hydroxide is substituted for sodium hydroxide in the neutralization, is questionable, because of the lack of a carbonate correction.

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THE ABNORMALITY OF STRONG ELECTROLYTES AND THE IONIZATION THEORY OF GHOSH[1]

BY JAMES KENDALL

Many attempts have been made during the past 30 years to account for the failure of the Ostwald dilution law $\mu_v^2/\mu_\infty \cdot (\mu_\infty - \mu_v).v = k$ to reproduce the ionization of strong electrolytes. It has been suggested, for example, that the degree of ionization is not correctly represented by the conductivity ratio μ_v/μ_∞, that the ionization equilibrium is not correctly represented by the equation $RX \rightleftharpoons R^+ + X^-$, or that the law of mass action is not applicable to the equilibrium between ions and undissociated molecules. The only alternative theory that has been received with any great degree of favor, however, is one recently developed by Ghosh,[2] which rejects the fundamental assumptions of Arrhenius entirely. It is the purpose of the present article to give a critical analysis of the arguments advanced by Ghosh and others in support of this theory.

The Postulates of Ghosh.—The theory, as applied to a uni-univalent salt RX in solution, is based upon the following postulates: (1) the electrolyte is completely dissociated at all dilutions into oppositely charged radicals R^+ and X^-; (2) the arrangement of these charged particles in the solution is analogous to the marshaling of atoms in a simple cubic crystal lattice; (3) the oppositely charged radicals of a salt-molecule RX form a completely saturated electrical doublet, and the work necessary to separate them is the electrical work done in moving them from their fixed mean distance in the solution to an infinite distance apart; (4) a radical is free to conduct the current only if its kinetic energy is greater than half the work required to separate it from its partner; (5) the distribution of velocities among the particles is according to Maxwell's law.

For salts of other valence types, and for acids and bases, other postulates are made, which will be referred to later. The essential point in the theory of Ghosh is that strong electrolytes are wholly dissociated in solution, partly into *free* and partly into *bound* ions, only the former being capable of conducting the current. The ratio μ_v/μ_∞ consequently ex-

[1] Presented, in part, at the St. Louis meeting of the American Chemical Society, April 14, 1920.

[2] Ghosh, *J. Chem. Soc.*, 113, 449, 627, 707, 790 (1918); 117, 823, 1390 (1920).

presses the *proportion of free ions*, and Ghosh, with the help of the above postulates, derives an equation for the variation of μ_v with dilution for each type of strong electrolyte which, it is claimed, is in satisfactory agreement with the experimental data. The agreement is, in point of fact, so striking, and so many additional confirmatory points are adduced that Ghosh's conclusion that the validity of the postulates has been thoroughly established is *apparently* perfectly justified. It is true that objections have been raised by Partington[3] and by Chapman and George[4] against certain of Ghosh's assumptions, but the general trend of physical chemists at the present time is obviously towards the acceptance of his theory.[5] Mention may be made, in particular, of articles by Noyes and MacInnes[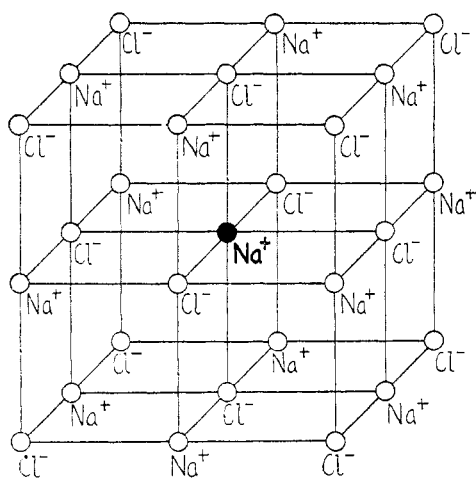6] and by Hill.[7] The fact that the main points of Ghosh's theory are in close harmony with Langmuir's recent work on atomic structure and valence[8] and with the latest results obtained from the examination of salt crystals by X-ray analysis[9] has undoubtedly predisposed many investigators in its favor.

Fig. 1.

If it could be shown, however, that the postulates of Ghosh are inconsistent with one another, that they are at variance with carefully established experimental data, that the equations which Ghosh employs do not follow from his postulates, or that the agreement between these equations and the results of experiment is fictitious, then the theory in its present form would of necessity become unacceptable. In the following pages it will be shown that the theory is indeed vulnerable at all of the above points, and that many of Ghosh's conclusions must in consequence be modified or rejected.

[3] Partington, *Trans. Faraday Soc.*, **15**, 111 (1919).

[4] Chapman and George, *Phil. Mag.*, [VI] **41**, 799 (1921).

