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THE PHYSICAL PROPERTIES OF AQUEOUS SALT SOLUTIONS IN RELATION TO THE IONIC THEORY.[*]

IT is generally recognized that the further progress of physical science will be greatly facilitated by a better systematization of the knowledge already accumulated, and this is true in an especially high degree of the newly developed branch of science in which this section is directly interested. It has, therefore, seemed to me that the most valuable contribution that I could make toward the solution of the present problems of physical chemistry in correspondence with the aims of this Congress, would be a formulation of the present status of some of our knowledge relating to important classes of phenomena which are being actively investigated, but which have not yet received a final interpretation. It was my original hope to discuss several such classes of phenomena; but the effort involved in the collation and criticism of the available data connected with the problem which was first studied, forced me to confine my attention to that alone. This problem concerns *the physical properties of aqueous salt solutions in relation to the ionic theory.* This is the subject which I shall attempt to present to you: I hope that its importance and the greater definiteness that can be given to its treatment may compensate for the somewhat limited scope of this paper.

Permit me to say in advance that I have

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[*] Address delivered at St. Louis before the Section of Physical Chemistry of the Congress of Arts and Science.

studied this subject primarily from an empirical standpoint, and that it will be my aim to present to you a series of generalized statements of the experimental results, formulated in such a way as to show their relation to the important hypotheses connected with the ionic theory. Unfortunately, it will not be possible in this address to reproduce, or even fully refer to, the data upon which these conclusions are based—a defect serious in a work of this kind, which will be remedied in a subsequent publication. I shall, however, try to show the general character of the evidence for each conclusion, and the degree of accuracy within which it has been confirmed. I wish to add that I have been most ably assisted in the preparation of the material upon which paper is based, by Dr. J. W. Brown and Dr. M. S. Sherrill, of the Massachusetts Institute of Technology.

The principles to be first presented have reference to two of the main hypotheses which are commonly employed in quantitative applications of the ionic theory. One of these hypotheses is that *the migration-velocities of the ions of a salt do not vary appreciably with its concentration, at least up to a moderate concentration; and consequently, that the degree of ionization is equal to the ratio of the equivalent conductivity at the concentration in question to the limiting value of the equivalent conductivity at zero concentration*—a ratio which I will hereafter call simply the conductivity-ratio. The other hypothesis is that *ions, and also the un-ionized molecules accompanying them, produce an osmotic pressure substantially equal to the pressure exerted by the same number of gaseous molecules at the same temperature, at least up to a moderate concentration;* a hypothesis which may be more briefly expressed by the statement that the osmotic-pressure constant for dissolved electrolytes is identical with the gas-constant. It is evident that with the help of this hypothesis we can calculate, either from measurements of osmotic pressure or from those of any other property which is thermodynamically related to osmotic pressure, the number of mols in the solution resulting from one formula weight of salt, that is, the quantity which van't Hoff has represented by the letter *i*. From the latter, provided the ionization is not complicated by the formation of complex molecules or ions, the degree of ionization is readily derived.

The first of these hypotheses can not be independently tested, because no direct method of determining the change of migration-velocity with the concentration, is known. But the following principle, which has an important significance with reference to the *relative* influence of concentration on the velocities of different ions, has been established by measurements of the concentration-changes at the electrodes attending the electrolysis of salt solutions.

The transferrence number, or ratio of the conductivity of one ion to the sum of the conductivities of both ions, is constant within one per cent., between the concentrations of 1/200 *and* 1/10 *normal, for all salts thus far accurately investigated, except lithium chloride, the halides of bivalent metals and cadmium sulphate.*

This principle holds true, according to the results of various investigators, in the case of potassium and sodium chlorides, hydrochloric and nitric acids, silver nitrate, barium nitrate, potassium sulphate and copper sulphate—thus in the case of salts of the three different ionic types, which I will speak of as the uni-univalent, the uni-bivalent and the bi-bivalent types, in correspondence with the valences of the two ions composing the salt.

Two conclusions are to be drawn from this result. The first is that complex ions are not present in important quantity in the solutions of these salts. And the second is that the migration velocities of the two ions of a salt vary by the same percentage amount, if they vary at all, with changes in its concentration. It is scarcely admissible, however, to regard this last fact even as an indication that the hypothesis of constant migration velocities is correct; for any change in the character of the liquid medium might well affect the velocities of different ions not far from equally.

