent addition of the one or the other ion has the same action on the solubility of a binary electrolyte:

SOLUBILITY OF THALLOUS CHLORIDE (25°).

(Noyes, 1890.)

Concentration of the Addition.	Addition: $TlNO_3$	Addition: HCl
0	0.0161	
0.0283	0.0083	0.0084
0.0560	0.0057	0.00565
0.147	0.0033	0.0032

With very insoluble salts, such as AgCl, the quantity in solution may be looked upon as very nearly completely dissociated, on account of its great dilution, so that only

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[1] Zeitschr. physik. Chem., **4**, 372 (1889).

[2] Ibid., **6**, 241 (1890).

[3] Ibid., **13**, 588 (1894).

a minimum portion of the quantity dissolved is undissociated substance, while the major portion is present as ions. If, for example, we reduce to $\frac{1}{10}$ the $Ag^{\cdot}$ ion concentration of a saturated AgCl solution by the addition of HCl (i.e., Cl'), it is practically equivalent to reducing the total amount of silver ($Ag^{\cdot}$ ions + undissoc. AgCl) present in the solution to $\frac{1}{10}$, even, if strictly speaking, the quantity of the undissociated AgCl is not changed at all in its concentration by the addition.

Let us now consider conversely a mixture of two electrolytes, each of which contains an ion of a difficultly soluble substance, for example $AgNO_3$ and KCl, and discuss the conditions, when and how much of the difficultly soluble substance is formed. In any case the quantity of undissociated AgCl becomes

$$k\cdot(\mathrm{AgCl})=(\mathrm{Ag}^{\cdot})(\mathrm{Cl}').$$

If either the $Ag^{\cdot}$ or Cl' ions or even both ions are very dilute, so that the concentration (AgCl) formed from these may be smaller than that required for saturation, then no precipitate of AgCl is produced, for not until we have $(\mathrm{Ag}^{\cdot})(\mathrm{Cl}') \gtreqless L$ can solid AgCl separate; from there on, however, an increase of either the one or the other kind of ion no longer produces an increase of the ionic product, since the value L is its maximum value. If both ions are present in equal quantity, then $(\mathrm{Ag}^{\cdot})=(\mathrm{Cl}')=\sqrt{L}$, the solubility of the silver chloride in water (more exactly, after subtracting the undissociated AgCl). The value of this solubility product L, which of course varies for different substances, is of fundamental significance in the formation and conversion of precipitates.[1] Several examples will show this.

If AgCl reacts with KI, AgI and KCl are formed. How far does this reaction go? In the common solution of the four substances the $Ag^{\cdot}$, Cl' equilibrium demands

$$(Ag^{\cdot}) = \frac{L_{AgCl}}{(Cl')},$$

and the $Ag^{\cdot}$, I' equilibrium,

$$(Ag^{\cdot}) = \frac{L_{AgI}}{(I')};$$

hence we have

$$\frac{L_{AgCl}}{L_{AgI}} = \frac{(Cl')}{(I')} = K.$$

That is, the interaction proceeds until the ratio of the $(Cl'):(I')$ ions has reached the constant value K, the quotient of the two solubility products. If therefore we use for the precipitation of any $Ag^{\cdot}$ solution a potassium chloride and iodide mixture in the ratio $(Cl'):(I') = L_{AgCl}:L_{AgI}$, then the difficultly soluble salts also precipitate in this ratio until the remaining $Ag^{\cdot}$ concentration satisfies both solubility products. If we further add KI to this equilibrium, this would disturb the equilibrium ratio $(Cl'):(I')$, and consequently the reaction $AgCl + I' = AgI + Cl'$ takes place, until the old value $(Cl'):(I')$ is attained; but also the reverse, the addition of KCl converts some AgI into AgCl with the production

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[1] See in particular Findlay, Zeitschr. physik. Chem., **34**, 413 (1900).

of I′. This latter change, however, will have to take place to only a very slight extent in order to raise the I′ concentration to the value of the equilibrium, since L_{AgI} is very much smaller than L_{AgCl}; according to Goodwin,[1] the latter is 1.56×10^{-10} and the former 0.94×10^{-16}, so that the concentration ratio of the equilibrium (Cl′) : (I′) must be equal to 1600000. From this it follows that even with the greatest concentrations of potassium chloride, practically speaking, no appreciable quantities of potassium iodide are left, but are as good as entirely consumed in the conversion of AgCl into AgI.[2]

An exactly analogous case occurring in analytical chemistry is Mohr's method for chlorine titration by means of silver solution with chromate addition. Silver chromate as well as chloride is difficultly soluble; however, the latter much more so than the former, so that the equilibrium ratio of the concentrations (CrO_4'') : (Cl′) is very large. As long, then, as we have present in the solution to be titrated much Cl′ as compared with the small amount of CrO_4'' (serving as indicator), essentially only AgCl can precipitate upon the addition of Ag˙ ions. Finally, when so much Cl′ has thereby been removed from solution (practically speaking, all) that the chromate ions can take part in the precipitation, the deep-brown silver chromate is formed alongside the white chloride. Conversely, in any solution containing an appreciable concentration of chloride, the brown precipitate of

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[1] l. c.

[2] In case the precipitates form solid solutions with one another, the relations are changed; compare F. W. Küster and Thiel, Zeitschr. anorg. Chem., **19**, 81; **23**, 25, **24**, 1; **33**, 129 (1899–1903).

Ag_2CrO_4 is completely converted into AgCl and soluble chromate, a fact employed in sounding ocean depths by means of a patent sounding instrument. In this, glass tubes are used closed at one end and lined on the inside with silver chromate; these are lowered into the ocean. As high as the sea-water enters the tube, corresponding to the pressure of the depth, the silver chromate is converted into white chloride, and the brown-white line of demarcation between the two permits the calculation of the compression to which the air within the tube was subjected at the greatest depth.

If we have two salts of the same metal, approximately equal as to insolubility, in equilibrium with a solution, then under all conditions we must also have in the solution an approximately equal concentration of the precipitating anions, or if they are not equal such equality must be brought about by one precipitate being changed into the other.

For example, if we have silver chloride present in a solution of silver nitrate, and precipitate the silver ions of the nitrate with the aid of KCNS, we obtain AgCNS as a second precipitate. So long as the precipitation of the silver is not complete, the solution will not be capable of containing sulphocyanate anions; as soon, however, as the first excess of sulphocyanate ions is added the equilibrium with the AgCl is disturbed, because suddenly the ratio $(CNS'):(Cl')$ in the solution is shifted very much in favor of CNS′. The equilibrium then adjusts itself in such a way that the excess of CNS′ ions reacts with AgCl to form AgCNS and Cl′ ions until the necessary $(Cl'):(CNS')$ concentration ratio is re-established. The result is that a sulphocyanate excess is not shown at once by the ferric indicator reaction, and in order to attain this, that is, prevent the reaction of the sulphocyanate with the AgCl, it is necessary in the Volhard chlorine titration method to remove the AgCl by filtration before the addition of sulphocyanate.

The greater the solubility product or the solubility of a precipitate is, the greater—for a given concentration of one of its ions—the other ion, contained in the "precipitating agent," must become before separation of the precipitate sets in.

The extreme of insolubility is probably that of the sulphides, which require as precipitating ions the sulphur ions S''. These S'' ions are contained in greatest concentration in the alkali sulphides, somewhat less in ammonium sulphide on account of hydrolysis, very much less in hydrogen sulphide, which, according to Walker,[1] splits up to a just measurable extent into the ions $H^{\cdot}$ and HS'. A 0.1-NH_2S solution, which is one almost saturated with H_2S at a pressure of 1 atm., contains only 0.000075 [2] mole HS' ions per liter; these in turn are further dissociated to an extremely limited extent according to the equation $HS' = H^{\cdot} + S''$. Hence the concentration of the S'' ions in an H_2S solution is exceedingly small and is made still smaller by the addition of acid, whose $H^{\cdot}$ ions force down the HS' ions to concentration magnitudes of about 10^{-9}. In spite of this, the inconceivably small S'' concentrations resulting are sufficient to enable a

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[1] Zeitschr. physik. Chem., **32**, 137 (1900); Journ. Chem. Soc., **77**, 5 (1900).

[2] $=\sqrt{5.7 \times 10^{-8} \times 0.1}$ (see p. 55).

whole series of metals to so easily reach their solubility products that they are precipitated even from their most dilute solutions.

It is plain to see now why we group qualitative analysis according to these sulphide solubilities, for:

1. The most insoluble sulphides are formed even with the few S″ ions of a strongly acid hydrogen sulphide solution, that is, they do not dissolve in acids (Pb, Ag, Hg, Cu, Bi, As, Pt, Au). In other words, they send so few S″ ions into solution that even with the high H˙ concentration of strong acids no H_2S is produced.

2. The very insoluble sulphides (Cd, Sn, Sb) are partly but not completely precipitated from a strongly acid solution, i.e., very small metal ion concentrations no longer give a precipitate with the extremely small S″ concentration, or the sulphides are dissolved (form H_2S) by concentrated acids.

3. The appreciably soluble sulphides (Zn, Co, Ni) precipitate only from neutral or H_2S solutions acidified with a weak acid, but usually not completely until the H˙ concentration of the liberated acid is reduced by means of sodium acetate, for example (see p. 71), thereby increasing the HS′ and S″ concentrations.

4. The markedly soluble sulphides (Mn, Fe) require for their precipitation high S″ concentration, which is only attainable in alkaline solution, i.e., a solution poor in H˙ (ammonium sulphide, sodium sulphide). Even weak acids such as acetic acid possess sufficient H˙ ions to form H_2S with the S″ ion of the aqueous solution of Mn or Fe sulphide—in other words, to dissolve the sulphide.

Of interest is also the behavior of difficultly soluble oxides and hydroxides, which, in so far as they are soluble in water, produce in addition to the particular cathion the anions O'' and OH' respectively. On account of the presence of water the equilibrium condition, $(H^{\cdot})^2 \cdot (O'') = k$ and $(H^{\cdot}) \cdot (OH') = k_w$ respectively (see p. 55), must always be fulfilled. This equilibrium constant is extremely small, so the $H^{\cdot}$ concentrations of the weakest acids are in most cases sufficient to dissolve, with the formation of H_2O, these difficultly soluble substances. Therefore only the most insoluble oxides (and hydroxides) are not dissolved in acids to an approximately quantitative extent, especially when the acid is at the same time a weak one.

