

Equivalent Conductivities at 0° in Absolute Units.

m = number of Gram-equivalents of Solute per thousand grams of Solution.

m .	$m^{\frac{1}{2}}$.	KCl.	$\frac{1}{2}\text{BaCl}_2$.	$\frac{1}{2}\text{K}_2\text{Cr}_2\text{O}_7$.	$\frac{1}{2}\text{CuSO}_4$.	$\frac{1}{2}\text{MgSO}_4$.
0·00001	0·0215	807	746	813	696	699
0·00002	0·0272	807	746	804	692	694
0·00005	0·0358	807	745	781	684	685
0·0001	0·0464	806	742	763	674	676
0·0002	0·0585	806	739	740	660	663
0·0005	0·0791	803	731	722	633	639
0·001	0·100	800	723	714	602	614
0·002	0·126	796	711	709	563	579
0·005	0·171	787	690	708	500	512
0·01	0·215	776	669	704	445	468
0·02	0·271	761	645	695	388	417
0·03	0·311	752	629	685	357	387
0·05	0·368	740	607	669	326	353
0·10	0·464	723	581	643	282	309
0·20	0·585	705	554	615	243	270
0·40	0·737	692	530	—	205	229
0·50	0·794	690	522	—	192	222
1·0	1·000	690	496	—	160	188
1·2	1·063	694	490	—	152	176
1·5	1·145	—	481	—	145	161
2·0	1·260	—	472	—	135	136
3·0	1·442	—	—	—	—	94·5

“The Resistance of the Ions and the Mechanical Friction of the Solvent.” By FRIEDR. KOHLRAUSCH, Foreign Member R.S.
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(Translated into English for Dr. Kohlrausch by Dr. L. Austin.)

Messrs. Bousfield and Lowry in their interesting paper, “The Influence of Temperature on the Conductivity of Electrolytic Solutions,”* have discussed a hypothesis recently advanced by me. In this I stated the probability that the conductivities of all aqueous solutions approach, with decreasing temperature, a zero value at about the same temperature, and that the cause of this phenomenon is to be looked for in the disappearance of the fluidity of water. This hypothesis was very briefly mentioned, as it were, in parenthesis, in the midst of the discussion of the numerical data which formed the main portion of the paper.†

* Bousfield and Lowry, ‘Roy. Soc. Proc.’ vol. 70, p. 42, 1902.

† Kohlrausch, “Über den Temperatureinfluss auf das elektr. Leitvermögen von Lösungen, insbesondere auf die Beweglichkeit der einzelnen Ionen im Wasser,” ‘Sitz. Ber. Berlin Akad.’ 1901, p. 1028.

I beg the honour of laying before the Royal Society the following more complete consideration of the subject.

The above-mentioned article had for its object the study, from careful measurements made at my request by Mr. Déguisne,* of the influence of temperature on completely dissociated, that is, infinitely dilute aqueous solutions of strong electrolytes, and the deduction from this of the temperature coefficients of the single ions.

Mr. Déguisne expresses the influence of temperature on the conductivity κ , starting from 18° as a mean temperature, in the form of the quadratic interpolations equation

$$\kappa_t = \kappa_{18}[1 + \alpha(t - 18) + \beta(t - 18)^2]$$

and shows that this closely represents his observations between 2° and 34° C. I shall confine myself to the consideration of this formula.

(1.) *Numerical values.*—In the table, under Λ is given the equivalent conductivity of infinitely dilute solutions,† then the coefficients α and β for 1/1000 and, for the neutral salts, observed by Déguisne, α also for