Important evidence in regard to this hypothesis and that stating that ions and the un-ionized molecules associated with them have a normal osmotic pressure is, however, furnished by the agreement of the ionization values derived, on the one hand, from the conductivity-ratio, and, on the other, from the properties thermodynamically related to osmotic pressure. Three of these properties have been measured with sufficient accuracy with certain electrolytes to make the results of significance, namely, the freezing-point lowering, the electromotive force of concentration cells, and the heat of solution in relation to change of solubility with the temperature. Under the assumption that osmotic pressure and gaseous pressure are equal under identical conditions, a relation between each of these properties and the degree of ionization of an electrolyte can be derived with the help of the second law of energetics. Then, either this ionization value may be directly compared with the conductivity ratio; or, assuming provisionally that the latter is a correct measure of ionization, the magnitude of the property in question may be calculated, and the result compared with that obtained by direct measurement. In the case of the freezing-point lowering, I have adopted the first of these methods. For the five salts for which both reliable freezing-point determinations and accurate conductivity measurements at 0° exist, the ionization values corresponding to both of these properties have been computed. Especial attention was given to the selection of the best value of the freezing-point lowering constant and to the extrapolation of the conductivity for zero concentration, the details of which can not be here described. The results may be summarized as follows:

In case of the two uni-univalent salts and the three uni-bivalent salts hitherto carefully investigated, the ionization values derived from freezing-point lowering do not differ from those derived from conductivity, between the concentrations of 1/200 *and* 1/4 *normal, by more than two or three per cent.*

The five salts referred to are potassium and sodium chlorides, potassium and sodium sulphates and barium chloride. The two sets of values for potassium chloride, for which an abundant experimental material exists, exhibit no pronounced or systematic differences; but for the other four salts the freezing point leads to values which are in general from two to three per cent. higher at all concentrations than the conductivity ratio. The fact that these differences do not, as a rule, increase with increasing concentration indicates that they may be due to some constant experimental error, or to an error in the extrapolated conductivity value.

Accurate measurements have been made by Jahn of the electromotive force of concentration cells consisting of two silver or mercury electrodes covered with silver chloride or mercurous chloride, one of which is immersed in a weak solution and the other in a strong solution of sodium or potassium chloride. These measured values were compared by him with those calculated from the thermodynamic relation between electromotive force and the concentrations and degrees of ionization of the salt in the cell. Unfortunately, however, the thermodynamic relation employed involved the assumption that the ionization varies with the concentration in accordance with the mass-action law—an assumption which is known not to be true of the ionization values derived from conductivity. The assumption is, therefore, an irrational one —one by which the question at issue is prejudged. What should be done in calculating the electromotive force so as to determine whether the conductivity ratio gives ionization values consistent with the measured electromotive forces, is evidently to assume that the ionization changes with the concentration in the way that the conductivity indicates that it does. Arrhenius recognized this error and partially corrected for it by a method of approximation. I have repeated the calculations by an exact thermodynamic formula based on an empirical law expressing the change of the conductivity ratio with the concentration, to which I will refer later. The results are summed up in the statement that, *when the conductivity-ratio is assumed to represent the degree of ionization of the salt, the calculated values of the electromotive force of concentration cells exceed the measured ones by only about one per cent. in the case of potassium and sodium chloride between the concentrations of* 1/600 *and* 1/20 *normal.* The measured electromotive force corresponds to an ionization value at the latter concentration about one per cent. less than the conductivity ratio.

The thermodynamic relation involving heat of solution has been accurately tested with only one salt—potassium perchlorate; but since it is a different salt from those used in the other experiments and since its concentration was fairly high—one eighth normal—the result is of interest. It was found that the *measured heat of solution was less by only 1.1 per cent. than that calculated under the assumption that the conductivity ratio is equal to the degree of ionization.* The measured heat of solution corresponds to an ionization value 2½ per cent. lower than the conductivity ratio.

With respect to these small deviations of the results obtained by the three methods of comparison, it is important to note that they lie in opposite directions, the freezing-point lowering corresponding to larger values of the ionization, and the measured electromotive forces and heat of solution to smaller ones than the conductivity-ratio. This fact makes it almost certain that they are due to experimental errors. Nevertheless, further exact measurements of all these properties are highly desirable.