A case of this was found by Jaeger[1] in dissolving HgO in H_2F_2. Here he found the ratio of the free acid remaining in the solution equilibrium to be $(H_2F_2) : (HgF_2) = 3.6$ as a mean. It is easy to see that this equilibrium is nothing more than a hydrolytic one, which is only distinguished from the former instances in that the base HgO liberated by the action of H_2O on the salt HgF_2 attains its saturation concentration and therefore enters equation (15) (p. 90) with constant active mass

$$\frac{(\text{Acid}) \cdot (\text{Base})}{(\text{Salt})} = \text{Hydrolytic Constant } k = \frac{(H_2F_2) \cdot (HgO)}{(HgF_2)},$$

so that, as found, $(H_2F_2) : (HgF_2)$ has a constant value (3.6).[2]

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[1] Zeitschr. anorg. Chem., **27**, 26 (1901).

[2] From which by (15), knowing the solubility of HgO, the dissociation constant of H_2F_2 could be calculated.

The solution of a precipitate is usually based upon the fact that one ion of the substance added unites with one ion of the difficultly soluble substance to form an undissociated body, and thereby disturbs the solubility product of the original precipitate. For instance, if we have a suspension of $BaCO_3$ in water, there are present dissolved in the water sufficient $Ba^{\cdot\cdot}$ and CO_3'' ions so that we have

$$(Ba^{\cdot\cdot}):(CO_3'')=L_{BaCO_3}.$$

An addition of acid, $H^{\cdot}$ ions, forms undissociated carbonic acid with the weak CO_3'' ions, whereby the CO_3'' concentration is reduced and a corresponding amount of the dissolved undissociated $BaCO_3$ is ionized; then, however, the undissociated part ceases to be saturated, and consequently more solid $BaCO_3$ passes into solution.

In general in the same way every precipitate not too insoluble and containing the anion of a very weak acid (carbonates, sulphides, cyanides, phosphates, oxalates, etc., and especially hydroxides) must be dissolved by $H^{\cdot}$ ions (acids), in that the anions are consumed in the production of the undissociated weak acids, among which water is to be counted.

Analogously the solvent action of ammonia and its derivatives upon the precipitates of many heavy metals is explained. The metal ions in these cases are to a very great extent taken up by the amines to form complex "amine" ions, and are thereby removed from participation in the solubility product, which in turn strives to re-establish itself at the expense of the undissociated portion of the dissolved solid, resulting in a solution of the precipitate.

Complex-forming ions, such as cyanogen and iodine ions, have a somewhat different kind of solvent action on cyanides (Cu, Ag, Cd, Ni, etc.) and iodides (Pb, Hg^{II}, Ag), because they take up the undissociated portions of these as a "neutral part,"[1] so that the solid must pass into solution in order to keep up the concentration of saturation.

Special attention has been attracted to several cases, more in the nature of curiosities, in which, by the interaction of a difficultly soluble (heavy metal) oxide and a neutral salt, alkaline reaction appears, i.e., OH' ions are formed. This, for example, takes place between HgO and KI. The dissociation theory also explains this phenomenon very simply. Let us consider the oxide ion equilibrium, which, since oxides are formed from metal $M^{\cdot}$ and OH' ions, may be formulated thus:

$$(M^{\cdot})(OH') = L_O,$$

in which L_O represents the solubility product of the oxide. Accordingly, every electrolyte, which consumes the cathions $M^{\cdot}$ either for the formation of a difficultly soluble compound (as AgI) or for a complex formation (as HgI_4'', $Ag(CN)_2'$, PbI_3', BF_4'), must bring about an increase of the OH' concentration, that is, an alkaline reaction.

So among others the following cases may be predicted, and are confirmed experimentally.[2]

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[1] See Abegg and Bodländer, Zeitschr. anorg. Chem., **20**, 471 (1899).

[2] Heinrich Biltz, in his "Experimentelle Einführung in die anorganische Chemie" (Kiel, 1898), p. 86, maintains that $HgO + 2KCN$ is

APPEARANCE OF BASIC REACTION BY INTERACTION OF NEUTRAL COMPOUNDS.

(Bersch, 1891 [Ostwald's Zeitschr., 8, 383]; Abegg, 1903.)

Oxide.	Neutral Salt.		Reaction Product.
PbO	Potassium	iodide	PbI_2
"	"	bromide	$PbBr_2$
$Fe(OH)_3$	"	fluoride	FeF_3 (undissoc.) (*L*)
"	"	oxalate	$Fe(C_2O_4)_3'''$ (complex) (*L*)
$Cu(OH)_2$	"	tartrate	Fehling ion (complex) (*L*)
"	"	sulphocyanate	Cu-sulphocyanate complex (*L*)
"	"	thiosulphate	Cu-thiosulphate complex (*L*)
Ag_2O	"	iodide	AgI
"	"	bromide	AgBr
"	"	chloride	AgCl
"	"	thiosulphate	Ag-thiosulphate complex (*L*)
HgO	"	iodide	HgI_4'' complex (*L*)
"	"	bromide	$HgBr_4''$ complex (*L*)
"	"	chloride	$HgCl_4''$ complex (*L*)
"	"	oxalate	Hg-oxalate complex (*L*)
"	"	thiosulphate	Hg-thiosulphate complex
$Cd(OH)_2$	"	iodide	$(CdI_2)n$ } inner complex, very little dissoc. (*L*)
"	"	bromide	$(CdBr_2)n$
"	"	chloride	$(CdCl_2)n$
$B(OH)_3$	"	fluoride	BF_4' complex (*L*)

All these reaction products, of course, do not react with alkalis to separate metal hydroxides.

A reverse curiosity, the appearance of an acid reaction upon the mixing of neutral $AgNO_3$ with alkaline Na_2HPO_4, is explained in an exactly analogous way by

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probably the only reaction of the kind. However, the above considerations of the case, based on the ionic theory, give, as we see, numerous reactions. The still more numerous cases in which KCN as a result of complex formation brings about alkaline reaction are purposely omitted, since, on account of the alkaline reaction of the KCN to begin with, they are not as striking as the above produced with absolutely neutral salts. In the cases marked (*L*) in the table, solution of the oxide occurs; in the others, conversion into a more difficultly soluble salt.

the ionic theory. The latter salt contains the ions $Na^{\cdot}$ and HPO_4'', and this anion dissociates with the separation of $H^{\cdot}$ ions, according to the equation

$$HPO_4'' \rightleftarrows H^{\cdot} + PO_4'''.$$

This dissociation is, however, exceedingly slight as long as appreciable amounts of OH' ions are present, owing to the hydrolysis of the Na_2HPO_4, which is due to the weakness of the anion. Since by the previous equation and the law of mass action

$$(H^{\cdot}) = k \cdot \frac{(HPO_4'')}{(PO_4''')},$$

the concentration of the $H^{\cdot}$ ions grows with diminishing PO_4''' ions, and the $Ag^{\cdot}$ ions remove these PO_4''' ions by precipitating Ag_3PO_4, so accordingly the addition of $AgNO_3$ must produce acid reaction.

As for the rest, the appearance of alkaline reaction is absolutely analogous to the appearance of acid reaction when we use a neutral salt such as $CuSO_4$, $HgCl_2$, or $AgNO_3$ to remove by means of its cathion (through producing insoluble sulphide) the S'' ions from H_2S and so force the hydrogen of the same to become ionic. This is usually described as decomposition of the salt and liberation of its acid by H_2S. In place of H_2S, of course any weak acid will serve which gives difficultly soluble metal compounds, i.e., such whose saturated solutions contain very few metal ions. The previously discussed case of Na_2HPO_4 is therefore only a special case of this general manifestation.

The salts of very insoluble hydroxides, such as those of $Al^{\cdot\cdot\cdot}$, $Cr^{\cdot\cdot\cdot}$, and $Fe^{\cdot\cdot\cdot}$, also give an acid reaction with the neutral water, because their cathions consume the OH' of the latter—a phenomenon that we have already learned to recognize as hydrolysis.

The common feature of all these reactions is that the metals and the acid anions combined with OH' and $H^{\cdot}$ respectively are contained in considerably smaller concentration in the compounds produced (precipitate, complex, or undissociated substance).

Heterogeneous equilibria may also appear in conjunction with hydrolysis, as shown by the action of water on tin, plumbic, bismuth, antimony, and the strongly dissociated mercurous and mercuric salts (nitrate and chlorate). Here the OH' ions of the water combine with the very weak cathions to form difficultly soluble basic salts, which precipitate as soon as hydrolysis has produced such quantities of them that they exceed the concentration of saturation. As a matter of course, acid reaction ($H^{\cdot}$ ions) appears here also and places a limit upon the hydrolysis.

The hydrolyzing OH' ions may by the addition of acid be so reduced at the very outset that no appreciable hydrolysis and hence no precipitation of basic salt takes place. This fact is likewise made use of in analytical chemistry.

Just as precipitating reactions, and through them the heterogeneous equilibria, play a leading part in analytical chemistry, so the knowledge of the numerical values of the solubility products L_s for the various precipitates is of primary importance. A series of determinations of this kind have been made by Goodwin,[1] Immerwahr,[2]

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[1] Zeitschr. physik. Chem., **13**, 641 (1894).

[2] Zeitschr. f. Elektrochem., **7**, 477 (1901).

Noyes,[1] Kohlrausch and Rose,[2] Bodländer,[3] Sherrill,[4] v. Ende,[5] Küster and Thiel, and others,[6] and the following figures are taken from these:

SATURATION CONCENTRATIONS AND SOLUBILITY PRODUCTS OF DIFFICULTLY SOLUBLE SALTS.

