ON THE DISSOCIATION OF SUBSTANCES DISSOLVED IN WATER

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In a paper submitted to the Swedish Academy of Sciences, on the 14th of October, 1895, Van't Hoff proved experimentally, as well as theoretically, the following unusually significant generalization of Avogadro's law:†

"The pressure which a gas exerts at a given temperature, if a definite number of molecules is contained in a definite volume, is equal to the osmotic pressure which is produced by most substances under the same conditions, if they are dissolved in any given liquid."

Van't Hoff has proved this law in a manner which scarcely leaves any doubt as to its absolute correctness. But a difficulty which still remains to be overcome, is that the law in question holds only for "most substances"; a very considerable number of the aqueous solutions investigated furnishing exceptions, and in the sense that they exert a much greater osmotic pressure than would be required from the law referred to.

If a gas shows such a deviation from the law of Avogadro, it is explained by assuming that the gas is in a state of dissociation. The conduct of chlorine, bromine, and iodine, at higher temperatures is a very well-known example. We regard these substances under such conditions as broken down into simple atoms.

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* *Ztschr. Phys. Chem.*, **1**, 631, 1887.

† Van't Hoff, *Une propriété générale de la matière diluée*, p. 43; *Sv. Vet-Ak-s Handlingar*, **21**, Nr. 17, 1886. [Also in *Archives Néerlandaises* for 1885.]

The same expedient may, of course, be made use of to explain the exceptions to Van't Hoff's law; but it has not been put forward up to the present, probably on account of the newness of the subject, the many exceptions known, and the vigorous objections which would be raised from the chemical side, to such an explanation. The purpose of the following lines is to show that such an assumption, of the dissociation of certain substances dissolved in water, is strongly supported by the conclusions drawn from the electrical properties of the same substances, and that also the objections to it from the chemical side are diminished on more careful examination.

In order to explain the electrical phenomena we must assume with Clausius* that some of the molecules of an electrolyte are dissociated into their ions, which move independently of one another. But since the "osmotic pressure" which a substance dissolved in a liquid exerts against the walls of the confining vessel, must be regarded, in accordance with the modern kinetic view, as produced by the impacts of the smallest parts of this substance, as they move, against the walls of the vessel, we must, therefore, assume, in accordance with this view, that a molecule dissociated in the manner given above, exercises as great a pressure against the walls of the vessel as its ions would do in the free condition. If, then, we could calculate what fraction of the molecules of an electrolyte is dissociated into ions, we should be able to calculate the osmotic pressure from Van't Hoff's law.

In a former communication "On the Electrical Conductivity of Electrolytes," I have designated those molecules whose ions are independent of one another in their movements, as active; the remaining molecules, whose ions are firmly combined with one another, as inactive. I have also maintained it as probable, that in extreme dilution all the inactive molecules of an electrolyte are transformed into active.† This assumption I will make the basis of the calculations now to be carried out. I have designated the relation between the number of active molecules and the sum of the active and inactive molecules, as the activity coefficient.‡ The activity coefficient of an

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* Clausius, *Pogg. Ann.*, **101**, 347 (1857); *Wied. Elektr.*, **2**, 941.

† *Bihang der Stockholmer Akademie*, **8**, Nr. 13 and 14, 2 Tl. pp. 5 and 13; 1 Tl., p. 61.

‡ *l. c.*, 2 Tl., p. 5.

electrolyte at infinite dilution is therefore taken as *unity.* For smaller dilution it is less than *one,* and from the principles established in my work already cited, it can be regarded as equal to the ratio of the actual molecular conductivity of the solution to the maximum limiting value which the molecular conductivity of the same solution approaches with increasing dilution. This obtains for solutions which are not too concentrated (*i. e.,* for solutions in which disturbing conditions, such as internal friction, etc., can be disregarded).

If this activity coefficient (α) is known, we can calculate as follows the values of the coefficient i tabulated by Van't Hoff. i is the relation between the osmotic pressure actually exerted by a substance and the osmotic pressure which it would exert if it consisted only of inactive (undissociated) molecules. i is evidently equal to the sum of the number of inactive molecules, plus the number of ions, divided by the sum of the inactive and active molecules. If, then, m represents the number of inactive, and n the number of active molecules, and k the number of ions into which every active molecule dissociates (*e. g.,* $k=2$ for KCl, *i. e.,* K and Cl; $k=3$ for $BaCl_2$ and K_2SO_4, *i. e.,* Ba, Cl, Cl, and K, K, SO_4), then we have:

$$i=\frac{m+kn}{m+n}.$$

But since the activity coefficient (α) can, evidently, be written $\frac{n}{m+n}$:

$$i=1+(k-1)\alpha.$$

Part of the figures given below (those in the last column), were calculated from this formula.

On the other hand, i can be calculated as follows from the results of Raoult's experiments on the freezing-point of solutions, making use of the principles stated by Van't Hoff. The lowering (t) of the freezing-point of water (in degrees Celsius), produced by dissolving a gram-molecule of the given substance in one litre of water, is divided by 18.5. The values of i thus calculated, $i=\frac{t}{18.5}$, are recorded in next to the last column. All the figures given below are calculated on the assumption that one gram of the substance to be investigated was dissolved in one litre of water (as was done in the experiments of Raoult).

In the following table the name and chemical formula of the substance investigated are given in the first two columns, the value of the activity coefficient in the third (Lodge's dissociation ratio*), and in the last two the values of i calculated by the two methods: $i=\frac{t}{18.5}$ and $i=1+(k-1)\alpha$.

The substances investigated are grouped together under four chief divisions: 1, non-conductors; 2, bases; 3, acids; and 4, salts.

NON-CONDUCTORS.