[5] For example, at a recent symposium on the present position of the ionization theory [*Trans. Faraday. Soc.*, **15**, 1–178 (1919)], the opinion was expressed by Sand (p. 171), "it seemed not improbable that Ghosh's theory would rank as the most important advance in the theory of electrolytic conduction since the enunciation of the Ostwald-Planck dilution law." See also Walker, "Introduction to Physical Chemistry," Macmillan and Co., 1919, p. 266.

[6] Noyes and MacInnes, THIS JOURNAL, **42**, 239 (1920).

[7] Hill, *ibid.*, **43**, 254 (1921).

[8] Langmuir, *J. Ind. Eng. Chem.*, **12**, 386 (1920); THIS JOURNAL, **42**, 274 (1920).

[9] "Ann. Reports Chem. Soc.," **16**, 209 (1919); **17**, 2 (1920).

Inconsistency of the Postulates.—The second and the third postulates of Ghosh are absolutely incompatible. If the marshaling of the oppositely-charged particles of a salt such as sodium chloride in solution is analogous to the arrangement of the atoms in the crystalline structure (see Fig. 1), then no positively charged particle Na^+ is specifically attached to any particular negatively charged particle Cl^- to give a salt-molecule $NaCl$ or to form a completely saturated electrical doublet. Any atom will be kept in a definite mean position in the cubic lattice by the electrical forces exerted between it and all of the surrounding atoms, and cannot form a neutral doublet with any one of the 6 oppositely charged atoms in immediate proximity to it without destroying the whole basis of the crystal structure.

Ghosh's calculation of the electrical work required to separate "the component ions of a salt-molecule," where E is the charge on each ion, D the dielectric constant of water, and r the distance between oppositely charged ions, leads therefore to an entirely incorrect result.

Calculation of the Electrical Work Necessary to Separate the Component Ions of a Gram-molecule.—The true value of A, the electrical work necessary to disperse to infinite dilution the component radicals of a gram-molecule of dissolved salt, if arranged according to the cubic space lattice, may be obtained as follows.

Consider one particular atom, such as the central Na^+ in Fig. 1, and sum up the work necessary to disperse the atoms immediately surrounding it, taking into account only the force exerted between each atom and the central Na^+. There are, first of all, 6 Cl^- particles at a distance r. The work to separate these to an infinite distance is $6\ E^2/Dr$. The cubes shown in the diagram also contain, however, 12 Na^+ particles at a distance $\sqrt{2}\ r$, and 8 Cl^- particles at a distance $\sqrt{3}\ r$. The total work required to disperse the particles forming these cubes is therefore

$$\frac{E^2}{Dr} \cdot \left(6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}}\right) = 2.134 \frac{E^2}{Dr}.$$

The particles in more remote cubes must next be considered. If we pack one more layer of cubes all around those represented in the diagram, and sum up the work necessary to disperse each particle, as before, we obtain for this second layer of particles

$$\frac{E^2}{Dr} \cdot \left(-\frac{6}{2} + \frac{24}{\sqrt{5}} - \frac{24}{\sqrt{6}} - \frac{12}{\sqrt{8}} + \frac{24}{\sqrt{9}} - \frac{8}{\sqrt{12}}\right) = -0.617 \frac{E^2}{Dr}.$$

Continuing out into space, we obtain for the next four layers the values

$$+ 0.398 \frac{E^2}{Dr}, -0.295 \frac{E^2}{Dr}, + 0.234 \frac{E^2}{Dr} \text{ and } -0.192 \frac{E^2}{Dr} \text{ respectively.}$$

The work for successive layers is therefore opposite in sign and steadily diminishing in magnitude. The rate of diminution, after the second layer,

is very nearly expressed by the simple relation (layer work) × (layer number) = constant.

We are therefore able to evaluate the work necessary to separate one particular particle from all surrounding particles; it is the limit of the convergent series

$$\frac{E^2}{Dr} \cdot (2.134 - 0.617 + 0.398 - 0.295 + 0.234 - 0.192 + \ldots \ldots) = 1.75\frac{E^2}{Dr}.$$

Now, in one gram-molecule of dissolved salt there are $2N$ particles, N being Avogadro's number. The total electrical work A necessary to disperse these will be $A = 1.75\ NE^2/Dr$. (The factor 2 falls out of this equation, since in summing up the *total work* the force necessary to separate any 2 particles is considered twice, once for the first and once for the second particle.)

The value here obtained is significantly different from that derived by Ghosh, NE^2/Dr. Consequently all of the equations employed by Ghosh, which utilize the relation $A = NE^2/Dr$, stand in need of correction.

The Distribution of Velocities.—Ghosh has calculated that the number of free ions in a gram-molecule of dissolved salt is given by the expression $2N \cdot e^{-\frac{A}{2RT}}$. It has been shown by Chapman and George[4] that this calculation is erroneous. Maxwell's law for the distribution of velocities leads to an entirely different and much more complicated expression for the number of particles which possess a kinetic energy in excess of the critical value.[10] All of the equations employed by Ghosh which utilize the above expression for the number of free ions stand also, therefore, in need of correction.