Ag_2O	$Ag^{\cdot}$	$=1.5 \times 10^{-4}$	$L_s=$ — —
$AgIO_3$	“	$=1.9 \times 10^{-4}$	“ $=3.6 \times 10^{-8}$
$AgCl$	“	$=1.25 \times 10^{-5}$	“ $=1.56 \times 10^{-10}$ (25^c)
$AgSCN$	“	$=1.1 \times 10^{-6}$	“ $=1.2 \times 10^{-12}$
$AgBr$	“	$=6.6 \times 10^{-7}$	“ $=4.35 \times 10^{-13}$ (25^c)
AgI	“	$=1.0 \times 10^{-8}$	“ $=1.0 \times 10^{-16}$ “
Ag_2CrO_4	“	$=1.7 \times 10^{-4}$	“ $=1.0 \times 10^{-11}$ (18^c)
$TlCl$	$Tl^{\cdot}$	$=1.6 \times 10^{-2}$	“ $=2.65 \times 10^{-4}$ (25^c)
$TlBr$	“	$=2.0 \times 10^{-3}$	“ $=4.0 \times 10^{-6}$ “
$TlBr$	“	$=8.7 \times 10^{-3}$	“ $=7.6 \times 10^{-5}$ (68.5^c)
$TlSCN$	“	$=1.5 \times 10^{-2}$	“ $=2.25 \times 10^{-4}$ (25^c)
Tl_2SO_4	“	$=9.0 \times 10^{-2}$	“ $=3.6 \times 10^{-4}$
$CuCl$	$Cu^{\cdot}$	$=1.1 \times 10^{-3}$	“ $=1.2 \times 10^{-6}$
$CuBr$	“	$=2.0 \times 10^{-4}$	“ $=4.15 \times 10^{-8}$
CuI	“	$=2.25 \times 10^{-6}$	“ $=5.1 \times 10^{-12}$
Hg_2Cl_2	$Hg_2^{\cdot\cdot}$	$=1.0 \times 10^{-6}$	“ $=3.5 \times 10^{-18}$ (25^c)
Hg_2Br_2	“	$=7.0 \times 10^{-8}$	“ $=1.3 \times 10^{-21}$
Hg_2I_2	“	$=3.0 \times 10^{-10}$	“ $=1.2 \times 10^{-28}$
Hg_2SO_4	“	$=8.5 \times 10^{-4}$	“ $=3.0 \times 10^{-10}$
$HgCl_2$	$Hg^{\cdot\cdot}$	$=0.9 \times 10^{-5}$	“ $=2.6 \times 10^{-15}$
$HgBr_2$	“	$=2.7 \times 10^{-7}$	“ $=8.0 \times 10^{-20}$
HgI_2	“	$=2.0 \times 10^{-10}$	“ $=3.2 \times 10^{-29}$
$PbCl_2$	$Pb^{\cdot\cdot}$	$=2.0 \times 10^{-2}$	“ $=1.0 \times 10^{-4}$
$PbBr_2$	“	$=2.0 \times 10^{-2}$	“ $=6.0 \times 10^{-6}$
PbI_2	“	$=1.8 \times 10^{-3}$	“ $=1.0 \times 10^{-7}$
$PbSO_4$	“	$=1.5 \times 10^{-4}$	“ $=2.2 \times 10^{-8}$

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[1] Zeitschr. physik. Chem., **6**, 241 (1890); **42**, 336 (1903).

[2] Ibid., **12**, 241 (1893)

[3] Zeitschr. anorg. Chem., **31**, 474 (1902).

[4] Zeitschr. physik. Chem., **43**, 705 (1903).

[5] Zeitschr. anorg. Chem., **26**, 129 (1901).

[6] Ibid., **24**, 57 (1900), and **33**, 129 (1903); see also Wilsmore, Zeitschr. physik. Chem., **35**, 305 (1900).

ANOMALY OF STRONG ELECTROLYTES.

While in the preceding discussions it is safe to say the law of mass action, as applied to an extended series of reactions between ions and undissociated substances, found its excellent verification, yet it seems in one especially simple and important case to utterly fail, namely, in the dissociation of the so-called strong electrolytes—the salts—and the strong acids and bases. Whether we derive the degree of dissociation of these electrolytes from the conductivity $\left(\alpha=\frac{\Lambda}{\Lambda_0}\right)$ or from the freezing-point $\left(\alpha=\frac{i-1}{n-1}\right)$, we arrive at values for the expression $\frac{\alpha^2 \cdot c}{1-\alpha}$ of the law of mass action which for the different concentrations c decidedly deviate from the demanded constant, and therewith prove that, for some reason, either the law of mass action is to be modified for these electrolytes, or the methods for the determination of the degree of dissociation α in these cases give incorrect values.

Recently this vulnerable spot of the dissociation theory has been very assiduously investigated and discussed, and we are indebted to Jahn in particular for a series of brilliant measurements of precision. He attempted to get at the degree of dissociation by a third method, namely, that of the measurement of concentration chains. Up to this time this method had hardly been used, because of its lack of sensitiveness for purposes of ordinary accuracy.

It would take us too far to give here the theoretical considerations which rest on the exact application of thermodynamics, especially as up to the present we can by no means look upon the problem as solved. There is a tendency on the one hand to assume that in the solutions of strong electrolytes the ratio of the equivalent conductivities for different concentrations cannot give the degree of dissociation accurately, because, in consequence of the variable friction, the mobility of the ions varies in the solutions according to the amount of salt contained and cannot be assumed as equal. On the other hand, the osmotic methods (depression of the freezing-point, etc.) might fail, for reasons which may be of a physical as well as of a chemical nature.

Nernst and Jahn[1] find the physical reasons in that there exists in the solution an interaction between the ions and the undissociated molecules, which counteracts their mutual independence and so causes the osmotic pressure to be different from that which, according to van't Hoff's law, corresponds to the concentration.

From the fact that the osmotic laws hold for non-electrolytes and weak electrolytes, Jahn draws the conclusion that such an interaction between the undissociated molecules may be neglected. He further makes it plausible that the ions have no marked influence on each other, since the electrostatic attractions of the unlike-charged are just counteracted by the repulsions of the like-charged; that is, there would be left only the interaction of the undissociated molecules with the ions, which would have to be considered accountable for the devia-

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[1] Zeitschr. physik. Chem., **33**, 545, **35**, 1; **37**, 490; **38**, 487; **41**, 257 (1900–1902).

tion of the osmotic pressure from van't Hoff's law. The mathematical form in which this is to take place has been shown in the latest investigation of Jahn, just referred to. The result is that the dissociation constant is not given by the formula

$$\frac{n^2}{N-n}=k, \text{ but should be expressed by } \frac{n^2}{N-n}\cdot e^{\frac{a(2n-N)}{n_0}}=k,$$

in which N is the total molecular concentration, n the ionic concentration, n_0 the molecular concentration of the solvent, e the base of natural logarithms, and a the characteristic constant of the interaction named.

That this formula agrees well with the freezing-point determinations is shown by the following calculation of Jahn, using Abegg's freezing-point determinations on KCl with the selection of a suitable a value:

N	0.0237	0.0354	0.0469	0.0583	0.0697	
n	0.0208	0.0302	0.0384	0.0463	0.0525	
$\frac{n^2}{N-n}\cdot e^{\frac{a(2n-N)}{n_0}}$	0.132	0.147	0.141	0.141	0.125	Mean: 0.137

The applicability of Jahn's equation only shows, however, as Jahn himself states, that the physical explanation is correct as to formulation. Indeed, it seems to us that a number of considerations demand another interpretation of these complicated relations. The physical point of view should lead to the conclusion that the interaction between ions and molecules should manifest itself with all strongly dissociated electrolytes; at least, it would not be clear why this influence should assume markedly different values for substances of a similar degree of dissociation.

But after all among Ostwald's[1] extended material there are to be found a number of strongly dissociated acids, such as dichloracetic acid, maleic acid, cyanacetic acid, and various bromine-substituted amidobenzene-sulphonic acids, for which Ostwald's simple dilution law, even up to degrees of dissociation as high as 98%, gives good constants. The following summarization contains some figures pertaining thereto; under 100α we have the degrees of dissociation in percentages up to those for which the dissociation constant k holds, and under v the dilutions for which the value 100α holds:

STRONG ELECTROLYTES WHICH OBEY THE DILUTION LAW.

	$10^2 \cdot k$	100α	v
Cl_2-acetic acid	5.14	93.4	256
CN-acetic acid	0.37	>82.1	1024
Maleic acid	1.17	92.8	1024
o-NH_2-benzene-sulphonic acid	0.33	>80	1024
(1:2:5) Br-NH_2-benzene-sulphonic acid	1.67	97	1652
(1:2:4:5) Br_2-NH_2-benzene-sulphonic acid	7.9	97.8	556
(1:3:4:5) Br_2-NH_2-benzene-sulphonic acid	2.5	96	1150

Again, other acids show the behavior characteristic of strong electrolytes in spite of great analogy in composition. In any case, according to this, it is not very likely that the high degree of dissociation essentially determines the deviation from the law of mass action, and certainly in the cases of the above-tabulated acids, at least, the conductivity is to be looked upon as a correct measure of the degree of dissociation.

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[1] l. c.; see p. 29.

Further, the physical assumption of Jahn still owes us an explanation as to whether or not the interaction which exists between many ions and few molecules (strongly dissociated substances) is not likewise observable between many molecules and few ions (weak electrolytes), as every analogy would lead us to expect.

The chemical facts which come into consideration for an explanation of the anomaly are on the one hand the formation of inner complexes, and on the other the hydration of the ions.

The formation of inner complexes was discovered by Hittorf[1] on cadmium salts in their transference behavior during electrolysis, and since then has been accepted as the explanation for the variability of the transference number with the dilution. It consists in an addition of the undissociated molecules to one of the ions of the electrolyte, and the extent to which it takes place depends on the concentration of the two components of the complex (ion and undissociated part). A quantitative investigation of inner-complex formation has not been possible thus far, but in addition to the investigations of Hittorf, those of Bredig,[2] Noyes,[3] and especially those of Steele[4] should be mentioned, which have experimentally placed the fact beyond doubt. Of these, Steele especially discusses in detail the necessity of this assumption of Hittorf.

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[1] Pogg. Ann., **106**, 385 and 546 (1859).

[2] Zeitschr. physik. Chem., **13**, 262 (1894).

[3] Ibid., **36**, 63 (1901).

[4] Ibid., **40**, 722 (1902).

