

THE THEORY OF ELECTROLYTIC DISSOCIATION AS VIEWED IN THE LIGHT OF FACTS RE- CENTLY ASCERTAINED¹

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INTRODUCTION

The theory of electrolytic dissociation as advanced by Arrhenius² in 1887 is based primarily upon the facts that the molecular conductivity of solutions increases with the dilution, that substances which when dissolved conduct electricity, also have abnormally low molecular weights in such solutions when tested by osmotic or freezing- or boiling-point methods, and that the so-called degree of dissociation may be calculated from the electrical conductivity or the results of the molecular weight determinations. In his original article Arrhenius states that the phenomena of electrolysis, when viewed from the standpoint of thermodynamics, require the assumption of the presence of free ions, as was pointed out by Clausius, and that the heats of neutralization of acids and bases in dilute solutions and the various physical properties of salt solutions, which are well known to be additive in character, support the electrolytic dissociation hypothesis. The effect which the publication of that memorable article of Arrhenius had, need not to be dwelt upon at length here. Suffice it to recall that its author sought to save van't Hoff's theory of solutions from having but a limited application, and at the same time to bring into correlation facts that had hitherto been entirely isolated. Chemists and physicists alike

¹ Published also in the Bulletin of the University of Wisconsin, Science Series No. 4, 2, 247 (1901).

² Zeit. phys. Chem. 1, 629 (1887).

were astonished by the audacity of the assumption made by this investigator of recognized ability. The theory at once met with great opposition, notably in England, and it was by no means received with open arms on the continent. But the hypothesis inspired experimental investigation, and the results of this phenomenal activity (which at first centered in Ostwald's laboratory at Leipzig, but spread rapidly to other parts of Germany, to various other countries of Europe and to America) soon silenced opposition in Germany, and gradually diminished it also in England. It must not be supposed, however, that this silence meant that all were convinced. The silence seemed to result on the one hand because of a recognition of the futility of the debate with the knowledge of existing facts, and because of a recognition of, if not an admiration for, the enthusiasm displayed by the adherents of the theory,—enthusiasm that bore fruitful results in experimental investigations of various physical, chemical and physiological properties of solutions, which results were ingeniously interpreted in the light of the new theory.

It was at first only in the case of aqueous solutions of the ordinary acids, salts and bases that van't Hoff's theory of solutions met its difficulties; and when Arrhenius pointed out that these solutions are conductors of electricity, and assumed that the dissolved substances are electrolytically dissociated into free ions, these solutions were on this basis shown to support the theory. Arrhenius calculated the troublesome factor i (which van't Hoff had found it necessary to introduce to make the behavior of the above mentioned solutions conform to the gas equation) from the electrical conductivity on the one hand and from molecular weight determinations on the other, the resulting figures showing an agreement to within 5 to 15 percent, according to his estimation. In view of the few experimental data at hand in 1887, and the fact that many of them had not been determined with accuracy, the poor agreement, of a goodly number of values at least, was readily overlooked in view of the generalities that the theory sought to bring, generalities which were soon incorporated without proper qualifications into text-books. The

electrolytic solutions with which Arrhenius made his comparisons and deductions were without exception aqueous solutions. The non-aqueous solutions known at that time were practically non-conductors of electricity; and in dilute solutions at least, they generally conformed fairly well in their behavior to van't Hoff's theory of solutions. (Indeed it was not until Raoult began his famous work on the freezing-points of non-aqueous solutions that it was discovered that molecular weights could be calculated from the lowering of the freezing-point.) In view of the facts then known, the idea gradually gained ground in the minds of those holding van't Hoff's theory and Arrhenius' auxiliary hypothesis concerning the nature of electrolytes, that non-aqueous solutions in general yield "normal" molecular weights for the solutes, and that they are "of course" non-conductors of electricity. This notion took root with surprising rapidity and the natural result was that investigations of electrical conductivity, of electromotive forces and of electrolysis in non-aqueous solutions was entirely neglected.¹ When in 1895 I had the great privilege of working in the inspiring atmosphere of Ostwald's laboratory, I upon one occasion asked the genial director of the institute why the electrical conductivity of non-aqueous solutions was not studied; the reply was, "*Die nicht-wässrigen Lösungen leiten ja nicht.*" So it was hardly a surprise when in 1899 the new edition of Ostwald's *Grundriss der allgemeinen Chemie* appeared, containing on pages 390 and 391 the sweeping, unqualified, italicized statement, "*Jedesmal wenn ein gelöster Stoff von den Lösungsgesetzen in solchem Sinne abweicht, dass sein osmotischer Druck (oder die diesem proportionale Gefrierpunkts- oder Siedepunkts-änderung) grösser ist, als seinem Molekulargewicht entspricht, so zeigt er auch elektrolitische Leitfähigkeit und umgekehrt.*" It is to be noted that Reychler's book on physical chemistry, a much less compendious volume, the English translation of which appeared early in 1899,

¹ On the other hand it was at once assumed that free ions exist whenever a substance conducts electricity with accompanying chemical decomposition, be that substance a gas, a molten salt, or a solid.

nevertheless contains a very fair consideration of the work that had at that time been accomplished in the study of non-aqueous solutions.

Behavior of non-aqueous electrolytic solutions

Before entering upon the experimental part of this paper, I desire to call attention briefly to the import of some of the work on non-aqueous conducting solutions as bearing upon the theory of electrolytic dissociation. In the first place many cases have been found in which the molecular conductivity decreases with increased dilution. This is true for instance of solutions of NaI and NaBr in benzonitrile,¹ of AgNO₃ in piperidine,² of FeCl₃ in pyridine,³ of FeCl₃ in benzaldehyde³ and of CoI₂ in POCl₃.⁴ In other cases the molecular conductivity at first increases and then again decreases with the dilution, as for instance in solutions of FeCl₃ in paraldehyde,¹ of CBr₃COOH in POCl₃.² Again many solutions have been found in which the solute according to molecular weight determinations is undissociated, and which nevertheless possess excellent power of conducting electricity. So AgNO₃ has a normal molecular weight⁵ in pyridine and benzonitrile, and yet it conducts⁶ fairly well in these solvents. According to Dutoit and Friderich,⁷ CdI₂, LiCl, NaI, HgCl₂ and NH₄CNS have normal molecular weights in acetone, and yet these solutions are conductors of electricity. Walden⁸ has found that KI, NaI, RbI, NH₄I and KCNS conduct well in liquid SO₂ and yet have abnormally large molecular weights in this solvent; while S(CH₃)₃I, N(CH₂)₄I have molecular weights in this solvent which hardly differ from the theoretical more than do the molecular weights of non-electrolytes examined in SO₂. Walden himself says concerning this, "*ganz*

¹ Euler. Zeit. phys. Chem. **28**, 619 (1899).

² Lincoln. Jour. Phys. Chem. **3**, 457 (1899).

³ Kahlenberg and Lincoln. Ibid. **3**, 12 (1899).

⁴ Walden. Zeit. anorg. Chem. **25**, 213 (1900).

⁵ Werner. Ibid. **15**, 1 (1897).

⁶ Kahlenberg and Lincoln. l. c. Also Lincoln. l. c.

⁷ Bull. Soc. Chim. Paris, (3), **19**, 334 (1898).

⁸ Ber. chem. Ges. Berlin. **32**, 2862 (1899).

unerwartet ist jedoch die doppelte Molekulargrösse für die Elektrolyte 4-7, was ganz aus dem Rahmen des Geforderten herausfällt und nicht ohne Weiteres mit der üblichen Auffassung vereinbar ist." Franklin and Kraus¹ have found that while NH_4NO_3 , NaNO_3 and KI dissolved in liquid ammonia are excellent conductors of electricity, the boiling-points of the solutions, like those observed by Walden in SO_2 , are not nearly as high as they ought to be on the basis of the assumption that electrolytic dissociation takes place. Again lately Nicolo Castoro² found by means of the freezing-point method that AgNO_3 , CdCl_2 , HgCl_2 , and ZnCl_2 have normal molecular weights in urethane. I have made a few preliminary tests on the first three of these salts which showed that their solutions in urethane are conductors of electricity. Very recently Innes³ found the molecular weights of succinic, salicylic and tartaric acids to be normal in pyridine according to the boiling-point method. These acids undoubtedly form salts which redissolve in the excess of the solvent. Preliminary tests have assured me that all three of these solutions are fairly good conductors of electricity. The tartaric acid solution conducts best, as might have been expected.

While in many cases the molecular conductivity of non-aqueous solutions increases with the dilution, this increase is generally relatively slight. It has generally been impossible to calculate the degree of dissociation of substances in non-aqueous solutions from the conductivity, because in these solutions the molecular conductivity commonly either diminishes with the increase of dilution, or it increases slightly with the dilution exhibiting no tendency to reach a maximum, or it remains practically constant, or soon reaches a maximum with so low a value that completeness of dissociation can not consistently be assumed. These facts will become evident to the reader by a perusal of the figures contained in the original articles above cited. I have

¹ Amer. Chem. Jour. 20, 836 (1898).

² Gazz. chim. Ital. 28, II, 317 (1898).

³ Jour. Chem. Soc. 79, 261 (1901).

already discussed at some length the difficulty of calculating the degree of dissociation in non-aqueous solutions,¹ and shall therefore simply add here that the calculation of the degree of dissociation from molecular weight determinations is in the case of non-aqueous solutions also impracticable, because the molecular weights are, as a rule, normal or greater than normal in spite of the fact that the solutions conduct well, and that the boiling-point constant of the solvent is so high that dissociation certainly ought to be indicated, if it were present.

It is a well known fact also that molecular weights determined according to cryoscopic or ebullioscopic methods at times increase with the dilution, again at other times they do not change much with the dilution, and at still other times they decrease as the dilution increases. The latter behavior only is in harmony with the theory of solutions and the theory of electrolytic dissociation. Furthermore, occasionally simple substances show abnormally low molecular weights and yet their solutions are not conductors of electricity. This I have found to be true, for instance, in the case of solutions of diphenylamine in methyl cyanide,— results as yet unpublished.

The osmotic theory of the galvanic cell, which uses the dissociation hypothesis as a basis, also naturally meets great difficulties when applied to chains containing non-aqueous solutions.²

In the face of these facts the theory of electrolytic dissociation is untenable in the case of non-aqueous solutions. While chemists have frequently in conversation admitted this to be true, I have also often been told, "But in the realm of aqueous solutions the theory concords with the facts so well." This led me to investigate the behavior of aqueous solutions somewhat further.

Experimental part

The general plan of the investigation was to determine the boiling-points of aqueous solutions of typical, common, chemical compounds from low to very high concentrations, in order to see

¹ Jour. Phys. Chem. 3, 379 (1899).

² See Kahlenberg. Jour. Phys. Chem. 3, 395 (1899). Ibid. 4, 709 (1900).

how the molecular weight changes with the concentration, and at the same time to measure the electrical conductivity of such solutions at or near their boiling-points. This would enable one to make much more accurate comparisons between the values of the degree of dissociation as calculated from conductivity and molecular weight, than by the but too common practice of comparing coefficients deduced from conductivity results obtained at room temperature with those reckoned from boiling- or freezing-point experiments. The work of making the conductivity measurements at high temperatures and the corresponding boiling-point determinations was undertaken by Mr. Arthur A. Koch, to whose diligence and care the numerous tables (2 and 12 to 31 inclusive) given below are due. Again it was part of the plan to measure the conductivity of such solutions at 0° and at the same time to make molecular weight determinations by the cryoscopic method, and then to compare the degrees of dissociation found according to the two methods.¹ All the conductivity determinations at 0° were made by Mr. Roy D. Hall, the results of whose work are contained in Table 1 below.