	Λ .	α for		β .
		1/10000.	1/1000.	
KCl.....	130.1	0.0216	0.0217	+0.000066
KF.....	111.3	..	226	069
KNO ₃	126.4	210	211	062
K ₂ SO ₄	133.4	223	223	077
KOH.....	239	..	190	033
NH ₄ Cl.....	130	219	219	068
NaCl.....	109.0	228	227	084
NaF.....	90.2	..	240	100
NaNO ₃	105.3	220	221	075
Na ₂ SO ₄	112.2	234	234	097
NaC ₂ H ₃ O ₂	78.5	..	242	110
NaC ₂ H ₉ O ₂	69.2	..	244	111
LiCl.....	98.9	..	233	091
BaCl ₂	121.7	227	226	083
Ba(NO ₃) ₂	118.1	221	220	076
AgNO ₃	115.8	216	216	+0.000067
HCl.....	383	..	165	-0.000015
HNO ₃	380	..	163	-0.000017

1/10000 normal solutions, corrected by me for the impurity of the water. Mr. Déguisne has kindly furnished me with the data regarding the water in each of his solutions. After applying these corrections the values for 1/10000 and 1/1000 normal do not continue to show the systematic changes, which from the observations appeared to

* Déguisne, "Temperatur-Koefficienten des Leitvermögens sehr verdünnter wässriger Lösungen," 'Dissertation, Strassburg,' 1893.

† Kohlrausch u. v. Steinwehr, 'Sitz. Ber. Berlin, Akad.,' 1902, p. 581.

make the reduction to completely dissociated solutions very uncertain, but now show only differences of irregular sign within the limits of the errors of observation.

From this we may assume that the true values of the coefficients for the concentration $1/10000$ would be practically the same as those for complete dissociation. But, as a matter of fact, in the case of such dilute solutions considerable uncertainty underlies the observations themselves, on account of the variations of the solutions with time, as well as the corrections for the conductivity of the water, on account of its magnitude and somewhat uncertain theoretical basis. These facts are especially true in the case of the acids. Therefore, the values found for the concentration $1/1000$, in which these two sources of error need scarcely be considered, must be looked upon as experimentally much more accurate. Then too, the condition of ionization of very dilute solutions of weak salts is always somewhat uncertain on account of possible hydrolytic action. In order to treat all electrolytes alike, I shall therefore choose the coefficients α and β of the concentration $1/1000$.

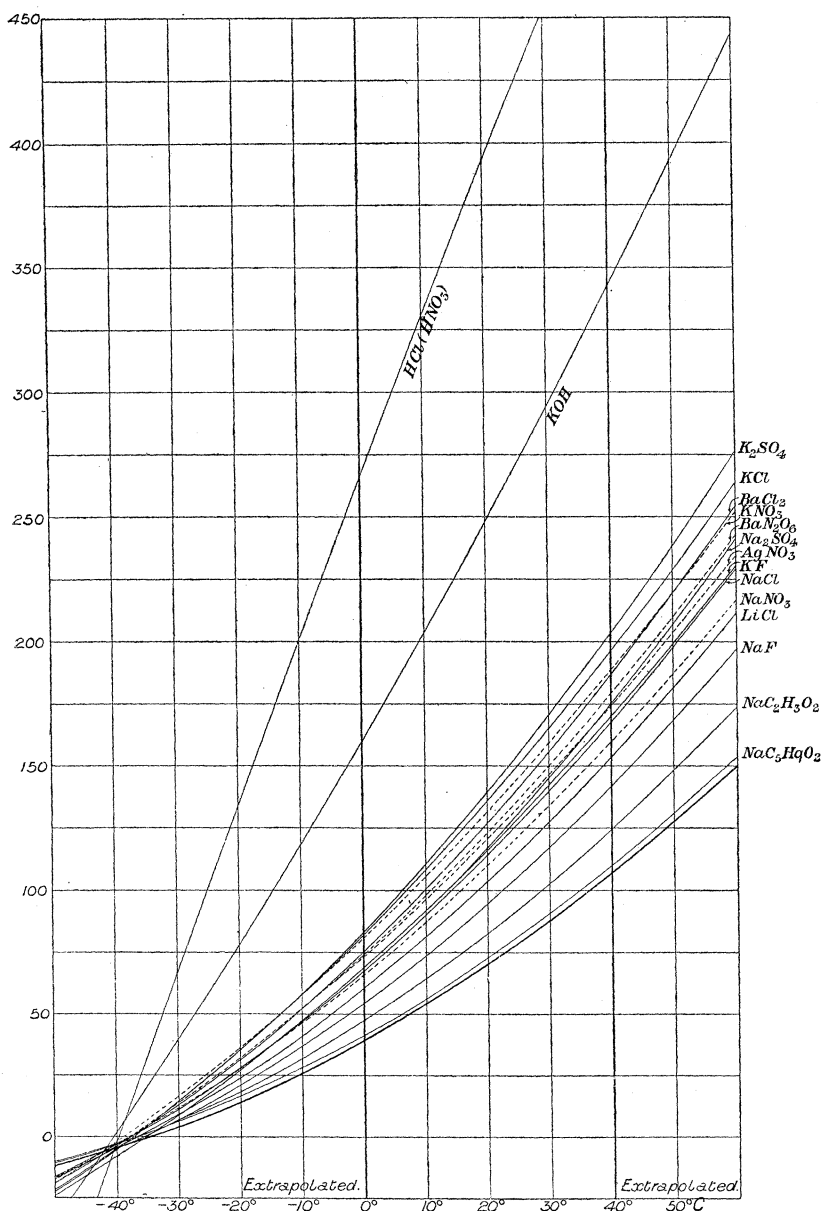
The errors which may arise from the fact that these solutions lack from 2 to 5 per cent. of complete dissociation cannot at present be avoided. Since the values of the constants themselves differ but little from those for a concentration of $1/10000$, we may assume that these errors are not great. The material is not yet complete enough to allow the application of the corrections proposed by Mr. Whetham. The values may indeed be capable of improvement, but I am of the opinion that the following conclusions drawn from them are in the main correct.