That inner-complex formation is present even in the salts of very positive metals is made highly probable by the existence of such double salts as $K_3Na(SO_4)_2$ (glaserite), $KMgCl_3$ (carnallite), etc. We shall therefore have to take into consideration, even in the case of salts such as NaCl, etc., the possibility of an ionic formation such as, say, $Na^{\cdot}$ and $NaCl_2'$. With salts of metals of less electro-affinity, ionic formations of that kind are beyond doubt, as was experimentally demonstrated in every direction for $CoCl_2$, $CuCl_2$, $ZnCl_2$, etc., in the nice research of Donnan, Bassett, and Fox.[1]

It is well also to call attention to the fact that in the exact equation as developed by Jahn [2] for the electromotive force of concentration chains there is, in addition to the logarithmic factor with the ratio of the ionic concentrations, another factor proportional to the difference of the ionic concentrations. Such a factor would have to be present in case of the existence of ionic hydrates in order to give due consideration to the water combined with the ions [3] in the work of their transport from one concentration to the other.

The formation of inner complexes would reduce the concentration of the independent molecules so that the osmotic methods (freezing-point, etc.) would give smaller *i* values, as well as smaller α values, than demanded by

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[1] Trans. Chem. Soc., **81**, 944 (1902).

[2] Zeitschr. physik. Chem., **41**, 276 (1902).

[3] Compare Dolezalek, Theorie des Bleiakkumulators, p. 35 (Halle, 1901); also translation, Theory of the Lead Accumulator, p. 65 (Wiley & Sons, 1904); and F. Haber, Zeitschr. physik. Chem., **41** 399 (1902).

the law of mass action; accordingly, the dissociation constants, as calculated by means of the freezing-points, should diminish with increasing concentration. This agrees, for example, with the experience[1] on $RbNO_3$, though usually one observes in the constant thus calculated decidedly the reverse course.

Just as with their own undissociated molecules, the ions also form complexes with the solvent (hydrates), whose existence is likewise supported by extended experimental evidence.[2] Such a formation of hydrates, in distinction from the formation of inner complexes, would leave the number of moles of the dissolved electrolyte unchanged, while that of the solvent would be diminished, and so with increasing concentration one would reach an accelerated increase of the molecular concentration ratio, electrolyte : water, which agrees qualitatively with the course of the dissociation constants calculated from the freezing-points.[3] Even if the quantitative foundation for this explanation is wanting, it is still noteworthy and seems to speak in favor of the chemical explanation that cæsium nitrate, a salt of whose ions, according to a theory of Abegg and Bodländer (see later on p. 161), one is led to expect a minimum tendency to form complexes and hydrates, gives degrees of dissociation according to its freezing-point depressions, as determined by W. Biltz,[4] which are entirely in accord with the law of mass action, as the following table shows:

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[1] W. Biltz, Zeitschr. physik. Chem., **40**, 217 (1902).

[2] For literature, see Biltz, l. c., p. 214.

[3] For examples, see Jahn, l. c.

[4] l. c., p. 218.

CÆSIUM NITRATE.

c	$\frac{\Delta}{c}$	$i=\frac{\Delta}{1.85c}$	$\alpha=i-1$	$\frac{\alpha^2 c}{(1-\alpha)}=k$	
0.00766	3.66	1.98	0.98	0.33	
0.0194	3.61	1.95	0.95	0.35	
0.0465	3.53	1.91	0.91	0.41	
0.0988	3.35	1.81	0.81	0.34	
0.142	3.24	1.75	0.75	0.32	Mean: 0.34
0.210	3.15	1.704	0.704	0.35	
0.299	3.037	1.64	0.64	0.34	
0.386	2.914	1.575	0.575	0.30	
0.434	2.92	1.578	0.578	0.34	

Since the degrees of dissociation taken from the conductivity $\left(\alpha=\frac{\Lambda}{\Lambda_0}\right)$ of cæsium nitrate by W. Biltz and Jul. Meyer gave markedly greater values than the above and also led to no constant for $\frac{\alpha^2 c}{(1-\alpha)}$, it is plain to see that the conductivity in the case of this and no doubt many other salts is not a correct measure of the dissociation, while before (see p. 124), in regard to a number of acids of moderate strength, we were forced to the opposite conclusion.

With the anomalous strong electrolytes it seems that the conductivity in almost every instance gives the semblance of too high degrees of dissociation. Thus, for example, according to Biltz and Meyer, $CsNO_3$ gives

for c	$=0.25$	$0.125N$
Freezing-point	$\alpha=0.67$	0.78
Conductivity	$\alpha=0.76$	0.82

that is, with growing concentration we have a very marked increase in the discrepancy. This may, as Jahn assumes, be due to a decreasing ionic friction in the more concentrated solutions; however, several conclusions following from this are not, as tested by Sackur,[1] borne out by experiment.

We see, then, that this material still demands extended and searching investigation, but so much at least it seems we may say at present with reasonable certainty, that the law of mass action will prove itself, as usual, to hold absolutely also for strong electrolytes, as soon as we come into possession of perfect methods for obtaining the real ionic concentrations or degrees of dissociation.

As to strong electrolytes we must console ourselves, in so far as a complete molecular theoretical explanation is concerned, with the hope of a possibly near future; however, let us in addition mention several attempts to express the course of their conductivities in a mathematical formula. Rudolphi[2] was the first to give an equation for this, which was later transformed by van't Hoff and Kohlrausch[3] into

$$\frac{\alpha^3 \cdot c}{(1-\alpha)^2}=k,$$

in which, as hitherto, $\alpha=\frac{\Lambda}{\Lambda_0}$. The physical significance of this formula is:

$$(\text{Ionic concentration})^3=k\cdot(\text{Undissoc.})^2.$$

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[1] Zeitschr. f. Elektrochem., **7**, 475 (1901).

[2] Zeitschr. physik. Chem., **17**, 385 (1895).

[3] Ibid., **18**, 301, 662 (1895).

In order to give an idea of the extent to which this equation conforms to the observations, the following small table may be offered:

CONSTANTS OF VAN'T HOFF'S DILUTION LAW FOR STRONG BINARY ELECTROLYTES.

(van't Hoff, 1895.)

v	KNO_3 (18°)	$MgSO_4$ (18°)	HCl (18°)	KCl (99.4°)	KCl (18°)	NaCl (18°)	KBr (18°)	v	LiCl (18°)
2	1.63	—	4.41	1.83	2.49	1.87	2.44	2	1.27
4	1.67	0.162	4.87	1.79	2.23	1.71	2.55	10	1.16
8	1.68	0.156	4.43	1.76	2.1	1.6	2.28	20	1.07
16	1.72	0.151	4.72	1.92	1.94	1.4	2.38	33.3	1.02
32	1.82	0.151	5.29	1.9	1.87	1.43	2.41	100	0.92
64	1.88	0.158	—	1.78	1.72	1.38	2.72	—	—

For the sake of completeness we must mention an investigation by Storch,[1] who assumed that the dilution law is represented by a formula in which any power of the ionic concentration is written proportional to any other power of the concentration of the undissociated portion. In the formula of van't Hoff the ratio of these powers is 3:2, that is, equal to 1.5. Storch found by extended calculations that the power ratios, which are reproduced as nearly as possible in the conductivity observations, are somewhat different for the different electrolytes, KCl, KI, KOH, KNO_3, HCl, HNO_3, $MgSO_4$, $CuSO_4$, H_2SO_4, K_2SO_4, $BaCl_2$, $ZnCl_2$, varying, however, only between 1.40 and 1.577, so that in any case they approach very closely the value 1.5 of the van't Hoff formula. The close agreement with observed values makes it possible

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[1] Zeitschr. physik. Chem., **19**, 13 (1896).

to foresee that the formula,[1] for the present purely empirical, will some day give an interesting relationship between the real degree of dissociation and the $\frac{\Lambda}{\Lambda_0}$ values.

Before dismissing the question of the variability of the degree of dissociation with the concentration, it is necessary to inform ourselves as to the concentrations up to which the equation of the law of mass action or the so-called dissociation isotherm does hold. We may say, a priori, that it cannot hold without limits, for if we continuously increase the concentration of the electrolyte, in the first place we depart from the field of "ideal dilute" solutions, in which alone the van't Hoff laws for the osmotic pressure hold strictly, and secondly, the replacing of the solvent by dissolved electrolyte alters more and more the medium in which the equilibrium has to establish itself. We can no more expect of this reaction than of any other that it be independent of the nature of the solvent. The same conclusion follows from the consideration that in so far as we are dealing with dissolved electrolytic liquids for the limiting case of highest concentration, i.e., water-free electrolytes, the concentration of the ions must be extremely small, since even pure liquids, according to a rule to be mentioned later (see p. 155), possess only a very small conductivity of their own.

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[1] The recent attempt of Roloff (Zeitschr. angew. Chem., 1902, Heft 22–24, also separately published by Springer, Berlin, 1902) to establish a theoretical basis on the ground of the assumption of a variable dissociation of the water itself stands in direct contradiction to the facts, for the ionic product of water, even in concentrated solutions of electrolytes, has been found by the most diverse methods (see p. 56) to be entirely constant.

The field of these more concentrated solutions has recently been the subject of interesting researches by Wolf[1] and Rudorf,[2] whose results may best be discussed with the aid of one of the examples studied, namely, that of acetic acid. It was shown that the addition of acetic acid to any electrolyte acts in such a way as to reduce the mobility of the ions of the latter by a definite amount, proportional to the concentration of the acetic acid. This reduction of mobility is equal to about 9.3% per normal strength of the acid, so that, for instance, in a mixture of sodium chloride + 1-normal acetic acid the conductivity of the sodium chloride, no matter in what concentration it is present, is 9.3% less than in pure water. Since this influence upon the mobility of ions has shown itself to be entirely independent of their nature, nothing is easier than to assume that the acetic acid also affects the mobility of its own ions in the same measure, so that in a 1 normal acetic acid, for example, the value of the equivalent conductivity must again be less by 9.3% than if the same number of ions moved in pure water, as is the case at infinite dilution (Λ_0). In order, therefore, to get at the real degree of dissociation, the equivalent conductivity Λ for the high concentration is to be increased by the correction due to the retarding influence which the presence of the undissociated acid brings about. In fact, Abegg found that the constancy of the expression

$$\frac{(\text{Corr. }\Lambda)^2 \cdot c}{\Lambda_0 \cdot (\Lambda_0 - \text{Corr. }\Lambda)} = \text{Const.}$$

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[1] Zeitschr. physik. Chem., **40**, 253 (1902).