SUBSTANCE.	FORMULA.	α	$i=\frac{t}{18.5}$.	$i=1+(k-1)\alpha$.
Methyl alcohol	CH_3OH	0.00	0.94	1.00
Ethyl alcohol	C_2H_5OH	0.00	0.94	1.00
Butyl alcohol	C_4H_9OH	0.00	0.93	1.00
Glycerin	$C_3H_5(OH)_3$	0.00	0.92	1.00
Mannite	$C_6H_{14}O_6$	0.00	0.97	1.00
Invert sugar	$C_6H_{12}O_6$	0.00	1.04	1.00
Cane-sugar	$C_{12}H_{22}O_{11}$	0.00	1.00	1.00
Phenol	C_6H_5OH	0.00	0.84	1.00
Acetone	C_3H_6O	0.00	0.92	1.00
Ethyl ether	$(C_2H_5)_2O$	0.00	0.90	1.00
Ethyl acetate	$C_4H_8O_2$	0.00	0.96	1.00
Acetamide	$C_2H_3ONH_2$	0.00	0.96	1.00

BASES.

SUBSTANCE.	FORMULA.	α	$i=\frac{t}{18.5}$.	$i=1+(k-1)\alpha$.
Barium hydroxide	$Ba(OH)_2$	0.84	2.69	2.67
Strontium hydroxide	$Sr(OH)_2$	0.86	2.61	2.72
Calcium hydroxide	$Ca(OH)_2$	0.80	2.59	2.59
Lithium hydroxide	$LiOH$	0.83	2.02	1.83
Sodium hydroxide	$NaOH$	0.88	1.96	1.88
Potassium hydroxide	KOH	0.93	1.91	1.93
Thallium hydroxide	$TlOH$	0.90	1.79	1.90
Tetramethylammonium hydrate	$(CH_3)_4NOH$	——	1.99	——

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* Lodge, On Electrolysis, *Report of British Association*, Aberdeen, 1885, p. 756 (London, 1886).

BASES—(*continued*).

SUBSTANCE.	FORMULA.	a	$i=\frac{t}{18.5}$.	$i= 1+(k-1)a$.
Tetraethylammonium hydrate	$(C_2H_5)_4NOH$	0.92	——	1.92
Ammonia	NH_3	0.01	1.03	1.01
Methylamine	CH_3NH_2	0.03	1.00	1.03
Trimethylamine	$(CH_3)_3N$	0.03	1.09	1.03
Ethylamine	$C_2H_5NH_2$	0.04	1.00	1.04
Propylamine	$C_3H_7NH_2$	0.04	1.00	1.04
Aniline	$C_6H_5NH_2$	0.00	0.83	1.00

ACIDS.

SUBSTANCE.	FORMULA.	a	$i=\frac{t}{18.5}$.	$i= 1+(k-1)a$.
Hydrochloric acid	HCl	0.90	1.98	1.90
Hydrobromic acid	HBr	0.94	2.03	1.94
Hydroiodic acid	HI	0.96	2.03	1.96
Hydrofluosilicic acid	H_2SiF_6	0.75	2.46	1.75
Nitric acid	HNO_3	0.92	1.94	1.92
Chloric acid	$HClO_3$	0.91	1.97	1.91
Perchloric acid	$HClO_4$	0.94	2.09	1.94
Sulphuric acid	H_2SO_4	0.60	2.06	2.19
Selenic acid	H_2SeO_4	0.66	2.10	2.31
Phosphoric acid	H_3PO_4	0.08	2.32	1.24
Sulphurous acid	H_2SO_3	0.14	1.03	1.28
Hydrogen sulphide	H_2S	0.00	1.04	1.00
Iodic acid	HIO_3	0.73	1.30	1.73
Phosphorous acid	$P(OH)_3$	0.46	1.29	1.46
Boric acid	$B(OH)_3$	0.00	1.11	1.00
Hydrocyanic acid	HCN	0.00	1.05	1.00
Formic acid	$HCOOH$	0.03	1.04	1.03
Acetic acid	CH_3COOH	0.01	1.03	1.01
Butyric acid	C_3H_7COOH	0.01	1.01	1.01
Oxalic acid	$(COOH)_2$	0.25	1.25	1.49
Tartaric acid	$C_4H_6O_6$	0.06	1.05	1.11
Malic acid	$C_4H_6O_5$	0.04	1.08	1.07
Lactic acid	$C_3H_6O_3$	0.03	1.01	1.03

SALTS.