In order to fill certain gaps in the series of the coefficients, I have added to the electrolytes investigated by Déguisne my own observations on $1/1000$ normal solutions of potassium and sodium fluoride, sodium acetate and lithium chloride. The coefficients here are derived only for the temperatures 10° , 18° , and 26° , and will therefore be less accurate than in Déguisne's results.

(2.) *Values of the Conductivity at Different Temperatures.*—My conclusion, that by extrapolating the quadratic formula below 0° , the conductivities of all electrolytes approach a zero value within a narrow range of temperature, rested upon an empirically established connection between the coefficients α and β . I will introduce here, however, the more easily followed graphic representation (fig. 1) plotted from the single coefficients. The extrapolated portions of all sixteen curves converge toward the same region and pass through zero between -35° and -41° .*

* NH_4Cl would nearly coincide with KCl ; MgSO_4 on account of the large changes in its coefficient with increasing dilution is uncertain and therefore omitted; it would probably lie near Na_2SO_4 .

FIG. 1.



In regard to the lowest curve, cf. 4. The fact that the greatest differences exist for KOH and KF may be connected with the smaller accuracy of these curves. But on this we will lay no stress.

(3.) *Discussion of Results.*—We may derive from the above fact the certainty that the individual differences of the electrolytes come under a common law, the degree of accuracy of which must, however, remain unsettled. This law I have stated as follows: for dissociated aqueous solutions the coefficient β of the quadratic member can be approximately expressed in terms of the coefficient α of the linear member, in the form $\beta = C(\alpha - A)$, where C and A are constants common to all electrolytes. One sees at once that this law is identical with the other; all curves of the expression $(1 + \alpha t + \beta t^2)$ pass through the same point, having for its abscissa $-1/C$.*