The Variation in the Proportion of Free Ions with Dilution.—The equation which Ghosh finally derives from his five postulates is

$$\frac{N.E^2.\sqrt[3]{2N}}{D.\sqrt[3]{v}} = 2RT\ ln\frac{1}{\alpha}$$

where α is the proportion of free ions at dilution v. For aqueous solutions at 18°, this reduces to

$$\log \alpha = -0.1616/\sqrt[3]{v}.$$

Since $\alpha = \mu_v/\mu_\infty$ (or, more accurately, $\mu_v\eta_v/\mu_\infty\eta_\infty$, where η_v and η_∞ are the viscosities of the solution and the solvent respectively), the validity of this relationship can be directly tested against the experimental data.

Two separate points are here involved. In the first place, *all electrolytes of the same type should give identical values for* μ_v/μ_∞ *at any given dilution.* In the second place, *the variation of* μ_v/μ_∞ *with dilution should be as represented by the above equation.*

[10] See Jeans, "The Dynamical Theory of Gases," Cambridge Univ. Press, 1916, pp. 34–5.

Are All Electrolytes of the Same Type Equally Ionized?—This point has been called in question by Partington,[8] who presents extensive data to show that considerable divergences exist in the experimental values of μ_v/μ_∞ for different electrolytes. In reply, Ghosh[11] objects to the values of μ_∞ employed by Partington, and deduces alternative values for the alkali chlorides which make μ_v throughout the range $v = 10$ to $v = 5000$ practically identical in all cases.

It is impossible to settle this dispute satisfactorily at the present time, since the value for μ_∞ derived for any electrolyte depends upon the form of the equation used to extrapolate the experimental data to infinite dilution, and the choice of any particular equation largely predetermines the issue. It is true that many chemists[12] have preceded Ghosh in postulating identical ionization values for restricted series of salts of similar character at high dilutions, and that the deviations which become evident at higher concentrations may quite plausibly be ascribed to specific effects, such as changes in ionic mobilities. At concentrations approaching normal, indeed, the diameter of the ions becomes appreciable with respect to the distance between them, and salts which furnish ions of large diameter might be expected to give significant and specific variations from the simple equations of Ghosh. All this being granted, the position of advantage in the μ_∞ controversy still appears to lie with Partington. The values for μ_∞ employed by Partington are all taken *directly* from Kohlrausch, as extrapolated by him from his own data. The values employed by Ghosh *assume* that the careful conductivity measurements of Kohlrausch and his co-workers at high dilutions are in error to the extent of $1-2\%$, and it is extremely unlikely that this assumption is justified.[13]

In the case of potassium chloride, indeed, we have positive evidence in favor of Partington. The value of μ_∞ which Kohlrausch obtains for this salt is 129.90. The value deduced by Ghosh is 132.2. The recent determinations of Washburn and Weiland,[14] carried out to a remarkable degree of precision at exceedingly high dilutions, lead to the value 129.64.

Is the Variation of Ionization with Dilution Represented by the Equation of Ghosh?—The experimental data for potassium chloride are shown in Table I, p. 722 From $v = 10$ to $v = 500$ the equivalent conductivities of Kohlrausch and Maltby[15] have been taken, the usual viscosity corrections being applied. From $v = 1000$ to $v = 10000$ the

[11] Ghosh, *Trans. Faraday Soc.*, **15**, 154 (1919).

[12] For example, Noyes and Falk, THIS JOURNAL, **34**, 475 (1912). Lewis, *ibid.*, **34**, 1643 (1912). Washburn, *ibid.*, **40**, 151 (1918).

[13] See Kendall, *ibid.*, **39**, 19 (1917).

[14] Washburn and Weiland, *ibid.*, **40**, 131 (1918).

[15] Landolt-Börnstein, "Tabellen," 1912, p. 1102.

results are those of Washburn and Weiland.[16] The end-value of the latter investigators has been used throughout.

The values for α derived from Ghosh's equation are given in the third column. The last columns headed "α (Corrected)" show respectively: (I) the values for α obtained when the expression $A = 1.75\ NE^2/Dr$ is substituted for that employed by Ghosh, (II) the values for α obtained when the Chapman and George correction is made, (III) the effect of both of the above corrections.