From a theoretical standpoint these three methods are based on the same hypotheses, namely, that the osmotic pressure constant for ions and un-ionized molecules is identical with the gas-constant; that the conductivity-ratio is a correct measure of ionization, and that complex molecules or ions are not present in the solution. The concordance of the results furnishes, therefore, a strong confirmation of the correctness of these fundamental hypotheses. The only alternative conclusion is that an error in one of these hypotheses is compensated by an error of opposite effect in one of the others; but it seems very improbable that such a compensation could occur in the case of so many salts of different chemical nature and different types through the range of concentration (1/200–1/4 normal) for which the agreement of the experimental results has been shown to hold true. It is certainly more consistent with the modern methods of science to adopt these simpler hypotheses which are in full accord with the considerable number of facts thus far known, than deliberately to introduce more complicated assumptions for which there is at present no experimental warrant.

The combination of these hypotheses with the experimental values of the quantities involved at varying concentrations makes necessary the further conclusion that the *degree of ionization of salts, whether derived from the conductivity-ratio or from thermodynamic relations involving the equality of the osmotic pressure constant and the gas constant does not vary with the concentration even approximately in accordance with the law of chemical mass action.*

This empirical consequence of the fundamental hypotheses of the ionic theory has led several investigators to raise a theoretical objection to them, it being contended that the laws of thermodynamics require that the validity of these hypotheses involves that of the mass action law itself. This apparent inconsistency between the inductive and deductive conclusions makes it probable that some unproved, erroneous assumption is tacitly involved in the theoretical derivation. That there is in fact a possible alternative, which has, I believe, been previously overlooked in the thermodynamic discussions, will be evident from the following considerations. The thermodynamic relations between ionization and freezing point, electromotive force, or heat of solution involve only the assumption that the work done in reversibly separating water from a solution at constant concentration is equal to that done in producing the same volume-change in a gas, which implies, of course, that the ions and un-ionized molecules have in the presence of each other normal osmotic pressures. On the other hand, the derivation of the mass action law equation is based on cyclical processes which necessarily involve the separate introduction and removal of the un-ionized molecules and of the ions into or from solutions of different concentrations, and it further involves the assumption that this introduction or removal of molecules or ions can be effected by the application of an external pressure equal to that osmotic pressure which each of them possesses in the mixture, that is, the possibility is ignored that the separation of the molecules from the ions may itself give rise to some new force, and may involve, consequently another quantity of work than that corresponding to the osmotic pressure. The ionic theory would evidently predict a result of this kind if an attempt were made to separate the positive ions from the negative, even though their osmotic pressures when present together were perfectly normal; and it is quite conceivable, even though the reason for it be not apparent, that the separation of the un-ionized molecules from the ions, with which they may be in electrical as well as chemical equilibrium, should involve an abnormal quantity of work. The assertion that the validity of the osmotic pressure principle necessarily implies that of the mass action law is, therefore, unwarranted from a deductive standpoint; while the inductive evidence, pointing strongly as it does to the substantial correctness of the former principle and the complete inadequacy of the latter one, makes it highly probable that the *separation of un-ionized molecules from ions does involve the expenditure of other work than that corresponding to their osmotic pressures.*

Since the ionization does not change with the concentration in accordance with the mass action law, it is natural to inquire what the law of its change is. This matter has been investigated from an empirical standpoint by several investigators with the help of the conductivity data. The results justify the statement of the following principles:

The un-ionized fraction of a salt as determined from the conductivity ratio is proportional to the cube-root of its total concentration or to that of its ion-concentration, between 1/2,000 and 1/10 normal, in the case of both uni-univalent and uni-multivalent salts. That is, $1 - \gamma = Kc^{\frac{1}{3}}$