SUBSTANCE.	FORMULA.	a	$i=\frac{t}{18.5}$.	$i=$ $1+(k-1)a$.
Potassium chloride	KCl	0.86	1.82	1.86
Sodium chloride	$Na\,Cl$	0.82	1.90	1.82
Lithium chloride	$Li\,Cl$	0.75	1.99	1.75
Ammonium chloride	$NH_4\,Cl$	0.84	1.88	1.84
Potassium iodide	KI	0.92	1.90	1.92
Potassium bromide	$K\,Br$	0.92	1.90	1.92
Potassium cyanide	$K\,CN$	0.88	1.74	1.88
Potassium nitrate	$K\,NO_3$	0.81	1.67	1.81
Sodium nitrate	$Na\,NO_3$	0.82	1.82	1.82
Ammonium nitrate	$NH_4\,NO_3$	0.81	1.73	1.81
Potassium acetate	$CH_3\,COOK$	0.83	1.86	1.83
Sodium acetate	$CH_3\,COONa$	0.79	1.73	1.79
Potassium formate	$H\,CO\,OK$	0.83	1.90	1.83
Silver nitrate	$Ag\,NO_3$	0.86	1.60	1.86
Potassium chlorate	$K\,Cl\,O_3$	0.83	1.78	1.83
Potassium carbonate	$K_2\,CO_3$	0.69	2.26	2.38
Sodium carbonate	$Na_2\,CO_3$	0.61	2.18	2.22
Potassium sulphate	$K_2\,SO_4$	0.67	2.11	2.33
Sodium sulphate	$Na_2\,SO_4$	0.62	1.91	2.24
Ammonium sulphate	$(NH_4)_2\,SO_4$	0.59	2.00	2.17
Potassium oxalate	$K_2\,C_2\,O_4$	0.66	2.43	2.32
Barium chloride	$Ba\,Cl_2$	0.77	2.63	2.54
Strontium chloride	$Sr\,Cl_2$	0.75	2.76	2.50
Calcium chloride	$Ca\,Cl_2$	0.75	2.70	2.50
Cupric chloride	$Cu\,Cl_2$	——	2.58	——
Zinc chloride	$Zn\,Cl_2$	0.70	——	2.40
Barium nitrate	$Ba\,(NO_3)_2$	0.57	2.19	2.13
Strontium nitrate	$Sr\,NO_3)_2$	0.62	2.23	2.23
Calcium nitrate	$Ca\,(NO_3)_2$	0.67	2.02	2.33
Lead nitrate	$Pb\,(NO_3)_2$	0.54	2.02	2.08
Magnesium sulphate	$Mg\,SO_4$	0.40	1.04	1.40
Ferrous sulphate	$Fe\,SO_4$	0.35	1.00	1.35
Copper sulphate	$Cu\,SO_4$	0.35	0.97	1.35
Zinc sulphate	$Zn\,SO_4$	0.38	0.98	1.38
Cupric acetate	$(C_2\,H_3\,O_2)_2\,Cu$	0.33	1.68	1.66
Magnesium chloride	$Mg\,Cl_2$	0.70	2.64	2.40
Mercuric chloride	$Hg\,Cl_2$	0.03	1.11	1.05
Cadmium iodide	$Cd\,I_2$	0.28	0.94	1.56
Cadmium nitrate	$Cd\,(NO_3)_2$	0.73	2.32	2.46
Cadmium sulphate	$Cd\,SO_4$	0.35	0.75	1.35

The last three numbers in next to the last column are not taken, like all the others, from the work of Raoult,* but from the older data of Rüdorff,† who employed in his experiments very large quantities of the substance investigated, therefore no very great accuracy can be claimed for these three numbers. The value of α is calculated from the results of Kohlrausch,‡ Ostwald§ (for acids and bases), and some few from those of Grotrian‖ and Klein.¶ The values of α, calculated from the results of Ostwald, are by far the most certain, since the two quantities which give α can, in this case, be easily determined with a fair degree of accuracy. The errors in the values of i, calculated from such values of α, cannot be more than 5 per cent. The values of α and i, calculated from the data of Kohlrausch, are somewhat uncertain, mainly because it is difficult to calculate accurately the maximum value of the molecular conducting power. This applies, to a still greater extent, to the values of α and i calculated from the experimental data of Grotrian and Klein. The latter may contain errors of from 10 to 15 per cent. in unfavorable cases. It is difficult to estimate the degree of accuracy of Raoult's results. From the results themselves, for very nearly related substances, errors of 5 per cent., or even somewhat more, do not appear to be improbable.

It should be observed that, for the sake of completeness, all substances are given in the above table for which even a fairly accurate calculation of i by the two methods was possible. If now and then data are wanting for the conductivity of a substance (cupric chloride and tetramethylammonium hydrate), such are calculated, for the sake of comparison, from data for a very nearly related substance (zinc chloride and tetraethylammonium hydrate), whose electrical properties cannot differ appreciably from those of the substance in question.

Among the values of i which show a very large difference from one another, those for hydrofluosilicic acid must be

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* Raoult, *Ann. Chim. Phys.*, [5], **28**, 133 (1883); [6], **2**, 66, 99, 115 (1884); [6], **4**, 401 (1885). [*This volume*, p. 52.]

† Rüdorff, Ostwald's *Lehrb. all. Chem.*, I., 414.

‡ Kohlrausch, *Wied. Ann.*, **6**, 1 and 145 (1879); **26**, 161 (1885).

§ Ostwald, *Journ. prakt. Chem.*, [2], **32**, 300 (1885); [2], **33**, 352 (1886); *Ztschr. Phys. Chem.*, **1**, 74 and 97 (1887).

‖ Grotrian, *Wied. Ann.*, **18**, 177 (1883).

¶ Klein, *Wied. Ann.*, **27**, 151 (1886).

especially mentioned. But Ostwald has, indeed, shown that in all probability, this acid is partly broken down in aqueous solution into $6HF$ and SiO_2, which would explain the large value of i given by the Raoult method.

There is one condition which interferes, possibly very seriously, with directly comparing the figures in the last two columns—namely, that the values really hold for different temperatures. All the figures in next to the last column hold, indeed, for temperatures only a very little below 0° C., since they were obtained from experiments on inconsiderable lowerings of the freezing-point of water. On the other hand, the figures of the last column for acids and bases (Ostwald's experiments) hold at 25°, the others at 18°. The figures of the last column for non-conductors hold, of course, also at 0° C., since these substances at this temperature do not consist, to any appreciable extent, of dissociated (active) molecules.

An especially marked parallelism appears,* beyond doubt, on comparing the figures in the last two columns. This shows, *a posteriori*, that in all probability the assumptions on which I have based the calculation of these figures are, in the main, correct. These assumptions were:

1. That Van't Hoff's law holds not only for *most*, but for *all substances*, even for those which have hitherto been regarded as exceptions (electrolytes in aqueous solution).

2. That every electrolyte (in aqueous solution), consists partly of active (in electrical and chemical relation), and partly of inactive molecules, the latter passing into active molecules on increasing the dilution, so that in infinitely dilute solutions only active molecules exist.

