

XXXVIII.—*The Abnormality of Strong Electrolytes.*  
*Part I. Electrical Conductivity of Aqueous Salt*  
*Solutions.*

By JNANENDRA CHANDRA GHOSH.

VAN'T HOFF discovered that aqueous solutions of electrolytes show an abnormal osmotic pressure. For such solutions, as is well known, the equation  $PV=iRT$  holds good. Arrhenius suggested that  $i=(1-a)+na$ , where  $a$  is the degree of dissociation and  $n$  the number of ions into which a molecule dissociates. According to Arrhenius, there is, therefore, an equilibrium between ions and undissociated molecules in solution. Ostwald attempted to apply the law of mass action to this case of chemical equilibrium, but his dilution law,  $\frac{a^2}{(1-a)V} = K$  fails absolutely in the case of strong

electrolytes. Various hypotheses have been put forward to explain this anomaly, for example, hydration of ions, change in ionic friction with dilution, formation of complexes, action of salts, change in the dielectric constant of the solvent, interaction between molecules and ions, etc. None, however, has been found to be satisfactory. It appears to the present author that the fundamental suggestion of Arrhenius, postulating the co-existence of undissociated molecules and ions in solution, is probably not valid. The question of chemical equilibrium does not enter into the question at all in the case of strong electrolytes. In solutions of strong electrolytes only ions are present, and the attractive forces between ions are only governed by the physical laws of electrostatic attraction. On the basis of this simple assumption, a quantitative interpretation of the increase of molecular conductivity with dilution will be given.

*Number of Free Ions in a Solution containing a Gram-molecule of Salt from the Classical Kinetic Theory.*—According to a well-known theorem of the kinetic theory of gases, there is a simple relation between the total number of molecules and the number which can perform the work required to displace a molecule from the sphere of mutual attraction. In applying this theorem to calculate the number of free ions in a solution containing a gram-molecule of salt, we may proceed thus:—A salt solution, where only ions are present, is perfectly analogous to a gaseous system. The electrical attraction between the oppositely charged ions corresponds with the molecular forces in an imperfect gas. Due to this attraction, a field of force exists in the interior of a salt solution, the potential of which may be represented by  $A$ , that is,  $A$  is the work done when the ions constituting a gram-molecule go beyond one another's sphere of attraction. The ions in a solution are, of course, endowed with a kinetic energy of translation, the distribution of velocities being governed by Maxwell's law. As the work done in escaping from the electrical field inside the solution must be derived from the kinetic energy of the ions, only those ions can escape which have a kinetic energy greater than the work to be done. The problem before us is, therefore, to determine what fraction of the total number of ions has a velocity greater than the critical velocity  $v_0$ , where  $\frac{1}{2}mv_0^2 = \frac{A}{nN}$ . Here  $N$  is Avogadro's number ( $6.16 \times 10^{23}$  Millikan's value),  $n$  the number of ions into which a molecule dissociates, and  $\frac{A}{nN}$  is therefore the work to be done by each ion before it can escape. Now if  $V'$  is the most probable speed of an ion, then the fraction we are considering is

represented by  $e^{-v_0^2/V^2}$  where  $e$  is the base of natural logarithm. Now if  $c$  is the square root of the mean of the squares of the speeds, we have  $c^2 = \frac{3}{2}V^2$ , and the required fraction becomes

$$e^{-\frac{1}{2}v_0^2/\frac{3}{2}c^2} = e^{-\frac{1}{3}n \cdot N \cdot mv_0^2/\frac{3}{2}n \cdot mc^2} = e^{-\frac{A}{nRT}}$$

(Since there are ions of different equivalent weights in the solution,  $m$  signifies the mean mass of an ion.)

