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XVIII. *Ionization, Ionic Velocities, and Atomic Sizes.*

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IT is well-known that in the theory of ions as given to us by Faraday, van't Hoff, Arrhenius, and Ostwald, there occur some gaps, which are very surprising if we consider the wonderful completeness of the theory apart from these, and also the advanced state of the kinetic theory. The gaps are:—(1) Ignorance of the cause of ionization. (2) Ignorance of the reason why Ostwald's law for the ionization of weak acids and bases does not apply to ordinary binary electrolytes. (3) Ignorance of the connexion between the ionic velocities and the other physical properties of the atoms.

The present paper is a contribution towards bridging these gaps, and consists of three parts, namely:—

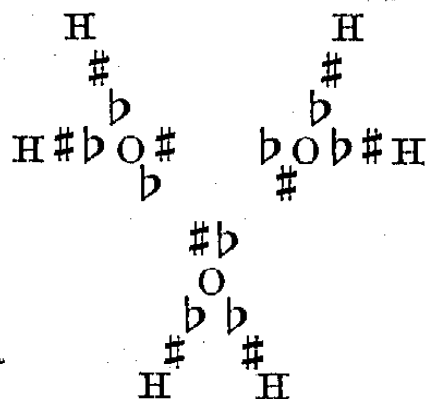
1. The cause of ionization.
2. The laws of ionization in binary electrolytes.
3. Deduction of ionic velocities from the other physical properties of the atoms, and their use as a definite means of calculating the absolute sizes of the atoms.

1. *The Cause of Ionization.*

To J. J. Thomson and Nernst we owe the sagacious suggestion that ionization of a solute is caused by the high dielectric capacity of a solvent, whereby the electric force between the oppositely charged atoms or radicals is sufficiently

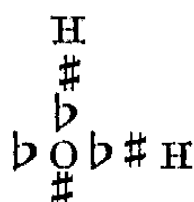
* Communicated by the Author.

reduced. Others have advanced the hypothesis that association of the molecules of the solvent is somehow the apparent cause of the dissociation of the solute molecule into ions. I think that both these suggestions can be combined in the proposition, that exceptionally high dielectric capacity, high power of ionization, and marked tendency to molecular association, are three effects traceable to the same cause, which I propose to call the latent or potential valency of certain atoms. Let us consider the case of water as a solvent. In a paper on the Molecular Constitution of Water (*Phil. Mag.* [5] vol. l. Nov. 1900), I have shown that while in steam we have H_2O , in ice we have $(H_2O)_3$, and in water a mixture of $(H_2O)_3$ and $(H_2O)_2$, varying with temperature. Now the dielectric capacity of steam is not so abnormal as that of water, being given by Lebedew (*Wied. Ann.* xlv.) as of the order 1.001 under ideal standard gas conditions, at which the index of refraction n is 1.00025. Maxwell's law $K=n^2$, or $K-1=n^2-1$, is therefore much more nearly complied with by steam than by ice and water in which K is of the order 80, while n^2 is only of the order 2. Obviously it is necessary for us to study the formula for ice or trihydrol in relation to the electrons which hold together the three H_2O constituents of its molecule, and similarly with $(H_2O)_2$. As it would be convenient to have symbols different from the operational + and - to distinguish the two sorts of electrons, I propose to use the musical types # for the + electron and b for the - electron, and ♯ for the neutron, which consists of the # and b united to form that electric doublet which gives to the æther its electric and magnetic properties. Trihydrol $(H_2O)_3$ would be represented graphically thus

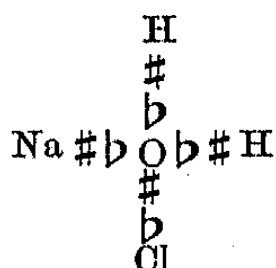


The usual chemical graphic bonds are replaced by the pairs of electrons required by electrical theory. This strictly symmetrical representation of the trihydrol molecule brings out the very important fact that, while oxygen appears as a tetrad, it is very different from the ordinary chemical tetrad,

since the four electrons attached to the oxygen atom are not of the same sort, there are three \flat electrons to one $\#$. If $(\text{H}_2\text{O})_3$ gets dissociated it will yield three parts



which could be more briefly represented by the formula $\# \text{O} \flat_3 (\# \text{H})_2$. From the graphic formula we see that in this one \flat and the $\#$ of the oxygen atom are not in positions of equilibrium, and will tend to rush together to form a neutron \natural , in which the \flat and $\#$ are much closer together than in their initial position when the dissociation of the $(\text{H}_2\text{O})_3$ first occurred. According to this conception H_2O in steam would be represented by the formula $\natural \text{O} \flat_2 (\# \text{H})_2$. But the change from $\# \text{O} \flat_3 (\# \text{H})_2$ to $\natural \text{O} \flat_2 (\# \text{H})_2$ would occupy some time, during which the \flat and the $\#$, which ultimately coalesce to form \natural , would be at a certain average distance apart, and would have a certain average electric moment obtained by multiplying the amount of either of the electrons by the average distance between them. This electric moment being much greater than that of the neutron confers on water its high dielectric capacity, though the special neutron in the steam molecule probably has a greater moment than that in æther. The field of electric force between \flat and $\#$ at their average distance apart is the direct cause of electrolytic dissociation produced by water. With a solute like $\# \text{NaCl} \flat$ we may expect to have



as an intermediate configuration from which the $\text{Na}\#$ and $\text{Cl}\flat$ are broken off, when too far apart to recombine.