The objections which can probably be raised from the chemical side are essentially the same which have been brought forward against the hypothesis of Clausius, and which I have earlier sought to show, were completely untenable.† A repetition of these objections would, then, be almost superfluous. I will call attention to only one point. Although the dissolved substance exercises an osmotic pressure against the wall of the vessel, just as if it were partly dissociated into its ions, yet

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* In reference to some salts which are distinctly exceptions, compare below, p. 55.

† *l. c.*, 2 Tl., pp. 6 and 31.

the dissociation with which we are here dealing is not exactly the same as that which exists when, *e. g.*, an ammonium salt is decomposed at a higher temperature. The products of dissociation in the first case (the ions) are charged with very large quantities of electricity of opposite kind, whence certain conditions appear (the incompressibility of electricity), from which, it follows that the ions cannot be separated from one another to any great extent, without a large expenditure of energy.* On the contrary, in ordinary dissociation where no such conditions exist, the products of dissociation can, in general, be separated from one another.

The above two assumptions are of the very widest significance, not only in their theoretical relation, of which more hereafter, but also, to the highest degree, in a practical sense. If it could, for instance, be shown that the law of Van't Hoff is generally applicable—which I have tried to show is highly probable—the chemist would have at his disposal an extraordinarily convenient means of determining the molecular weight of every substance soluble in a liquid.†

At the same time, I wish to call attention to the fact that the above equation (1) shows a connection between the two values i and α, which play the chief rôles in the two chemical theories developed very recently by Van't Hoff and myself.

I have tacitly assumed in the calculation of i, carried out above, that the inactive molecules exist in the solution as simple molecules and not united into larger molecular complexes. The result of this calculation (*i. e.*, the figures in the last column), compared with the results of direct observation (the figures in next to the last column), shows that, in general, this supposition is perfectly justified. If this were not true the figures in next to the last column would, of course, prove to be smaller than in the last. An exception, where the latter undoubtedly takes place, is found in the group of sulphates of the magnesium series ($Mg\,SO_4$, $Fe\,SO_4$, $Cu\,SO_4$, $Zn\,SO_4$, and $Cd\,SO_4$), also in cadmium iodide. We can assume, to explain this, that the inactive molecules of these salts are, in part,

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* *l. c.*, 2 Tl., p. 8.

† This means has already been employed. Compare Raoult, *Ann. Chim. Phys.*, [6], **8**, 317 (1886); Paternò and Nasini, *Ber. deutsch. chem. Gesell.*, 1886, 2527.

combined with one another. Hittorf,* as is well known, was led to this assumption for cadmium iodide, through the large change in the migration number. And if we examine his tables more closely we will find, also, an unusually large change of this number for the three of the above-named sulphates ($Mg\ SO_4$, $Cu\ SO_4$, and $Zn\ SO_4$) which he investigated. It is then very probable that this explanation holds for the salts referred to. But we must assume that double molecules exist only to a very slight extent in the other salts. It still remains, however, to indicate briefly the reasons which have led earlier authors to the assumption of the general existence of complex molecules in solution.

Since, in general, substances in the gaseous state consist of simple molecules (from Avogadro's law), and since a slight increase in the density of gases often occurs near the point of condensation, indicating a union of the molecules, we are inclined to see in the change of the state of aggregation, such combinations taking place to a much greater extent. That is, we assume that the liquid molecules in general are not simple. I will not combat the correctness of this conclusion here. But a great difference arises if this liquid is dissolved in another (*e. g.*, $H\ Cl$ in water). For if we assume that by dilution the molecules which were inactive at the beginning become active, the ions being separated to a certain extent from one another, which of course requires a large expenditure of energy, it is not difficult to assume, also, that the molecular complexes break down, for the most part, on mixing with water, which in any case does not require very much work. The consumption of heat on diluting solutions has been interpreted as a proof of the existence of molecular complexes.† But, as stated, this can also be ascribed to the conversion of inactive into active molecules. Further, some chemists, to support the idea of constant valence, would assume‡ molecular complexes, in which the unsaturated bonds could become saturated. But the doctrine of constant valence is so much disputed that we are scarcely justified in basing any conclusions upon it. The conclusions thus arrived at, that, *e.g.*, potassium chloride would have the formula $(KCl)_3$, L. Meyer

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* Hittorf, *Pogg. Ann.*, **106**, 547 and 551 (1859); *Wied. Elektr.*, **2**, 584.

† Ostwald, *Lehrb. all. Chem.*, I., 811; L. Meyer, *Moderne Theorien der Chemie*, p. 319 (1880).

‡ L. Meyer, *l. c.* p. 360.

sought to support by the fact that potassium chloride is much less volatile than mercuric chloride, although the former has a much smaller molecular weight than the latter. Independent of the theoretical weakness of such an argument, this conclusion could, of course, hold only for the pure substances, not for solutions. Several other reasons have been brought forward by L. Meyer for the existence of molecular complexes, *e. g.*, the fact that sodium chloride diffuses more slowly than hydrochloric acid,* but this is probably to be referred to the greater friction (according to electrical determinations), of sodium against water, than of hydrogen. But it suffices to cite L. Meyer's own words: "Although all of these different points of departure for ascertaining molecular weights in the liquid condition are still so incomplete and uncertain, nevertheless they permit us to hope that it will be possible in the future to ascertain the size of molecules."† But the law of Van't Hoff gives entirely reliable points of departure, and these show that in almost all cases the number of molecular complexes in solutions can be disregarded, while they confirm the existence of such in some few cases, and, indeed, in those in which there were formerly reasons for assuming the existence of such complexes.‡ Let us, then, not deny the possibility that such molecular complexes also exist in solutions of other salts—and especially in concentrated solutions; but in solutions of such dilution as was investigated by Raoult, they are, in general, present in such small quantity that they can be disregarded without appreciable error in the above calculations.