The conductivity determinations were made by means of the usual Kohlrausch method, a telephone being employed. An Arrhenius resistance cell was used for the dilute solutions and a U-shaped cell with platinized electrodes sufficiently far apart was employed for the concentrated solutions. All of the solutions were carefully made up to the proper volume at the temperature indicated. The measurements at 0° were made in a bath of melting ice surrounded by another very large bath of the same nature. In the immediate vicinity of the resistance cell a

¹ But few conductivity determinations at or near 100° could be found in the literature. For seven of the salts named in Table 2, Krannhals [*Zeit. phys. Chem.* **5**, 250 (1890)] determined the conductivity at 99.4° . He did not, however, as a rule, begin with as concentrated solutions as those represented by the corresponding salts in Table 2, and his series are frequently incomplete. As far as conductivity determinations at 0° are concerned, only a few scattered determinations could be found in the literature, which would not have been adequate for the purpose in hand. Molecular weight determinations of a goodly number of the salts under consideration are to be found in the literature, but they do not cover a sufficient range of concentration for the present purpose.

delicate thermometer was kept which remained very constant at 0° . At first it was attempted to measure the conductivity of solutions at 100° , but it was soon observed that small gas bubbles are so apt to form on the electrodes at this temperature as to introduce considerable error. It was found that at 95° this particular difficulty is not so prominent, and so the conductivity measurements at the higher temperature were made at 95° instead of at 100° . The resistance cell was immersed in a large paraffine bath whose temperature was carefully regulated at 95° .

The freezing-point determinations were made with a regular Beckmann's apparatus of large size, about 40 grams of water being used in each case. The solutions were cooled only from two to three-tenths of a degree below their freezing-points, and the crystallization was each time inaugurated by means of a point of ice. The boiling-point determinations were made with a Beckmann's apparatus of about double the ordinary size. Unless otherwise stated, appropriate Beckmann's thermometers graduated to 0.01° (made by F. O. R. Goetze in Leipzig) were used. It was at first thought best to surround the thermometer with a platinum cylinder in the boiling tube, as recommended by Jones, but it was soon found that this at times causes slight fluctuations in the boiling-point, apparently due to the fact that the solution within the cylinder is apt to be slightly more concentrated than that without.

The water used in the experiments was distilled water condensed in a block tin condenser. By drawing air freed from carbon dioxide through it for a long time its conductivity was reduced to 2×10^{-6} (or somewhat less) at room temperature. The conductivity of the water has been deducted in each case, after having been determined at the proper temperature of course. The substances used were all of the C. P. variety of standard makes, generally either Kahlbaum's or Schuchardt's. They were tested as to their purity, and as a rule were recrystallized. When the salt contained water of crystallization, the amount of this was ascertained, and the salt was weighed in the crystallized form for the molecular weight determination, the crystal water being added

to the solvent in making the computations, so that the latter are all based on the amount of anhydrous salt in the solutions. For the conductivity determinations the appropriate quantities of salt (also calculated on the basis of the anhydrous substance) of course simply had to be made up to the required volume at the proper temperature.

In Table 1 are given the results of the conductivity measurements at 0° , while in Table 2 the values obtained at 95° are presented. The numbers in each case indicate the equivalent conductivity (Λ_v) in reciprocal ohms. The value of v indicates the volume in liters in which a gram-equivalent is contained.

An inspection of Tables 1 and 2 shows that in each case Λ_v increases with the dilution, which fact has also been observed by other investigators¹ who determined the conductivity of these salts at 18° and 25° . The general manner in which the equivalent conductivity increases with the dilution can best be seen by charting the results in the form of curves. For the salts here under consideration, it is true in general that Λ_v increases with increase of v in a similar manner in the case of salts that are chemically analogous. Thus if curves be charted in which ordinates represent the volumes and abscissas the conductivities, these curves will have a similar trend in the case of the chlorides; the same will be true for the nitrates as a group; and again for the sulphates as a group. At the same time, the curves for the nitrates are very similar to those of the chlorides, but the sulphates have curves with more of a characteristic trend of their own. It was deemed unnecessary to present here the curves for all the salts in Tables 1 and 2. While they have all been plotted, it will suffice for the present purpose to reproduce curves of the various types of salts contained in the tables. As such typical salts have been selected NaCl , BaCl_2 , MgSO_4 and AgNO_3 . Figures 1 and 2 show the trend of the curves at 0° and at 95° respectively, the ordinates representing the cube roots of the volumes and the abscissas the equivalent conductivities. The

¹ Compare for instance the tables in Kohlrausch und Holborn, — *Das Leitvermögen der Elektrolyte*.

TABLE I
Electrical Conductivity at 0°
(Figures represent Λ_v in reciprocal ohms)

ν	NaCl	KCl	KI	BaCl ₂	KClO ₄	NaNO ₃	KNO ₃	AgNO ₃	Ba(NO ₃) ₂	Sr(NO ₃) ₂	K ₂ SO ₄	MgSO ₄	ZnSO ₄	MnSO ₄	CdSO ₄	NiSO ₄	CoSO ₄	FeSO ₄	CuSO ₄
1/4	31.0	24.5	..	27.2	7.0	7.1	..	6.7
1/2	41.8	63.9	69.3	38.7	..	34.7	..	35.3	..	23.5	..	13.0	12.6	12.1	11.4	13.1	..	12.1	12.3
1	47.4	65.6	69.5	44.0	..	46.5	..	44.5	..	32.1	..	17.6	16.3	15.8	15.0	17.8	15.5	16.3	15.9
2	50.8	67.3	69.7	47.0	..	48.0	..	48.3	..	38.4	48.4	21.2	21.7	19.2	18.3	21.6	18.7	19.6	19.0
4	53.3	69.0	69.9	50.6	55.4	49.0	60.6	53.3	41.9	43.2	52.6	25.2	24.7	23.4	21.3	25.3	22.0	23.0	22.4
8	55.7	70.6	71.5	53.8	60.2	52.8	63.8	57.8	45.6	47.8	56.7	29.5	28.3	26.1	25.0	28.9	25.7	28.1	26.2
16	57.9	73.0	73.5	57.0	63.2	55.7	66.6	60.1	50.4	51.3	61.8	33.7	32.2	31.2	29.5	33.9	30.2	31.4	31.0
32	59.5	75.0	76.5	60.0	65.6	57.6	70.2	63.7	55.2	55.5	65.2	38.7	37.0	35.8	34.3	39.0	34.7	36.3	35.9
64	60.9	76.6	77.7	63.5	67.7	59.7	72.7	66.6	59.3	58.4	68.8	43.3	41.9	41.0	40.3	44.8	40.0	41.7	41.2
128	62.3	77.7	78.9	65.9	69.0	61.1	73.9	67.8	62.6	61.9	71.5	47.9	47.5	46.3	45.6	50.8	45.6	47.2	46.8
256	64.2	78.9	79.4	71.0	70.3	62.3	75.5	68.8	64.9	63.1	74.8	52.7	52.9	51.4	50.5	56.0	50.6	52.1	51.9
512	65.3	79.6	79.8	72.3	71.5	63.5	75.9	69.7	66.7	64.5	75.6	56.6	56.8	56.3	56.2	59.6	55.2	56.0	56.3
1024	67.7	80.5	80.7	..	72.1	64.3	76.8	70.2	67.9	66.1	76.9	60.5	61.0	59.4	59.4	63.0	58.4	59.5	60.7
2048	67.8	80.9	72.5	65.2	77.7	70.7	68.0	67.9	78.0	63.6	64.4	62.8	62.4	64.6	61.7	62.0	63.2
4096	67.7	78.4	70.5	..	68.0	79.0	66.2	65.4	65.6	63.4	65.9	64.3	63.4	66.4
8192	67.8	65.9	65.5	64.7	64.9	67.3

TABLE 2
Electrical Conductivity at 95°
(Figures represent Λ_v in reciprocal ohms)

α	NaCl	KCl	KBr	KI	MgCl ₂	BaCl ₂	HgCl ₂	KClO ₃	KNO ₃	AgNO ₃	MgSO ₄	ZnSO ₄	MnSO ₄	CdSO ₄	NiSO ₄	CoSO ₄	FeSO ₄	CuSO ₄
1/4	115.9	169.1	121.9	114.3
1/2	156.1	213.2	222.8	216.3
1	206.7	261.0	245.4	252.8	158.7	146.3	185.9	198.1	180.5	75.6	64.2	58.2	52.5	70.8	64.8	60.6	58.8
2	215.5	271.9	265.3	261.7	183.4	171.1	1.93	208.3	216.6	205.0	91.1	76.7	70.0	63.6	84.5	74.7	74.3	67.9
4	236.3	284.8	286.0	274.3	197.5	193.9	2.12	235.6	251.3	228.7	103.7	87.8	84.7	74.6	98.7	87.8	89.2	76.8
8	267.5	289.5	296.4	296.3	222.6	218.5	3.98	248.7	269.4	244.4	121.0	104.0	100.4	88.6	114.2	107.8	103.5	92.2
16	271.5	313.2	317.7	305.4	235.1	240.4	5.24	266.2	288.2	252.4	142.7	123.2	119.6	109.7	133.4	123.9	125.5	108.7
32	277.2	334.4	325.8	315.1	257.7	276.1	8.78	284.1	304.6	286.8	169.7	149.4	141.4	131.2	157.7	144.7	144.2	133.8
64	288.9	360.3	338.1	331.6	272.1	297.1	14.40	300.0	320.4	293.7	194.7	172.0	171.2	152.2	183.2	178.0	173.0	150.5
128	302.6	363.9	340.4	341.4	278.6	308.1	18.60	310.3	323.1	303.0	227.4	202.9	197.3	185.6	213.0	209.6	211.5	180.8
256	310.0	373.5	343.9	348.2	285.2	326.0	28.77	320.8	330.1	309.0	259.6	232.1	236.4	225.1	253.4	241.0	250.3	218.9
512	318.8	401.8	351.5	357.5	290.9	338.9	45.90	327.7	338.7	319.3	295.4	257.4	275.4	261.7	298.6	282.7	275.9	246.8
1024	328.3	419.8	360.5	368.2	319.3	352.8	77.07	333.6	349.9	322.3	335.4	268.4	309.8	300.2	316.8	321.2	319.9	275.9
2048	339.1	433.3	375.0	389.8	317.1	363.1	106.2	337.9	349.6	343.4	338.6	277.6	338.0	357.0	359.6	383.4	413.1	298.3

shape of the curves of KCl and KI is similar to that of NaCl; the shape of the curves of ZnSO_4 , MnSO_4 , CdSO_4 , NiSO_4 , CoSO_4 , FeSO_4 and CuSO_4 closely resemble that of MgSO_4 , while KNO_3 and NaNO_3 have curves much like that of AgNO_3 . The great similarity between the curves of the chlorides and those of the nitrates has already been alluded to; this similarity is clearly shown by the curves represented in the figures. A comparison of Figs. 1 and 2 shows that at 95° the MgSO_4 curve is practically

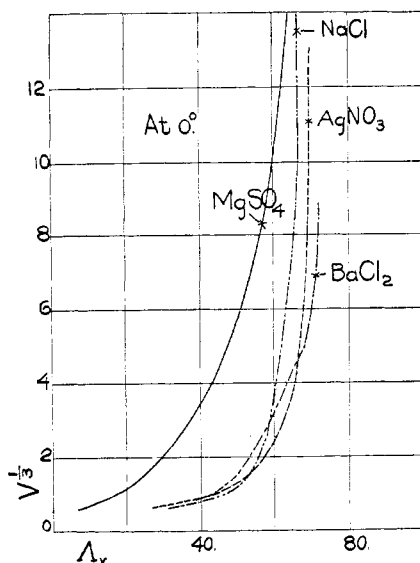


Fig. 1

a straight line, and that the curves of NaCl, BaCl_2 and AgNO_3 also exhibit a marked tendency to straighten out at the higher temperature. It should be stated in this connection, that the curve for CdSO_4 ¹ preserves more of its convexity toward the axis of abscissas at 95° than do the curves for the other sulphates. Curves that were chartered from data obtained for the same salts at 18° and at 25° showed a marked similarity² to those in

¹ This curve is not represented in the figures. The curve for HgCl_2 — also not represented — is practically a straight line at 95° .