We have now seen how high dielectric capacity, molecular association, and ionization in water are all consequences of the latent or potential valency of oxygen. But as this valency has the peculiar character of being associated with opposite electric charges in the atom, and gives us in $\# \text{O} \flat_3 (\# \text{H})_2$ a radical with electric charges, yet not an ion, because its charges are equal and opposite. I propose to call such a

radical or atom a stion, as in static electricity it bears the same important relation to dielectric capacity as the ion to conductivity in current electricity. The neutron and the stion differ as do the electron and the ion; the neutron and electron are the molecule and atom of electricity, the stion and the ion are atoms of matter with associated electrons.

According to this line of thought those substances which fail to conform to the law $K=n^2$ fail, when K is measured electrostatically, because they contain stions, which are doublets of exceptionally large electric moment.

We spoke above of the time taken by the $\#$ and \flat to rush together to form \sharp , and that they do so ultimately rush together is proved by the not very abnormal dielectric capacity of steam (Lebedew, *loc. cit.*), but before they settle down to the stationary state which characterizes them in the molecule of steam, they will revolve in their relative orbits, dissipating their energy till it falls to its stationary value. But a $\#Ob_3(\#H)_2$ group broken off from $\{\#Ob_3(\#H_2)\}_3$ in water can enjoy only a certain average time of independent existence. Again, given a number of stions with the electric axes of their doublets uniformly distributed as to direction, and a field of electric force suddenly created where they are, it will take a certain time for the axes to adjust themselves to the directions giving maximum dielectric capacity to the region. If the field of electric force is an alternating one, and if its period of alternation is only a fraction of the time required to produce maximum dielectric capacity, we see dielectric capacity must appear to be a function of the period of alternation, with limiting values $K=2$ and $K=80$. With an order of frequency about 10^8 per second Perot (*Compt. Rend.* 1894) found $K=2.04$, while with 10^6 alternations per second, J. Hopkinson and Wilson (*Proc. Roy. Soc.* lx.) found K to be less than 3. It would appear then that the time taken for the stion axes to be maximally directed in a field of electric force is of the order 10^{-6} second. This time would be an interesting subject of calculation if we knew more of the relations between electrons and atoms.

2. The Laws of Binary Electrolytes.

Let i be the degree of ionization of an electrolytic solution containing m gramme-equivalents of solute per litre of solution, or $1/m$ ($=v$) litres of solution per gramme-equivalent of solute, then Ostwald's well-known reasoning gives the rate of dissociation proportional to $m(1-i)$, say equal to $cm(1-i)$, and that of recombination equal to $c'm^2i^2$ with the condition

for equilibrium

$$cm(1-i) = c'm^2i^2$$

$$\therefore \frac{i^2}{1-i} = \frac{c}{c'} \cdot \frac{1}{m} = kv. \quad (1)$$

This is the simple mass-action formula which Ostwald found to be true for over 200 weak organic acids dissolved in water, and to fail completely for ordinary binary electrolytes. It is to be noticed that the solvent is supposed to exert no effect except in so far as it influences the values of c and c' . These being determined, the processes of dissociation and combination are supposed to go on as if the solute were in a vacuum.

Recently in volume xvii. of *Zeit. f. phys. Chem.* Rudolphi has given an empirical formula for the ionization of an ordinary binary electrolyte, namely,

$$i^2/(1-i) = kv^{\frac{1}{2}}, \quad (2)$$

which in vol. xviii. van't Hoff has proposed to replace by

$$i^3/(1-i)^2 = kv, \quad (3)$$

as perhaps a better and more easily interpreted form. In vol. xix. Storch uses $i^p/(1-i) = kv^{p-1}$, where p like k is a parameter varying from one electrolyte to another. Kohlrausch (*Beibl. Ann. d. Ph.* xxv. p. 35) finds

$$1 - 1/i^p = kv^{-\frac{1}{p}} \quad (4)$$

to be an accurate empirical formula for dilute solutions from $m = .1$ to $m = .0001$ ($v = 10$ to $v = 10^4$).

All these formulæ are empirical and applicable only to dilute solutions. In them i is taken to be given by the ratio of the specific molecular conductivity of the solution at strength m to that at infinitely small strength, that is at infinite dilution. Now, no stipulation is made here about the viscosity of solutions, because the formulæ apply only to dilutions where the difference of the viscosity of the solution from that of pure water can be merged in the experimental errors in the measurement of molecular conductivity. But to satisfactorily investigate dissociation in solutions we must be free to push the investigation to far higher strengths than hitherto, in fact right up to saturation, and therefore we must take account of the effect of viscosity on conductivity. It has been argued that because an electrolyte dissolved in a stiff jelly has nearly the same conductivity as a pure aqueous solution of the same strength, viscosity can be of little importance; but it is obvious that the correct inference is that in the jelly the water is so immersed in the gelatine

that it exhibits great viscosity and quasi-solidity as regards bulk movements, while to ions moving through its meshes quite freely the confined water exhibits almost only the viscosity of ordinary water. Many experiments could be mentioned to illustrate how the resistance of electrolytes is proportional to viscosity, other things being equal, but a reference to those of Manoulier (*Compt. Rend.* cxxx. p. 773) with mixtures of glycerine and water and CuSO_4 will suffice, as the importance of viscosity appears at once in the following elementary theoretical treatment.