Most of the properties of dilute solutions of salts are of a so-called additive nature. In other words, these properties (expressed in figures) can be regarded as a sum of the properties of the parts of the solution (of the solvent, and of the parts of the molecules, which are, indeed, the ions). As an example, the conductivity of a solution of a salt can be regarded as the sum of the conductivities of the solvent (which in most cases is zero), of the positive ion, and of the negative ion.§ In most cases this is controlled by comparing two salts of one

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* L. Meyer, *l. c.* p. 316.

† L. Meyer, *l. c.* p. 321. The law of Van't Hoff makes this possible, as is shown above.

‡ Hittorf, *l. c.* Ostwald's *Lehrb. all. Chem.*, p. 816.

§ Kohlrausch, *Wied. Ann.*, 167 (1879).

acid (*e. g.*, potassium and sodium chlorides) with two corresponding salts of the same metals with another acid (*e. g.*, potassium and sodium nitrates). Then the property of the first salt ($K\,Cl$), *minus* the property of the second ($Na\,Cl$), is equal to the property of the third (KNO_3), *minus* the property of the fourth ($Na\,NO_3$). This holds in most cases for several properties, such as conductivity, lowering of freezing-point, refraction equivalent, heat of neutralization, etc., which we will treat briefly, later on. It finds its explanation in the nearly complete dissociation of most salts into their ions, which was shown above to be true. If a salt (in aqueous solution) is completely broken down into its ions, most of the properties of this salt can, of course, be expressed as the sum of the properties of the ions, since the ions are independent of one another in most cases, and since every ion has, therefore, a characteristic property, independent of the nature of the opposite ion with which it occurs. The solutions which we, in fact, investigate are never completely dissociated, so that the above statement does not hold rigidly. But if we consider such salts as are 80 to 90 per cent. dissociated (salts of the strong bases with the strong acids, almost without exception), we will, in general, not make very large errors if we calculate the properties on the assumption that the salts are completely broken down into their ions. From the above table this evidently holds also for the strong bases and acids: $Ba\,(OH)_2$, $Sr\,(OH)_2$, $Ca\,(OH)_2$, $Li\,OH$, $Na\,OH$, $K\,OH$, $Tl\,OH$, and $H\,Cl$, $H\,Br$, $H\,I$, $H\,NO_3$, $H\,Cl\,O_3$, and $H\,Cl\,O_4$.

But there is another group of substances which, for the most part, have played a subordinate rôle in the investigations up to the present, and which are far from completely dissociated, even in dilute solutions. Examples taken from the above table are, the salts, $Hg\,Cl_2$ (and other salts of mercury), $Cd\,I_2$, $Cd\,SO_4$, $Fe\,SO_4$, $Mg\,SO_4$, $Zn\,SO_4$, $Cu\,SO_4$, and $Cu\,(C_2\,H_3\,O_2)_2$; the weak bases and acids, as NH_3, and the different amines, $H_3\,PO_4$, $H_2\,S$, $B\,(OH)_3$, $H\,CN$, formic, acetic, butyric, tartaric, malic, and lactic acids. The properties of these substances will not, in general, be of the same (additive) nature as those of the former class, a fact which is completely confirmed, as we will show later. There are, of course, a number of substances lying between these two groups, as is also shown by the above table. Let attention be here called to the fact that several investigators have been led to the assumption of a certain kind of complete dissociation of salts into their ions, by considering that the properties of substances of the first group, which have been investigated far more frequently than those of the second, are almost always of an additive nature.* But since no reason could be discovered from the chemical side why salt molecules should break down (into their ions) in a perfectly definite manner, and, moreover, since chemists, for certain reasons not to be more fully considered here, have fought as long as possible against the existence of so-called unsaturated radicals (under which head the ions must be placed), and since, in addition, it cannot be denied that the grounds for such an assumption were somewhat uncertain,† the assumption of complete dissociation has not met with any hearty approval up to the present. The above table shows, also, that the aversion of the chemist to the idea advanced, of complete dissociation, has not been without a certain justification, since at the dilutions actually employed, the dissociation is never complete, and even for a large number of electrolytes, (the second group) is relatively inconsiderable.

After these observations we now pass to the special cases in which additive properties occur.

1. *The Heat of Neutralization in Dilute Solutions.*—When an acid is neutralized with a base, the energies of these two substances are set free in the form of heat; on the other hand, a certain amount of heat disappears as such, equivalent to the energies of the water and salt (ions) formed. We designate with ( ) the energies for those substances, for which it is unimportant for the deduction whether they exist as ions or not, and with [ ] the energies of the ions, which always means the energies in dilute solution. To take an example, the following amounts of heat are set free on neutralizing $Na\,OH$ with $\frac{1}{2}\,H_2\,SO_4$ (1), and with $H\,Cl$ (2), and on neutralizing $K\,OH$ with $\frac{1}{2}\,H_2\,SO_4$ (3), and with $H\,Cl$ (4) (all in equivalent quantities, and on the previous assumption of a complete dissociation of the salts):

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* Valson, *Compt. rend.*, **73**, 441 (1871); **74**, 103 (1872); Favre and Valson, *Compt. rend.*, **75**, 1033 (1872); Raoult, *Ann. Chim. Phys.*, [6], 4, 426.