² Such similarity has also been pointed out at various times by other observers.

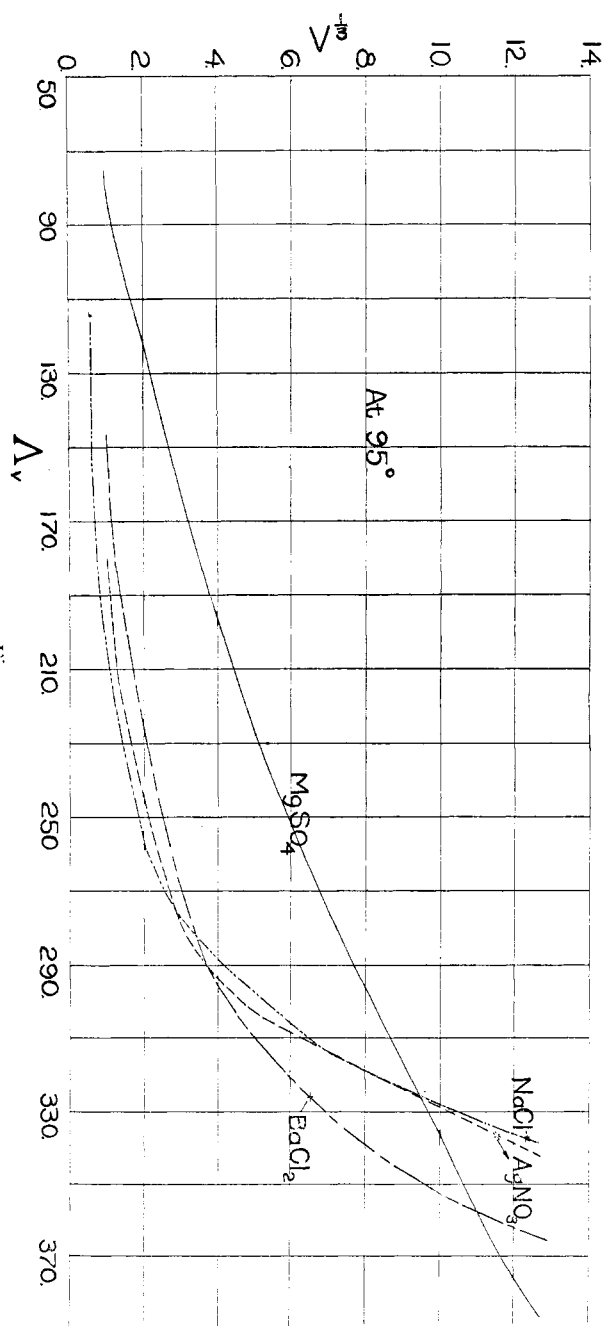


Fig. 2

Fig. 1 at (at 0°), and indicate that the change in the shape of the curves at 0° and at 95° takes place gradually as the temperature rises. It should be clearly borne in mind that the curves for even very closely analogous salts are not perfectly parallel; all that can be said of them is that they are similar in trend.

The results of the freezing-point determinations are given in Tables 3 to 11. The headings of the tables are self-explanatory. In calculating the molecular weights 18.9° was assumed as the lowering of the freezing-point caused by the presence of one gram-molecule in 100 grams of water.

Tables 3 to 11 do not contain all the salts represented in Table 1. The freezing-points of barium chloride solutions have lately been determined by Jones and Chambers¹ between approximately the concentrations 0.1 and 0.6 normal, as have also those of the chlorides and bromides of other alkaline earths. Table 3, giving the results obtained with NaCl, indicates that for the concentrations investigated (0.2 to 1.0 normal approximately) the molecular weight is practically constant. For about 0.2 normal the molecular weight was found to be 32.6, which corresponds to a dissociation of 79.4 percent; for an approximately normal solution the molecular weight was found to be 31.7, which corresponds to a dissociation of 84 percent. These two results represent the extreme variations of the values in Table 3. For the average value of the six determinations, 32.2, the dissociation is 81 percent. According to Table 1 the degree of dissociation (calculated according to the usual formula $\frac{\Lambda_v}{\Lambda_\infty}$) is about 79 percent for the 0.2 normal solution and 70 percent for the normal solution.² The degrees of dissociation 79 percent and 70 percent correspond, respectively, to the molecular weights

¹ Amer. Chem. Jour. 23, 89 (1900).

² In calculating the degrees of dissociation from the conductivity the values of the conductivity at infinite dilution were taken either directly from the highest values given in the table of conductivities; or when the trend of the curve (which was in all cases charted) required it, from the careful extrapolation of the curve.

TABLE 3¹
Sodium Chloride (NaCl). Mol. wt. 58.5

Amount NaCl in 100 g. water	Lowering of the freezing-point	Molecular weight
1.195	0.693	32.6*
2.550	1.512	31.9
2.970	1.750	32.1*
3.927	2.300	32.3*
4.914	2.866	32.4
5.741	3.395	31.7*

TABLE 4
Magnesium Sulphate (MgSO₄). Mol. wt. 120.4

Amount MgSO ₄ in 100 g. water	Lowering of the freezing-point	Molecular weight
0.699	0.154	85.8
1.517	0.314	91.3
2.550	0.480	100.4
5.994	1.006	112.6
6.961	1.165	112.9
9.246	1.527	114.5

TABLE 5
Zinc Sulphate (ZnSO₄). Mol. wt. 161.5

Amount ZnSO ₄ in 100 g. water	Lowering of the freezing-point	Molecular weight
1.602	0.258	117.4
5.026	0.625	152.0
8.962	1.030	164.5
10.930	1.246	165.8
13.675	1.493	173.1
16.935	1.922	166.5

¹ The four determinations marked * in this table were made in this laboratory by Mr. G. M. Wilcox. The other two determinations were made by the writer.

TABLE 6
Manganous Sulphate (MnSO_4). Mol. wt. 151.1

Amount MnSO_4 in 100 g. water	Lowering of the freezing-point	Molecular weight
1.941	0.293	125.2
2.502	0.391	131.0
5.120	0.687	140.9
10.843	1.399	146.5
18.572	2.591	135.5

TABLE 7
Cadmium Sulphate (CdSO_4). Mol. wt. 208.1

Amount of CdSO_4 in 100 g. water	Lowering of the freezing-point	Molecular weight
3.071	0.313	185.5
8.608	0.742	219.3
15.640	1.322	223.6
22.647	1.968	217.5
26.120	2.330	211.9

TABLE 8
Nickelous Sulphate (NiSO_4). Mol. wt. 154.8

Amount NiSO_4 in 100 g. water	Lowering of the freezing-point	Molecular weight
1.077	0.189	107.8
2.364	0.351	127.3
4.332	0.557	147.0
5.896	0.779	143.1
10.443	1.284	153.7
16.030	1.984	152.7

TABLE 9
Cobaltous Sulphate (CoSO_4). Mol. wt. 155.1

Amount CoSO_4 in 100 g. water	Lowering of the freezing-point	Molecular weight
1.457	0.209	131.8
2.982	0.390	144.5
4.927	0.600	155.2
9.657	1.067	171.2
14.143	1.587	168.5

TABLE 10
Ferrous Sulphate (FeSO_4). Mol. wt. 152.1

Amount FeSO_4 in 100 g. water	Lowering of the freezing-point	Molecular weight
2.270	0.316	135.8
2.651	0.376	133.3
6.502	0.794	154.8
8.980	1.072	158.4
13.849	1.655	158.2

TABLE 11
Copper Sulphate (CuSO_4). Mol. wt. 159.7

Amount CuSO_4 in 100 g. water	Lowering of the freezing-point	Molecular weight
1.835	0.300	115.6
3.312	0.405	154.6
5.443	0.743	163.9
9.242	0.996	175.4
14.210	1.569	171.2

32.7 and 34.4. It is clear then, that the degree of dissociation for the most dilute solution tested is found to be the same by freezing-point and conductivity methods to within the experimental error of the former method. But the dissociation increases rapidly with the dilution according to the conductivity, whereas the freezing-point results show, that it at least remains constant, if it does not diminish with the increase of the dilution, within the limits tested. C. Dieterici¹ has shown by his very careful measurements of the diminution of the vapor tension of NaCl solutions at 0° that between the limits 0.1 and 1.0 normal the molecular diminution of the vapor tension decreases as the dilution increases. R. W. Wood² found that the degree of dissociation of KCl, while nearly the same by cryoscopic and conductivity methods at a concentration slightly above 0.1 normal, increases more rapidly with the dilution according to the latter than according to the former method.

In the case of MgSO_4 (Table 4) the solutions examined varied in concentration from about 0.1 to 1.5 normal, the degree of dissociation for the most dilute solution being 40 percent and for the most concentrated only 5 percent. According to the conductivity determinations (Table 1) the corresponding degrees of dissociation are 44 and 22 percent respectively. The discrepancy between the dissociation as determined by the two methods then, while relatively rather small at first, increases enormously with the concentration within the limits investigated.

Zinc sulphate (Table 5) shows no dissociation according to the freezing-point determinations when the solutions contain a gram-equivalent or more of the salt per liter, and yet zinc sulphate solutions have an electrical conductivity nearly the same as that of the equivalent solutions of MgSO_4 (Table 1). The most dilute solution represented in Table 5 yielded a molecular weight of 117.4, corresponding to a dissociation of 38 percent; the conductivity method yields about 40 percent. For the normal solution, where the dissociation is nil according to the cryoscopic work, it is 24 percent according to the conductivity.

¹ Wied. Ann. **62**, 616 (1897).

² Zeit. phys. Chem. **18**, 522 (1895).

Manganous sulphate (Table 6) at first shows an increase of molecular weight with the increase of concentration and then a decrease. This also appears in the case of ZnSO_4 (Table 5), though less markedly. Again CdSO_4 (Table 7) shows this behavior in a marked degree, while NiSO_4 (Table 8), CoSO_4 (Table 9) and CuSO_4 (Table 11) show it slightly, and possibly also FeSO_4 (Table 10). The electrical conductivity of MnSO_4 solutions increases regularly with the dilution, as does that of solutions of all the other sulphates investigated. It is clear that according to conductivity determinations the dissociation constantly increases with the dilution in the case of the particular sulphates, just enumerated, whereas according to the cryoscopic determinations there is at first a decrease of dissociation with increase of concentration and then an increase of dissociation with increase of concentration. The most dilute solution of MnSO_4 tested (about 0.25 normal) gave a molecular weight of 125.2, corresponding to 21 percent dissociation, the conductivity method yields about 35 percent. When the molecular weight is 146.5 the dissociation is 3 percent, — the conductivity indicates 20 percent.