or $1 - \gamma = K(c\gamma)^{\frac{1}{3}}$ where γ is the degree of ionization, c the concentration, and K a constant. The first of three functions was proposed by Kohlrausch, the second by Barmwater. Owing to the relatively small variation of the ionization, these two functions can not differ much as to their constancy, but on the whole the experimental data indicate that the second function is somewhat more constant. The average deviations of the actual measurements from the values corresponding to this function are ¼ per cent. in the case of ten uni-univalent salts, ⅓ per cent. in the case of nine uni-bivalent salts and also ⅓ per cent. in the case of three uni-tri and uni-quadrivalent salts. The maximum deviations are two or three times as great. It is of interest to note that the strong mineral acids, hydrochloric and nitric, behave like salts in this respect. These functions have been shown to apply to potassium and sodium chlorides through a range of temperature extending from 18° to 306°. They do not apply at all closely to such salts of the bi-bivalent type as magnesium and copper sulphates, perhaps owing to appreciable hydrolysis. Nor do they represent satisfactorily the experimental data for any kind of salts at the very low concentrations lying between 1/100,000 and 1/2,000 normal, nor at concentrations higher than 1/5 normal.

The experimental results are also well expressed by the statement that *in the case both of uni-univalent and uni-bivalent salts between the concentrations of* 1/10,000 *and* 1/5 *normal, the concentration of the un-ionized molecules is proportional to the concentration of the ions raised to a constant power, varying somewhat with the salt and the temperature, but as a rule only between the limits of* 1.43 *and* 1.56. That is,

$$c(1-\gamma) = K(c\gamma)^n, \text{ where } n > 1.43 \text{ and } < 1.56.$$

This general function was first applied by Storch, and was afterwards further discussed by Euler and Bancroft. It has the advantage over the previous ones that it represents the data with accuracy even up to the highest dilutions, and therefore can be used for obtaining the limiting conductivity at zero concentration.

The applicability to the salts of different types of either of these principles governing the change of ionization with the concentration leads to the important conclusion that *the form of the concentration function is independent of the number of ions into which the molecules of the salt dissociates.* This remarkable fact, though previously recognized, has not been sufficiently emphasized, and it has been often ignored in discussions of the cause of the deviation of the ionization of salts from the requirements of the mass action law. It seems to me to show almost conclusively that chemical mass action has no appreciable influence in determining the equilibrium between ions and un-ionized molecules. How complete the contradiction with the mass action law is, may be illustrated by citing the specific facts that for di-ionic, tri-ionic and tetra-ionic salts this law requires that the concentration of the un-ionized molecules be proportional to the square, the cube, and the fourth power, respectively, of the concentration of the ions, while the experimental data show that it is approximately proportional to the 3/2 power of that concentration, whatever may be the type of salt.

Having seen in what manner the degree of ionization varies when the concentrations of both ions of the salt are simultaneously varied by dilution, it is of interest to determine the effect of changing the concentration of either ion separately. A study of the conductivity and the freezing-point of mixtures of two salts having one ion in common throws much light upon this question, for the following simple principle has been found to represent this phenomenon: *The conductivity and the freezing-point lowering of a mixture of salts having one ion in common are those calculated under the assumption that the degree of ionization of each salt is that which it would have if present alone at such an equivalent concentration that the concentration of either of its ions were equal to the sum of the equivalent concentrations of all the positive or negative ions present in the mixture.*

This somewhat complicated statement may be illustrated by the following example: Suppose that a mixed solution is 0.1 normal with respect to sodium chloride and 0.2 normal with respect to sodium sulphate, and that it is 0.18 normal with reference to the positive or negative ions of these salts. The principle then requires that the ionization of either of these salts in the mixture be the same as it is in water alone when its ion-concentration is 0.18 normal.

This principle in regard to the conductivity of mixtures, which has been definitely stated by Arrhenius, is shown by the existing data to hold true almost, if not quite, within the small experimental error of the determinations both for mixtures of salts of the same type and for those of salts of different types up to a concentration of at least 1/2 normal. Experiments confirming this principle have been made upon eight pairs of uni-univalent salts by Arrhenius, Manson and Barmwater. In addition, the principle has been shown by several Canadian investigators, Archibald, McKay and Barnes, to hold true for mixtures of potassium and sodium sulphates, potassium and copper or magnesium sulphates (up to 0.1 normal), potassium sulphate and chloride, barium and sodium chlorides, and zinc and copper sulphates—thus for almost every possible typical combination of uni-uni, uni-bi and bi-bivalent salts. That the same principle is true of the freezing point lowering is shown by the measurements of Archibald with mixtures of potassium and sodium sulphate. This proves that the phenomenon really has reference to the degree of ionization and that it does not arise from a possible variation in the migration-velocities of the ions.