Let us regard an ion as a sphere of radius a_1 moving with ionic velocity V through a solution of viscosity η , then for the frictional resistance R experienced by the sphere, if there is no slipping at its surface, we have by Stokes's formula

$$R = 6\pi V \eta a_1. \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Now if the fall of electric potential is at the rate dE/dx in the direction of motion of the $\#$ ion when a current is traversing the solution, then the force on each such ion is $e dE/dx$ where e is its charge. For steady ionic velocity V the condition is

$$e \frac{dE}{dx} = 6\pi V \eta a_1. \quad . \quad . \quad . \quad . \quad . \quad (6)$$

For the \flat ions with velocity U we have likewise

$$-e \frac{dE}{dx} = 6\pi U \eta a_2.$$

In a c. c. of solution 10^{-3} *mi* molecules are split up into as many ions of each sort, and the current C per cm.^2 is

$$\begin{aligned} C &= 10^{-3}mie(V - U) \\ &= 10^{-3}mie \cdot \frac{1}{6\pi\eta} \left(\frac{1}{a_1} + \frac{1}{a_2} \right) \frac{dE}{dx}, \quad . \quad . \quad . \quad (7) \end{aligned}$$

therefore by Ohm's law and the definition of specific conductivity the latter is

$$10^{-3}mie^2 \cdot \frac{1}{6\pi\eta} \cdot \left(\frac{1}{a_1} + \frac{1}{a_2} \right),$$

and λ the specific molecular conductivity is given by

$$\lambda = ie^2 \cdot \frac{1}{6\pi\eta} \cdot \left(\frac{1}{a_1} + \frac{1}{a_2} \right). \quad . \quad . \quad . \quad . \quad . \quad (8)$$

If η is taken to be constant, as is usually done with dilute solutions, V and U are both constant for all dilutions, if

$dE/dx=1$; and if at infinite dilution i is assumed to become 1, then i is given by the ratio of the specific molecular conductivity at strength m to that at strength $1/\infty$. But for solutions in general we take η_0 to be the viscosity of the solvent, and η to be that of a solution of strength m , and if again we assume that i becomes 1 at infinite dilution when λ becomes λ_0 , then

$$i = \frac{\lambda\eta}{\lambda_0\eta_0}.$$

Thus the ionization is found by multiplying the usual λ/λ_0 by η/η_0 .

Now this simple theory must have been written down by many a physicist and found to be wanting, for it makes the ionic velocities of the different atoms at infinite dilution stand to one another inversely as their radii, a result which a brief study of data as to ionic velocities and relative atomic sizes shows to be not verified.

But we need to introduce a correction into the too simplified equation (6). The electron of the ion must be treated as if it were embedded in the atom, which has a different dielectric capacity from that of the water or other solvent.

Now if K_0 is the dielectric capacity of water, and K that of the matter of the atom of our ion, and if all the ions gathered into a single slab at right angles to the current would give it a thickness t in a distance D between the electrodes whose potentials are E_1 and E_2 , then the electric force in the slab F_1 would be K_0/K times that in the water, which may be denoted by F , and

$$\begin{aligned} E_1 - E_2 &= F(D - t) + F_1 t \\ &= F(D - t + tK_0/K), \end{aligned}$$

$$\therefore F_1 = \frac{K_0}{K} \frac{1}{1 - \frac{t}{D}(1 - \frac{K_0}{K})} \cdot \frac{E_1 - E_2}{D}.$$

As $(E_1 - E_2)/D$ is the same as dE/dx of our previous reasoning, we find the electric force acting on the electron of the ion to be $K_0/K \{1 - t/D(1 - K_0/K)\}$ times what we assumed it to be according to the ordinary too simplified method of treating ions in the theory of electrolysis. We therefore amend equation (8) to the following form:—

$$\lambda = ie^2 \cdot \frac{1}{6\pi\eta} \cdot \left(\frac{1}{K_1 a_1} + \frac{1}{K_2 a_2} \right) \frac{K_0}{1 - (1 - K_0/K_1)t_1/D - (1 - K_0/K_2)t_2/D}. \quad (9)$$

This introduces some interesting considerations. In the first place it shows that the dielectric capacity of each electrolytic solution must be taken into account in a complete investigation of ionization. It should be noticed that t/D is proportional to the strength of the solution. The dielectric capacity of solutions demands special investigation. But if we consider only solutions so dilute that t/D may be neglected, we find from (9) that in different solvents the specific velocity of a given ion must vary as K_0/η . Now Whetham has pointed out (*Phil. Mag.* [5] xxxviii., xlv.) that with water, methyl alcohol, and ethyl alcohol as solvents, the conductivities for a given electrolyte are approximately as K_0/η , one estimate of $\lambda\eta/K_0$ for the three substances in an arbitrary unit giving the relative values 1, 0.9, and 1.1, and another giving 1, 1.2, and 1.3, the conductivities standing in the ratios of 1 to .73 and .34. Whetham considers the dielectric capacity of the solvent to have most bearing on its ionizing power, in accordance with the suggestion of J. J. Thomson, but according to our reasoning the effect of dielectric capacity on ionization is secondary to its immediate effect on ionic velocities. But Whetham's results verify in a broad way our equation (9) when applied to very dilute solutions.

It is important to remark that this equation might appear to violate the law of the conservation of energy by seeming to make the work done in carrying a charge e from potential E_1 to E_2 in a very dilute solution to be $K_0e(E_1 - E_2)/K$ instead of $e(E_1 - E_2)$. But the difficulty disappears if energy $(K_0/K - 1)e(E_1 - E_2)$ is assumed to be taken from the dielectric. The total energy ultimately given to the dielectric is $e(E_1 - E_2)$ in the form of the heat generated by the friction of the ion carrying the charge e . Evidently the dielectric has a profound role to play in ionic matters. It should be noticed that the introduction of K the dielectric capacity of the atom into the expression for ionic velocity is important, and is to be returned to in the final section.