It is practically useless to make the comparison in the case of CdSO_4 (Table 7) for the cryoscopic determinations show no dissociation except in the most dilute solution tested; whereas, as stated above, the conductivity of the solutions is excellent and increases regularly with the dilution. The most dilute solution, in which a molecular weight of 185.5 was found, would contain the salt dissociated to the extent of 12 percent; the conductivity results yield about 30 percent.

Nickel sulphate is practically undissociated according to cryoscopic determinations (Table 8) when the solution is about 10 percent strong. The conductivity at about this strength indicates 22 percent dissociation. The molecular weight of the most dilute solution investigated corresponds to 43 percent dissociation; the conductivity indicates 42 percent.

In the case of CoSO_4 the freezing-point indicates no dissociation in a solution about 5 percent strong or stronger (Table

g), whereas the conductivity determinations show about 26 percent dissociation when the observed molecular weight is 155.2. In the most dilute solution the molecular weight found is 131.8 corresponding to 18 percent dissociation; the conductivity indicates about 34 percent.

According to cryoscopic determinations FeSO_4 also is undissociated in about 6 percent solutions or over (Table 10). When the observed molecular weight is 154.8 the conductivity nevertheless indicates 24 percent dissociation. The most dilute solution shows a molecular weight of 135.8, or 12 percent dissociation; the conductivity indicates 30 percent.

Copper sulphate is also undissociated in 5 percent solutions or over (Table 11). When the molecular weight observed equals 163.9, which corresponds to no dissociation, the conductivity indicates about 22 percent dissociation. In the most dilute solutions tested, the molecular weight found, 115.6, corresponds to 38 percent dissociation; the conductivity indicates about 32 percent.

From the foregoing it is evident that with the exception of a few instances (and these at certain special concentrations) the agreement between the value of the degree of dissociation as calculated from the freezing-point of the solutions and that deduced from their conductivity must in general be pronounced poor, even in the case of the most dilute solutions tested; while in the somewhat stronger solutions there is no agreement at all, many of the cryoscopic determinations showing no dissociation, whereas the conductivity indicates quite appreciable dissociation.

Arrhenius¹ in his original tables presents figures from cryoscopic data indicating no dissociation for MgSO_4 , FeSO_4 , CuSO_4 , ZnSO_4 and CdSO_4 , whereas the electrical conductivity (he used the results obtained at room temperatures) showed considerable dissociation, which substantially agrees with the results above recorded for the stronger solutions. Cadmium iodide, as Arrhenius shows, exhibits a similiar behavior. Arrhenius seeks to explain away the discrepancy in the case of the sulphates men-

¹ l. c.

tioned by assuming that the inactive or undissociated molecules in the solutions are polymerized; and he seeks to base this assumption on the fact that Hittorf¹ found that the migration numbers of MgSO_4 and ZnSO_4 show a considerable variation with the concentration, which was also found to be true — though much more markedly — in the case of CdI_2 , for which Hittorf assumed double molecules in the solution in order to explain the phenomena he observed. The latter also clearly states that he applies the same explanation to the other salts of the magnesia series, for their migration numbers also vary considerably with the concentration. This at first seems to justify perfectly the position taken by Arrhenius. However, the latter has not applied the explanation to all the salts of the magnesia series as he ought to, but he has simply assumed polymerized molecules in the case of those salts that did not behave according to his theory. He ought to assume polymerized molecules in the case of MgCl_2 for instance, for Hittorf found the migration numbers of this salt strongly dependent upon the concentration as he did those of MgSO_4 . But it happens that to assume polymerized molecules in the case of MgCl_2 would be very inconvenient for Arrhenius' theory, as his calculations of the factor i show; and so he did not make the assumption which he, in order to be consistent, ought to have made. In the case of CaCl_2 , BaCl_2 , $\text{Ca}(\text{NO}_3)_2$, $\text{Ba}(\text{NO}_3)_2$ Hittorf likewise found the migration numbers strongly dependent upon the concentration, yet Arrhenius does not assume polymerized molecules for these as he ought, to be consistent, for these salts agree better with his theory when such an assumption is not made. To assume polymerization of the molecules of such salts as MgCl_2 , CaCl_2 and BaCl_2 would lead to the greatest difficulty also in harmonizing the freezing-point results obtained by Jones and Chambers² with the dissociation theory; for they have found that the molecular lowering shows a minimum between the

¹ Pogg. Ann. 106, 547 (1859).

² Amer. Chem. Jour. 23, 89 (1900). Compare also in this connection Chambers and Frazer. Ibid. 23, 512 (1900).

strengths 0.1 and 0.2 normal, and that in concentrated solutions the lowering is as great or greater than the theoretical lowering, if the compounds were completely electrolytically dissociated. Jones and Chambers seek to harmonize their "abnormal" freezing-point lowerings by assuming that the salts form hydrates in the solutions. There can hardly be any doubt that the salts in question unite with water to form hydrates; but when the authors seek to use this to explain the "abnormally" low freezing-points of solutions, it might be well to remind them that the dissociation theory itself was promulgated to explain "abnormally" low freezing-points of solutions, and that since they have found the theory unable to do this and have reached out to the hydrate theory for help, it might be well in the face of the facts to acknowledge freely the weakness of the dissociation theory, and to proceed to explain the facts on the basis of the hydrate theory alone. If it be urged that the solutions conduct electricity and therefore the salts must be electrolytically dissociated,—the answer is, they must be, only if the dissociation theory be assumed.

Attention must now be directed especially to the careful determinations of C. Dieterici,¹ who measured the lowerings of the vapor tensions of a series of aqueous solutions of electrolytes and non-electrolytes at 0°. He found that for CaCl_2 the molecular lowering of the vapor tension diminishes strongly with the increase of dilution, and then at about 0.1 normal it again increases with the dilution. He also emphasizes the fact that the very careful freezing-point work of Loomis² and of Ponsot³ shows a minimum of the molecular lowering of the freezing-point at nearly the same concentration. The work of Jones and Chambers above cited also corroborates this. Between the concentrations 0.1 and 1.0 normal, to which Dieterici's work is really limited, he found that for the substances tested (H_3PO_4 , H_2SO_4 , NaCl , CaCl_2 , cane sugar, dextrose and urea) the molec-

¹ l. c.

² Wied. Ann. 51, 500 (1894); Ibid. 57, 495 (1896); Ibid. 60, 523 (1897).

³ Recherches sur les congélations Gauthiers-Villars, Paris (1896).

ular lowering of the vapor tension diminishes as the dilution increases, which is the opposite of that which the theory of Arrhenius requires. In view of this fact Dieterici rightfully refrains from even attempting to make a further comparison between the degree of dissociation as calculated from the vapor tension measurements on the one hand and the conductivity on the other. The reader is also referred to the able critical consideration of the very careful freezing-point determinations of various investigators, which is contained in Dieterici's article.

Attention is now called to the results of the boiling-point determinations (Tables 12 to 29). For a number of the most important salts represented in these tables, two, and in a few instances three or four series of determinations were made by Mr. Koch, in order to be perfectly sure of the facts.

In Table 12, giving the results for NaCl, it appears that the molecular weight decreases steadily with the increase of concentration,¹ becoming in the strong solutions less than half the theoretical molecular weight. The facts then indicate that the dissociation of common salt would increase with the concentration and that in solutions above about 20 percent the molecule would break up into more than two parts, which is impossible on the basis of the atomic theory as generally accepted. The behavior of NaCl is clearly diametrically opposed to that which we should expect according to the theory of electrolytic dissociation. The electrical conductivity of NaCl solutions increases regularly with the dilution as Table 2 shows. From the character of the boiling-point results, it is clearly out of the question to make even an attempt to compare the dissociation as calculated from the molecular weight determinations with the dissociation as deduced from the electrical conductivity measurements.

What has been said concerning NaCl applies also to KCl (Table 13), KBr (Table 14) and KI (Table 15). The molecular weights of these salts continually diminish with increase of concentration, finally becoming less than half the theoretical,

¹ The same fact is also demonstrated by the determinations of Landsberger and Biltz. *Zeit. anorg. Chem.* 17, 452 (1898).

TABLE 12
Sodium Chloride (NaCl). Mol. wt. 58.5
(Series 1)

Amount NaCl in 100 g. water	Rise of the boiling-point	Barometric pressure	Molecular weight
1.139	0.197	747.7 mm	33.4
4.167	0.744	747.1	32.4
5.524	1.002	747.0	31.9
8.254	1.553	"	30.0
11.010	2.157	746.9	29.5
15.910	3.304	"	27.8
20.520	4.495	746.8	26.4
(Series 2)			
2.900	0.499	743.6	33.6
6.006	1.082	743.5	32.1
7.103	1.690	"	30.6
12.625	2.514	"	29.0
15.640	3.231	"	28.0
18.530	4.032	"	26.7
20.130	4.471	"	26.0
(Series 3) ¹			
1.256	0.195	754.0	33.5
2.500	0.390	"	33.3
3.793	0.598	"	32.5
5.046	0.820	"	32.0
6.299	1.031	"	31.8
8.792	1.474	"	31.0
11.409	1.970	"	30.1
(Series 4)			
10.090	1.68	743.7	31.5
12.902	2.23	"	30.4
15.631	2.77	"	29.6
19.043	3.70	743.4	27.0
22.950	4.56	"	25.8
25.320	5.28	"	25.2
28.697	6.17	"	24.4
31.242	6.82	"	24.1

¹ The results in Series 3 are those of Mr. G. M. Wilcox. In Series 4, a thermometer graduated to tenths, which readily permitted the hundredths to be estimated with the aid of a lens, was used, the temperature range being greater than that of the Beckmann's thermometer.

TABLE 13
Potassium Chloride (KCl). Mol. wt. 74.59
(Series 1)

Amount KCl in 100 g. water	Rise of the boiling-point	Barometric pressure	Molecular weight
2.122	0.293	737.6 mm	41.9
5.124	0.700	"	42.3
9.012	1.247	"	41.8
13.990	2.004	"	40.4
20.170	2.975	"	39.2
24.160	3.653	"	38.2
27.720	4.266	"	37.7
31.840	5.009	"	36.8
(Series 2)			
1.911	0.255	744.0	43.3
4.052	0.554	"	42.3
7.225	0.986	"	42.4
11.620	1.625	743.9	41.3
16.520	2.406	744.0	39.4
21.350	3.206	"	39.5
26.130	3.911	744.2	38.5
30.370	4.756	744.1	37.1
(Series 3) ¹			
5.676	0.65	736.1	45.4
7.427	0.91	"	42.4
10.001	1.25	"	41.6
12.447	1.59	736.2	40.7
15.949	2.05	"	40.5
19.676	2.60	"	39.6
23.937	3.18	"	39.1
27.174	3.75	736.3	37.7
30.868	4.30	"	37.3
34.901	5.00	"	36.2
38.491	5.60	736.2	35.7
42.268	6.28	"	35.0
45.862	6.88	"	34.7
48.935	7.60	"	34.2

¹ In Series 3 the thermometer graduated to tenths was used.