Of special interest is the relation of this principle to the validity of the mass action law. Almost all investigators of the conductivity of mixtures have concluded from the fact that upon mixing solutions of equal ion-concentration there is no change in ionization, that the results do conform to this law. Yet it is scarcely conceivable that this law can apply to mixtures of salts in which the concentration of one ion is varied while maintaining that of the other constant, in view of the fact that it is known not to hold true for the variations of the concentrations of both ions produced by dilution. And in reality this conclusion, if regarded as a general expression of the facts, is entirely unwarranted. It is true that for certain typical combinations of salts—those for which from one molecule of each salt results by ionization not more than one ion of the kind not common to the salts—the principle here stated does coincide with the requirements of the mass-action law. But for combinations not so characterized the mass-action law predicts, as is readily seen upon formulating the equations, a conductivity of the mixture widely divergent from that actually found, and, therefore, from that expressed by the principle under consideration. This last statement applies, for example, to the mixtures before referred to of potassium sulphate with sodium sulphate, and of potassium sulphate with copper or magnesium sulphate, the first of which have been studied with respect both to their conductivity and freezing point.

The law of chemical mass action here again shows itself entirely inapplicable to the phenomena connected with the ionization of salts. That some investigators have thought that the deviations from this law indicated by the conductivity were only apparent, and that they were attributable to variations in the migration velocity, has arisen, no doubt, from the fact that they have confined their attention to di-ionic salts, and have failed to recognize, on the one hand, the striking divergences from it exhibited by tri-ionic salts, and, on the other, the substantial correspondence of the conductivity and freezing-point results.

Combining this principle in regard to the ionization of mixed salts in solution with the empirical concentration law of Storch for single salts, we are led to the conclusion that the ratio of the concentration of the un-ionized part to the product of the concentrations of the two ions (but in the case of tri-ionic salts *not* raised to a power corresponding to the requirements of the mass action law) is a function of the sum of the equivalent concentrations of all the ions in the solution and of that alone.* This ratio is, moreover, roughly inversely proportional to the square root of the total ion-concentration.

The correctness of this principle is further demonstrated by the fact that with its aid, also, the conductivity of a mixture of two salts without a common ion can be computed from their separate conductivities. This is shown by the conductivity measurements, made by Archibald and more recently by Sherrill, upon mixtures of potassium chloride and sodium sulphate, or of sodium chloride and potassium sulphate. Up to at least 0.2 normal concentration, the agreement between the observed and calculated values is within 0.5 per cent. On the other hand, the divergence of the observed values from the requirement of the mass-action law amounts to many per cent.

It seems appropriate at once to supplement these principles in regard to the form of the concentration function by a statement of two general rules which have been found to express the magnitude of the ionization of salts of different types. These rules, unlike the preceding principles, are only crude approximations; but, nevertheless, they prove of some assistance in rough applications of the ionic theory, and undoubtedly possess an important theoretical significance, not yet recognized. They may be stated as follows: (1) *The decrease of ionization with increasing concentration is roughly constant in the case of different salts of the same type; and* (2) *the un-ionized fraction at any definite molal concentration is roughly proportional to the product of the valences of the two ions in the case of salts of different types.* Thus, at 0.1 normal concentration the mean value of the degree of ionization for 17 uni-univalent salts measured at 18° is 83.3 per cent., the average deviation of the separate values from this mean is 2.1 per cent., and the maximum deviation of any of them is 5.4 per cent. of the mean value; while for fourteen uni-bivalent salts the mean value is 69.8 per cent., the average deviation 5 per cent. of this, and the maximum deviation about 10 per cent. of it. The un-ionized fraction in 1/20 molal solution is 13½ per cent. for these univalent salts; 30 per cent., or about twice as great, for the uni-bivalent salts; and 60 per cent., or about four times as great, for the three bi-bivalent salts investigated (zinc, magnesium and copper sulphates). The salts of mercury

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* This is expressed mathematically by the following equation, in which c_1 and c_2 represent the equivalent concentrations of the two salts, and γ_1 and γ_2 their degrees of ionization in the presence of each other:

$$\frac{c_1\gamma_1(c_1\gamma_1 + c_2\gamma_2)}{c_1(1-\gamma_1)} = K_1(c_1\gamma_1 + c_2\gamma_2)^{n-1}$$

and cadmium are pronounced exceptions to the rule.