As  $nN$  is the total number of ions, the number of free ions

$$= nNe^{-\frac{A}{nRT}} \quad \dots \quad (1)$$

*Conductivity of Salt Solutions.*—It is well known that Ohm's law holds good for electrolytic conduction. No energy is therefore lost in overcoming the forces of mutual attraction between ions. Any hypothesis put forward to explain the phenomenon of electrolytic conduction must take into consideration this fundamental fact. According to Arrhenius, the molecular conductivity of a salt solution at infinite dilution is at a maximum, because there the salt is entirely dissociated into ions. With diminishing dilution the molecular conductivity diminishes, because the salt is only partly dissociated and hence the number of ions is less. On the hypothesis that in aqueous solutions we have only ions present subject to forces of electrical attraction, a neat explanation can also be given. Since during electrolytic conduction no energy is lost in overcoming the forces of electrical attraction, only those ions take part in the conduction of electricity which by virtue of their kinetic energy can overcome the forces of mutual attraction. These are also the ions which can be liberated on the electrode surface. The rest are inactive so far as electrical conduction is concerned. At any dilution, the number of free conducting ions is equal to

$$n \cdot N \cdot e^{-\frac{A}{nRT}}$$

where  $A$  is the work at that dilution. The molecular conductivity is proportional to this number. At infinite dilution  $A$  is zero, since the ions are outside one another's sphere of attraction, and therefore the number of conducting ions is  $nN$ . Therefore

$$\frac{\mu_o}{\mu_{\infty}} = \frac{nNe^{-\frac{A}{nRT}}}{nN} = e^{-\frac{A}{nRT}} \quad \dots \quad (2)$$

or

$$A = nRT \log_e \frac{\mu_{\infty}}{\mu_o} \quad \dots \quad (2')$$

*The Electrical Work Necessary to Separate the Component Ions of a Gram-molecule at Various Dilutions.*

(a) *The Arrangement of Ions in Solution.*—In the interior of a solution, the electrical forces between ions are balanced. In order that this equilibrium condition may be attained, the ions should arrange themselves in a definite fashion. It is necessary that they should adopt a geometrical disposition of perfect regularity, as do the atoms when they assume a crystalline structure, under the forces of mutual attraction. This does not necessarily mean that the ions in solution are devoid of any kinetic energy whatsoever. What we assume here is that the mean disposition of the oppositely charged ions should conform to some patterns in space. According to Ostwald, the conditions of the salt molecule in the crystalline state is not far removed from the state of solution. Indeed, there is not much difference between a crystalline salt and the same in a molten condition as regards their electrochemical properties. Thus, the experiments of Graetz (*Ann. Phys. Chem.*, 1890, [iii], 40, 18) have shown that there is no sudden change in electrical conductivity as we pass from the solid to the fused state.

It may well be that even the forces which group the atoms of a solid salt according to a definite space-lattice are electrical in nature. In the first place, therefore, we make the perfectly reasonable assumption that the marshalling of the ions of a salt in a state of solution is analogous to the arrangement of its atoms in the crystalline structure.

(b) *The Forces of Electrical Attraction between Ions.*—For the calculation of the electrical work it is necessary to make another assumption. In solution, an ion takes up a definite mean position because of the forces of electrical attraction exerted by oppositely charged ions surrounding it.

We may, however, suppose that the component ions of a salt-molecule form a completely saturated electrical doublet. When a univalent ion tends to pass out of solution, the solution becomes electrified with an opposite unit charge and attracts it as a whole. By assuming the existence of electrical doublets we only locate the centre of attraction inside the solution. The work necessary for separating the component ions of a molecule is the electrical work done in moving the ions constituting a doublet from their fixed mean distance in the solution to an infinite distance apart. Thus for an aqueous solution of a binary salt like potassium

chloride, the electrical work necessary for separating the potassium and chlorine ions

$$= \frac{E^2}{D.r} \dots \dots \dots (3)$$

where  $E$  is the charge on each ion,  $D$  the dielectric constant of water, and  $r$  the distance between the oppositely charged ions at that dilution.

For salts of the type of barium chloride, there are two electrical doublets associated with each molecule, Cl-Ba-Cl. Now let us remove the two chlorine ions successively from the sphere of influence of the barium ion. For the first chlorine ion, the electrical work is  $\frac{E^2}{D.r}$ , the same as is necessary for separating the components of a doublet in potassium chloride solutions. The removal of the second chlorine ion is much more difficult. This ion is attracted by two opposite charges, and hence the work due to electrical attraction is  $\frac{2E^2}{D.r}$ . The work necessary for separating the component ions of a molecule of barium chloride is therefore

$$\frac{3E^2}{D.r} \dots \dots \dots (4)$$

For salts of the type of magnesium sulphate the electrical work is

$$\frac{4E^2}{D.r} \dots \dots \dots (5)$$

for each ion here carries two unit charges. Now, if we can determine the value of  $r$  for these types of salt at various dilutions,  $A$  is known, and therefore the ratio  $\frac{\mu_v}{\mu_\infty}$ , which is equal to  $e^{-\frac{A}{nRT}}$  can at once be calculated.