TABLE 14
Potassium Bromide (KBr). Mol. wt. 119.1
(Series 1)

Amount KBr in 100 g. water	Rise of the boiling-point	Barometric pressure	Molecular weight
2.614	0.206	740.2 mm	66.0
5.504	0.433	"	66.1
9.593	0.763	"	65.4
16.503	1.351	"	63.7
23.393	1.968	"	61.8
28.177	2.413	"	60.7
33.278	2.899	"	59.7
38.497	3.425	"	58.4
43.418	3.932	"	57.4
47.065	4.312	"	56.8
51.204	4.778	"	55.7

(Series 2)

3.380	0.244	739.5	72.0
5.656	0.449	"	65.5
9.422	0.725	"	67.6
13.488	1.066	"	65.8
17.978	1.437	"	65.0
22.310	1.854	"	62.6
26.485	2.249	"	61.2
30.440	2.677	"	59.1
34.760	3.115	"	58.0
39.785	3.656	"	56.6
45.367	4.267	"	55.3
49.066	4.735	"	53.9

TABLE 15
Potassium Iodide (KI). Mol. wt. 166
(Series 1)

Amount KI in 100 g. water	Rise of the boiling-point	Barometric pressure	Molecular weight
2.803	0.155	736.1 mm	94.0
7.032	0.397	"	92.1
10.801	0.620	"	90.6
14.923	0.870	"	89.2
19.782	1.184	"	86.9
24.537	1.494	736.0	85.4
29.244	1.812	"	83.9
33.666	2.134	"	82.6
39.059	2.511	"	80.9
47.611	3.159	"	78.4
(Series 2) ¹			
4.174	0.23	740.6	94.3
6.177	0.33	740.4	97.3
12.929	0.72	"	93.3
19.024	1.10	"	89.8
26.237	1.58	740.0	86.4
35.003	2.14	"	85.0
43.059	2.74	739.4	81.6
66.253	4.67	"	73.4
77.17	5.55	739.5	72.1
85.71	6.36	"	70.0
92.73	7.02	"	68.6
104.80	8.02	"	67.9

¹ The thermometer graduated to tenths was used in this series.

TABLE 16
Magnesium Chloride (MgCl_2). Mol. wt. 95.26

Amount MgCl_2 in 100 g. water	Rise of the boiling-point	Barometric pressure	Molecular weight
3.371	0.416	750.1 mm	42.1
6.199	0.850	750.0	37.9
9.156	1.351	749.0	35.2
13.869	2.380	750.0	30.3
16.802	3.164	749.8	27.6
20.422	4.243	749.8	25.0
22.056	4.720	749.6	24.3

TABLE 17
Barium Chloride (BaCl_2). Mol. wt. 208.3
(Series 1)

Amount BaCl_2 in 100 g. water	Rise of the boiling-point	Barometric pressure	Molecular weight
4.078	0.242	742.8 mm	89.7
8.777	0.525	"	86.9
13.422	0.825	"	84.7
18.619	1.174	742.9	82.5
24.076	1.586	"	78.9
32.025	2.243	"	74.2
40.468	2.970	"	70.9
47.879	3.625	"	68.7
54.519	4.157	"	68.2

(Series 2)

3.397	0.208	752.8	84.9
8.290	0.496	"	86.6
13.612	0.839	"	84.4
19.868	1.293	"	79.9
27.071	1.909	"	75.5
35.036	2.517	"	72.4
38.843	2.877	"	70.2
44.255	3.362	"	68.5
48.130	3.737	"	67.0
53.863	4.157	"	67.3

TABLE 18
Mercuric Chloride (HgCl_2). Mol. wt. 270.9

Amount HgCl_2 in 100 g. water	Rise of the boiling-point	Barometric pressure	Molecular weight
3.341	0.056	751 mm	310.1
8.580	0.143	"	312.0
15.463	0.248	750.9	324.2
24.858	0.376	"	343.8
34.90	0.496	750.8	366.4
45.87	0.600	750.6	397.6
52.59	0.645	750.5	423.1

TABLE 19¹
Potassium Chlorate (KClO_3). Mol. wt. 122.6

Amount KClO_3 in 100 g. water	Rise of the boiling-point	Barometric pressure	Molecular weight
3.743	0.34	738.8 mm	57.2
8.121	0.65	"	66.4
12.837	1.01	738.6	66.0
17.116	1.31	"	67.9
23.484	1.72	738.4	70.9
29.689	2.10	"	76.7
35.42	2.49	738.1	73.9
42.96	2.98	"	74.9
48.92	3.43	737.6	74.1

¹ This series of determinations was made with the thermometer graduated to tenths.

TABLE 20
 Potassium Nitrate (KNO_3). Mol. wt. 101.2
 (Series 1)

Amount KNO_3 in 100 g. water	Rise of the boiling-point	Barometric pressure	Molecular weight
2.789	0.248	741.1 mm	58.5
6.058	0.518	"	60.8
9.727	0.822	"	61.5
14.798	1.207	"	63.8
21.333	1.706	741.2	65.0
27.095	2.123	"	66.4
33.80	2.577	"	68.2
41.54	3.079	"	70.2
49.42	3.570	741.3	72.0
57.20	4.027	741.4	73.9
62.83	4.357	"	75.0
(Series 2)			
4.286	0.378	744.5	59.1
8.434	0.725	744.6	60.5
13.068	1.101	"	61.7
19.740	1.603	"	64.0
28.056	2.212	"	66.0
35.54	2.710	744.8	68.2
44.53	3.275	744.9	70.7
53.37	3.795	"	73.1
61.64	4.309	"	74.4
70.76	4.677	"	78.7

TABLE 21
Silver Nitrate (AgNO_3). Mol. wt. 170.0
(Series 1)

Amount AgNO_3 in 100 g. water	Rise of the boiling-point	Barometric pressure	Molecular weight
3.893	0.197	739.4 mm	102.8
11.926	0.570	"	106.3
23.342	1.066	"	113.9
35.08	1.523	"	119.8
45.89	1.915	"	124.6
56.30	2.249	"	129.9
68.68	2.636	"	135.5
83.38	3.047	"	142.3
99.74	3.521	"	147.3
110.22	3.755	"	152.6
122.33	4.060	"	156.7
136.26	4.398	"	161.1
(Series 2)			
8.315	0.422	738.8	102.4
16.289	0.772	738.7	109.7
25.137	1.091	"	119.8
30.61	1.526	"	131.3
45.39	1.887	"	125.4
54.32	2.178	"	135.9
65.40	2.516	"	135.2
74.52	2.790	"	138.9
86.43	3.143	738.5	143.0
99.71	3.496	738.4	148.3
115.23	3.900	"	153.7
136.46	4.431	"	160.2

TABLE 22

Magnesium Sulphate (MgSO_4). Mol. wt. 120.4

Amount MgSO_4 in 100 g. water	Rise of the boiling-point	Barometric pressure	Molecular weight
2.733	0.097	739.3 mm	146.5
7.236	0.281	"	168.6
27.58	0.524	"	273.7
36.91	0.925	"	207.5
43.47	1.455	"	155.4
52.77	1.984	"	138.3
60.52	3.220	"	97.7
64.39	3.316	739.4	101.0
72.28	3.630	"	105.9

TABLE 23

Zinc Sulphate (ZnSO_4). Mol. wt. 161.5

Amount ZnSO_4 in 100 g. water	Rise of the boiling-point	Barometric pressure	Molecular weight
2.886	0.080	743.0 mm	187.6
6.647	0.169	"	204.5
10.139	0.266	"	198.2
13.389	0.372	"	201.1
17.713	0.461	"	199.8
22.202	0.591	"	190.5
25.199	0.690	"	189.9
28.249	0.811	"	181.1
30.47	0.899	742.0	176.3
32.89	0.995	"	171.9
35.18	1.122	"	163.0
37.36	1.240	"	156.7
39.83	1.381	"	150.0
41.30	1.459	"	147.2
44.56	1.671	"	138.7

TABLE 24
Manganous Sulphate (MnSO_4). Mol. wt. 151.1

Amount MnSO_4 in 100 g. water	Rise of the boiling-point	Barometric pressure	Molecular weight
3.713	0.114	739 mm	169.4
7.132	0.193	"	192.2
10.250	0.282	"	194.1
14.464	0.373	"	201.7
19.349	0.520	"	193.5
24.209	0.678	"	185.7

TABLE 25
Cadmium Sulphate (CdSO_4). Mol. wt. 208.1

Amount CdSO_4 in 100 g. water	Rise of the boiling-point	Barometric pressure	Molecular weight
4.563	0.105	741.3 mm	225.8
10.972	0.215	"	265.4
15.090	0.287	"	273.5
20.662	0.356	"	301.7
24.76	0.385	"	334.4
27.77	0.494	"	292.3
32.93	0.604	"	283.5
36.76	0.699	"	273.4
41.28	0.820	"	261.8
47.38	0.988	"	249.3
53.47	1.164	"	239.4

TABLE 26
Nickelous Sulphate (NiSO_4). Mol. wt. 154.8

Amount NiSO_4 in 100 g. water	Rise of the boiling-point	Barometric pressure	Molecular weight
2.766	0.096	737 mm	149.8
5.255	0.169	"	161.7
7.676	0.230	"	173.5
11.196	0.336	"	173.3
15.135	0.448	"	175.7
17.943	0.536	"	174.1
20.847	0.641	"	169.1
23.143	0.738	"	163.1
25.525	0.841	"	157.8
27.159	0.939	"	150.4
29.021	1.042	"	144.8
31.144	1.190	"	136.1
32.705	1.302	"	130.6
34.461	1.389	"	129.0
35.165	1.576	"	118.7
37.733	1.734	"	113.2

TABLE 27
Cobaltous Sulphate (CoSO_4). Mol. wt. 155.1

Amount CoSO_4 in 100 g. water	Rise of the boiling-point	Barometric pressure	Molecular weight
2.107	0.068	736 mm	160.8
4.446	0.110	"	205.3
8.744	0.201	"	226.1
9.596	0.262	"	190.5
12.936	0.346	"	194.3
16.134	0.449	"	186.3
20.600	0.568	"	188.6
22.151	0.626	"	184.0
24.070	0.694	"	180.8
26.150	0.772	"	175.7
28.745	0.876	"	170.8
32.841	1.055	"	161.9

TABLE 28
Ferrous Sulphate (FeSO_4). Mol. wt. 152.1

Amount FeSO_4 in 100 g. water	Rise of the boiling-point	Barometric pressure	Molecular weight
3.245	0.093	738 mm	181.4
6.704	0.182	"	191.6
9.222	0.243	"	197.3
13.087	0.343	"	198.4
15.810	0.412	"	199.5
17.962	0.483	"	193.4
22.806	0.545	"	212.6
24.452	0.633	"	200.9
26.645	0.713	"	194.3
28.788	0.805	"	185.6
30.692	0.899	"	181.7
32.768	0.994	"	171.4
35.346	1.099	"	167.2

TABLE 29
Cupric Sulphate (CuSO_4). Mol. wt. 159.7

Amount CuSO_4 in 100 g. water	Rise of the boiling-point	Barometric pressure	Molecular weight
3.356	0.091	742.9 mm	191.8
7.811	0.189	742.7	214.9
12.208	0.186	"	221.5
15.952	0.374	742.6	221.8
22.914	0.571	"	208.7
27.466	0.708	742.5	201.8
32.356	0.874	"	192.5
36.449	1.042	742.4	181.9
39.57	1.192	742.2	172.6
44.03	1.414	"	158.4
48.63	1.692	741.9	149.5
52.02	1.916	741.8	140.9
56.95	2.283	741.7	129.7
64.14	2.903	"	114.9
68.98	3.363	"	106.7
73.77	3.768	"	101.8

whereas the conductivities increase regularly with the dilution (Table 2). It is interesting to note the similarity of the behavior of the haloid salts of the alkalies, to which attention has been previously directed in a general way.