A far more extensive material for testing these rules is furnished by the measurements made at 25° between the concentrations of 1/32 and 1/1024 normal. In the case of the uni-univalent salts, data exist at this temperature and these concentrations for 36 inorganic salts, about 65 sodium salts of organic acids, and about an equal number of hydrochlorates of organic bases. A consideration of all these data shows that, with only three or four exceptions not of a pronounced character, the values of the degree of ionization of all these salts in 1/32 normal solution lie between the limits of 84 and 90 per cent. and are fairly uniformly distributed throughout this range of 6 per cent. For 67 uni-bivalent salts the corresponding limits of the ionization values are 72 and 81 per cent. while for only four such salts do the values lie beyond these limits. For the 6 uni-trivalent salts investigated the range is from 67 to 76 per cent.; for the three uni-quadrivalent salts, from 59 to 63 per cent.; and for twelve bi-bivalent salts, from 49 to 63 per cent., while three such salts show more considerable variations. The values of the un-ionized fraction corresponding to the mean of these two limits for the different types of salts at the same equivalent concentration increase somewhat more slowly than the product of the valences of the ions. The proportionality becomes a fairly close one, however, when the salts are compared at the same molal, instead of the same equivalent concentration. Thus, with the help of the Kohlrausch concentration-function, it is calculated from the preceding values that the un-ionized fractions in 1/32 molal solution are as follows: 13 per cent. for the uni-univalent salts, 29½ per cent. for the uni-bivalent salts, 41 per cent. for the uni-trivalent salts, 62 per cent. for the uni-quadrivalent salts, 55 per cent. for the bi-bivalent salts, which are seen to be approximately the required multiples of the constant factor 14.

Before leaving this subject it should be stated that the results conform, on the whole, about equally well with the rule that *the decrease of equivalent conductivity* (*instead of ionization*) *is roughly constant for salts of the same type;* and when the comparison is made at the same equivalent concentration, distinctly better to the rule that the *decrease of equivalent conductivity is proportional to the product of the valences of the ions for salts of different types.* (When compared at the same *molal* concentration, however, this rule does not apply.) These rules were originally stated by Ostwald. They differ not inconsiderably from those expressing the change in ionization, namely, to an extent corresponding to the variations of the conductivities at extreme dilution. The deviations are so irregular, however, that from an empirical standpoint the choice between the two pairs of rules is arbitrary. In either form these rules seem to justify the inference that the degree of ionization of salts, unlike that of the organic acids and bases, is not primarily a specific chemical property determined by chemical affinity, but that it is determined, at least in the main, by the magnitude of the electric charges on the ions.

The establishment of the principle in regard to the ionization of a mixture of salts has a direct bearing on the phenomenon of the effect of one salt on the solubility of another with a common ion. It has been usually assumed that in a (not too concentrated) saturated solution the un-ionized molecules of the salt always have the same concentration, and secondly that the product of the *ion*-concentrations (each raised to a power corresponding to the number resulting from one molecule) also retains the same value. And the experimental results in several cases have been shown to accord fairly well with these two hypotheses. Yet their simultaneous validity is quite inconsistent with the principle in regard to the ionization in mixtures. In fact, when considered in the light of this principle, the existing data lead to the conclusion that the former hypothesis is not even approximately true, and that the latter one, at any rate in cases where the ionization is far from complete, is affected by a considerable error. One example may be cited: when thallium chloride and bromate, each of which alone has a solubility of about 1/40 normal in water at 40°, are simultaneously present as solid phases, the solubility of each is reduced by the other to an extent which shows that the concentration of the un-ionized molecules is diminished by about 15 per cent. and that the product of the ion-concentrations is increased by about 5 per cent. This case is a typical one; but what the quantitative law of the influence in question is, can only be determined by a further study of the phenomenon. In the case of tri-ionic salts, the ion-concentration product is even approximately constant, only when the square—not when the first power—of the concentration of the univalent ion is employed. This has been shown by experiments with lead iodide in the presence of potassium iodide, with lead chloride in that of other chlorides and with calcium hydroxide in that of ammonium chloride.