TABLE I

Proportion of Free Ions

Potassium chloride in water at 18°

v	α (Expt.)	α (Ghosh)	α (Corrected)		
			I	II	III
10	0.8625	0.8410	0.7393	0.9511	0.8950
50	0.9245	0.9041	0.8380	0.9775	0.9494
100	0.9440	0.9230	0.8691	0.9838	0.9638
500	0.9741	0.9542	0.9213	0.9926	0.9834
1000	0.9816	0.9634	0.9370	0.9946	0.9883
5000	0.9926	0.9784	0.9626	0.9972	0.9945
10000	0.9953	0.9829	0.9702	0.9980	0.9959

It will be seen that the equation used by Ghosh gives values somewhat lower than the experimental throughout the whole dilution range. The application of the first correction leads to much lower values. The second correction, on the other hand, gives results considerably higher than the experimental. The two corrections together largely cancel each other's effect, and a series of values is obtained only slightly higher than the experimental. The differences at the higher concentrations, however, are far beyond the limits of experimental error.

It does not follow, of course, from the above table that Ghosh's theory is fundamentally invalid. Further modification of the postulates might very conceivably suffice to bring the calculated and experimental values into satisfactory agreement. At this point we may profitably note, with respect to the fifth postulate, that Maxwell's law for the distribution of velocities is derived on the assumption that the particles are not electrically charged and are perfectly free to move in space. Its extension to positively and negatively charged particles, the mean disposition of which conforms to a definite space-lattice, certainly requires justification.

Whether Ghosh's second postulate—that the arrangement of the oppositely-charged radicals of a salt in solution is according to a definite space-lattice—is itself acceptable, is a point we shall return to later. In the sections immediately succeeding, the concordance claimed by Ghosh to exist between the equations resulting from his theory and the observations of previous workers will be examined. In order to make the criticisms on the various topics discussed quite independent of those which

[16] Ref. 14, p. 146.

have preceded, Ghosh's original equations are used throughout. So many different points are involved that the treatment of each is necessarily brief and, for space considerations, the argument is confined almost entirely to uni-univalent electrolytes.

The Variation of Equivalent Conductivity with Dilution.—To avoid the difficulty introduced by the uncertainty in μ_∞, Ghosh prefers to test the validity of his equation for uni-univalent electrolytes in aqueous solution at 18°,

$$\log \alpha = -0.1616/\sqrt[3]{v}$$

by throwing it into the form

$$\log \mu_v - \log \mu_{100} = 0.1616 \left(\frac{1}{\sqrt[3]{100}} - \frac{1}{\sqrt[3]{v}} \right).$$

The value of μ_v for the dilution $v = 100$ is thus made the basis of calculation for μ_v at other dilutions, and incidentally is also used to evaluate μ_∞.

Equations of a similar nature are derived by Ghosh for salts of two other valence types, barium chloride and magnesium sulfate, under the assumption that the space-lattice arrangement of the charged particles in solution corresponds in each case to the crystal structure. All three equations are tested[17] against the experimental data of Kohlrausch, and the agreement between the observed and calculated values of μ_v for dilutions from $v = 10$ to $v = 5000$ is characterized as "remarkably good," "rarely greater than 1 per cent."

Is this agreement really remarkable? Let us take the first salt listed, potassium chloride. According to the figures given, μ_v varies throughout the whole concentration range by 17.1 units only, from 112.0 at $v = 10$ to 129.1 at $v = 5000$. If now we assume, as Ghosh does, that the calculated and observed values of μ_v are *identical* at a point in the middle of this narrow range, *i. e.*, 122.5 at $v = 100$, the concordance of calculated and observed values becomes more a matter of necessity than of merit. When μ_v varies from μ_{100} at the utmost by only 10%, as is the case with all of the uni-univalent electrolytes tested by Ghosh, then a divergence of 1 unit, which is frequent in the table, is equivalent to an error of 1 in 10. The fundamental validity of the equation can scarcely be confirmed by evidence of this character; all that has been demonstrated is that it reproduces the observed results fairly well over a restricted range, and other interpolation equations[18] are known which possess equal, if not superior, accuracy over the same interval.

If we could prove satisfactory agreement over a more extended range, the above criticism would naturally no longer hold. At concentrations above $v = 10$, however, μ_v loses much of its theoretical significance, in

[17] Ghosh, *J. Chem. Soc.*, **113**, 455-6 (1918).
[18] See Washburn, Ref. 12, p. 122.

consequence of the increasing magnitude of the arbitrary corrections necessary for viscosity and ionic mobility changes. At concentrations below $v = 5000$, on the other hand, few determinations of sufficient precision are available. It is highly significant that the equation cannot be extended, in the case of potassium chloride, to give agreement with the very accurate determinations of Washburn and Weiland[14] between $v = 1000$ and $v = 100,000$. The calculated values deviate more and more from the observed as the dilution is increased, the final μ_∞ values differing by as much as 2%, far beyond the limits of experimental error.