[2] Ibid., **43**, 257 (1903).

is fulfilled up to considerably higher values for *c* than is the case when the correction is not introduced. The following values are taken from the investigation of Rudorf, who took up the subject more exactly:

Acetic Acid (25°). $\varLambda_0 = 397$.

c	*Λ*	*k* (uncorr.)	Corr.-factor.	*k* (corr.)
0.019	12.3	1.88	1.002	1.88
0.039	8.57	1.85	1.004	1.87
0.078	6.08	1.84	1.007	1.87
0.157	4.23	1.81	1.015	1.86
0.313	2.97	1.76	1.029	1.86
0.627	2.01	1.62	1.059	1.82
1.254	1.29	1.33	1.118	1.67

The range of the reaction constants, or in other words the field within which the affinity manifestations of the ions possess the same intensity as in pure water or at extreme dilution, extends in this case to about 0.6-normal concentration. At higher concentrations where the constant, even by introducing the corrected *Λ* value, assumes other values than for dilute solutions, this deviation is undoubtedly to be attributed to the changing of the medium. And indeed I may draw the conclusion from Rudorf's investigation just alluded to, that this constant, variable with the medium, possesses the chemical significance belonging to it according to its derivation; for the same also regulates the ratios of the quantity of acetic acid ions and the undissociated acid, when the acetate ions are altered by the addition of strongly dissociated acetates.

INFLUENCE OF PRESSURE AND TEMPERATURE ON DISSOCIATION.

Now that we have considered in the preceding pages the influence of concentration on the degree of dissociation of electrolytes, the question arises, Upon what other additional influences is dissociation dependent? A general answer is given by the so-called thermodynamic principle of Le Chatelier, according to which, action on a system in equilibrium by an agent from without brings about a reaction that works against this external action. If, then, we attempt to increase by compression the pressure on such a system, that one of the two reactions in equilibrium (decomposition into ions or combination of ions to form undissociated molecules) will take place which gives a diminution in volume, for thereby the condition of stress in the system caused by the pressure is reduced. At the suggestion of Arrhenius, a fine piece of research pertaining to this influence was carried out by the Russian Fanjung,[1] whom, we regret to say, death claimed all too early. He worked with pressures as high as 260 atmospheres. The observed increases in conductivity for the highest pressures amount at most to about 9%, depending upon how great is the volume-difference between the

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[1] Zeitschr. physik. Chem., **14**, 673 (1894).

undissociated and dissociated acids (mostly organic). They are found to be in best agreement with the values calculated from this volume-difference. It is plain to see, however, that the pressure variations occurring in every-day life have no effect in any way noteworthy on the dissociation of electrolytes.

On the other hand, the influence that temperature changes may have on dissociation is very marked. If we wish to determine this from a study of the conductivities, it is necessary, in the first place, to consider the superimposed influence of the changed ionic friction or ionic mobility discussed on p. 35 and following pages. The conductivity changes conditioned on mobility evidently are not linked with a temperature influence on the degree of dissociation, for the variation in conductivity caused by variation in temperature can be attributed, and in fact in many cases is to be attributed, essentially to changed ionic mobility, without the degree of dissociation of the electrolyte having at the same time undergone any alteration. To put it mathematically, in the expression $\alpha = \frac{\Lambda}{\Lambda_0}$ not only Λ but Λ_0 as well is changed in the same ratio by the temperature.

Again, the temperature influence on the dissociation is given by applying the principle of Le Chatelier. The addition of heat will alter the degree of dissociation in the direction of that reaction which absorbs heat; that is, in case the ionic dissociation is endothermic the dissociation will increase upon heating; in case it is exothermic it will decrease. A number of methods may be employed to determine the heat effect of ionic decomposition or the heat of dissociation (ionization), which are based on the previously mentioned law of the thermo-neutrality of strong electrolytes. According to this law, the mixing of two electrolytes produces no heat effect when all of their constituents continue in the ionic state after mixing. Take, for example, the electrolytes $KC_2H_3O_2$ and HCl, and let us assume, contrary to the facts, that upon mixing they do not form undissociated acetic acid, but that the acetate′ and H˙ ions continue to exist alongside of each other; then in this case the mixing would not involve a heat of reaction. However, the heat of reaction occurring in reality is to be attributed directly to the circumstance that H˙ and acetate′ ions unite to produce undissociated acetic acid, and so we have in this heat of reaction between potassium acetate and hydrochloric acid the immediate heat effect of the formation of undissociated acetic acid from its ions. The negative value would therefore represent the heat of dissociation of acetic acid. This method of determining the heat of dissociation may be described as the mixing of two strongly dissociated compounds, of which each contains one of the ionic components of the weakly dissociated substance whose heat of dissociation is sought, and which in the process of mixing is formed in the undissociated state.

Another method, very similar in principle to the one just mentioned, is based on the fact alluded to above (see p. 59), that the neutralization of strong acids and bases by one another always produces the same heat effect, 13700 cal. per gram-equivalent. Deviations from this heat of neutralization, which essentially represents the heat effect of the formation of water from H˙ and OH′

ions, are to be found whenever weak acids or bases are neutralized by one another, as the table below shows.

The deviations explain themselves in that, in addition to the formation of water, a further reaction takes place. Since the neutral salt solution formed is strongly dissociated according to the general rule, while before neutralization one of its ionic components was appreciably undissociated, being combined with one of the ions of water, it follows that in such a neutralization a dissociation of the weak electrolyte employed must result at the same time. The equation of such a reaction will best elucidate the facts. For that purpose let us consider, say, the neutralization of NaOH by acetic acid, and assume as an approximation that NaOH is completely dissociated, while only the

Heats of Neutralization.

(Thomsen.)

By NaOH.		By HCl.	
Weak Acids.		*Weak Bases.*	
Metaphosphoric acid	14300 cal.	Ammonia	12200 cal.
Hypophosphorous acid	15100 "	Methylamine	13100 "
Hydrofluoric acid	16300 "	Dimethylamine	11800 "
Acetic acid	13400 "	Trimethylamine	8700 "
Chloracetic acid	14300 "		
Dichloracetic acid	14800 "		
Strong Acids.		*Strong Bases.*	
HCl	13700 cal.	LiOH	13800 cal.
HBr	13700 "	NaOH	13700 "
$HClO_3$	13800 "	$Ba(OH)_2$	13900 "
HNO_3	13700 "	Tetramethylammonium hydroxide	13700 "

(small) fraction α per mole of the acetic acid is present in the form of ions, and the larger portion $(1-\alpha)$ is in undissociated combination with the $H^{\cdot}$ ions. If now we mix one mole of each of the two substances and write the equation in such a way that we separate the ions and undissociated portions from each other, then the neutralization equation will read:

$$1\ \text{Na}^{\cdot}+1\ \text{OH}'+\alpha\ \text{H}^{\cdot}+\alpha\ \text{Acetate}'+(1-\alpha)\text{H acetate}$$
$$=1\ \text{Na}^{\cdot}+1\ \text{Acetate}'+\text{H}_2\text{O}+a\ \text{cal.}$$

If we combine with it the further assumed equation

$$1\ \text{Na}^{\cdot}+1\ \text{OH}'+1\ \text{H}^{\cdot}+1\ \text{Acetate}'$$
$$=1\ \text{Na}^{\cdot}+1\ \text{Acetate}'+\text{H}_2\text{O}+13700\ \text{cal.},$$

which would apply if acetic acid were a strong, almost completely dissociated acid, we get, by subtracting the first equation from the second, the following simple expression:

$$(1-\alpha)\text{H}^{\cdot}+(1-\alpha)\ \text{Acetate}'$$
$$=(1-\alpha)\text{H acetate}+(13700-a)\ \text{cal.}$$

or

$$\text{H acetate}=\text{H}^{\cdot}+\text{Acetate}'+\frac{a-13700}{1-\alpha}\ \text{cal.}$$

That is, the observed heat of reaction a diminished by 13700 cal. represents the heat of dissociation for $1-\alpha$ moles of the weak acid or base when we neutralize the same by a strong base or acid and divide the heat effect, diminished by 13700 cal., by $1-\alpha$. With a weak acid $1-\alpha=1$, very nearly, α being very small.

Experimentally this way of obtaining the heat of dissociation is not very advantageous, because it generally gives the sought magnitude as a small difference of two large heat effects, so that the experimental errors play a very important part in this difference. It is unlike the previous method in that we start with the weakly dissociated compound and end with the strongly dissociated salt of the same; that is, to a certain extent it is the reverse of the first, in which we prepare the undissociated substance from the strongly dissociated salt by means of a strongly dissociated acid or base. The heats of dissociation obtained by either of these two methods may serve to calculate the influence of temperature change on the degree of dissociation by employing the thermodynamic equation derived by Arrhenius,[1]

$$\frac{dlnk}{dT} = \frac{W}{RT^2},$$

in which k signifies the dissociation constant, W the heat of dissociation, T the absolute temperature, and R the gas constant in calorimetric units (1.99).

It is true Arrhenius followed the reverse course, in that he calculated the heat of dissociation W from the variability with the temperature of the conductivity or of the dissociation constant k, and compared it with the results obtained by the methods indicated above. From these conceptions of Arrhenius it was possible to predict an interesting case of conductivity: that with electrolytes whose heat of dissociation is strongly positive, rise in temperature is followed by such marked reduction in the degree of dissociation that the increase in conductivity resulting from the enhanced ionic mobility is covered up. In fact, in this way it has been possible, in cases like

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[1] Zeitschr. physik. Chem., 9, 339 (1892).

phosphoric and hypophosphorous acids, to establish experimentally such reductions in conductivity. This was the more striking since it was generally thought that the characteristic difference between electrolytic and metallic conductivity was the negative temperature coefficient of the latter, i.e., reduction in conductivity with rise in temperature.

In the following table a series of heats of dissociation is given, from a consideration of which, however, nothing in the way of a relationship between these values and the chemical nature of the substances has resulted. It is worthy of note nevertheless that they are all markedly variable with the temperature.

HEATS OF DISSOCIATION.

(Arrhenius, 1889, 1892; Thomsen, 1882; Baur, 1897.)

(Exothermic dissociation taken negative, as is customary in thermodynamics.)