The molecular weight of MgCl_2 too decreases with the increase of concentration (Table 16), finally becoming less than one-third the theoretical value. This salt would then have to dissociate into more than three ions and that in concentrated solutions. On the other hand the conductivity increases with the dilution. It is again clearly useless to attempt a comparison of the degree of dissociation as computed from the observed molecular weights and the conductivity.

What has been stated concerning MgCl_2 applies exactly to BaCl_2 (Table 17), so that further comments about the behavior of the latter salt are superfluous. It is interesting to note that these two salts of analogous composition exhibit a similar behavior, which resembles closely that of the haloid salts of the alkalies.

Mercuric chloride (Table 18) shows no dissociation by the boiling-point method. The behavior of mercuric chloride differs from that of the salts last mentioned in that its molecular weight increases with the concentration. Of course, with this behavior polymerization of the molecules with increase of concentration could consistently be assumed; it could further be assumed that some of the molecules not yet polymerized are electrolytically dissociated and thus the observed phenomena could, with these assumptions, be brought into harmony with existing conceptions, at least qualitatively. The electrical conductivity of the solutions of this salt (Table 2) though relatively low, increases regularly with the dilution.

The boiling-point determinations for KClO_3 (Table 19) were made with a thermometer graduated to tenths, so that the measurements are relatively less accurate than those in which the Beckmann thermometer was used. The results are sufficient to indicate, however, that in the case of this salt the molecular weight increases with the concentration, which is at least quali-

tatively in harmony with that which the dissociation hypothesis requires. The degree of dissociation corresponding to a molecular weight of 66 is 88 percent, whereas for the same strength of solution the conductivity results (Table 2) indicate a dissociation of not more than 70 percent. No special stress is laid upon this comparison, however, because the Beckmann instrument was not employed in making the determinations.

In the case of KNO_3 (Table 20) we again have an increase of molecular weight with increase of concentration, which agrees qualitatively with the requirements of the dissociation theory. For the most dilute solution tested the molecular weight is 58.5, which corresponds to 73 percent dissociation; from the conductivity results (Table 2) the dissociation for this concentration is about 72 percent, — a satisfactory agreement. For a normal solution the molecular weight found is about 61.7, corresponding to 64 percent dissociation; the conductivity results yield 56 percent.

Silver nitrate (Table 21) also shows an increase of molecular weight with increase of concentration, which behavior agrees qualitatively with the dissociation theory. The most dilute solution tested yielded a molecular weight of 102.8, corresponding to a dissociation of 65 percent; the conductivity results yield about 67 percent, — an acceptable agreement. For a normal solution the molecular weight is about 110, corresponding to 54 percent dissociation; the conductivity determinations indicate 52 percent, — again a very fair agreement. It happens then, that the behavior of potassium and silver nitrate agrees much better with the demands of the dissociation theory at the boiling-point of the solutions than at the freezing-point.¹ It will be noted that these nitrates behave alike and that solutions of KClO_3 apparently exhibit a behavior similar to that of the nitrates.

The sulphates (Tables 22 to 29) again show great similarity in their general behavior. In the case of MgSO_4 (Table 22) the molecular weight begins with a value somewhat above the theoretical, — which indicates no dissociation; then it increases

¹ Compare for instance Arrhenius' table. 1. c.

at first with the concentration, and finally it decreases with increase of concentration after having passed through a maximum, the values in the strongest solutions becoming less than the theoretical. There is clearly no irregularity in the conductivity values (Table 2) to even suggest such a behavior. What has been said about MgSO_4 applies also to ZnSO_4 (Table 23), NiSO_4 (Table 26), and CuSO_4 (Table 29). The same general behavior is also exhibited by MnSO_4 (Table 24), CdSO_4 (Table 25), CoSO_4 (Table 27), and FeSO_4 (Table 28), except that the molecular weights of these salts, while first increasing and then decreasing with the increase of concentration, always remain above the theoretical values. As Table 2 shows there is nothing in the conductivity results to lead one to expect such a behavior. A comparison of the freezing-point results (Tables 4 to 10) with those obtained by the boiling-point method (Tables 22 to 29) shows that the molecular weight of the sulphates is less by the former than by the latter method in the case of corresponding concentrations. So that if it be assumed that these sulphates are polymerized in their solutions, it follows that this polymerization is greater at the boiling-points of the solutions than at their freezing-points, which seems unlikely.

It was thought to be of interest in this connection to investigate the behavior of a non-electrolyte. Cane sugar was selected, the results obtained with which by the boiling-point method are given in Table 30. The results indicate clearly that the molecular weight diminishes appreciably as the concentration increases. Strong sugar solutions, however, do not — as is well known — conduct electricity in consequence thereof. The solution was finally tested with Fehling's solution to see whether any sugar had become inverted during the process of boiling, but no invert sugar was found. On the other hand, a series of boiling-point determinations of solutions of H_3BO_3 (Table 31) shows that the molecular weight remains practically constant for very considerable changes in the concentration of this substance, considering its low molecular weight. The freezing-points of solutions of H_3BO_3 ¹ show that the molecular weight is lower at 0°

¹ Compare Kahlenberg und Schreiner. *Zeit. phys. Chem.* **20**, 548 (1896).

TABLE 30
Cane Sugar ($C_{12}H_{22}O_{11}$). Mol. wt. 342

Amount $C_{12}H_{22}O_{11}$ in 100 g. water	Rise of the boiling-point	Barometric pressure	Molecular weight
20.75	0.30	736.6 mm	360
29.51	0.42	"	366
36.15	0.55	"	342
42.69	0.70	"	310
49.38	0.75	"	335
57.35	0.91	"	328
65.97	1.13	"	304
77.77	1.41	"	280
92.97	1.77	737.1	273
103.4	2.06	737.4	261
113.4	2.20	737.6	268
114.9	2.32	"	258
125.1	2.57	"	253
137.8	2.90	"	247
149.1	3.20	"	242
159.9	3.48	"	239
167.5	3.70	"	236
175.1	3.84	737.9	237
187.1	4.25	"	229
197.7	4.56	738.5	226
207.1	4.80	"	225
222.0	5.20	739.0	222
236.9	5.60	"	220
248.0	5.92	"	218
259.1	6.11	"	221
266.7	6.41	"	216
276.2	6.71	739.1	214
289.4	7.10	739.0	212

than at 100° ; and its solutions at the lower temperature really ought to be somewhat better conductors of electricity (according to the dissociation hypothesis) than they are.

Discussion

The difficulties which the theory of electrolytic dissociation encounters in explaining the phenomena in aqueous solutions are really insurmountable. We have seen that there are solutions which are excellent electrical conductors, and yet the molecular weight determinations show a normal molecular

weight of the dissolved substance. It is clear that while in some cases the molecular weight increases with the concentration, thus according at least qualitatively with the theory, in other cases the molecular weight decreases with the increase of the concentration, finally becoming less than what it ought to be even on the assumption that electrolytic dissociation is complete. Again, in other cases, the molecular weight at first increases with the concentration and then it diminishes as the concentration increases. And these phenomena are observed in solutions, the conductivity of which steadily increases with the

TABLE 31¹
Boric Acid (H_3BO_3). Mol. wt. 62

Amount H_3BO_3 in 100 g. water	Rise of the boiling-point	Barometric pressure	Molecular weight
3.161	0.26	743 mm	63.2
5.264	0.42	"	65.2
8.746	0.72	"	63.0
12.040	1.01	"	62.2
14.098	1.18	"	62.1
16.600	1.41	"	61.2
19.956	1.67	"	62.1
23.896	2.00	"	62.1
26.500	2.13	742.5	64.5
29.295	2.41	"	63.2
33.793	2.82	"	62.3
36.407	3.01	"	62.9

increase of the dilution. I have not given any examples of aqueous solutions in which the molecular conductivity does not increase regularly with the dilution; but such cases do exist. So for instance the molecular conductivity of aqueous solutions of the alkaline hydroxides first increases with the dilution and then decreases as the dilution increases.²

From the facts here presented in the case of aqueous solu-

¹ In this series, which was really only a preliminary one, the thermometer graduated to tenths was used.

² The determinations of Kohlrausch show this phenomenon. See also the measurements of Kahlenberg and Lincoln. Jour. Phys. Chem. 2, 87 (1898).

tions and those detailed above in the case of non-aqueous solutions, it follows that there is no such connection between the freezing-points and boiling-points of solutions on the one hand, and their electrical conductivity on the other, as is claimed by the theory of electrolytic dissociation of Arrhenius. In numerous cases not even a qualitative agreement exists. A careful scrutiny of Arrhenius' original table reveals the fact that while in a certain number of instances the agreement of the values of the factor i , as computed from cryoscopic measurements and from conductivity determinations is acceptable, in many cases it is poor, and again in others it is entirely wanting. To be sure Arrhenius bases this table upon measurements which he deemed might in some cases contain large errors; but later experimental work has really only served to emphasize the presence of such discrepancies. Further we have seen that investigations of non-aqueous and of aqueous solutions have in reality yielded a host of facts which even the most ardent adherents of the dissociation theory have not been able to harmonize with it. For some facts, to be sure, explanations have been offered upon the basis of auxiliary assumptions which frequently had no root in facts, having been created simply to save the dissociation theory from being pronounced untenable.