† In reference to the different hypotheses of Raoult, compare, *l. c.*, p. 401.

$$(Na\,OH)+\tfrac{1}{2}(H_2\,SO_4)-(H_2\,O)-[Na]-[\tfrac{1}{2}\,SO_4]. \qquad (1)$$
$$(Na\,OH)+(H\,Cl)-(H_2\,O)-[Na]-[Cl]. \qquad (2)$$
$$(K\,OH)+\tfrac{1}{2}(H_2\,SO_4)-(H_2\,O)-[K]-[\tfrac{1}{2}\,SO_4]. \qquad (3)$$
$$(K\,OH)+(H\,Cl)-(H_2\,O)-[K]-[Cl]. \qquad (4)$$

(1)−(2) is, of course, equal to (3)−(4), on the assumption of a complete dissociation of the salts. This holds, approximately, as above indicated, in the cases which actually occur. This is all the more true, since the salts which are farthest removed from complete dissociation—in this case $Na_2\,SO_4$ and $K_2\,SO_4$—are dissociated to approximately the same extent, therefore the errors in the two members of the last equation are approximately of equal value, a condition which, in consequence of the additive properties, exists more frequently than we could otherwise expect. The small table given below shows that the additive properties distinctly appear on neutralizing strong bases with strong acids. This is no longer the case with the salts of weak bases with weak acids, because they are, in all probability, partly decomposed by the water.

HEATS OF FORMATION OF SOME SALTS IN DILUTE SOLUTION, ACCORDING TO THOMSEN AND BERTHELOT.

	$H\,Cl$ $H\,Br$ $H\,I$	$H\,NO_3$	$C_2\,H_4\,O_2$	$CH_2\,O_2$	$\tfrac{1}{2}\,(CO\,OH)_2$
$Na\,OH$	13.7	13.7 (0.0)	13.3 (−0.4)	13.4 (−0.3)	14.3 (+0.6)
$K\,OH$	13.7	13.8 (+0.1)	13.3 (−0.4)	13.4 (−0.3)	14.3 (+0.6)
NH_3	12 4	12.5 (+0.1)	12.0 (−0.4)	11.9 (−0.5)	12.7 (+0.3)
$\tfrac{1}{2}\,Ca\,(OH)_2$	14.0	13.9 (−0.1)	13.4 (−0.6)	13.5 (−0.5)	——
$\tfrac{1}{2}\,Ba\,(OH)_2$	13.8	13.9 (+0.1)	13.4 (−0 4)	13.5 (−0.3)	——
$\tfrac{1}{2}\,Sr\,(OH)_2$	14.1	13.9 (−0.2)	13.3 (−0.8)	13.5 (−0.6)	——

	$\tfrac{1}{2}\,H_2\,SO_4$	$\tfrac{1}{2}\,H_2\,S$	HCN	$\tfrac{1}{2}\,CO_2$
$Na\,OH$	15.8 (+2.1)	3.8 (−9.9)	2.9 (−10.8)	10.2 (−3.5)
$K\,OH$	15.7 (+2.0)	3.8 (−9.9)	3 0 (−10.7)	10.1 (−3.6)
NH_3	14.5 (+2.0)	3.1 (−9.3)	1.3 (−11.1)	5.3 (−7.1)
$\tfrac{1}{2}\,Ca\,(OH)_2$	——	3.9 (−10.1)	——	——
$\tfrac{1}{2}\,Ba\,(OH)_2$	——	——	——	——
$\tfrac{1}{2}\,Sr\,(OH)_2$	——	——	——	——

As can be seen from the figures inclosed in brackets (which represent the difference between the heat tone in question and the corresponding heat tone of the chloride), they are approximately constant in every vertical column. This fact is very closely connected with the so-called thermo-neutrality of salts; but since I have previously treated this subject more directly, and have emphasized its close connection with the Williamson-Clausius* hypothesis, I do not now need to give a detailed analysis of it.

2. *Specific Volume and Specific Gravity of Dilute Salt Solutions.*—If a small amount of salt, whose ions can be regarded as completely independent of one another in the solution, is added to a litre of water, the volume of this is changed. Let x be the quantity of the one ion added, and y that of the other, the volume will be approximately equal to $(1+ax+by)$ litres, a and b being constants. But since the ions are dissociated from one another, the constant a of the one ion will, of course, be independent of the nature of the other ion. The weight is, similarly, $(1+cx+dy)$ kilograms, in which c and d are two other constants characteristic for the ions. The specific gravity will then, for small amounts of x and y, be represented by the formula:

$$1+(c-a)\,x+(b-d)\,y,$$

where, of course, $(c-a)$ and $(b-d)$ are also characteristic constants for the two ions. The specific gravity is, then, an additive property for dilute solutions, as Valson† has also found. But since "specific gravity is not applicable to the representation of stöichiometric laws," as Ostwald‡ maintains, we will refrain from a more detailed discussion of these results. The determination of the constants a and b, etc., promises much of value, but thus far has not been carried out.

The changes in volume in neutralization are closely related to these phenomena. It can be shown that the change in volume in neutralization is an additive property, from considerations very similar to those above for heat of neutralization. All the salts investigated (K_1- Na- NH_4-) are almost completely dissociated in dilute solutions, as is clear from the above table (and is even clearer from the subsequent work of Ostwald), so that a very satisfactory agreement for these salts can be expected. The differences of the change in volume in the

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* *l. c.*, 2 Tl., p. 67.

† Valson, *Compt. rend.*, **73**, 441 (1871); Ostwald, *Lehrb. all. Chem.*, I., 384.

‡ Ostwald, *ibid.*, I., 386.

formation of the salts in question, from nineteen different acids, are also found to be nearly constant numbers.* Since bases which form salts of the second group have not been investigated, there are no exceptions known.