From equation (9) with the assumption that at infinite dilution $i=1$ we can write the general value of i thus:—

$$i = \frac{\lambda\eta}{\lambda_0\eta_0} \{1 - (1 - K_0/K_1)t_1/D - (1 - K_0/K_2)t_2/D\} \dots (10)$$

To realize the order of magnitude of the effect of dielectric capacity here, let us consider the case of an electrolytic ion having the same volume as a molecule of H_2O in a solution containing 0.1 gramme-equivalent of it per litre, then, in round numbers, we can say that we have $10^4/18 = 555$ molecules of H_2O to each ion, so $t/D = 1/555$. For an ordinary

ion we may take K as of the order 2, while K_0 is 80, and therefore $(1 - K_0/K)t/D$ is of the order $1/14$; for $m = .01$, this expression will be $1/140$, for $m = .001$ it will be $1/1400$. For dilute solutions it is therefore negligible, but for solutions of the order $m = .01$ it cannot safely be neglected, especially in the study of formulæ where $1 - i$ plays an important part, for though the error in i may be relatively small, that in $1 - i$ may be relatively large. In the case of an ion for which K is larger, say 20 instead of 2, then the effect of dielectric capacity becomes less important. But this line of thought does not lead direct to the explanation of the diverse behaviour discovered by Ostwald for weak acids and ordinary binary electrolytes; because if a large value of K secures that i measured in the usual way is nearly correct for CH_3COO in acetic acid, it ought also to act in the same way for sodium acetate, and so bring this electrolyte under Ostwald's law for weak acids like acetic, whereas sodium acetate ranges itself with the ordinary binary electrolytes. It seems to me that the following is a probable explanation why Ostwald's formula applies to weak acids. Many of these acids are known to polymerize. Acetic acid is probably $(\text{CH}_3\text{COOH})_2$, and when dissolved in water is partly dissociated into CH_3COOH , which is practically all ionized into CH_3COO and H at the dilutions of Ostwald's experiments. The conductivity measurements of Ostwald thus give him the amount of $(\text{CH}_3\text{COOH})_2$ which has been dissociated into CH_3COOH , and his law for acetic acid is probably the expression for equilibrium between di-acetic acid and the products of its dissociation, namely, mono-acetic acid. A similar explanation will apply to all his cases of weak acids. In the case of acetates like that of sodium, we must consider that the polymerization is not so stable in the presence of water as that of acetic acid, and that in dilute solutions the di-acetate is practically all dissociated into mono-acetate, in which form the acetate is usually assumed to be present in aqueous solutions, and, finally, that with the acetates it is really the dissociation into CH_3COO , and Na or K that we investigate by means of conductivities, and not as in acetic acid the relative amounts of diacetate and monoacetate.

As it has been shown that we must have an experimental investigation of dielectric capacity in solutions before we can determine ionizations satisfactorily, I do not propose to dwell at length on the wealth of existing data, but a brief discussion of a few typical solutions is necessary. The solutions chosen are those of NaCl , BaCl_2 , CaCl_2 , $(\text{NH}_4)_2\text{SO}_4$, and ZnSO_4 . For solutions of NaCl we have the latest

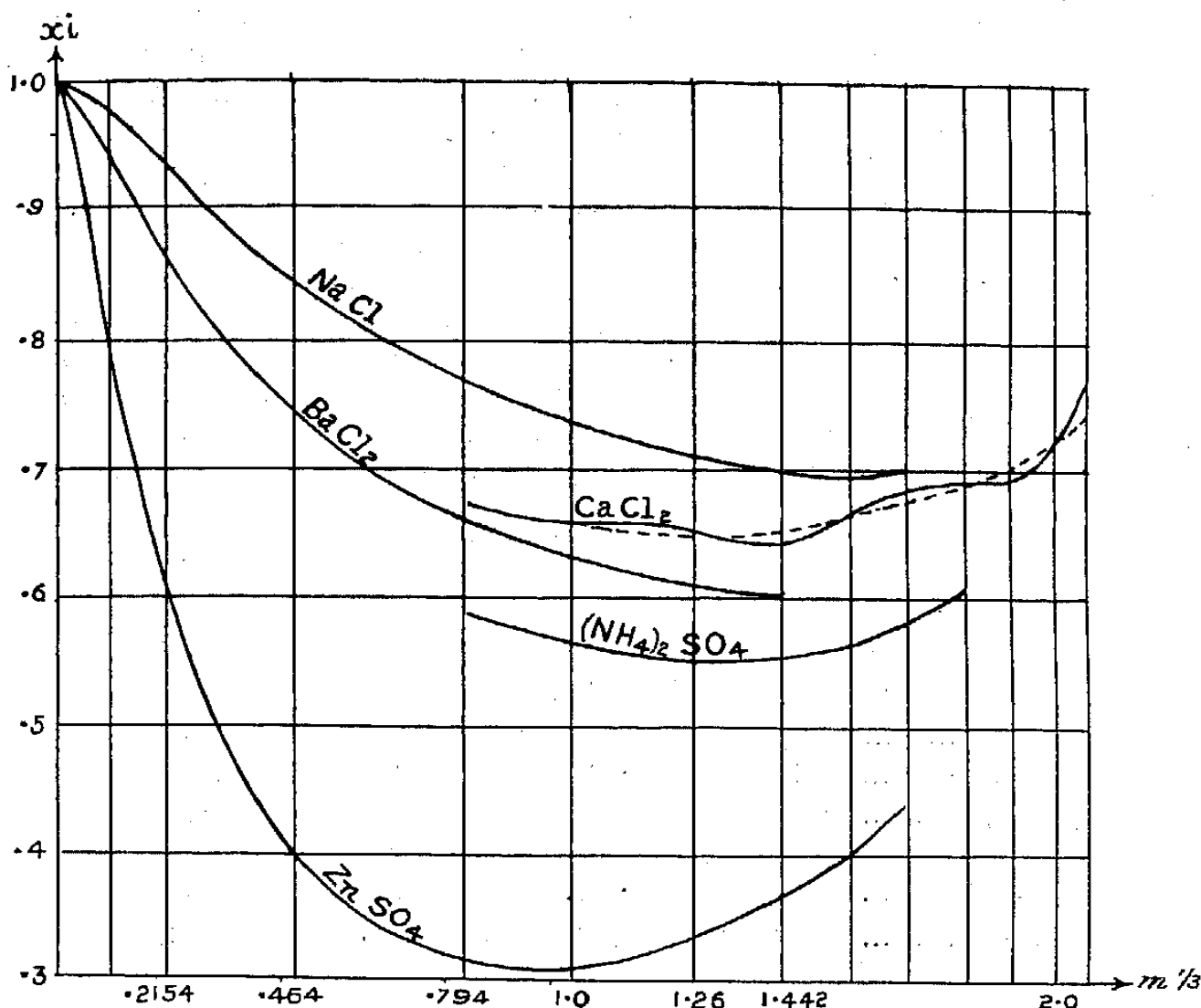
determinations of Kohlrausch (*Beibl.* xxv.) for strengths from $m = \cdot 0001$ to $m = \cdot 1$ at 18°C. , with which we can join on his previous determinations from $m = 1$ to $m = 5$. Kohlrausch estimates the specific molecular conductivity of NaCl at infinite dilution in water as $108\cdot99 \text{ cm}^{-1} \text{ ohm}^{-1}$. We need give then only λ/λ_0 in the following table along with η_0/η found by interpolation from Hosking's data (*Phil. Mag.* [5] xlix.), the viscosity of water at 18° being taken as $\cdot 01059 \text{ c.g.s.}$