In the majority of cases, indeed, the actual agreement between calculated and observed values for μ_v between $v = 10$ and $v = 5000$ is by no means so striking as indicated by Ghosh in his three tables. Comparison of these tables with the original data of Kohlrausch and his co-workers[19] discloses the fact that *in no fewer than 39 out of 75 instances the value for μ_v (obs.) presented by Ghosh differs from that recorded by Kohlrausch.* The difference frequently exceeds a whole unit. The remarkable agreement claimed by Ghosh is therefore largely fictitious.

The Temperature-coefficient of the Ratio μ_v/μ_∞.—The next point considered by Ghosh[20] is the variation in the ratio μ_v/μ_∞ with temperature, due to the variation in the dielectric constant of water. The experimental data for potassium chloride at $18°$ and $100°$ are utilized to show that the observed diminution of μ_v/μ_∞ at a fixed dilution with increase of temperature corresponds with the variation calculated from the Ghosh equation. For the dielectric constant of water at $100°$, the value 52.6 is employed. The data for μ_v/μ_∞ at two dilutions, $v = 12.5$ and $v = 100$, at $18°$ and $100°$ are tabulated, and it is noted once more that the "coincidence" between the calculated and observed values is "remarkable."

It is unfortunate for the theory of Ghosh, therefore, that all of the calculated values in this table are wrong. At $18°$ the errors of calculation are relatively small; for $v = 12.5$ Ghosh's equation gives $\mu_v/\mu_\infty = 0.852$ (instead of 0.854), while for $v = 100$ it gives 0.923 (instead of 0.930). At $100°$, however, the equation utilized by Ghosh for the variation of the dielectric constant of water with temperature[21] really leads to the value 58.4, not to 52.6. The *true* calculated values for μ_v/μ_∞ at $100°$ according to the equation of Ghosh are, at $v = 12.5$, 0.841 (instead of 0.826) and, at $v = 100$, 0.917 (instead of 0.909).

In addition to this, the experimental figures for the ionization of potassium chloride at $18°$ are not accurately transcribed, the value given

[19] Kohlrausch, "Gesammelte Abhandlungen," Barth, Leipzic, 1911, vol. 2; Landolt‧ Börnstein, "Tabellen," 1912.

[20] Ref. 17, p. 457.

[21] Ref. 15, p. 1213.

by Noyes and Coolidge[22] at $v = 12.5$ being 0.873 (instead of 0.870) and, at $v = 100$, 0.942 (instead of 0.940).

These corrections, it will be noted, vitiate entirely the claim made by Ghosh that the diminution of the ratio μ_v/μ_∞ with increase in temperature has been quantitatively explained.

The Electrical Conductivity of Non-aqueous Solutions.—The whole of Ghosh's second paper[23] is devoted to this topic; 28 tables of data are presented, and it is again concluded that the validity of the equations is "completely confirmed." The experimental results employed are mainly from the work of Carrara[24] and of Walden.[25] In order to obtain satisfactory agreement between calculated and observed values for Walden's "normal electrolyte" tetra-ethyl-ammonium iodide, however, Ghosh finds it necessary to assume that this salt, in most non-aqueous solvents, first *polymerizes* and then *dissociates not as a binary but as a ternary electrolyte*, giving the ions $2NEt_4^+$ and I_3^- The same assumption is made for sodium and potassium iodides in acetonitrile and in pyridine, respectively, while for ammonium iodide in acetone an additional postulate is involved, namely that the NH_4^+ ions are displaced diagonally towards the I_2^- ions in the space lattice.

These assumptions have been attacked by Partington[26] as purely arbitrary, and there is no question that Ghosh chooses his polymerizing solvents in a most peculiar manner. Thus tetra-ethyl-ammonium iodide is regarded as a binary electrolyte in acetaldehyde and acetone, liquids with dielectric constants of approximately 20, while in formamide, a solvent closely resembling water, with a dielectric constant of 84, the same salt is treated as a ternary electrolyte.

Obviously, if variants of the normal space lattice are admissible, it will always be possible to select one which will lead to an equation reproducing the observed values for μ_v for any particular solution within the limits of experimental error, especially when the error limits are relatively large, the range of dilutions is small, the variation in μ_v throughout this range is small, and the equation is thrown into a form which makes μ_v (calc.) and μ_v (obs.) identical in the middle of the range. What positive evidence, then, does Ghosh adduce in support of his new assumptions to rescue them from the suspicion of being merely arbitrary?

The statement that iodine tends to form univalent complex ions such as I_3^- and I_5^- has no bearing at all upon the ability of iodine ion to unite

[22] Noyes and Coolidge, *Carnegie Inst. Pub.*, **63**, 53 (1907). The reference given by Ghosh [*Z. physik. Chem.*, **46**, 323 (1903)] does not contain any of the experimental values which he employs.

[23] Ref. 17, p. 627.