(c) *Calculation of the Distance between Ions in Solutions of Binary Salts.*—The distance between the oppositely charged ions in an aqueous solution can be very simply determined on the assumption previously made. Take, for example, the case of potassium chloride. Bragg has actually measured the distance between the planes 100, 110, 111 of this cubic crystal, and has found that it is the simple cubic lattice to which the arrangement of the atoms conforms. We therefore expect that in solutions, also, the sets of points corresponding with the mean position of the ions form a cubic space-lattice. It is obvious that in a cubic lattice there is only one point, that is, one ion, associated with a unit cell, the distance between the oppositely charged ions being

the linear dimension of the unit cell. Since there are  $2N$ -ions, the total volume occupied by  $2N$ -unit cubes  $= 2N \cdot r^3 = V$  (c.c. containing a gram-molecule), therefore

$$r = \sqrt[3]{\frac{V}{2N}} \text{ and } A = \frac{N \cdot E^2 \sqrt[3]{2N}}{D \cdot \sqrt[3]{V}} \quad \dots (6)$$

$$= 2RT \log_e \frac{\mu_\infty}{\mu_v} \quad \dots \dots \dots (7)$$

where  $E = 4.7 \times 10^{-10}$  [E.S.U.] and  $D = 81$  at  $18^\circ$ .

For salts like ammonium chloride or potassium nitrate, where complex univalent radicles are encountered, we are also justified in assuming that the distance between ions at equivalent dilutions is approximately the same as in the case of potassium chloride solutions.

(d) *Calculation of the Distance between Ions in Solutions of Salts like Barium Chloride.*—Crystals of calcium fluoride, the constitution of which is perfectly analogous to that of barium chloride, have been thoroughly investigated by Bragg (*Proc. Roy. Soc.*, 1914, A, **89**, 474). In a fluorspar crystal, the calcium atoms are arranged in a face-centred cube lattice, whilst the fluorine atoms occupy the centres of the small cubes. This structure explains how, for each calcium atom, two fluorine atoms may be arranged to form a cubic lattice. Assuming that the arrangement of the barium and chlorine ions in solution corresponds with the fluorspar lattice, we find that each unit cube of the lattice is associated with half an ion of barium. If  $r$  be the linear dimension of the unit cube, since there are  $N$ -barium ions,  $2N \cdot r^3 = V$  (c.c. containing a gram-molecule), therefore

$$r = \sqrt[3]{\frac{V}{2N}}$$

The chlorine ions, from analogy, should occupy the centres of unit cubes, hence the distance between the barium ion and the chlorine is  $\frac{\sqrt{3}}{2} r$ . Therefore the electrical work required to separate the components of a gram-molecule is equal to

$$\begin{aligned} & \frac{3NE^2 \cdot 2 \cdot \sqrt[3]{2N}}{D \cdot \sqrt{3} \cdot \sqrt[3]{V}} \text{ ergs} \\ & = 3RT \log_e \frac{\mu_\infty}{\mu_v} \quad \dots \dots \dots (8) \end{aligned}$$

(e) *Calculation of the Distance between Ions in Solutions of Salts like Magnesium Sulphate.*—No definite structure has yet been assigned to crystals of magnesium sulphate. The fundamental lattice is, of course, not cubic, but a rhombohedron.

It is possible that, owing to the forces of electrical attraction being greater, the oppositely charged ions constituting a doublet should come together as close as possible. Since, however, we are dealing with a salt, the valency volumes of the ions of which are, according to Barlow and Pope's theory, twice as great as that of a univalent ion, the distance between the doublets should be greater than that in the case of potassium chloride. In solution we may take the cube as the fundamental lattice, without introducing any serious error. The above conditions are satisfied if we imagine that the unit cube is formed only by two oppositely charged ions placed at the adjacent corners. The unit cell becomes thus associated with only one-fourth of an ion, as in the cube-centred lattice. If  $r$  be the linear dimension of the unit cube at dilution  $V$ , then  $8N \cdot r^3 = V$  (c.c. containing a gram-molecule) or

$$r = \sqrt[3]{\frac{V}{8N}}.$$

$r$  is also the distance between the component ions of a doublet. Therefore the electrical work

$$A = \frac{4 \cdot N \cdot E^2 \sqrt[3]{8N}}{D \sqrt[3]{V}} = 2RT \log_e \frac{\mu_{\infty}}{\mu_v} \quad \dots \quad (9)$$