The proposed constants have the following values, taking 18°C. as the point from which the temperature is reckoned, $C = 0.0163$, $A = 0.0174$. The convergence takes place at the point where $t - 18 = -1/0.0163 = -61$, or $t = -43^\circ$. On account of the small difference between C and A , this point lies not far from the zero axis. If C and A were identical, the extrapolation according to the quadratic formula would show that the conductivity of all electrolytes becomes zero at the same temperature. Introducing this critical temperature t_0 , all electrolytes could be nearly represented by a formula containing but two individual constants,

$$\kappa_t = P(t - t_0) + Q(t - t_0)^2.$$

On the one hand, I consider it impossible that the inequality of A and C , and the resulting deviations from a common point of convergence on the zero axis are produced by errors of observation. Even the circumstance that we have no completely dissociated solutions can scarcely have so great an influence. On the other hand, it appears very improbable that the approximate equality of the constants A and C is purely accidental. The deduction that the extrapolated curves all have a nearly common point of convergence appears to me especially worthy of notice in that this point lies approximately at the zero value of the conductivity. The importance of this is still more increased by the fact that if the mobility of the water particles be extrapolated according to the same formula, it becomes zero at about the same temperature (cf. 4).

(4.) *Variations of the Fluidity of Water with Temperature.*—The relations which have just been mentioned concerning the motions of the ions in water assume a greater interest when they are compared with the mobility of the water particles themselves. The fluidity (the reciprocal of the viscosity) of water when calculated in the same way as the conductivity, with the quadratic formula, is represented by the lowest curve.

That the best observations on the fluidity of water agree excellently

* The coincidence in the drawing differs a little from this, because each of the expressions is multiplied by its corresponding A .

at moderate temperatures with the quadratic interpolation formula, already applied by Poiseuille, has long been known to me. The literary priority regarding this observation belongs, however, to Messrs. Bousfield and Lowry.

In my calculations I have made use of the values chosen by Mr. Heydweiller,* as the most probable between the limits of 0° and 30° . These values were selected from different observers, especially Messrs. Thorpe and Rodger. Since the constants were calculated for this range of temperature, they have practically the same signification for the fluidity of water as the former constants for the conductivity.

The formula

$$\phi_t = 55.68 + 1.981t + 0.0105t^2 \text{ C.G.S.}$$

or

$$\phi_t = 94.74[1 + 0.0249(t - 18) + 0.000111(t - 18)^2] \text{ C.G.S.}$$

represents the fluidity ϕ within the limits of the table, 0° to 30° , with a maximum error of $1/1000$, that is, with about the same degree of accuracy as Déguisne's formula for the conductivity. As far as 90° the error would not exceed $1/100$.

The curve represented in the figure instead of having the factor 94.74 (which has no reference to the conductivity), was given the arbitrary factor 67.0 in order to give the curve the desired position close to the lowest curve of conductivity, that of sodium valerate.

The coincidence of the two curves is striking, indeed the coefficients 0.0249 and 0.000111 differ little from those of sodium valerate 0.0244 and 0.000111.† The curves of conductivity are cut by the fluidity curve approximately in the same region to which they converge. The curve of fluidity passes through zero at $-34^{\circ} \text{ C.} \ddagger$

Messrs. Bousfield and Lowry calculated from the measurements of Thorpe and Rodger the coefficients 0.0251 and 0.000115. This curve differs very little from mine, especially in the neighbourhood of the crossing point.

* Mr. Heydweiller calculated at my request the table for the 'Lehrbuch der Praktischen Physik' (Tab. 20a, 1901).

† The same would apply for Déguisne's observations on Na_2HPO_4 (0.0241 and 0.000105) and on $\text{NaHC}_4\text{H}_4\text{O}_4$ (0.0241 and 0.000109), which, however, on account of the unknown constitution of these salts in solution, I have left out of account.

Messrs. Bousfield and Lowry further called attention to the fact that the temperature change which I have found for ordinary distilled water (practically a very dilute solution of CO_2) corresponds with the temperature change of fluidity.

‡ It is also to be mentioned that Messrs. Lyle and Hosking, from their interesting observations on the viscosity and the electrical resistance of 0.1 to 4 normal solutions of NaCl between 0° and 100° draw the conclusion: "The curves so arrived at are remarkable, in that they indicate that for solutions of the strengths experimented with, both the fluidity and the sp. mol. conductivity vanish at a temperature of -35.5° C. " The manner of extrapolation is not dealt with.—'Phil. Mag.,' May, 1902, p. 496.