TABLE I.—NaCl Solutions.

m	$1/\infty$	$\cdot 0001$	$\cdot 001$	$\cdot 01$	$\cdot 1$	1	2	3	4	5
$m^{1/3}$...	$0\cdot 0$	$\cdot 0464$	$\cdot 10$	$\cdot 2154$	$\cdot 464$	$1\cdot 0$	$1\cdot 26$	$1\cdot 442$	$1\cdot 587$	$1\cdot 710$
λ/λ_0	$1\cdot 0$	$\cdot 9918$	$\cdot 9770$	$\cdot 9354$	$\cdot 8443$	$\cdot 6822$	$\cdot 594$	$\cdot 517$	$\cdot 450$	$\cdot 391$
η_0/η	$1\cdot 0$	$1\cdot 0$	$1\cdot 0$	$\cdot 9995$	$\cdot 995$	$\cdot 927$	$\cdot 832$	$\cdot 736$	$\cdot 645$	$\cdot 558$
$xi = \lambda\eta/\lambda_0\eta_0$...	$1\cdot 0$	$\cdot 9918$	$\cdot 977$	$\cdot 936$	$\cdot 849$	$\cdot 736$	$\cdot 715$	$\cdot 701$	$\cdot 697$	$\cdot 700$
xi calc....	$1\cdot 0$	$\cdot 983$	$\cdot 964$	$\cdot 925$	$\cdot 851$	$\cdot 741$	$\cdot 712$	$\cdot 701$	$\cdot 697$	$\cdot 699$

x is put for $1/\{1 - (1 - K_0/K_1)t_1/D - (1 - K_0/K_2)t_2/D\}$ which for the small values of m differs so little from $1\cdot 0$ that xi may be taken to give an approximate value of i for very dilute solutions. In the second row values of $m^{1/3}$ have been given, because Kohlrausch found several years ago that for dilute solutions λ/λ_0 is a linear function of $m^{1/3}$, so that xi must also be nearly a linear function of $m^{1/3}$ when m is small. But the rest of the data show that xi reaches a minimum value at nearly the strongest solution. In the graph of these data, given in the figure (p. 171) with $m^{1/3}$ as abscissa and xi as ordinate, we see that the graph instead of being a straight line for small values of $m^{1/3}$ is a curve with a point of inflexion separating two parts of small opposite curvature. Some graphs given by Whetham (*Proc. Roy. Soc.* 1900) for λ/λ_0 show the same effect. Kohlrausch's straight line is the simplest approximation to this part of the curve; but the whole graph looks like a parabola which at small values of $m^{1/3}$ gets distorted. The cause of the distortion is probably this. Kohlrausch pointed out that in experiments on molecular conductivity for dilute solutions it is necessary to subtract from the conductivity of the solution that of the solvent, assuming that the conductivity of the solvent is not altered by the addition of the solute. Now, for a liquid like water which contains $(\text{H}_2\text{O})_3$ and $(\text{H}_2\text{O})_2$ in delicately equilibrating amount, it is not safe to assume that its conductivity is not altered by the mere presence of a small amount of electrolyte. The fact that the electrolyte is dissociated makes it probable that the slight ionization and conductivity of water are altered by the presence of the electrolyte. In fact it is well

known that some strong acids appear to have maximum molecular conductivities before infinite dilution is attained.