From the equations (7), (8), and (9), which contain no unknown quantities whatever,  $\frac{\mu_v}{\mu_{\infty}}$  can be at once calculated for any dilution. In the following tables it will be shown how the observed values of  $\mu_v$  at 18° agree with those calculated from the above equations. The value of  $\mu_{\infty}$  cannot be determined experimentally, but is generally obtained by extrapolation. In the tables, the value of  $\mu_{\infty}$  has been calculated from the observed values of  $\mu_v$  for 0.01*N*-solutions, and this theoretical value of  $\mu_{\infty}$  has then been utilised in calculating  $\mu_v$  at other dilutions. The observed values of  $\mu_v \cdot \nu$  are from the tables of Kohlrausch and co-workers.

TABLE I.

*V* = Dilution in litres.

Salt.	$\mu_{\infty}$ calc. from $\mu_{100}$	$\nu = 10.$	20.	100.	1000.	5000.	
KCl .....	132.2	$\left\{ \begin{array}{l} \mu_v \text{ calc.} \\ \mu_v \text{ obs.} \end{array} \right.$	111.7 112.0	115.7 115.9	122.5 122.5	127.7 127.6	129.2 129.1
		$\left\{ \begin{array}{l} \mu_v \text{ calc.} \\ \mu_v \text{ obs.} \end{array} \right.$	93.1 92.0	96.5 95.7	102.0 102.0	106.4 106.5	108.0 107.8
LiCl .....	99.6	$\left\{ \begin{array}{l} \mu_v \text{ calc.} \\ \mu_v \text{ obs.} \end{array} \right.$	84.0 82.4	87.1 86.1	92.1 92.1	96.2 96.5	97.5 97.8
		$\left\{ \begin{array}{l} \mu_v \text{ calc.} \\ \mu_v \text{ obs.} \end{array} \right.$	114.3 113.6	—	125.2 125.2	130.6 130.6	132.5 132.0

TABLE I.—(continued).

*V = Dilution in litres.*

Salt.	$\mu_{\infty}$ calc. from $\mu_{100}$		<i>v</i> = 10.	20.	100.	1000.	5000.
NH <sub>4</sub> Cl ...	132.0	$\mu_v$ calc.	111.3	115.4	122.1	127.4	129.3
		$\mu_v$ obs.	110.7	115.2	122.1	127.3	128.8
KBr .....	134.5	$\mu_v$ calc.	113.6	117.7	124.4	129.7	131.7
		$\mu_v$ obs.	114.2	117.8	124.4	129.4	130.9
KI .....	133.5	$\mu_v$ calc.	112.7	116.7	123.4	128.7	130.6
		$\mu_v$ obs.	113.9	117.2	123.4	128.2	129.5
KNO <sub>3</sub> ...	127.9	$\mu_v$ calc.	107.8	111.2	118.1	123.3	124.8
		$\mu_v$ obs.	105.0	110.0	118.1	122.9	124.3
NaNO <sub>3</sub> ...	105.0	$\mu_v$ calc.	88.5	91.8	97.1	101.3	102.8
		$\mu_v$ obs.	87.4	91.4	97.1	101.8	103.3
C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> K	101.6	$\mu_v$ calc.	85.9	88.9	94.0	98.1	99.6
		$\mu_v$ obs.	84.0	87.7	94.0	98.3	99.6

The agreement is remarkably good. The difference between the observed and the calculated values is rarely greater than 1 per cent.

TABLE II.

*V = Equivalent dilution in litres.* *$\mu_v$  and  $\mu_{\infty}$  are equivalent conductivities.*

Salt.	$\mu_{\infty}$ calc. from $\mu_{100}$		<i>v</i> = 10.	20.	100.	1000.	5000.
BaCl <sub>2</sub> .....	124.3	$\mu_v$ calc.	92.0	97.3	107.7	116.2	119.5
		$\mu_v$ obs.	92.2	96.8	107.7	116.9	119.8
Sr·Cl <sub>2</sub> .....	121.6	$\mu_v$ calc.	89.3	95.2	105.4	113.8	116.9
		$\mu_v$ obs.	90.2	94.4	105.4	114.5	117.5
CaCl <sub>2</sub> .....	119.1	$\mu_v$ calc.	87.5	93.2	103.2	111.4	114.6
		$\mu_v$ obs.	87.9	92.8	103.2	111.5	114.4

The difference between the theoretical and the observed values is never greater than 1 per cent.