[24] Carrara, *Gazz. chim. ital.*, [i] **26**, 119 (1896).

[25] Walden, *Z. physik. Chem.*, **54**, 129 (1906).

[26] Ref. 2, p. 113.

with itself to form a divalent ion $I_2^=$. Furthermore, as we shall see later, Ghosh's equation for uni-univalent electrolytes in solvents of low dielectric constant fails just as inevitably with other salts as it does with iodides. It is true, as Ghosh remarks, that the consensus of opinion among electrochemists is generally in favor of complex molecules in non-aqueous solutions. This opinion, however, is based on the fact that freezing-point depressions and boiling-point elevations obtained for salts in solvents of low dielectric constant are abnormally small,[27] and it has been clearly established in recent articles by Hildebrand[28] that such abnormalities must be ascribed, in general, to differences in the internal pressures of the components of the solution, *not* to association of the solute. The only other argument advanced by Ghosh in proof of the abnormality of tetra-ethyl-ammonium iodide in certain solvents is that "the exact coincidences between the observed and calculated values leave no room for doubt as to the mode of dissociation." This argument loses weight when it is found, once more, on examination of the original tables, that *in as many as 31 instances in this article Ghosh's values for μ_v (obs.) do not agree with the actual experimental data.*

The Molecular Number i and the Clausius Theorem.—In his third article,[29] Ghosh combines his equation: $A = 2RT \ln 1/\alpha$ with the Clausius theorem:[30] $PV = {}^2/_3$ kinetic energy $- {}^1/_3$ virial and derives, for a uni-univalent salt in aqueous solution, the following expression for the molecular number i

$$i = 2\left(1 - \frac{1}{3} \ln \frac{1}{\alpha}\right).$$

He then purports to show that this expression gives better agreement with the experimental values for i, as obtained from freezing-point depression measurements for binary electrolytes, than does the Arrhenius equation $i = 1 + \alpha$. Similarly successful comparisons having been made for typical ternary salts, Ghosh concludes that the validity of his fundamental equations has now been completely demonstrated; "in fact, a complete theory of dilute salt solutions has been propounded."

In point of fact, however, Ghosh never tests the Arrhenius equation connecting experimental conductivity ratios with experimental freezing-point depression abnormalities at all. To evaluate i at various dilutions he substitutes, in both of the above equations, not the *experimental* value for α, μ_v/μ_∞, but the *theoretical* value for α calculated from his own equation.

[27] See Turner, "Molecular Association," Longmans, Green and Co., 1915, pp. 46-8.

[28] Hildebrand, This Journal, **38**, 1452 (1916); **42**, 2180 (1920).

[29] Ref. 17, p. 707.

[30] Compare Milner, *Phil. Mag.*, [vi] **23**, 551 (1912); **25**, 747 (1913).

$$\frac{N.E^2.\sqrt[3]{2N}}{D.\sqrt[3]{v}} = 2\,RT\,ln\,\frac{1}{\alpha}.$$

All that Ghosh really shows, therefore, is that this equation gives values for α which vary with dilution in such a manner that the expression $2\left(1 - \frac{1}{3}ln\frac{1}{\alpha}\right)$ reproduces the freezing-point depression values for i more closely than does the expression $1 + \alpha$. The values obtained from this latter expression, however, are far from being identical with those derived from the experimental conductivity data for uni-univalent salts,[31] as may be seen from the following table. The calculated values for the expression $2\left(1 - \frac{1}{3}ln\frac{1}{\alpha}\right)$ and the experimental freezing-point depression values[32] for i are also here included.

TABLE II

MOLECULAR NUMBER i FOR SALTS OF TYPE RX

v	2	5	10	20	50	100
$i = 1 + \alpha$ (calc. from Ghosh equation).	1.748	1.808	1.844	1.875	1.906	1.924
$i = 1 + \alpha$ (expt. from conductivity)....	1.771	1.821	1.855	1.885	1.918	1.938
$i = 2\left(1 - \frac{1}{3}ln\frac{1}{\alpha}\right)$	1.806	1.859	1.887	1.910	1.934	1.947
i (expt. from freezing-point depression).	1.804	1.837	1.865	1.887	1.925	1.937

From this table it is evident that the Arrhenius equation: $i = 1 + \alpha$, where $\alpha = \mu_v/\mu_\infty$ (expt.), gives better agreement with the freezing-point depression data than does the Ghosh-Clausius equation, except at the highest concentration $v = 2$. The deviations at the higher concentrations, indeed, are only such as might be expected from the fact that van't Hoff's law $\pi V = RT$ cannot be valid for strong electrolytes.[33] As the dilution is increased, the superiority of the Arrhenius expression becomes manifest. This superiority is indisputably confirmed on examination of the later and more accurate freezing-point depression data of Adams[34] and of Hall and Harkins.[35]

The Ionization of Strong Acids.—Aqueous solutions of strong acids like hydrochloric acid and of strong bases like potassium hydroxide give much higher values for μ_v/μ_∞ than do uni-univalent salts at equivalent dilutions, and do not exhibit even approximate agreement with the equation of Ghosh. In his fourth paper,[36] Ghosh attempts to account for

[31] Noyes and Falk, Ref. 12, p. 476.