3. *Specific Refractivity of Solutions.*—If we represent by n the index of refraction, by d the density, and by P the weight of a substance, $P\frac{n-1}{d}$ is, as is well known, a value which, when added for the different parts of mixtures of several substances, gives the corresponding value for the mixture. Consequently, this value must make the refraction equivalent an additive property also for the dissociated salts. The investigations of Gladstone have shown distinctly that this is true. The potassium and sodium salts have been investigated in this case just as the acids themselves. We take the following short table on molecular refraction equivalents from the *Lehrbuch* of Ostwald:†

	POTASSIUM.	SODIUM.	HYDROGEN.	$K-Na$.	$K-H$.
Chloride.....	18.44	15.11	14.44	3.3	4.0
Bromide.....	25.34	21.70	20.63	3.6	4.7
Iodide.......	35.33	31.59	31.17	3.7	4.2
Nitrate......	21.80	18.66	17.24	3.1	4.5
Sulphate....	30.55	——	22.45	——	2×4.1
Hydrate.....	12.82	9.21	5.95	3.6	6.8
Formate.....	19.93	16.03	13.40	3.9	6.5
Acetate......	27.65	24.05	21.20	3.6	6.5
Tartrate.....	57.60	50.39	45.18	2×3.6	2×6.2

The difference $K-Na$ is, as is seen, almost constant throughout, which was also to be expected from the knowledge of the extent of dissociation of the potassium and sodium salts. The same holds also for the difference $K-H$, as long as we are dealing with the strong (dissociated) acids. On the contrary, the substances of the second group (the slightly dissociated acids), behave very differently, the difference $K-H$ being much greater than for the first group.

4. Valson‡ believed that he also found additive properties

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* Ostwald, *Lehrb. all. Chem.*, I., 388.

† Ostwald, *l. c.*, p. 443.

‡ Valson, *Compt. rend.*, **74**, 103 (1872); Ostwald, *l. c.* p. 492.

of salt solutions in *Capillary Phenomena.* But since this can be traced back to the fact that the specific gravity is an additive property, as above stated, we need not stop to consider it.

5. *Conductivity.*—F. Kohlrausch, as is well known, has done a very great service for the development of the science of electrolysis, by showing that conductivity is an additive property.* Since we have already pointed out how this is to be understood, we pass at once to the data obtained. Kohlrausch gives in his work already cited, the following values for dilute solutions:

$K=48$, $NH_4=47$, $Na=31$, $Li=21$, $Ag=40$, $H=278$, $Cl=49$, $Br=53$, $I=53$, $CN=50$, $OH=141$, $F=30$, $NO_3=46$, $Cl\,O_3=40$, $C_2\,H_3\,O_2=23$, $\frac{1}{2}\,Ba=29$, $\frac{1}{2}\,Sr=28$, $\frac{1}{2}\,Ca=26$, $\frac{1}{2}\,Mg=23$, $\frac{1}{2}\,Zn=20$, $\frac{1}{2}\,Cu=29$.

But these values hold only for the most strongly dissociated substances (salts of the monobasic acids and the strong acids and bases). For the somewhat less strongly dissociated sulphates and carbonates of the univalent metals (compare above table), he obtained, indeed, much smaller values: $K=40$, $NH_4=37$, $Na=22$, $Li=11$, $Ag=32$, $H=166$, $\frac{1}{2}SO_4=40$, $\frac{1}{2}\,CO_3=36$; and for the least dissociated sulphates (the metals of the magnesium series), he obtained the following still smaller values: $\frac{1}{2}\,Mg=14$, $\frac{1}{2}\,Zn=12$, $\frac{1}{2}\,Cu=12$, $\frac{1}{2}\,SO_4=22$.

It appears, then, that the law of Kohlrausch holds only for the most strongly dissociated salts, the less strongly dissociated giving very different values. But since the number of active molecules also increases with increase in dilution, so that at extreme dilution all salts break down completely into active (dissociated) molecules, it would be expected that, at higher dilutions, the salts would behave more regularly. I showed, also, from some examples that "we must not lay too much stress upon the anomalous behavior of salts (acetates and sulphates) of the magnesium series, since these anomalies disappear at greater dilutions."† I also believed I could establish the view that conductivity is an additive property,‡ and I ascribed to the conductivity of hydrogen in all acids (even in the poorest conducting, whose behavior was not at all compatible with this view), a value which was entirely independent of the

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* Kohlrausch, *Wied. Ann.*, **6**, 167 (1879); *Wied. Elek.*, **1**, 610; **2**, 955.

† *l. c.*, 1 Tl., p. 41.

‡ *l. c.*, 2 Tl., p. 12.

nature of the acid. This, again, was accomplished only with the aid of the conception of activity. The correctness of this view appears still more clearly from the later work of Kohlrausch,* and of Ostwald.† Ostwald attempts to show in his last work upon this subject, that the view that conductivity is additive is tenable without the aid of the activity conception, and he succeeds very well for the salts which he employed (potassium, sodium, and lithium), because these are, in general, very nearly completely dissociated, and especially at very great dilutions. This result receives further support from the fact that analogous salts of the univalent metals, if they are very closely related to one another, are dissociated to approximately the same extent at the same concentrations. But if we were dealing with salts of less closely related metals we should obtain very different results, as is shown distinctly by previous investigations. As Ostwald ‡ himself says, the law of Kohlrausch does not hold for the acids, but we must add to it the conception of activity if we would have it hold true. But this law does not apply to all salts. A closer investigation of copper acetate would, indeed, lead to considerable difficulties.§ This would be still more pronounced if we took into account the mercury salts, since it appears from the investigations of Grotrian,‖ as if these gave only a very small fraction of the conductivity derived from this law, even in extreme dilutions. It is apparent that not all of the salts of the univalent metals conform to this law, since, according to Bouty,¶ potassium antimonyl tartrate, in 0.001 normal solution, conducts only about one-fifth as well as potassium chloride. From the law of Kohlrausch it must conduct at least half as well as potassium chloride. But if we make use of the activity conception, the law of Kohlrausch holds very satisfactorily, as is shown by the values of i in the above table for weak bases and acids, calculated on the basis of this law, and also for $HgCl_2$ and $Cu(C_2H_3O_2)_2$. They agree very well with the values of i derived from the experiments of Raoult.