This seems to be only an exaggerated manifestation of the change of curvature shown in our graph for NaCl solutions, and to be ascribable to the same cause, namely our present inability to estimate the change in the ionization of the water brought about by the presence of the electrolytic solute. In spite of the experimental refinements in recent measurements of electrical conductivities, our knowledge of the molecular conductivities of solutions at infinite dilution is less definite than most physical chemists have assumed it to be. If we take the NaCl graph to be a parabola whose vertex is the point $m^{1/3} = 1.62$, $\xi_i = 0.697$, we find its equation to be

$$\xi_i - 0.697 = 0.1155(1.62 - m^{1/3})^2, \quad \dots \quad (11)$$

the values of ξ_i given by this being entered up in Table I. as ξ_i calc. The discrepancies between the actual and calculated values of ξ_i are probably due to the distortion of

the graph, which has been already discussed. As, theoretically, α must generally diminish with increasing values of m , because K_0/K is generally large compared to 1, it follows from the existence of a minimum value for αi that i must have a minimum value. This is important, because a formula like Ostwald's for weak acids could not give such a result. It appears that even when we can measure i , and especially $1-i$, with the requisite accuracy, we shall not be able to use Ostwald's formula for binary electrolytes.

The data for the other typical solutions are contained in Table II., the results being graphed in the figure. The conductivities are Kohlrausch's, and the viscosities derived by interpolation from Sprung's measurements (*Pogg. Ann.* clix.) and Grotrian's for ZnSO_4 (*ibid.* clx.). The temperature is 18°C ., at which the equivalent conductivities at infinite dilution in $\text{cm}^{-1} \text{ ohm}^{-1}$ are :—

$\frac{1}{2}\text{BaCl}_2$.	$\frac{1}{2}\text{CaCl}_2$.	$\frac{1}{2}(\text{NH}_4)_2\text{SO}_4$.	$\frac{1}{2}\text{ZnSO}_4$.
123·2	118·9	133·9	117·2

TABLE II.

$\frac{1}{2}\text{BaCl}_2$.										
m	·01	·1	1·0	3·0						
$m^{1/3}$	·2154	·464	1·0	1·442						
λ/λ_0	·868	·743	·567	·420						
η_0/η	·999	·989	·895	·698						
$xi=\lambda\eta/\lambda_0\eta_0$...	·869	·751	·634	·602						
xi calc.	·859	·751	·630	·607						
$\frac{1}{2}\text{CaCl}_2$.										
m	·5	1	2	3	4	5	6	7	8	9
$m^{1/3}$	·794	1·0	1·26	1·442	1·587	1·71	1·82	1·91	2·0	2·08
λ/λ_0	·622	·566	·484	·414	·356	·298	·245	·197	·153	·116
η_0/η	·927	·863	·741	·649	·537	·437	·353	·285	·214	·150
$xi=\lambda\eta/\lambda_0\eta_0$...	·671	·656	·653	·638	·662	·682	·693	·691	·716	·776
$\frac{1}{2}(\text{NH}_4)_2\text{SO}_4$.										
m	·5	1	2	3	4	5	6			
λ/λ_0 ...	·557	·511	·449	·406	·368	·331	·295			
η_0/η ...	·946	·902	·813	·731	·647	·568	·487			
xi	·589	·566	·552	·556	·569	·583	·607			
$\frac{1}{2}\text{ZnSO}_4$.										
m	·00001	·01	·1	1	3	5				
$m^{1/3}$	·02154	·2154	·464	1	1·442	1·71				
λ/λ_0	·962	·621	·391	·226	·132	·0742				
η_0/η	1·0	·997	·968	·724	·357	·168				
xi	·962	·623	·404	·312	·370	·443				
xi calc.	·909	·565	·402	·308	·347	·440				

These tables and their graphs bring out more clearly the important fact that αi or $\lambda\eta/\lambda_0\eta_0$ passes through a minimum. The curves are parabolic, those for BaCl_2 , $(\text{NH}_4)_2\text{SO}_4$, and ZnSO_4 having axes inclined to the axis of αi . The sinuosities of the CaCl_2 curve are smoothed out in the dotted curve. The equations for the BaCl_2 and ZnSO_4 graphs are respectively

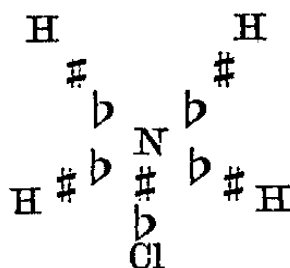
$$(\cdot969m^{1/3} - i - \cdot350)^2 = 7\cdot18i + \cdot824m^{1/3} - 5\cdot35 \quad (12)$$

$$(\cdot969m^{1/3} - i - \cdot442)^2 = 3\cdot51i + \cdot403m^{1/3} - 1\cdot433 \quad (13)$$

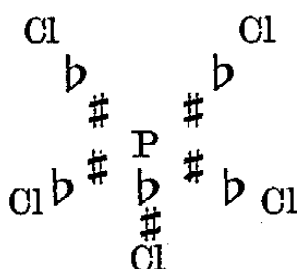
with which the values marked αi calc. in Table II. have been found. For reasons which are obvious after what has been said in discussing the NaCl graph, little importance attaches to these equations. The main point about the graphs is that they make it plain that αi attains a minimum value at a certain strength of the solution. In interpreting the form of these equations we must first consider how $m^{1/3}$ and $m^{2/3}$ come in. On general principles it is clear that they do not enter because of a direct dependence of ionization on the distance apart of the molecules of solute, which is proportional to $m^{-1/3}$. It is possible that the $m^{1/3}$ enters on account of the following train of circumstances. The solute molecules in a watery solution, such as that of NaCl , probably change a certain amount of $(\text{H}_2\text{O})_3$ into $(\text{H}_2\text{O})_2$, as is shown by the occurrence of shrinking on solution, and they also probably dissociate into $\# \text{Ob}_2(\# \text{H})_2 \flat$ a number of trihydrol molecules. Let y be the average part of each second for which $\# \text{Ob}_2(\# \text{H})_2 \flat$ is separate, $1-y$ the part for which it is combined with others, then the actions producing fresh stions do so at a rate $c(1-y)m$, while those forming trihydrol out of the stions do so at a rate $c'y^3m^3$, and for equilibrium $c(1-y)m = c'y^3m^3$, and when y is small, $y^3 \propto m^{-2}$ and y varies as $m^{-2/3}$.