[32] Noyes and Falk, THIS JOURNAL, 32, 1027 (1910).

[33] See Washburn, ibid., 32, 485 (1910); and, more particularly, Bates, ibid., 37, 1421 (1915).

[34] Adams, ibid., 37, 495 (1915).

[35] Hall and Harkins, ibid., 38, 2658 (1916).

[36] Ref. 17, p. 790.

this by postulating that the ratio μ_v/μ_∞ is not, for acids and bases dissolved in water, the true expression for the proportion of free ions, since the water molecules also take an active part in the transmission of the current. It is assumed that a hydrogen ion or an hydroxyl ion, striking against a molecule of water, may cause the latter to undergo dissociation into H^+ and OH^-, and that one of these unites with the original ion to regenerate a molecule of water while the other shoots off as a charged particle. If this process of dissociation and recombination is instantaneous, the electric charge is thus carried instantaneously through a distance proportional to the diameter of the water molecule, and the apparently abnormal mobilities of the hydrogen and hydroxyl ions in aqueous solution are explained.

This is an old suggestion of Arrhenius.[37] It introduces several points of difficulty. Why should the impacts of other ions on these dissociable water molecules be entirely innocuous? Why should the mobilities of other ions approach those of H^+ and OH^- at high temperatures, as has been shown by Noyes and his co-workers?[38] One would rather expect the opposite, since water molecules should be more readily dissociable as the temperature is raised, and the impacts between them and H^+ and OH^- ions are certainly more violent. How can the fact that the ratio μ_v/μ_∞ for hydrochloric acid at high temperatures is *less* that that of potassium chloride at an equivalent dilution[39] be explained? Finally, since it is admitted[40] that the constituent radicals of the water molecule are oppositely charged, why should these radicals also not attempt to take up a space-lattice arrangement and contribute towards the production of free ions in all aqueous solutions?

The last of these points—the rôle of the solvent in ionization—will be taken up in the concluding sections. Let us assume, for the present, that Ghosh's new postulate is valid, and examine the consequences.

First of all, assuming that the true value of α for strong acids like hydrochloric acid at any given dilution is the same as that of uni-univalent salts, Ghosh develops an equation by which the real mobility U_{H^+} of the hydrogen ion and the conductivity C_1 due to the water may be evaluated from conductivity data. For acids, $U_{H^+} = 152$ and $C_1 = 198.5$ at $25°$; for bases, $U_{OH^-} = 109$ and $C_1 = 66$. Tables are given to show that the calculated variation of μ_v with dilution for strong acids and bases, when these values are substituted in Ghosh's equation, is always in agreement with the experimental data within 0.5%. Unfortunately the experimental values for μ_v, in any single case, vary only from 3 to 6% throughout

[37] Arrhenius, "Theories of Solutions," Yale University Press, 1912, p. 139.

[38] Noyes, *et al.*, *Carnegie Inst. Pub.*, **63**, 336 (1907).

[39] Ref. 38, p. 339.

[40] Ghosh, Ref. 11, p. 159.

the range of dilutions examined, so that the test is not very stringent. More definite support for the validity of his contention that the true value for α is the same for strong acids and bases as for salts is sought by Ghosh[40] from the work of Ellis[41] on activity-coefficients by the electromotive-force method. Reference to a table recently published by Noyes and MacInnes[42] will show, however, that the most accurate data in this important field, *including the results of Ellis*, indicate conclusively that the activity-coefficients for hydrochloric acid, potassium hydroxide and potassium chloride diverge considerably, and are in no single case in agreement with the calculated values of Ghosh.

The Ionization of Weak Acids.—Still more convincing evidence against Ghosh's theory is obtained from the results of its application to typical weak electrolytes like acetic acid. These are assumed to give both undissociated molecules and ions in solution, their ionization equilibria being expressed by the equation: $(\alpha x)^2/(1-x).v = k$, where x is the fraction dissociated and α the proportion of free ions in this fraction. For any ionic concentration x/v, α can be calculated, and is so very nearly equal to 1 at all dilutions (according to Ghosh) that the above equation becomes identical with Ostwald's dilution law for very weak acids.

The *actual data for acetic acid* at 25° are presented in Table III below. The first column shows the dilution and the second the observed conductivity.[43] In the third and fourth columns x and α, as calculated from the equations of Ghosh, are shown. The fifth column gives the dissociation constant derived from these values, the last column the dissociation constant obtained on the basis of the original Arrhenius theory.