The fact is therefore established that the temperature change of the fluidity of water is nearly the same as that of the conductivity of dissociated aqueous solutions of electrolytes which have a large temperature coefficient. Even if nothing more was known than this fact, the question of a connection between the electrolytic and the mechanical motion in water must be considered a matter for serious discussion.

(5.) *Discussion of the Extrapolation.*—Extrapolation of an empirical formula over a wide range can never be considered as necessarily representing the truth. This is especially true in a case like the present, where at low temperatures it is applied to a state of matter other than that for which the formula was originally deduced. It is *à priori* impossible for the formula to hold where its extrapolation gives to the conductivity or the fluidity a value zero. Since these quantities are from their very nature positive, negative values are physically impossible. Therefore the cutting of the zero axis by the curve at an acute angle is *à priori* inadmissible, just as, for example, the assumption is inadmissible that the Joule heating effect is proportional to the current strength, or that the kinetic energy is proportional to the velocity. A quantity from its nature positive can, as it becomes zero, have a finite differential quotient as function of another quantity, only when the other quantity cannot vary beyond the critical point. This can be considered identical with the impossibility of negative values. In reality the conductivity and the fluidity must reach the zero value in a curve which is tangent to the axis of temperature. (Becoming zero through a discontinuous process as in freezing is, of course, something entirely different.)

Therefore the quadratic formula, in spite of the fact that it shows such a remarkably wide range of applicability, must be replaced by another expression before the zero value is reached.

The above explanation shows that my view of the "critical temperature" of the fluidity and the conductivity of water as derived from the quadratic formula, does not materially differ from that of Messrs. Bousfield and Lowry. This temperature is only a quantity by which one constant of the ordinary formula can be replaced; but the importance of the constant now introduced is verified, in that now the individualities of the ions, if they do not entirely vanish, at any rate disappear except for small differences. Further, the remarkable fact follows, that approximately the same constant may be introduced in the temperature formula of the viscosity of water. This number, entering as a temperature, may therefore be called a fundamental constant of water, of course with the reservation which follows from the fact that it varies by several degrees in the different cases.* (Cf. 3.)

* The objection that the use of such a constant may be responsible for the

(6.) *Other Formule.*—Among the former attempts to derive an empirical formula from the behaviour in ordinary temperatures, which does not *a priori* lose its significance as the conductivity or the fluidity approaches zero, that of Slotte, $\phi = \phi_0 (1 + bt)^n$, must be given the first place. This has recently assumed a greater importance on account of the extensive work of Thorpe and Rodger. Here, in the case of the fluidity, the condition that $d\phi/dt = 0$ where $\phi = 0$ is fulfilled, for here everywhere $n > 1$. For the conductivity, however, nothing is gained, since in the case of the acids $n < 1$, and there $d\kappa/dt = \infty$ for $\kappa = 0$; there is, therefore, no object in recalculating our results according to this formula. However, in a former paper I have given the preference to Slotte's formula in a remark concerning fluidity. To try to bring the coefficients of this formula into a relationship with those of the quadratic formula was indeed not allowable.

(7.) *Experimental Indications.*—The attempt to draw conclusions in regard to the region near the zero value from the course of the phenomenon in the region where the fluidity &c. have values of considerable magnitude, would have, of course, very little prospect of success. But perhaps the attempt to follow the fluidity of water or the conductivity of dilute solutions down to lower temperatures would be more successful than we think, if made in closed vessels of small dimensions.

Up to the present time we are acquainted only with phenomena from which uncertain conclusions from analogy can be drawn. The idea may be pretty certainly held as probable, that the viscosity and the electrical resistance finally increase more slowly than the quadratic formula extrapolated would indicate. In regard to viscosity, I remember the investigations of Tammann on the freezing of over-cooled liquids, and Ostwald's observations on salol. The phenomenon of the gradual solidification of alcohol at low temperatures also leads to the same conclusion.