I will close by calling your attention to a remarkable principle in regard to the properties of salt solutions, of a character quite distinct from those thus far considered. That many properties of dilute salt solutions can be expressed as the sum of values assigned once for all to the constituent radicals or ions was long ago recognized, and has often been cited as a corollary from the ionic theory. That this additivity of properties persists up to fairly high concentrations is a fact, however, that has received scant consideration, owing to its apparent lack of relationship to that theory. This fact is shown strikingly in the case of certain highly specific optical properties which are ordinarily found to be dependent in a high degree on molecular structure. Thus, the experimental data fully warrant the statement of the principle that *the optical activity and the color of salts in solution, when referred to equivalent quantities, are independent of the concentration and therefore of the degree of ionization of the salts and are additive with respect to the properties of the constituent ions even up to concentrations where a large proportion of the salt is in the un-ionized state.* Abundant data might be cited in support of this principle, especially with reference to optical activity. But I can only illustrate the character of the evidence by presenting a few of the results obtained by Walden with the salts of α-brom camphor sulphonic acid. In 1/30 normal solution he found the following values of the molal rotary power:

Lithium salt	275
Sodium salt	272
Potassium salt	273
Thallium salt	273
Acid itself	273
Beryllium salt	274
Zinc salt	272
Barium salt	272

The values are seen to be substantially identical, although the conductivity shows the acid to have an un-ionized fraction of 7 per cent., the salts of the univalent metals one of 16 per cent., and those of the bivalent metals one of 30 per cent., and although the un-ionized molecules present contain in some cases the elements hydrogen, lithium and beryllium of very small atomic weights, and in two others the elements thallium and barium of large atomic weights.

If there were not other evidence to the contrary, the existence of this general principle, which is also applicable to many other properties, would almost warrant the conclusion that the salts are completely ionized up to the concentration in question, and that the decrease in conductivity is due merely to a change in migration velocity. But, in view of the apparently conclusive evidence against such a hypothesis, we can only conclude that the form of union represented by the un-ionized molecules of salts differs essentially from ordinary chemical combination, it being so much less intimate that the ions still exhibit their characteristic properties, in so far as these are not dependent upon their existence as separate aggregates.

These then are the empirical principles to which a critical analysis of the experimental data leads. Upon these principles must be based the rational, theoretical explanation of the phenomena in question. The discovery of that explanation constitutes one of the most important of the present problems of physical chemistry.

ARTHUR A. NOYES.

THE FIELD OF LOGIC.*

CURRENT tendencies in logical theory make a determination of the field of logic fundamental to any statement of the general problems of the science. In view of this fact, I propose in this paper to attempt such a determination by a general discussion of the relation of logic to mathematics, psychology and biology, especially noting in connection with biology the tendency known as pragmatism. In conclusion, I shall indicate what the resulting general problems appear to be.

I.

There may appear, at first, little to distinguish mathematics in its most abstract, formal and symbolic type from logic. Indeed, mathematics as the universal method of all knowledge has been the ideal of many philosophers, and its right to be such has been claimed of late with renewed force. The recent notable advances in the science have done much to make this claim plausible. A logician, a non-mathematical one, might be tempted to say, that in so far as mathematics is the method of thought in general, it has ceased to be mathematics; but, I suppose, one ought not to quarrel too much with a definition, but should let mathematics mean knowledge simply, if the mathematicians wish it. I shall not, therefore, enter the controversy regarding the proper limits of mathematical inquiry. I wish to note, however, a tendency in the identification of logic and mathematics which seems to me to be inconsistent with the real significance of knowledge. I refer to the exaltation of the freedom of thought in the construction of conceptions, definitions and hypotheses.

The assertion that mathematics is a 'pure' science is often taken to mean that it is in no way dependent on experience in the construction of its basal concepts. The space with which geometry deals may be Euclidean or not, as we please; it may be the real space of experience or not; the properties of it and the conclusions reached about it may hold in the real world or they may not; for the mind is free to construct its conception and definition of space in accordance with its own aims. Whether geometry is to be ultimately a science of this type must be left, I suppose, for the mathematicians to decide. A logician may suggest, however, that the propriety of calling all these conceptions 'space' is not as clear as it ought to be. Still further, there

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* Address before the Section of Logic, International Congress of Arts and Science, Universal Exposition, St. Louis.