TABLE III.

*V = Equivalent dilution in litres.* *$\mu_v$  is equivalent conductivity.*

Salt.	$\mu_{\infty}$ calc. from $\mu_{100}$		<i>v</i> = 10.	20.	100.	1000.
MgSO <sub>4</sub> .....	114.7	$\mu_v$ calc.	48.1	57.6	76.6	95.1
		$\mu_v$ obs.	50.1	57.0	76.6	100.2
ZnSO <sub>4</sub> .....	110.0	$\mu_v$ calc.	46.0	55.1	73.4	91.0
		$\mu_v$ obs.	46.2	53.5	73.4	98.0
CuSO <sub>4</sub> .....	108.0	$\mu_v$ calc.	45.2	53.0	72.2	89.6
		$\mu_v$ obs.	45.0	51.4	72.2	101.6

At  $V=100$  the discrepancy is very large. Below  $V=100$  the agreement is quite good. At high dilutions the conductivity is much greater than the calculated value, because of the undoubted hydrolysis of the salts—the interaction between ions and water molecules.

*The Temperature-coefficient of the Ratio  $\frac{\mu_v}{\mu_\infty}$ .*—We have seen how the observed values of  $\mu_v$  agree with those calculated from the equations (7), (8), and (9). There is every reason to believe that the laws of electrical attraction are independent of temperature. The equations, which yield very satisfactory results at  $18^\circ$ , should also hold good at higher temperatures. In our equation for binary electrolytes,

$$A = \frac{N \cdot E^2 \cdot \sqrt[3]{2N}}{D \cdot \sqrt[3]{V}} = 2kT \log_e \frac{\mu_\infty}{\mu_v}$$

if the variation of the dielectric constant of water with temperature be known,  $\frac{\mu_v}{\mu_\infty}$ , can be easily calculated for any temperature. According to Drude, the variation of the dielectric constant of water with temperature between  $0^\circ$  and  $76^\circ$  is given by the following formula:

$$D_t = D_{18} \{1 - 0.00436(t - 18) + 0.0000117(t - 18)^2\}.$$

Assuming that this formula holds good up to  $100^\circ$ , the dielectric constant of water at  $100^\circ = 52.6$ . Table IV shows how the calculated values of  $\frac{\mu_v}{\mu_\infty}$  at various temperatures agree with the observed data of Noyes and Coolidge (*Zeitsch. physikal. Chem.*, 1903, **46**, 323).

TABLE IV.

Salt.	T°.		$v = 12.5.$	$= 100.$
KCl.	18°	$\left\{ \begin{array}{l} \frac{\mu_v}{\mu_\infty} \text{ calc.} \\ \frac{\mu_v}{\mu_\infty} \text{ obs.} \end{array} \right.$	85.4 per cent.	93.0 per cent.
			87.0 ,,	94.0 ,,
	100°	$\left\{ \begin{array}{l} \frac{\mu_v}{\mu_\infty} \text{ calc.} \\ \frac{\eta_r}{\mu_\infty} \text{ obs.} \end{array} \right.$	82.6 ,,	90.9 ,,
			82.6 ,,	91.1 ,,

The coincidence is remarkable. The diminution of the ratio  $\frac{\mu_v}{\mu_\infty}$  with increase in temperature may thus be quantitatively explained.

In conclusion, reference should be made to one important point, namely, the question of weak electrolytes. They are invariably either acids or bases. The abnormally high conductivity of hydrogen and hydroxyl ions leaves no room for doubt that here there is a chemical interaction between solvent and solute molecules. Ostwald's dissociation constant is probably related in some way to the constant of these specific chemical reactions.

I take this opportunity of offering my best thanks to Mr. J. N. Mukherjee, M.Sc., for many valuable suggestions. My best thanks are also due to Prof. P. C. Rây.

PHYSICO-CHEMICAL LABORATORY,  
UNIVERSITY COLLEGE OF SCIENCE,  
CALCUTTA.

[Received, July 18th, 1917.]

---