Numerous observations of the same kind in regard to electrical behaviour are also recorded. The very slow increase of the conductivity of glass with increasing temperature is well known. A quantitative determination of this has been made by Messrs. Bousfield and Lowry. But how far a heterogeneous mixture like glass can be considered parallel to a dilute ionised solution is doubtful. In the same way, experiments such as those of Lehmann on the electrolysis

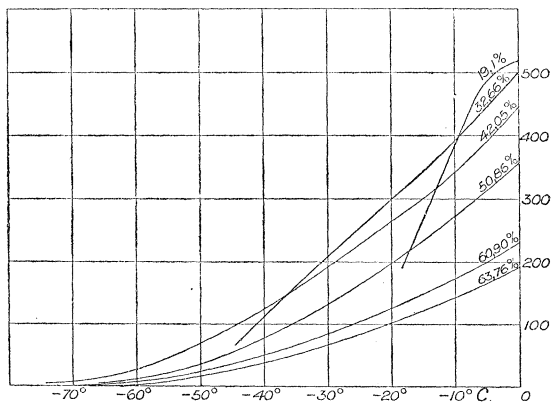
introduction of errors is without much weight; it is, at any rate, practically the same case as that of the gas formula. This is written, making use of the absolute zero, $vp = \text{const.} (t_0 + t)$, where $t_0 = 273$, although it is certain that the result $v = 0$ for $t = -t_0$ is false, so that the formula must assume another form before v approaches its zero value. The constant of the gas formula loses its significance at the point where the gas passes into the liquid state. The same is true for the temperature constant of the fluidity, which we have introduced, when it passes out of the liquid state.

of solid silver iodide, or those of W. Kohlrausch on its conductivity at different temperatures, scarcely form a basis for conclusions in regard to solutions in water, particularly as the behaviour of silver chloride and silver bromide is quite different from that of silver iodide.

In addition, it is difficult to compare substances which are so highly concentrated, in comparison with ordinary electrolytes, with dilute solutions. All these conductivities reduced in the ratio of the concentration, as, for example, the measurements made on hot glass of large surface and small thickness by means of the potentiometer, would probably have to be considered zero, that is, smaller than the errors of observation, in comparison with our dilute salt solutions at moderate temperatures.

Of the greatest interest for our problem are the recently published measurements of electrical conductivity as far as -70°C. , which Mr. Kunz* was led to make through my remarks on the relation between conductivity and temperature. He was unfortunately unable (as was I also) to sufficiently over-cool dilute solutions, and the measurements were therefore made on strong solutions of sulphuric acid of at least 4 gr. equiv./litre. Notwithstanding the fact that no certain conclusions can be drawn in regard to dilute solutions, Mr. Kunz's values are of sufficient interest to represent graphically. The curves are marked with the percentage concentration of the solutions (fig. 2).

FIG. 2.



The conductivity of the strongest solutions sinks gradually with the temperature, and reaches at -70° a relatively small value. It is impossible to follow the more dilute solutions to so low a temperature on account of their freezing. But it is evident from the observations that the more dilute they are, the more rapid is the rate of change of the

* 'Comptes Rendus,' vol. 135, 1902, p. 788.

conductivity, so that it may be supposed that the 19 per cent. solution would reach a relatively negligible value at a much higher temperature than the stronger solutions, if it were possible to follow it.

Mr. Kunz adopts the view that the electrical resistance is due to friction. It is his opinion, indeed, that the conductivity would disappear only at the absolute zero of temperature; this conclusion can hardly be supported by his observations, as his lowest temperatures are still $+200^{\circ}$ absolute.

(8.) *The Temperature Coefficients of the Single Ions.*—For these* I have recently published values. It is of importance to us that the temperature coefficients of univalent monatomic ions appear to be functions of mobility, decreasing as the mobility increases. Complex and multivalent ions as groups deviate from this series, so that in this relationship we have a new criterion for univalent elemental ions. The largest temperature coefficients of the ions approach that of water.