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* Kohlrausch, *Wied. Ann.*, **26**, 215 and 216 (1885).

† Ostwald, *Ztschr. Phys. Chem.*, **1**, 74 and 97 (1887).

‡ Ostwald, *l. c.* p. 79.

§ My work, already cited. 1 Tl., p. 39.

‖ Grotrian, *Wied. Ann.*, **18**, 177 (1883).

¶ Bouty, *Ann. Chim. Phys.*, [6], **3**, 472 (1884).

6. *Lowering of the Freezing-Point.*—Raoult[*] shows, in one of his investigations, that the lowering of the freezing-point of water by salts can be regarded as an additive property, as would be expected, in accordance with our views for the most strongly dissociated salts in dilute solutions. The following values were obtained for the activities of the ions:

GROUP.		
1st.	Univalent (electro) negative ions (radicals)..	20 (Cl, Br, OH, NO_3, etc.)
2d.	Bivalent “ “ “	11 (SO_4, CrO_4, etc.)
3d.	Univalent (electro) positive “ “	15 (H, K, Na, NH_4, etc.)
4th.[†]	Bivalent or polyvalent “ “ “	8 (Ba, Mg, Al_2, etc.)

But there are very many exceptions which appear because of unusually small dissociation even in the most dilute solutions, as is seen from the following table:

	Calculated.	Observed.		Calculated.	Observed.
Weak acids.............	35	19	Lead acetate...........	48	22.2
$Cu(C_2H_3O_2)_2$...........	48	31.1	Aluminium acetate.....	128	84.0
Potassium antimonyl tartrate................	41	18.4	Ferric acetate...........	128	58.1
Mercuric chloride.......	48	20.4	Platinic chloride.......	88	29.0

We know, from experiments on the electrical conductivity of those substances which are given in the first column, that their

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[*] Raoult, *Ann. Chim. Phys.*, [6], **4**, 416 (1885).

[†] All ions have the same value 18.5, according to the views already explained. Raoult has, evidently, ingeniously forced these substances under the general law of the additivity of freezing-point lowering, by assigning to the ions of the less dissociated substances, as $MgSO_4$, much smaller values (8 and 11 respectively). The possibility of ascribing smaller values to the polyvalent ions is based upon the fact that, in general, the dissociation of salts is smaller the greater the valence of their ions, as I have previously maintained (*l. c.*, 1 Tl., p. 69; 2 Tl., p. 5). "The inactivity (complexity) of a salt solution is greater, the more easily the constituents of the salt (acid and base) form double compounds." This result is, moreover, completely confirmed through subsequent work by Ostwald (*Ztschr. Phys. Chem.*, **1**, 105 to 109). It is evident that if we were to give the correct value. 18.5, to the polyvalent ions, the salts obtained from them would form very distinct exceptions. (Probably a similar view in reference to other additive properties could be correctly brought forward.) Although Raoult has, then, artificially forced these less strongly dissociated salts to conform to his law, he has not succeeded in doing so with all of the salts, as is pointed out above.

molecules are very slightly dissociated. The remaining substances are closely related to these, so that we can expect them to behave similarly, although they have not been investigated, electrically, up to the present. But if we accept the point of view which I have brought forward, all of these substances, the latter as well as the cases previously cited, are not to be regarded as exceptions; on the contrary, they obey exactly the same laws as the other substances hitherto regarded as normal.

Several other properties of salt solutions are closely connected with the lowering of the freezing-point, as Guldberg* and Van't Hoff† have shown. These properties are proportional to the lowering of the freezing-point. All of these properties—lowering of the vapor-pressure, osmotic pressure, isotonic coefficients,—are, therefore, to be regarded as additive. De Vries‡ has also shown this for isotonic coefficients. But since all of these properties can be traced back to the lowering of the freezing-point, I do not think it necessary to enter into the details of them here.

SVANTE ARRHENIUS was born February 19, 1859, near Upsala, Sweden. After leaving the Gymnasium in 1876, he studied in the University of Upsala until 1881. From 1881 to 1883 he worked at the Physical Institute of the Academy of Sciences in Stockholm. Having received the Degree of Doctor of Philosophy from the University of Upsala in 1878, he was appointed privat-docent in that institution in 1884.

A little later, the Stockholm Academy of Sciences granted Arrhenius an allowance that he might visit foreign universities. In 1888 he worked with Van't Hoff in Amsterdam, in 1889 with Ostwald in Leipsic, and in 1890 with Boltzmann in Gratz.

In 1891 he was called to Stockholm as a teacher of physics, in what is termed the Stockholm High School, but which, in reality, corresponds favorably with many of the smaller universities abroad. In 1895 he was appointed to the full professorship of physics in Stockholm, a position which he now holds.

Some of his more important pieces of work, in addition to

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* Guldberg, *Compt. rend.*, **70**, 1349 (1870).

† Van't Hoff, *l. c.* p. 20.

‡ De Vries, *Eine Methode zur Analyse der Turgorkraft*, Pringsheim's *Jahrbücher*, **14**, 519 (1883); Van't Hoff, *l. c.* p. 26.

that included in this volume, are : *The Conductivity of Very Dilute Aqueous Solutions* (Dissertation) ; *Theory of Isohydric Solutions ; Effect of the Solar Radiation on the Electrical Phenomena in the Earth's Atmosphere ; Effect of the Amount of Carbon Dioxide in the Air on the Temperature of the Earth's Surface.*

Arrhenius is also a member of a number of learned societies and academies.