Now the rate at which the stions $\# \text{Ob}_2(\# \text{H})_2 \flat$ form the labile compound $\text{Cl} \flat \# \text{Ob}_2(\# \text{H})_2 \flat \# \text{Na}$ will be proportional both to y and to m , that is to say, it varies as $m^{1/3}$, and therefore the index $1/3$ enters because of the 3 in the formula for trihydrol. Our equations connecting αi and $m^{1/3}$ are therefore equations of chemical equilibrium, expressing that a rate of combination denoted by a square is proportional to a rate of dissociation denoted by a linear, whence the parabolic graphs. It would not be profitable to follow this train of thought further, until the dielectric capacities of solutions have been quantitatively studied. The complete theory of the ionization of binary electrolytes in aqueous solutions is more complicated even than it has been hitherto supposed to be.

Similar considerations to those adduced for water must apply to other ionizing liquids. Take for example liquid NH_3 . The constitution of NH_4Cl suggests for it the formula



whence gaseous NH_3 , like steam, has a neutron associated with each molecule, though this neutron need not have the same electric moment as the neutrons of free æther. Liquid NH_3 may consist of di- or tri-ammonia, the molecules of which on dissociation yield stions $\# \text{Nb}_3(\# \text{H})_3 \text{b}$, whence the ionizing power of liquid NH_3 . For PCl_5 we can imagine the constitution



in which one of the Cl atoms is quite differently attached from the other four, being ready to form $\text{Cl}\# \text{bCl}$ and PCl_3 when PCl_5 dissociates. The easy dissociation of NH_4Cl would be explained in the same way, and probably a large part of the phenomena connected with variable valency could receive a similar electrical treatment.

3. *Ionic Velocities and Absolute Sizes of Atoms.*

For what is usually called the velocity ${}_1\lambda$ of an ion at any dilution we have from (9) the equation

$${}_1\lambda = ie^2 \cdot \frac{1}{6\pi\eta\alpha_1} \cdot \frac{K_0}{K_1} \cdot \frac{1}{1 - (1 - K_0/K_1)t_1/D - (1 - K_0/K_2)t_2/D} \quad (14)$$

At infinite dilution

$${}_1\lambda_0 = e^2 K_0 / 6\pi\eta\alpha_1 K_1. \quad . \quad . \quad . \quad . \quad . \quad (15)$$

Of the quantities entering into this last e^2 , α_1 and K_1 are not capable of direct physical measurement like the others, but if K_1 were known, then since we know M_1/e from the electrochemical equivalent of the ion of mass M_1 , and as $M_1 = 4\pi\rho_1\alpha_1^3$ where ρ_1 is the limiting density of the substance at absolute

zero, which can be closely estimated, equation (15) would become a definite one for a_1 the atomic radius. For an ion of valency ν , e^2 must be replaced by $\nu^2 e^2$ and ${}_1\lambda_0$ by $\nu {}_1\lambda_0$ and (15) becomes

$${}_1\lambda_0 = \nu e^2 K_0 / 6\pi\eta a_1 K_1. \quad (16)$$

We can derive values of K_1 from the relation $K_1 = N_1^2$, where N_1 is the index of refraction of the stuff of the atom. In a recent paper ("The Cause of the Structure of Spectra," Phil. Mag. [6] ii.) I have given values of N_1 for a number of metals of known density, which may be taken to be the limiting density, and so the data are to hand for calculating a_1 for a number of elements. But before proceeding to absolute values we can test how the equation behaves relatively for a number of elements. As e^2 , η , and K_0 are the same for all ions when we deal with infinitely dilute aqueous solutions, we must have ${}_1\lambda_0 a_1 K_1 / \nu$ the same for all ions. To test this relation we gather for several atoms and radicals in Table III. the values of N_1 , and of B which is the limiting volume of a gramme-atom or gramme-radical, of ${}_1\lambda_0$ according to Kohlrausch, and of ${}_1\lambda_0 B^{1/3} N_1^2 / \nu$ which by (16) is to be constant. The values of N_1 are derived from the refraction formula $(n-1)M/\rho = (N-1)B$ with the values of $(n-1)M/\rho$ given in the text-books as atomic refractions (see for example L. Meyer's 'Modern Chemistry'), and with values of B as given in "Further Studies on Molecular Force" (Phil. Mag. [5] xxxix.) and reproduced here. $\nu=2$ for Mg, Ca, Sr, Ba, and Zn, and $\nu=1$ for the rest.

TABLE III.