(9.) *The Electrolytic Resistance Considered as Friction of the Solvent.*—In the common view concerning the motion of the ions, an assumption is tacitly made which in other cases we do not consider justifiable. In the relative motions of adjacent particles we assume a discontinuity only in the case of friction between two rigid bodies where this by definition must occur. Even here it is impossible to deny that on the actual surfaces of contact there may be connected with the motion a rubbing away of particles which produces a continuous variation of velocity from one to the other.

When a fluid is in question, whether in contact with another fluid or with a solid, we concede no finite variation of velocity in two points at an infinitesimal distance from each other. The primitive assumption, until recently held to be correct, in the case of mercury on glass, that the fluid in actual contact with the solid moved with a finite velocity, would demand that the external friction be infinitesimal in comparison with the internal. This is now, to the best of my knowledge, entirely given up.† The idea of discontinuity, however, we employ in regard to the ions when we think of them as moving through the solvent without connection with it.

In addition to the objection of discontinuity there exist also the following difficulties in this assumption. In the first place, it is difficult to see how the electrical energy passes into the solvent in the form of heat, unless the latter takes part in the motion of translation. Further, it seems probable, from the fact of the ionisation of the salts,

* 'Sitz. Ber. d. Berlin. Akademie,' 1902, p. 572. The values here given are strengthened by the fact that a linear connection between α and β (cf. 3) appears *à priori* in the case of the single ions as well as in the case of electrolytes.

† Comp. Warburg, 'Pogg. Ann.,' vol. 140, 1870, p. 379. The "slipping" of rarefied gases on solid surfaces, established by Kundt and Warburg, being a separate phenomenon, need not be considered here.

that forces must exist between the ions and the water. Ciamician,* twelve years ago, concluded that this must lead to the hypothesis of a water-shell about the ion. The attempt was also made to measure this hydration, by using a method proposed by Nernst.

We may, therefore, look upon it as probable that the moving ion carries with it a mass of adhering solvent, just as a moving immersed solid carries with it a portion of the liquid, and we will endeavour on this basis to construct a new representation of electrolytic resistance. According to this the mechanics of electrolysis assume an appearance quite different from the old hypothesis of isolated ions. The resistance to motion takes place not directly between the solvent and the ions, not between H_2O and K or Cl, &c., but it is a phenomenon of friction between the particles of the solvent itself, modified by the fact that the accompanying shell of solvent may be thin enough to allow the ion to act through it, to a certain extent, upon the outer liquid.

It is impossible at first to make anything more than this rough sketch of the hypothesis, and the more so, as the expressions "continuous" and "discontinuous" must be especially defined if we are to apply them to molecular processes. The expression "continuous" stands from its very nature in contradiction to the atomic or molecular hypothesis; and in the case of solutions, and especially in electrolysis, a molecular representation seems to be the only one which is scientifically thinkable.

I hardly need after this to say that in our hypothesis we shall not claim to be able to differentiate strictly between the outer portions of the solution and those parts which have separated themselves from the rest as the accompanying atmosphere of the ion. A continuous change in the condition of motion from the moving ion to the solvent contradicts a strict differentiation. Fundamentally, however, the same is true for all atmospheres, even for that of the earth.

For the sake of brevity, we will retain the expression that an atmosphere of the solvent takes part in the motion of the ion. In the light of this hypothesis, I believe that all the phenomena which have been here described become so much clearer that this fact itself serves as a remarkable experimental support of the hypothesis.

(10.) *Hypotheses and Conclusions.*—The hypotheses are: About every ion moves an atmosphere of the solvent, whose dimensions are determined by the individual characteristics of the ion. The atmospheres of multivalent or compound ions differ from those of monatomic ions. Data are at present lacking for a more detailed representation.

The electrolytic resistance of an ion is a frictional resistance that increases with the dimensions of the atmosphere.† The direct action

* *Zeitschr. f. physikal. Chem.*, vol 6, 1890, p. 405.