	35°	21.5°
Acetic acid	− 386 cal.	+ 28 cal
Propionic acid	− 557 "	− 183 "
Butyric acid	− 935 "	− 427 "
Succinic acid	+ 445 "	+ 1115 "
Dichloracetic acid	− 2893 "	− 2924 "
Phosphoric acid	− 2458 "	− 2103 "
Hypophosphorous acid	− 4301 "	− 3745 "
Hydrofluoric acid	− 3549 "	—
Water	(10.14°) + 14247 "	(24.6°) + 13627 "

Interpolation-formula: $\frac{4045000}{(273+t)}$ after Kohlrausch and Heydweiller.

	5°	15°	25°	35°
Nitrourea	+5477	+3812	+3640	—
Nitrourethane	+3665	+3724	+2943	+2260
Amidotetrazole	+4724	+5258	+4593	+3865

The heat effects are in part positive, in part negative, and in many instances quite small, which is in keeping with the fact that frequently the dissociation into ions takes place without very great energy changes. The heats of dissociation of salts as calculated by Arrhenius are to be looked upon as uncertain, for the reason that (see p. 121) we are still in doubt on the dissociation of the same as calculated from the conductivities. The substances of special interest are those with very great heat of dissociation, because this corresponds to a great variation of the degree of dissociation with the temperature, as we saw above from the conductivities of the two acids of phosphorus. The most interesting substance in this regard, because the most extreme, is water, whose decomposition into ions absorbs the enormous quantity of 13700 cal. of heat. From this, according to the equation of Arrhenius, we can predict that the usually small temperature influence on the dissociation, and therewith on the conductivity, must be abnormally great in the case of water. Kohlrausch and Heydweiller, in their previously mentioned investigation, had occasion to test this conclusion of the dissociation theory. They calculated the temperature coefficient of the conductivity of pure water by the equation of Arrhenius and found it to be 5.8% per 1°,[1] while the otherwise largest known temperature coefficients are those of the salts, which at most scarcely amount to one half as much. The investigators named found the highest value for the temperature influence on the conductivity of water, that is, the influence peculiar to

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[1] Wied. Ann., **53**, 231 (1894).

water least contaminated, to be 5.3%, and they were able to calculate, by means of the deviation of this value from that theoretically found, that the purest water obtained by them still contained impurities to the extent of several thousandths of a milligram per liter. For the pure water the observations gave conductivities at the different temperatures which led to the degrees of dissociation contained in the following table:

DISSOCIATION OF WATER AT DIFFERENT TEMPERATURES.

(Kohlrausch and Heydweiller, 1894.)

	0°	2°	10°	18°	26°	34°	42°	50°	100°	
Ionic concentration/Liter. . .	0.35	0.39	0.56	0.80	1.09	1.47	1.93	2.48	8.5	$\times 10^{-7}$
k_w	0.12	0.15	0.31	0.64	1.2	2.15	3.7	6.15	72.0	$\times 10^{-14}$

We see how rapidly the dissociation of the water rises with the temperature, and that, for example, at 50° it is already more than three times greater than at the ordinary temperature. For the phenomenon of hydrolysis this fact is of very great importance, since, as we saw (p. 76), the degree of hydrolysis is determined by the ionic concentration raised to the second power, which is the water constant k_w. Correspondingly, hydrolysis greatly increases at higher temperatures. A whole series of chemical experiences may be explained on this basis. If, for example, we color a neutral ammonium salt solution with litmus and heat it, we observe that at higher temperatures a distinct red color sets in, indicative of the fact that an appreciable quantity of free hydrochloric acid has been separated, or, in the language of the dissociation theory, undissociated ammonium hydroxide has been formed from the ammonium ions and the hydroxyl ions of the water. A further phenomenon belonging here and made use of in analysis is the precipitation of difficultly soluble hydroxides by inducing the hydrolysis of their weak salts. This happens, for instance, in the precipitation of basic ferric acetate from a solution of ferric chloride by an alkali-acetate, and it may be of interest to consider this action somewhat more in detail. These last two salts we may look upon as markedly dissociated, notwithstanding the fact that the ferric chloride is considerably hydrolyzed on account of the weakness of its base, and so mixing them gives the ferric ions an opportunity to combine with the acetate ions. We have before us, then, such an electrolytic combination of two weak ions as was described on p. 89. The $H^{\cdot}$ ions, that in the case of the chloride bring the hydrolysis to a standstill, are checked in their formation by the acetate ions present, and in consequence hydrolysis sets in to a considerably greater extent and leads to the formation of a much larger amount of basic ferric acetate along with undissociated acetic acid. The raising of the temperature favors still further this hydrolysis, so that we are in position to increase the concentration of the undissociated ferric hydroxide to such a point that the solvent capacity of the water for this substance is passed, the solution becomes saturated, and all further formed hydroxide must precipitate. Chromic hydroxide and aluminium hydroxide, as is well known, are also precipitated by the hydrolysis of their solutions containing acetate.

To return once more briefly to heats of dissociation, the following deserves mention. In a number of cases it has been found that organic substances which are capable of acting either as an acid or a base must, before splitting up into ions, undergo a molecular rearrangement, that is, change into an isomeric form. We are indebted to the interesting investigations of Hantzsch for an entire series of examples of such so-called pseudo acids and bases, which in dissociating suffer this sort of rearrangement, and it seems as though in all of these electrolytic substances the heats of dissociation are especially large. These heats of dissociation manifest themselves either in the great variation of the degree of dissociation and the conductivity with the temperature, or in the heats of neutralization of these substances deviating considerably from the value 13700 cal. While there seem to be as yet no investigations pertaining to the latter fact, violuric acid and oximido-oxazolon offer two cases of the first kind, for which Guinchard[1] determined the variation of the dissociation constants with the temperature, and by means of this the heat of dissociation of violuric acid is calculated to be 3700 cal.[2]

The reaction of the intermolecular rearrangement preceding the dissociation must of course produce a certain heat effect, which appears as a part of the heat of dissociation. It is likely, therefore, that we are permitted to generalize to the extent of saying that intermolecular reaction and high heat of dissociation are bound together

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[1] Ber. d. deutsch. chem. Ges., **32**, 1723 (1899).

[2] Ibid., **33**, 393 (1900).

by a common cause. This holds without doubt not only for the two cases mentioned above, but in all probability for two other cases of high heat of dissociation given in the table (p. 140), namely, hydrofluoric acid and water, since hydrofluoric acid is essentially present in the form of the molecules H_2F_2, not only in the gaseous state but also in solution,[1] and must pass through the intermolecular reaction

$$H_2F_2 = 2HF$$

in order to dissociate into the ions $H^{\cdot}$ and F'. Also in the case of water a similar intermolecular reaction is more than probable, for the most varied facts have led to the conclusion that the water molecules in the liquid state are exceedingly strongly polymerized, so that they must likewise first break up into simple molecules of the formula H_2O in order to form $H^{\cdot}$ and OH' ions. We cannot, however, consider this relation between high heat of dissociation and inner reaction as altogether general, because the phenols and a number of other substances likewise show high heats of dissociation[2] without indications of the probability of intermolecular reactions. It seems of importance, nevertheless, that the fact of the presence of great heat of dissociation has recently led Hantzsch[3] to make the interesting discovery that the salts of phosphorous acid are capable of existing in the form

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[1] See Jaeger, Zeitschr. anorg. Chem., **27**, 28 (1901); Abegg and Herz, ibid., **35**, 129 (1903).

[2] See Hantzsch, Ber. d. deutsch. chem. Ges., **32**, 3073 (1899).

[3] Zeitschr. f. Elektrochem., **8**, 484 (1902).

of two structural isomers. That is, phosphorous acid also exists in two isomers of tautomeric form, and so for this acid it likewise appears that high heat of dissociation (great temperature coefficient of the conductivity, Arrhenius) is bound up with the possibility of intermolecular reaction.

NON-AQUEOUS SOLUTIONS.

All our previous discussions concerning dissociation have been confined to solutions in which water was the solvent. This was done not alone for the reason that the investigation of dissociation and conductivity was first carried through on aqueous solutions, but because here we have arrived at comparatively simple results, and because the property of behaving as an electrolyte is an especially conspicuous peculiarity of the particular compounds when dissolved in water. The capacity for ionic decomposition of those substances which have been recognized as electrolytes in water also makes its appearance more or less distinctly in other solvents. In fact, the nature of the solvent plays an exceedingly important rôle, so that it has been possible to arrange the various media in a series according to their " dissociating " power, which series agrees for most solutes.

One important advance in the question as to what other physical or chemical properties of substances the dissociating power of solvents is associated with was made by Nernst [1] and Thomson, and is based on a consideration of the dielectric constant. This constant of a medium is characteristic of the force with which two electrically charged bodies within this medium attract or repel each other; the greater the constant is the smaller becomes the

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[1] Zeitschr. physik. Chem., **13**, 531 (1894).

mutual force manifest between the electrically charged particles, the distance between the same remaining equal. Now the ions are also to be considered as such electrically charged parts, and accordingly the forces of attraction between the ions must become smaller, and their separation from one another easier, the higher the dielectric constant of the medium is. It follows that the dissociation of substances should be especially great in that medium with the highest dielectric constant. In the table are given the dielectric constants of a number of substances at ordinary temperature.

DIELECTRIC CONSTANTS.[1]

Hydrocyanic acid, HCN	95.0
Hydrogen peroxide, H_2O_2	92.8
Water, H_2O	81.0
Formic acid, $HCOOH$	57.0
Acetonitrile, CH_3CN	36.4
Nitrobenzene, $C_6H_5NO_2$	34.0
Methyl alcohol, CH_3OH	32.5
Propionitrile, C_2H_5CN	26.5
Benzonitrile, C_6H_5CN	26.0
Ethyl alcohol, C_2H_5OH	22.0
Liquefied ammonia, NH_3	22.0 **(−34°)**
Acetone, $(CH_3)_2CO$	20.7
Glycerine, $C_3H_5(OH)_3$	16.5
Liquefied sulphur dioxide, SO_2	14.8
Pyridine, C_5H_5N	12.4
Aniline, $C_6H_5NH_2$	7.2
Acetic acid, CH_3COOH	6.5
Chloroform, $CHCl_3$	5.0
Ether, $(C_2H_5)_2O$	4.4
Benzene, C_6H_6	2.3

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[1] Schlundt, Journ. Physic. Chem., 5, 165 (1901).—Drude, Zeitschr. physik. Chem., **23**, 308 (1897).—Linde, Wied. Ann., **56**, 563(1895).—Goodwin and de Kay Thompson, Phys. Review, **8**, 38 (1899).—Calvert, Drud. Ann., **1**, 483 (1900).—Coolidge, Wied. Ann., **69**, 125 (1899).—Mathews, Bibliography of Dielect. Consts., Journ. Physic. Chem., **9**, 667 (1905).