	Li.	Na.	K.	Rb.	Cs.	Mg.	Ca.	Sr.	Ba.	Zn.
${}_1\lambda_0 \dots$	35.5	44.4	65.3	67.3	67.8	48	53	54	57.3	47.5
$B \dots$	2	7.4	18.6	34.4	56	5.6	8.6	10.6	16.6	10.6
$N \dots$	2.9	1.65	1.44	1.41	1.24	2.25	2.21	2.28	1.95	1.96
${}_1\lambda_0 B^{1/3} N^2 / \nu$	375	235	360	435	400	215	265	310	277	200
	F.	Cl.	Br.	I.	H.	OH.				
${}_1\lambda_0 \dots$	46.1	65.9	67.5	66.7	318	174				
$B \dots$	9	19	26	36	4.5	9.5				
$N \dots$	1.16	1.56	1.65	1.76	1.37	1.44				
${}_1\lambda_0 B^{1/3} N^2 / \nu \dots$	130	430	545	680	980	765				
	HCOO.	CH ₃ COO.	C ₂ H ₅ COO.	C ₃ H ₇ COO.	C ₄ H ₉ COO.	C ₅ H ₁₁ COO.				
${}_1\lambda_0 \dots$	47.2	35.4	31.8	28.3	26.5	25.3				
$B \dots$	24.5	42	59.5	77	94.5	112				
$N \dots$	1.494	1.469	1.458	1.454	1.450	1.448				
${}_1\lambda_0 B^{1/3} N^2 / \nu \dots$	305	265	264	255	253	256				

Among the metals though ${}_1\lambda_0 B^{1/3} N^2 / \nu$ varies from 200 to 400, the approach to constancy appears remarkable when it is noticed that N^2 varies from 1.53 to 8.4, and $B^{1/3}$ from 1.26 to 3.8. In the six fatty acid radicals from formic to caproic the approach to constancy is satisfactory. In the halogen atoms ${}_1\lambda_0 B^{1/3} N^2 / \nu$ fails to approach constancy in a striking manner, ranging from 130 to 680. It is probable that the discrepancy here is due to the assumption that in these atoms $K = N^2$. If we remember that the halogens are heptads as well as monads, and that therefore each halogen atom contains three pairs of \sharp and \flat as neutrons, or as doublets, giving each the possibility of acting as a tri-stion, we can see that the assumption $K = N^2$ is unsafe. The exceptional behaviour of H and OH in having such large values as 980 and 765 for ${}_1\lambda_0 B^{1/3} N^2 / \nu$ is probably due to the fact that these are the ions of water itself. It is possible therefore that these two ions have their real ionic velocities largely increased by a sort of Grotthus-chain action, whereby an H or an OH, instead of passing through the space of a water molecule which is in front of it, simply combines with part of the molecule and liberates the other part at the other side, so that the same effect is produced as if the ion had traversed the space of the molecule with a higher velocity than the true ionic velocity.

To proceed with our equation (16) to the calculation of a_1 absolutely, let us fix our attention on the ion of Li. We must first convert ${}_1\lambda_0$ its ionic velocity per gramme equivalent G into the velocity of an atom by dividing by $3G/4\pi\rho_1 a_1^3$, which is the number of atoms in a gramme equivalent. Again, to express ${}_1\lambda_0$ in C.G.S. units we must multiply ${}_1\lambda_0$ cm.⁻¹ ohm⁻¹ by 10^{-9} to pass to the electromagnetic unit of resistance, and by 9×10^{20} to get the appropriate C.G.S. expression. Again, the electrochemical equivalent of hydrogen is .0001035 in E.M. units, and therefore for Li

$$M_1/e = .000725/3 \times 10^{10}$$

in electrostatic units. As $G/\rho_1 = B$ given along with ${}_1\lambda_0$ and N in Table III., we have for Li with $K_0 = 80$, $\nu = 1$, $\eta = .01059$, and $\rho_1 = 3.5$.

$$\left| \frac{4\pi}{3B} a_1^3 \times 35.5 \times 9 \times 10^{11} = (4\pi\rho_1 a_1^3)^2 \cdot \frac{9 \times 10^{20} \times 80}{.000725^2 \times 6\pi \times .01059 \times 2.9^2 a_1} \right|$$

$$\therefore a_1^2 = 3.8 \times 10^{-18},$$

$$a_1 = 2 \times 10^{-9},$$

$$\frac{4}{3}\pi a_1^3 = 7.5 \times 10^{-27}.$$

Now Kelvin's estimate of the volume of an ordinary molecule is between 3×10^{-25} and 10^{-28} c.c. with which the value just calculated for Li, the smallest of the ions in Table III., is in agreement. The molecular radius of ordinary gases, as found by the kinetic theory from measurements of gaseous viscosity, is of the order 5×10^{-8} cm., which is about 25 times our value of a_1 just found for the Li ion. The process of calculating the size of a molecule from its observed ionic velocity might prove helpful in the case of large organic ions such as physiologists have to deal with, for the molecular weight could be estimated from the size when other recognized methods of determining it fail. Ostwald's measurements of the ionic velocities of a large number of organic radicals (Wied. Ann. Beibl. xiii.) might supply useful material for a preliminary study in making equation (16) available for the estimation of very large molecular weights.

Melbourne, October 1901.

XIX. *On the Variation with Temperature of the Thermo-electromotive Force, and of the Electric Resistance of Nickel, Iron, and Copper, between the Temperatures of -200° and $+1050^\circ$.* By E. PHILIP HARRISON, University College, London*.

THE main objects of the investigation which forms the subject of this paper are as follows :—

To trace over as wide a range as possible the change with temperature of the thermoelectromotive force and the resistance of Nickel and Iron, *using in all experiments the same specimens of metal*; to investigate any singularities that may be present in the curves representing the change; and to determine whether they occur at the same temperature in each of the curves. It was originally intended to investigate the magnetic properties of the same specimens, but time has not sufficed for this.

SECTION I.

THERMOELECTRIC PROPERTIES.

(1) *Results of Previous Observers.*

In his researches on thermoelectricity† Tait gives the results of some of his measurements for iron which extended from 0° to the melting-point. The second portion of his iron

* Communicated by the Physical Society: read October 25, 1901.

† Proc. Roy. Soc. Edin. December 1873; 'Nature,' Rede Lecture, May 1st, 1873.

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