† The resistance of a sphere is proportional to its radius. Kirchhoff, 'Vorles. üb. math. Physik,' 1, 380, 1897 (herausgegeben von W. Wien).

between the ion and the outer portion of the solvent diminishes as the atmosphere becomes of greater thickness.

Conclusions.—(a.) The electrical resistance of an ion, expressed in mechanical units, must be of the same order of magnitude as the mechanical frictional resistance of a molecule of the solvent; a law whose assumption, as I some time ago showed, “leads to an expression for the distance between the molecules which is comparable with the usually accepted views in regard to this quantity.”*

(b.) The empirically discovered law that the temperature change of the resistance of the most sluggish ions is very like the temperature change of the viscosity of water, becomes now understandable. For ions of large resistance we must assume that the atmosphere is of considerable thickness, and hence the action of the ion itself on the outer portion of the solvent will be small. As a limiting case, for a very sluggish ion there will be only the friction of water against water, and the electrolytic resistance will have the same temperature coefficient as the viscosity of water, provided that the atmosphere itself does not change its dimensions with the temperature. If, however, the atmosphere become, for example, smaller with increasing temperature, the temperature gradient of the conductivity might be greater than that of the fluidity. According to the observations now at hand, this would seem to be the case for the slowest moving univalent ion Li. Even here, however, the differences scarcely exceed the errors of observation.

(c.) I now come to the remarkable relationship between the mobility of the ions and their temperature coefficients, which was mentioned in Section 8. This first led me to seek a general explanation for the electrolytic resistance in the idea of a water atmosphere, in order to escape being compelled to explain this otherwise unreconcilable fundamental characteristic of the ions as a *deus ex machina*.

Assuming as the single fundamental characteristic of each univalent monatomic ion the formation of a water atmosphere which varies according to the nature of the ion, the mobility of this complex on the one side, and its temperature coefficient on the other, will be functions of these atmospheric formations, and therefore both quantities must hold functional relations to each other. We know too little of the molecular forces at present to attempt to describe this connection more exactly. But for the case in which the water shell is so thick that the ion exerts no force beyond it, the resistance to motion becomes simply a matter of water friction, which explains the fact that the most sluggish ions have nearly the same temperature coefficients as the viscosity. In the case of smaller aggregations, we must remain content with the fact that we have at least the possibility of a fundamental explanation.

* ‘Göttinger Nachrichten,’ 1879, p. 1.

There are two experimental questions which are of importance although difficult to answer: first, whether the functional relationship is exact or only approximate, and second, whether the positive and negative ions are fully identical in regard to this relationship.

That the non-elementary ions also show as their greatest temperature coefficients that of water friction, but that they as groups differ from the elementary ions, is to be expected. The latter fact cannot be quantitatively explained. Here also it will be necessary to wait for more exact experimental data to settle the question.

(*d.*) Finally, the indication of the temperature formula that the mobility of all the ions converges towards zero (*cf.* 2 and 3) at about the same temperature, is a logical result, if the electrolytic resistance is in reality a mechanical friction. The fact that the formula for the fluidity of water takes part in this convergence, gives the hypothesis further support.

It does not seem at all impossible that the deviations from a strictly common zero point, found in extrapolating the different formulæ, have a systematic cause. These divergences seem to indicate that the more mobility an ion shows at ordinary temperatures, the more slowly relatively it loses the residue of its mobility as the solvent becomes more viscous. The mobility of the water molecules themselves becomes small at a comparatively high temperature, where such ions as K, Cl, NO₃, SO₄, and even more, OH and H still possess a considerable residue of electrolytic mobility. Such a relationship does not seem at all improbable.

In the foregoing pages I have sought to find a cause for the electrolytic resistance in the single fundamental characteristic of the ions, their hydration, that is, their ability to form atmospheres from the solvent. These views form a hypothetical sketch for the completion of which much is still wanting. It appears to me, however, complete enough to invite one to its experimental or theoretical continuation.