We see hereby that water must possess an abnormally high power of dissociation, since of all common solvents it has by far the greatest dielectric constant, and in general it seems that the order given in the table agrees approximately with that found in studying the ionic dissociation of electrolytes in various solvents by means of the conductivities. Of especial interest in this connection is an investigation of Centnerszwer,[1] who found the equivalent conductivities of potassium iodide and trimethyl sulphine iodide in HCN at 0° to be about four times as great as the corresponding figures for aqueous solutions. This is about as great as the equivalent conductivities of the best-conducting electrolytes, the acids in water solutions at 25°, and even if it does not necessarily follow (see later on) that the dissociation is greater than in water, nevertheless this is at least possible. If such were the case, it would be in best agreement with what one must expect according to the high dielectric constant of HCN.

On the other hand, however, these investigations have evidently shown that the dielectric constant cannot alone be the determining factor for the dissociation; moreover, purely chemical questions seem to be very vitally concerned. For example, according to the table of dielectric constants, it was to be expected that the solutions in benzonitrile and propionitrile would be equally dissociated and consequently also would show about the same conductivity. A comparison by Schlundt[2] of the conductivities of silver nitrate in these two dielectrically

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[1] Zeitschr. physik. Chem., **39**, 217 (1902).

[2] Journ. Physic. Chem., **5**, 168 (1901).

equal solvents, as measured by Lincoln, and Dutoit, gave large differences in the sense that the conductivity in propionitrile corresponds to a markedly greater ionic concentration. This fact and others are strikingly in accord with another assumption as to the reason for the difference in dissociating power, brought forward by Dutoit,[1] namely, the ability of the solvent to associate, forming polymerized molecules. Brühl,[2] for his part, finds a connection with the question whether or not the solutions contain atoms whose valences in the compound are not as yet completely saturated. These two views seem to me to mean practically the same thing, for the reason that evidently the ability to associate is conditioned upon the presence of unsaturated valences. For the two nitriles mentioned, the view that polymerization plays a part agrees excellently with the facts, in so far as the researches of Ramsay and Shields[3] have shown that propionitrile is considerably polymerized, while benzonitrile does not associate. The conclusions pertaining to ionic dissociation, derived from the conductivities in these non-aqueous solvents, are subject to considerable uncertainty, because in only a few cases and for only a few electrolytes have we been able to determine the values for Λ_0, the limit value of the equivalent conductivity for great dilution. Therefore the absolute values of the equivalent conductivity give only a very uncertain approximation for the degree of dissociation, and, strictly speaking, express

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[1] Compt. rend., **125**, 240; Bull. soc. chim. (3), **19**, 321 (1898).

[2] Ber. d. deutsch. chem. Ges., **28**, 2866 (1895); Zeitschr. physik. Chem., **27**, 319 (1898); **30**, 1 (1899).

[3] Zeitschr. physik. Chem., **12**, 433 (1893).

nothing more than that there are ions present in a solution, and in what way the number of ions varies in the same solvent with varying concentration. A comparison of different solvents with one another is altogether impossible under these conditions, since the conductivities (see p. 29) are dependent not only on the degree of dissociation but also very much upon the mobility of the ions, and this mobility stands in an entirely unknown relation to the nature of the solvent. For that reason the attempt has been made to employ the other method which in the case of aqueous solutions has been found to be serviceable, namely, to measure the degree of dissociation in these solvents by means of the osmotic pressures (from freezing-point, boiling-point, or vapor-pressure determinations). And indeed in many cases, for example solutions in the various alcohols, it has been demonstrated that electrolytes, or substances which possess conductivity in these solvents, also show an increased molar number (an abnormality factor $i > 1$), as is to be expected from the expression previously derived (see p. 9),

$$i = 1 + (n - 1) \cdot \alpha.$$

However, not only have i values been found (by osmotic methods) which appear much too small to be made to harmonize with the uncertain degrees of dissociation derived from the α values (electrically determined), but in a number of cases i values have been obtained that are even smaller than 1, in spite of the fact that the presence of conductivity proves the presence of an appreciable degree of dissociation. These facts, which have unnecessarily awakened doubt as to the foundations of the dissociation theory,[1] give us a clue to wherein consists the explanation of the anomalous behavior of the non-aqueous solutions. We may, for instance, maintain the relation between i and α if we admit the possibility that the undissociated molecules of the electrolyte associate to form polymerized molecules. Measurements have shown polymerization to be true of many other substances, and, for example, with organic acids this phenomenon has been repeatedly verified by the extensive investigations of Beckmann and others. With such association it is of course very possible that the reduction in the number of molecules caused thereby is greater than the increase which has its origin in the ionic decomposition. In this way for the present we can give an entirely satisfactory qualitative explanation for the seemingly very complicated relations of non-aqueous solutions. Likewise in keeping with this, as Nernst has already stated, is the fact that the serial order of the dissociating powers of solvents is the same, whether we base it on the electrolytic dissociation of simple molecules into ions or the non-electrolytic

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[1] See, for example, Journ. Physic. Chem., 5, 339 (1901). The author Kahlenberg is an enthusiastic opponent of the ionic theory, collecting facts with energy and great experimental skill which appear unexplainable by the theory. The possibility of suitably expanding the theory he unfortunately does not consider. It seems without purpose, however, to discard a theory so broadly established without putting a better one in its place. We are not accustomed to tearing down a habitable house because a few rooms are illy lighted, and putting ourselves out on the street, unless it be we can move into a better one. Any theory which desires to depose the one of Arrhenius has at the very outset the difficult task of bringing into a common field of view all the manifold facts which Arrhenius has taught us to summarize.

dissociation of polymerized molecules into simple ones. Accordingly, with decreasing power of dissociation, we must have, in non-aqueous solvents, as compared with water, not only a decrease of the dissociation into ions but also a decrease of the dissociation of polymerized molecules into simple ones, or, conversely expressed, the association into polymerized molecules must be favored. Whether the in part unsatisfactory agreement between the degrees of dissociation of aqueous solutions, as determined by osmotic and electric methods, can find an analogous explanation is still an open question. At any rate, it is worthy of note, as the approximate agreement proves, that in water association evidently seems to play quite a secondary rôle.

It is well to add that the probability of a participation of the solvent in the process of ionic dissociation, such as the formation of an addition product of solvent and ions, is variously supported by the experience with non-aqueous solutions. The assumption that the presence of free valences assists in determining the dissociation led Brühl to the conclusion that the ions are hydrated; and the results of Walden, that iodides and sulphocyanates have especially high solubilities in SO_2, with peculiar colorations of their SO_2 solutions, indicating the formation of new compounds,[1] point to the same conclusion. That this agrees with the facts is shown in a research by Fox,[2] who also proved the existence in aqueous solutions of such complex ions of the halogens and other anions with SO_2. The

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[1] Zeitschr. physik. Chem., **42**, 432 (1903).

[2] Dissert., Breslau, 1902; Zeitschr. physik. Chem., **41**, 458 (1902).

general result of the knowledge gathered thus far with non-aqueous solutions may for the present be summed up to the effect that the simplicity of conditions prevalent in aqueous solutions is here very much complicated by the phenomenon of the association of the non-ionized portion of the electrolyte. Hence the problems to be solved in this connection are, first, the determination of the amount of association of the electrolytes and, next, the Kohlrausch law for the additive nature of Λ_0. According to the equilibrium laws, it is no doubt permissible to assume that in non-aqueous solutions the ionic splitting-up, though in any case probably very slight, is caused by the great reduction, due to association, of the active masses of the simple molecules that alone are capable of ionizing. No doubt we might assert with equal right that in water the active mass of the undissociated molecules becomes too small, on account of the great ionization, to allow an appreciable association, since this latter is again proportional to the active mass of the simple molecules. But in many instances, for example with the organic carboxylic acids, the electrolytic dissociation is so slight even in water that the active mass of the undissociated molecules is not appreciably affected by it; that is, even if ionization is wanting, association would not increase in a sensible degree. So that in such cases we also find the association in water exceedingly small as compared with the other solvents, for which, according to the researches of Beckmann, the organic acids and alcohols already alluded to give the best evidence. This leads one to the assumption that the phenomenon of association is the chief phenomenon, and that ionization in non-aqueous solutions is so small, as a rule, essentially because of the great amount of association.

Finally, we may consider that case which deals with the amount of dissociation in pure substances as one of non-aqueous solvents, or, as we may term it, one of self-dissociation. Here it is a general rule that the electrolytic conductivity of pure substances is without exception exceedingly small, though, according to Walden,[1] it seems to increase with the polar difference of the atomic components. The amount of self-dissociation of water and the conductivity resulting therefrom have already been discussed (see p. 56). Conductivities of about the same order of magnitude have been observed for a whole series of other liquids of greatest possible purity, such as methyl and ethyl alcohol, sulphur dioxide, liquid ammonia, etc. But judging by the experiences of Kohlrausch and Heydweiller with water, it is difficult to say in how far the conductivities thus obtained are those of the absolutely pure substances, or to what extent possibly they are conditioned upon electrolytic impurities. It is worth mentioning in this connection that such substances as sulphuric acid, hydrochloric acid, etc., which in aqueous solutions belong to the best electrolytes, in the pure liquid form, on the contrary, possess an exceedingly small conductivity. The only known exceptions to this are the salts which in the melted state, that is as liquids, are very good electric conductors. It may be that this behavior is connected with a large dielectric constant of the salts in

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[1] Zeitschr. anorg. Chem., **25**, 225 (1890); see also Abegg, Christiania Vidensk. Selsk. Skrifter, 1902, No. 12, p. 8.

the molten state, although it has not been possible thus far to determine the same. In the solid state they show dielectric constants between 6 and 7, while all other solid substances, even water in the form of ice,[1] show only 1 to 3; and since liquids and melts always have higher dielectric constants, it does not seem improbable that the salt melts are exceedingly strong dielectrics. From this follows the probably very great self-dissociation which lies at the basis of the good conductivity of the salts, and according to the Thomson-Nernst rule is determined by their high dielectric constant. It is true at the high temperatures of the melted salts the ionic mobilities may be so great that it may not be necessary to consider the good conductivity as due to a marked dissociation. Especially in the case of water, where, as a result of the high dielectric constant, one might expect a greater self-dissociation, the very great association is in all likelihood essentially to blame, which takes away the simple molecules, the real material for the ionization.