The attempt has been made to explain all of the various properties of electrolytic solutions upon the basis of the theory of electrolytic dissociation. To these efforts attention must now be directed. The various additive properties of salt solutions as mentioned by Arrhenius and as detailed by Ostwald and by Nernst in their text-books are presented as supporting the dissociation theory. But it is clear that even if these additive properties could be explained on the basis of the dissociation theory, the theory could not be based on this alone, since additive properties are well known to exist in the case of true chemical compounds, where since there are no solutions under consideration, and since there is no electrical conductivity observable, the possibility of electrolytic dissociation is entirely out of the question. In the realm of physiology, where it at first seemed that

the theory of electrolytic dissociation would be particularly helpful, it has after all appeared that it can not cope with the facts.¹

The heats of neutralization of acids and bases in dilute solutions have been heralded as an argument in favor of the dissociation theory; but Crompton² has shown that the dissociation hypothesis is not only unnecessary to explain the heats of neutralization, but that it is really inadequate, for it does not bring the behavior of electrolytes, as far as heat changes that accompany the formation of salts in aqueous solution are concerned, into line with the behavior of non-electrolytes. It is unnecessary to dwell further upon the insurmountable difficulties which the dissociation theory meets in general in the realm of thermal chemistry. These difficulties have been sufficiently discussed by Reychler,³ whose conclusion is that, "above everything else we notice that *the hypothesis of free ions is in opposition to thermochemical observations.*"⁴

¹ In this connection the reader is referred in particular to the following articles and to the additional references that they in turn contain: L. Kahlenberg, The Taste of Acid Salts and Their Degree of Dissociation. Jour. Phys. Chem. 4, 33 (1900). T. W. Richards, The Relation Between the Taste of Acids and Their Degree of Dissociation. Ibid. 4, 207 (1900). L. Kahlenberg, The Taste of Acid Salts and Their Degree of Dissociation, II. Ibid. 4, 533 (1900). J. F. Clark, Electrolytic Dissociation and Toxic Action. Ibid. 3, 263 (1899). L. Kahlenberg and R. M. Austin, Toxic Action of Acid Sodium Salts on *Lupinus Albus*. Ibid. 4, 553 (1900). In reviewing the above articles for the Jour. Amer. Chem. Soc. and the Zeit. phys. Chem., Arthur A. Noyes has made the attempt to bring the facts into harmony with the dissociation theory. I will simply state here that I have no desire whatever to enter upon a discussion of these "explanations" of Mr. Noyes, the weakness of which is sufficiently apparent upon the face of them. The facts are before the reader and he can safely be left to judge for himself. I must request the reader, however, to refer to the original of the third article in the above list, or at any rate to use the review of it given in the Chemisches Centralblatt or the Jour. Chem. Soc. (London), since Noyes has omitted to mention an essential part of the very simple experiment upon which the argument is based and has then claimed that the experiment is irrelevant. Evidently Mr. Noyes, in his ardor to uphold the dissociation theory, did not see the full import of the experiment in question.

² Jour. Chem. Soc. 71, 951 (1897). See also Crompton's interesting article on Rotations of Optically Active Salts. Ibid. p. 946.

³ "Outlines of Physical Chemistry." (Translated by McCrae). Whitaker and Co. (1899), p. 214.

⁴ The italics are Reychler's.

The attempts to harmonize the theory of electrolytic dissociation with the law of mass action have signally failed in the case of the electrolytes *par excellence* as is well known, in spite of the fact that very earnest endeavors have been made in this direction for over a decade. In the case of weak organic acids to be sure a tolerable agreement between the law of mass action and the dissociation theory has been found by Ostwald. The fact that the dissociation hypotheses cannot be brought into harmony with the law of mass action is one of the strongest arguments against the theory. It is really unfortunate that in discussing problems of equilibrium into which strong electrolytes enter (their solubility for instance) the adherents of the dissociation theory should go right ahead with their mathematical equations and deductions as though the theory were in full accord with the law of mass action.¹

The chemical reactiveness of electrolytes has been explained by attempting to ascribe to the ions a peculiarly strong chemical activity on account of the electrical charges that are supposed to reside upon them.² The fact that a goodly number of substances will not react with each other when water is not present, and that they do react in aqueous solution, or at any rate when moist, has been called into requisition in this connection. While this behavior may be claimed to agree with the dissociation theory, it cannot be used as an argument to support the latter; for it is clear that many pure substances and mixtures of substances in which there are no grounds whatever for assuming the presence of ions, are nevertheless exceedingly reactive chemically, — take for instance many well known explosives as a striking example.

¹ Compare for instance the general and unqualified statements concerning the so-called solubility product contained in Ostwald's "Scientific Foundations of Analytical Chemistry," which the author applies to electrolytes to most of which it certainly does not apply unqualifiedly.

² A recent statement of H. C. Jones illustrates the extreme views that are entertained by some regarding this matter. He concludes a review of the work done on the dissociating power of solvents [*Amer. Chem. Jour.* **25**, 232 (1901)], with the statement, "The chemistry of atoms and molecules has thus given place to the chemistry of ions".

And on the other hand, it is a well recognized fact that, in many cases at least, salts, acids, and bases unite chemically with water and other solvents, and that any reaction which then takes place in solution is one between these new products; and that therefore such reactions might easily occur in presence of water, whereas the anhydrous substances might not react at all. It might be helpful to some to use the language of the dissociation theory and to say, for example, — the analytical test for chlorine ions is silver ions; instead of saying, — the analytical test for chlorine in the form of a soluble chloride is silver nitrate or any other soluble silver salt in which silver is the base; but that the new terminology, coupled with an attempt to apply the law of mass action to electrolytes in a way in which it certainly does not apply, forms a scientific foundation for analytical chemistry, is a position that is clearly untenable. The very fact that analytical chemistry has not received much benefit from Professor Ostwald's little book on "The Scientific Foundations of Analytical Chemistry", in the way of improving existing analytical methods and discovering new ones speaks for itself.

In connection with the dissociation hypothesis the solvent has been considered as having a peculiar "dissociating power". Water, then, yielding such excellent conducting solutions as it does, would have a very high degree of this dissociating power. The effort has been made by Nernst and by J. J. Thomson, practically simultaneously, to ascribe this strong dissociating power of water to its high dielectric constant which is about 80 at room temperatures. At the time when this was done relatively few solvents had been investigated that yielded solutions having considerable conductivity, and so it was perfectly easy to show that in the case of water, formic acid, alcohol, ether, and benzol, for example, the conductivity of the solutions in which these liquids are the solvents diminishes with the dielectric constant of the solvent.¹ The idea underlying the attempt to bring this hypothetical dissociating power into correlation with the

¹ Compare for instance Nernst's table, on page 365, of the third edition of his book, "Theoretische Chemie," F. Enke, Stuttgart (1900).

dielectric constant of the solvent is, that a high dielectric constant of the latter would make it more difficult for the electrically charged ions to neutralize their charges by reason of the electrostatic attraction existing between them. It is not claimed that the dissociating power is proportional to the specific inductive capacity of the solvent, but simply that it increases and diminishes with it, the exact mathematical relation being as yet unknown. Since the Nernst-Thomson rule has been put forth the electrical conductivity of various salts in a goodly number of solvents has been investigated.¹ While the dielectric constants of all the solvents tested were not known at the time so that a comparison could be made in all cases, in the majority of instances where the dielectric constants were known, the Nernst-Thomson rule was indeed corroborated.¹ At the same time a few striking exceptions were present. The relatively low dielectric constant of liquid ammonia² and the high conductivity³ of solutions of salts in it, speak powerfully against the Nernst-Thomson rule. It can hardly be argued that this high conductivity in liquid ammonia is due largely to the high rate with which the ions move because the conductivity of the solutions has been examined at the boiling-point of the solvent, -38° ; for liquid ammonia has a specific inductive capacity lower than that of alcohol and yet alcoholic solutions at their boiling-point have incomparably lower electrical conductivity than that observed in liquid ammonia solutions. Another striking exception to the Nernst-Thomson rule has recently been pointed out by H. Schlundt,⁴ who found the dielectric constants of butyronitrile and pyridine to be 20.3 and 12.4, respectively, and pointed out that nevertheless the solutions in the latter solvent are known to be the better conductors. Again liquid SO_2 which Walden⁵ has shown to yield excellent conducting solutions, has

¹ Compare Kahlenberg and Lincoln. *l. c.* Also Lincoln. *l. c.*, and the additional articles referred to in these papers.

² Goodwin and Thompson. *Physical Review*, **8**, 38 (1899).

³ Franklin and Kraus. *l. c.*

⁴ *Jour. Phys. Chem.* **5**, 157 (1901).

⁵ *l. c.*

a low dielectric constant¹ that would not lead one to expect such a behavior. The dielectric constant of liquid HCN was found by Schlundt² to be 95; this would lead one to expect this solvent to have a dissociating power greater than that of water. Preliminary tests which Mr. Schlundt and I have made show that solutions in liquid HCN are very much poorer conductors of electricity than corresponding aqueous solutions.³ On the other hand I have found that amyl amine with a specific inductive capacity of the order of that of chloroform⁴ yields fairly good conducting solutions. More striking proofs that the Nernst-Thomson rule is untenable could hardly be produced.⁵ The fact that the Nernst-Thomson rule can not be maintained takes away another pillar upon which the dissociation theory has been resting.

That the "dissociating power" of solvents is dependent upon the polymerization of their molecules, as claimed by Dutoit and Aston, is not in harmony with the facts in many cases, has clearly been shown by Kahlenberg and Lincoln.⁶ Again it has

¹ The exact value has been determined in this laboratory by Mr. Schlundt, who will report upon the same in connection with numerous measurements made on other solvents, among which are practically all the solvents investigated by Walden, l. c. Some older determinations of the dielectric constant of SO₂ have been found in the literature by Mr. Schlundt, which he will present in connection with his own work. Mr. Schlundt's article will appear in the October number of this Journal.

² l. c.

³ We hope soon to be able to publish exact conductivity measurements of solutions in liquid HCN and also of solutions in liquid cyanogen.

⁴ The exact value of the dielectric constant of amyl amine will be reported by Mr. Schlundt, whose list of determinations includes a fairly complete series of the substituted ammonias of both the fatty and aromatic series.

⁵ Nernst himself ("Theoretische Chemie," 3d Edition, p. 365) has realized the difficulty of harmonizing his rule with the far less striking instance that NaCl, KBr, etc., in formic acid (dielectric constant 62) solutions conduct almost as well as the corresponding aqueous solutions,—in which connection he remarks that other "specific influences" come into play. He states: "*Wahrscheinlich steht hier in erster Linie eine Association der Ionen mit Molekülen des Lösungsmittels.*" It is interesting to compare in this connection the treatment which the hydrate theory receives at the hands of the same writer, page 491.

⁶ l. c.

been maintained by Brühl¹ that "dissociating power" is possessed by such solvents as are unsaturated in character. It has been shown in this connection² that Brühl's position is untenable inasmuch as some solvents, which according to Brühl's view are unsaturated, and of which Brühl had predicted that they would yield conducting solutions, were found to yield solutions of high resistance. Later Brühl³ has entered the objection that he did not mean to assert, that whenever a solvent possesses spare valences it must necessarily yield conducting solutions. In other words, he claims that he did not mean to assert the converse of his original statement. Brühl cites in this connection that the statement, that whenever a compound is optically active it possesses an asymmetric carbon atom, is also not necessarily true when taken conversely. He apparently forgets, however, that in our knowledge of racemic mixtures and meso compounds, we have reasons why the converse of the latter statement is not necessarily true. A corresponding reason as to why his own statement should not hold in the converse has, however, not been furnished by Brühl.

The theory of electrolytic dissociation is at present at its best in explaining the phenomena of actual electrolysis. But it must nevertheless be admitted, that there are important phenomena of electrolysis which the theory does not explain satisfactorily. Thus if when for example a silver solution is electrolyzed, the process consists in each case of neutralizing the positive charge residing on silver ions (as far as the process at the cathode is concerned) as the theory claims, why do we always get poorly adhering crystalline deposits from certain solutions and dense, well-adhering deposits from others, the potential and the current density being the same. The writer has also observed certain phenomena which appear to him to be incompatible with the idea that during the process of electrolysis there is

¹ Zeit. phys. Chem. **18**, 514 (1895). Ibid. **27**, 317 (1898). Ber. chem. Ges. Berlin, **30**, 163 (1897).

² Kahlenberg and Lincoln. l. c.

³ Zeit. phys. Chem. **30**, 1 (1899).

a regular procession of charged, oriented, material particles in the solution. The study along this line is being pursued further, and it is hoped that the results may be ready for publication at some date in the near future. The study of the changes of concentration that take place around the electrodes in the electrolysis of non-aqueous solutions promises to yield results of unusual interest, especially as bearing upon the value of the dissociation theory in interpreting electrolytic phenomena. Since the time when Hittorf¹ determined the migration numbers of CdI_2 , ZnI_2 , and ZnCl_2 in absolute alcohol, and those of CdI_2 in amyl alcohol this field has not been cultivated. Now we know of a number of fairly good, and some cases of excellently conducting non-aqueous solutions in which the migration numbers await determination. This work has been begun in this laboratory.

It might not be superfluous to recall in connection with the claim that thermodynamics requires the dissociation theory, that Clausius who showed the discrepancy between the Grotthus theory and thermodynamics did not find it necessary to put forth such a radical hypothesis as that of Arrhenius. Again, Hittorf, on the basis of his studies of the migration of the ions, evidently did not think it necessary to frame a theory giving the term ion the meaning that it now has. Finally let the reader try to recall any real marked improvements or discoveries in the realm of electrolysis which are directly traceable to the influence of the dissociation theory. The function of E. M. F. in electrolysis, especially in electrolytic separations has been more strongly emphasized, but that is really about all. The importance of current density has early been pointed out by Bunsen, and as far as the influence of the temperature of the electrolyte upon the mechanical and chemical character of the deposit is concerned, we are still upon an empirical basis as before. It is very significant for instance, that in the latest edition of his work on quantitative analysis by electrolysis, Classen has devoted about four pages of the introductory part of the book to the ionic theory, and after that in the main body of the book we read

¹ l. c.

nothing more of that theory; the preparation of the solutions from which to get suitable deposits is very much upon the same empirical basis as ever. And it is also safe to say that electrolysis as used in the arts has not received much help from the theory of Arrhenius.

The dissociation theory has led to Nernst's theory of the E. M. F. of galvanic cells, which has already been referred to above. This theory is an attempt to explain the difference of potential between two electrolytes and to account for the difference of potential between an electrode and an electrolyte, and this not only qualitatively, but also quantitatively. Nernst's theory assumes that metals have a certain tendency to pass into the ionic condition, which tendency is termed the electrolytic solution tension of the metal. That which operates against this tendency is supposed to be the osmotic pressure of the ions of the metal already present in the solution, and the difference of potential between the metal and the electrolyte is the result of the action of these two forces; on the other hand, the difference of potential between two electrolytes is ascribed to the different rates with which the charged ions move. Nernst's formula really involves the assumption that the law of mass action is applicable to electrolytes in the sense required by the dissociation theory. That the law of mass action does not hold, however, in the case of electrolytes *par excellence*, has already been mentioned. By maintaining the correctness of Nernst's formula and thus assuming that the law of mass action does hold for such electrolytes, Jahn has arrived at the conclusion (as clearly he must) that $\frac{\Lambda_r}{\Lambda_x}$ does not correctly represent the degree of dissociation, and that the ionic velocities vary in dilute solutions. The latter is not, in many cases at least, in harmony with the facts. Arrhenius on the other hand stoutly defends his original $\frac{\Lambda_r}{\Lambda_x}$, which of course leads to a denial of the validity of the mass law as applied to the electrolytes in question. Ostwald, too, in the new addition of his *Grundriss* (p. 406) clearly inclines to-

ward maintaining the time-honored $\frac{\Lambda_v}{\Lambda_\infty}$ formula. The polemical discussion between Arrhenius and Jahn is still going on in the *Zeit. phys. Chem.*, and recently Nernst has also taken a hand in the debate. It seems at first rather deplorable that so much valuable energy is being expended in trying to decide which is the correct way to calculate the degree of dissociation, of which there are such excellent reasons to believe that it has no counterpart in reality. Naturally, then, insurmountable obstacles must arise in determining the value. These polemical discussions, however, are doing considerable good in that they emphasize how inadequate the dissociation theory really is, — they represent the beginning of the end of that theory.

It is true that as soon as the theory of electrolytic dissociation is declared invalid the original difficulty with the van't Hoff theory of solutions¹ recurs, namely the theoretical interpretation of the factor i . Whenever the factor i in the equation $PV = iRT$, is unity, we have the gas equation in its simplicity, as it holds for dilute solutions of the now classical cane sugar. When in any case i is less than unity and diminishes as the concentration increases, the assumption that polymerization of the dissolved molecules takes place can be made; but when i is greater than unity dissociation must be assumed. Arrhenius assumed so-called electrolytic dissociation; from which it followed that whenever a solution conducts electrolytically it requires a corresponding factor i greater than unity, — that this is by no means always the case has been sufficiently set forth above. Again, it has been shown above that in the case of cane sugar, for instance, a factor i which increases with the concentration must be introduced. There is no other logical theoretical significance to put upon this behavior than to assume that the stronger the sugar solution is the more the solute dissociates. This conclusion is absurd, — let alone the additional fact that sugar solutions do not conduct. And cane sugar is by no means the only

¹ Compare in this connection Crompton's explanation. *Jour. Chem. Soc.* 97, 925 (1897).

non-electrolyte that behaves thus. Attention has been directed to the fact that Dieterici found that the molecular lowering of the vapor tension of dextrose and urea also increases with the concentration like that of cane sugar.

I am well aware that the gas equation is supposed to hold strictly only for infinitely dilute solutions, just as it holds only for ideal gases, and that the solutions with which Dieterici worked varied between 0.1 and 1.0 normal, and that those used in experiments detailed above frequently were much stronger than normal. That a normal solution is nevertheless for many of the practical purposes of life a rather dilute solution will hardly be disputed. No one expects the gas equation to hold strictly for a normal solution or even for one considerably more dilute; but what one has a right to expect from the modern theory of solutions is, that with increasing concentration a solution should behave at least qualitatively as a gas does with increase of pressure. And this requirement is clearly not met, since while all gases behave alike under increase of pressure (so that van der Waals has been able to express their behavior by means of his well known equation) solutions as has been shown, often behave in the opposite manner in which a gas does, and this too, frequently in solutions that can not be termed concentrated. This demonstrates then that the van't Hoff law is at best only approximate and must be applied with great care. As Dieterici well says: "*Raoult hat seine Gesetze der Dampfspannungs- und Gefrierpunktsdepression durchaus nicht als absolut streng gültige Naturgesetze aufgestellt, sondern als nahezu zutreffende Erfahrungssätze, welche für die Zwecke der Molekulargewichtsbestimmung genau genug sind*".

We have seen above (and the literature is replete with records of facts illustrating the same point) that substances of similar chemical composition, when dissolved in the same solvents behave similarly, as far as the changes of the boiling- or freezing-points are concerned; this clearly shows that the influence of the chemical nature of the dissolved substance enters into the determination of the molecular rise of the boiling-point and the molecular lowering of the freezing-point.

In pressing the analogy between gases and solutions (which undoubtedly exists and from which at times valuable suggestions may be derived) it has often been forgotten that this is after all simply an analogy; and like other analogies it fails when carried too far. It is so easy to compare the process of dissolving a lump of sugar in a beaker of water with the expansion of a gas; — the analogy is at once apparent. In seeing it with the mind's eye one abstracts from the water and centers the attention entirely on the sugar. But it must be remembered that a gas will expand readily in *vacuo*, and that it will mix with any other gas or mixture of gases, while on the other hand, the lump of sugar will not dissolve when for instance benzene or absolute alcohol is poured over it. The process of solution of a substance and the expansion of a gas then, while possessing analogy, are in reality very different processes. And right here lies the difficulty with the theory of solutions. It neglects the all important rôle of the solvent. It fails to emphasize the fact that the process of solution takes place because of a mutual attraction between solvent and dissolved substance, and that this mutual attraction which is a function of the chemical nature of both solvent and dissolved substance, is the essence of the so-called osmotic pressure.¹ It is true that the thermodynamic considerations of van 't Hoff will hold whether the osmotic pressure be considered as the outcome of a mutual attraction of solvent and dissolved substance or as resulting from the bombardment of the molecules of the dissolved substance against the semi-permeable membrane. But if we choose to use the gas equation in working with solutions, it is very evident that the factor i must never be placed equal to unity (unless direct experimental evidence justifying this step is at hand) if exact results are desired, no matter whether we work with electrolytes or non-electrolytes. The dissociation theory, as has been shown, does not furnish a satisfactory explanation of the significance of i in

¹ Compare here the warning words of Lothar Meyer, in his article — *Das Wesen des osmotischen Druckes*. *Zeit. phys. Chem.* 5, 23 (1890). Also the reply of van 't Hoff. *Ibid.* p. 174 (1890).

the case of electrolytes. This value of i varies in all cases with the nature of the solvent and also in general, with the strength of the solution ; and it does not always vary to the same extent nor even in the same sense in different solutions. It is clear then, that when the simple equation $PV = RT$ is applied to a solution, only approximate results are obtained at best, unless experimental data are at hand showing that in the particular case and for the particular concentration under consideration i is actually equal to unity.

It must be fully and freely admitted that the dissociation theory has done much good in stimulating research in many lines. It has been fruitful in proportion to the amount of truth contained in it. Like other theories founded upon too narrow a basis of induction, it has gradually been outgrown, — the facts are too much for it. It would be difficult of course to say of any theory — even of one long ago discarded — that it is entirely worthless, and so the writer has no inclination to make such a statement concerning the dissociation theory. And further, he would not be understood as having the remotest intention to belittle in any way the work done by the enthusiastic adherents of the theory of electrolytic dissociation, for this will no doubt always form a bright page in the history of the development of chemistry and of science in general.

It is solely because of the rapid growth of the erroneous idea that the deductions drawn from the indiscriminate application of the simple gas equation to solutions and from the notion that all well-known facts harmonize with the theory of electrolytic dissociation, that I have felt compelled to call attention to the real status of the experimental facts underlying these deductions. It is hoped that this will stimulate to renewed experimental activity, for surely our theory of solutions leaves much to be desired. The analogy between gases and solutions does not help us to understand even moderately concentrated solutions; and whenever experimental work on such solutions is done, the assumption that there is chemical union between solvent and dissolved substance calls for recognition. That there is chemical

union between solvent and dissolved substance, in many cases at least, there can be no doubt; and as for the osmotic pressure, the outcome of that mutual attraction between solvent and dissolved substance, its various eccentricities and caprices, as exhibited even in moderately concentrated solutions, show clearly that it is closely related to, if not essentially identical with chemical affinity. Our hope in the study of solutions lies in the recognition of this. The problem of solutions is preeminently one for the chemist. Each solution will have to be examined separately, and then it will appear that chemically analogous solutes in the same solvent will have a similar behavior, the closeness of the agreement being determined by the degree of the analogy; and finally from such a study of solutions, which can and should begin with the most concentrated, the behavior of the most dilute solutions will appear as a limiting case, — and then we shall see the present theory of solutions in its true relation to the facts. And finally as far as the answer to the question, — What must be the relation between solvent and dissolved substance in order that the resulting solution may conduct electricity¹ is concerned, we are unfortunately as yet in the dark; just as we do not know why certain solids conduct electricity and others do not. The essence of electrical conduction in electrolytes and in metals is after all not so radically different as is frequently supposed. The further experimental investigation of the general problem of electrical conduction will, let us hope, ere long give us the true key to the situation.

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¹ The investigations of D. Konowalow [Wied. Ann. 49, 733 (1893)] are of special interest in this connection.