The determination of electrolytic dissociation based solely on conductivities, however, without knowledge of the specific resistances which the medium opposes to the transport of ions, must always be looked upon as extremely uncertain. So, for instance, the view has been frequently expressed or entertained that the salts in the solid form are not electrolytes, or at most possess only a very slight electrolytic dissociation. This is probably based on the observation that the solid salts have an exceedingly slight,

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[1] See Abegg, Wied. Ann., **65**, 229 (1898), and Zeitschr. f. Elektrochem., **5**, 353 (1899).

but nevertheless perfectly definite, conductivity, as determined by Warburg. The color of many solid salts, especially when they crystallize as hydrates, is very often identical with the specific ionic color of the chromophore constituent, and thus makes the presence of ions probable. The small conductivity in spite of the ions may easily be explained by the enormous frictional resistance to which the moving particles in their solids are subjected. The greatest promise of success in penetrating into the quantitative dissociation relations of non-aqueous solutions seems to be offered by studies in gradually varying solvents, as an example of which the research of Wolf, mentioned above (p. 132), may be cited. The first investigation with this object in view comes from Arrhenius,[1] who studied the influence of small amounts of non-conductors, such as alcohol, sugar, etc., on the conductivity and dissociation of various electrolytes. The chief result of this investigation is the establishing of the fact that the changing of the solvent also produces changes in the degree of dissociation, but of very different amounts, according to the nature of the electrolyte. The strongest dissociated electrolytes are affected very little in their degree of dissociation by slight changes of the medium, while the weak electrolytes are extremely sensitive to such changes, their degree of dissociation being reduced. Cohen[2] has confirmed the results of Arrhenius for strong electrolytes in the entire interval of solvent produced by mixing alcohol and water in various

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[1] Zeitschr. physik. Chem., **9**, 487 (1892).

[2] Ibid., **25**, 1 (1899).

proportions. He found that the degrees of dissociation in these cases do not seem to be influenced by the medium, at least in so far as the conductivity represents a correct measure of dissociation. We see, therefore, that it is less the nature of the solvent than that of the dissolved substance which is of influence here, and this leads us to a final consideration, whose subject is the important question, What sort of regularities exist between the endeavor of the electrolytes to dissociate and the nature of their components?

CHEMICAL NATURE AND IONIZATION TENDENCY OF THE ELEMENTS.

It has become apparent that of the elementary substances an entire series appears altogether, or at least by evident preference, in the form of ions. Thus, for example, there is not a single compound of the alkali and alkaline-earth metals which does not contain these metals for the greater part as independent ions, while others, again, such as most of the elements belonging to the carbon and nitrogen groups of the periodic system, are as good as unknown in the form of elementary ions. Furthermore, the difference in capacity for forming positive and negative ions is very striking: elements such as fluorine and chlorine never appear as positive ions, while the elements of the first two groups of the periodic system act exclusively as positive ions. In the middle groups the tendency to form ions disappears more and more, in place of which these elements assume an amphoteric character in that they give evidence of a participation in the ion formation of others combined with them, even though it has not been possible thus far to confirm an independent formation of ions.

A good illustration of the preceding statement is offered by nitrogen, which combined with four H atoms furnishes the cathion $NH_4^{\cdot}$ (ammonium), while in the form of HN_3 or HNO_3 it produces the anions N_3' and NO_3' respectively. Likewise phosphorus forms cathions in the phosphonium compounds as well as anions in the acids of phosphorus and the phosphides,[1] and again, sulphur shows a varying polar behavior in the sulphine bases and in sulphides or sulphuric acids. Furthermore, we are familiar with iodine independent, and also as an anion-former in many complex combinations, but nevertheless in addition it is capable, as taught by the existence of iodonium bases, of entering into the garb of a cathion.[2] It is possible in general to

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[1] Schenck, Ber. d. deutsch. chem. Ges., **36**, 979 (1903).

[2] Of such amphoteric electrolytes there are quite a number; thus, almost all hydroxides of the weak positive elements along with oxygen can form anions, so that their hydroxides are capable of producing simultaneously cathions of the element and anions of its oxygen complex. Among others, this is known to be the case with $Pb(OH)_2$, $Al(OH)_3$, $Cr(OH)_3$, $As(OH)_3$, $As(OH)_5$, $Be(OH)_2$, $Sn(OH)_2$, $Ge(OH)_2$ (cf. Hantzsch, Zeitschr. anorg. Chem., **30**, 289 [1902]; McCay, Journ. Amer. Chem. Soc., **24**, 667 [1902]), and is deserving of interest because upon dissociation OH' ions are formed on the one hand and $H^{\cdot}$ ions on the other, whose mutual concentrations in the presence of water are limited by the water constant k_w (see p. 55). In the coupled equilibrium, such as, for instance,

$$Pb^{\cdot\cdot} + 2OH' \leftrightarrows Pb(OH)_2 \leftrightarrows H^{\cdot} + PbO_2H',$$

an addition of strong bases (OH' ions) retards the production of $Pb^{\cdot\cdot}$ on account of the common OH' ions, that is, forces back the basic function of the hydroxide, while the consumption of $H^{\cdot}$ ions (as a result of the formation of water) increases the concentration of PbO_2''. In short, the acid nature (anion formation) is enticed forth, so to speak, which agrees with the experience on other amphoteric substances. It is also worth while to call special attention to the reaction, mentioned above (see p. 117), of boric acid with fluorides, in which the OH' concentration for the complex fluorides is brought forth by the consumption of the confirm, by reference to the periodic system, the fact that the tendency in each principal group to form cathions increases with increase in the atomic weight, or, what is the same thing, the tendency to form anions increases with diminishing atomic weight. In the horizontal rows, however, the tendency toward the formation of cathions diminishes with increasing atomic weight. Quantitative knowledge, at least of an approximate nature, is given by the study of the electromotive activity of the elements and of the decomposition voltages, or the amount of electrical energy necessary to deprive an ion of its charge. Not wishing to go farther here into these interesting questions, suffice it to refer again to the previously mentioned articles of Abegg and Bodländer on Electro-affinity, and Abegg on Valence.[1] Be it only noted that the tendency to form ions, or the electro-affinity, manifests itself also in the solubility relations[2] of the electrolytes and their capacity for forming complexes; that is, the disinclination to form ions is often associated with slight aqueous solubility or with great tendency to enter into complex ions, whereby the compound avoids the necessity of being subjected to the dissociating force of the water.

The observation that all reactions in which ions participate in measurable amounts—even the hydrolytic

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borate ions. This indicates the presence of a weak basic nature in boric acid. A number of organic amphoteric electrolytes have been more carefully studied by Winkelblech (see p. 55, alanine, amido. benzoic acid).

[1] Zeitschr anorg Chem., **20**, 453 (1899); Christiania Vidensk. Selsk. Skrifter, 1902, No. 12, p 8.

[2] Cl. Immerwahr, Zeitschr. f. Elektrochem., **7** 477 (1901),

actions of the exceedingly weakly dissociated water—proceed to their equilibrium with an immeasurably great velocity has induced the assumption that indeed every capacity to react is to be attributed to the presence of ions. A basis for this assumption has been thought to exist in the fact that reactions between non-electrolytes usually proceed with extreme slowness, corresponding to an immeasurably small, but not altogether lacking, dissociation. We may, by way of illustration, consider the hydrolysis of stannous chloride and stannic chloride. Both are dependent upon the action of the OH' ions of the water on the tin of the compound. The $SnCl_2$, which shows the presence of appreciable quantities of tin ions by the fact that during electrolysis metal separates as a result of the discharge of these ions, attains its state of hydrolytic equilibrium momentarily; while, on the other hand, the $SnCl_4$ contains no demonstrable—or rather extremely small—amounts of tin ions, and accordingly its hydrolysis goes on very slowly, as traced by Kowalevsky.[1] Analogous facts hold for the hydrolysis of $PtCl_4$ and $AuCl_3$, also for the hydrolytic splitting-up of the esters,[2] as observed by Kohlrausch.[3] The exceedingly interesting investigations of Brereton Baker [4] on the failure of gases to react when absolutely dry, as well as the non-dissociation of NH_4Cl and of Hg_2Cl_2, the failure of NH_3 and HCl, H_2 and Cl_2,

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[1] Zeitschr. anorg. Chem., **23**, 1 (1900).

[2] Zeitschr. physik. Chem., **36**, 641 (1901).

[3] Ibid., **33**, 257 (1900).

[4] Journ. Chem. Soc., **73**, 422; **77**, 646; **81**, 400 (1899–1902). See also Noyes, Zeitschr. physik. Chem., **41**, 11 (1902).

and H_2 and O_2 to react, and lastly the lack of electric conductivity, which we attribute to ionization—all this speaks likewise in favor of the assumption that capacity for reaction is due to ions.

A more recent investigation of Kahlenberg,[1] which offers as evidence against the above the instantaneous precipitations in non-aqueous solutions possessing no demonstrable conductivity, should be completed in the direction of striving to attain by all known means the absolute dryness so difficult to accomplish, as the experience of Baker shows. Until that has been done, we may only conclude that very great reaction velocities can be reached even with quantities of ions so small as to be beyond detection, and it would depend upon penetrating into the region of these small ionic concentrations, thus far inaccessible, in such a manner as to measure their small concentrations.

The dissociation theory has taught us to consider from a common point of view and to understand in their mutual relations an immense number of facts coming from the apparently most diverse regions of chemistry. Doubtless an equally great number of problems this theory has presented to science and has helped or helps in their solution. Its successes in the field of chemistry are no greater than in the field of physics, where the brilliant researches of Nernst have solved with its assistance the theory of diffusion and the hundred-year-old problem of the voltaic chain. Yes, one cannot resist the impression that the future of the theory will lead us directly to

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[1] Journ. Physic. Chem., **6**, 1 (1902).

the ultimate questions of chemistry, the essence of valence and the affinity forces; and so one can maintain that this conception of Arrhenius is one of the most significant and fruitful with which theoretical chemistry has ever been favored.

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