TABLE III

ACETIC ACID, 25°

v	μ_v	x	α	100 k (Ghosh)	100 k (Arrhenius)
13.57	6.086	0.01585	0.9613	0.001740	0.001845
27.14	8.591	0.02234	0.9655	0.001754	0.001851
54.28	12.09	0.03138	0.9693	0.001759	0.001849
108.56	16.98	0.04399	0.9727	0.001765	0.001849
217.1	23.81	0.06160	0.9757	0.001773	0.001851
434.2	33.22	0.08584	0.9784	0.001777	0.001849
868.4	46.13	0.1191	0.9809	0.001783	0.001850
1737.0	63.60	0.1640	0.9831	0.001790	0.001854

Evidently α diverges appreciably from unity throughout the whole range, although at the last dilution given the ionic concentration is less than 0.0001 N. In consequence of this variation in α with dilution, the theory of Ghosh involves a steady increase in the ionization constant, as illustrated by the figures in the fifth column. The exact applicability

[41] Ellis, THIS JOURNAL, **38**, 759 (1916).

[42] Ref. 6, p. 243.

[43] Kendall, *J. Chem. Soc.*, **101,** 1283 (1912).

of the Ostwald dilution law to weak acids like acetic acid and weak bases like ammonia must therefore be devoid of all theoretical basis, and the constant values for k obtained for so many weak electrolytes by so many different observers (as, for example, in the last column of the preceding table) are presumably entirely fortuitous! A more cogent argument *against* the validity of Ghosh's assumptions can scarcely be conceived.

The Ionization of Transition Acids.—Ghosh claims, however, to have demonstrated the applicability of his formula also to "the entire range of transition electrolytes." The equation developed for determining x for solutions of such electrolytes[44] is, it may be noted, erroneous, since it involves the use of the relationship $\alpha = 1 - K.(x/v)^{1/3}$, which is derived[45] under the condition that μ_v is only slightly less than μ_∞.

It has been shown by the present author[46] that the dissociation constants for transition acids decrease towards a limiting value k_∞ as the dilution is increased. The variation in α, calculated according to the Ghosh theory, is (as in the case of acetic acid above) in the opposite direction. The application of the Ghosh equation $(\alpha x)^2/(1-x).v = k$ to transition electrolytes consequently gives, owing to the counterbalancing of these two factors, a fairly satisfactory value for k throughout a limited dilution range. Nevertheless, if the examination is extended to high dilutions, where k (Arrhenius) is practically constant while α is still increasing, the inconstancy of k (Ghosh) becomes obvious. The stronger the acid, the more rapidly do the values for the latter expression increase. The first stages of this inevitable increase are quite evident in all of the four tables for transition acids presented by Ghosh, although in each case the data for the highest dilutions, where the variations in k become much more pronounced, are prudently omitted.

The Electrical Conductivity of Pure Salts in the Solid and Fused States.—Most of Ghosh's fifth paper[47] is occupied with the derivation of equations for the variation of the specific conductivity of a solid salt with temperature, and the presentation of experimental data in support of these equations. At first sight, the concordance of the observed figures with those calculated from Ghosh's final equation[48]

$$\frac{W_0(T_2 - T_1)}{2R} \left(\frac{1}{T_1 T_2} + \frac{1}{T_m{}^2} \right) = ln \frac{\mu_2 \sqrt{T_2}}{\mu_1 \sqrt{T_1}}$$

is indeed striking. On closer examination, however, it appears that it

[44] Ghosh, Ref. 17, p. 797. By good chance, Ghosh does not use this equation for calculating x and α in his tables for transition acids. The values given in these tables are consequently correct.

[45] Ref. 17, p. 795.

[46] Kendall, *J. Chem. Soc.*, **101**, 1290 (1912).

[47] Ghosh, *ibid.*, **117**, 823 (1920).

[48] The minus sign between the terms $1/T_1T_2$ and $1/T_m{}^2$ in this equation in Ghosh's article is evidently a typographical error.

is necessary to utilize the experimental values of μ at two temperatures T_1 and T_2 to evaluate W_0 (the work required to free the ions of a gram-molecule at absolute zero) for each salt. The figures for μ (calc.) and μ (obs.) are thus made identical at two points in the temperature range, and in Ghosh's tables comparative figures for μ are given only for from one to three other temperatures, in no case differing more than 50° from a fixed point. Since μ varies regularly with the temperature,[49] agreement between calculated and observed values under the above conditions is almost inevitable and does not necessarily establish the validity of several new assumptions which Ghosh introduces.

Only one of these assumptions will be considered here, namely, that W is zero at the melting-point T_m or, in other words, that fused salts are completely dissociated into *free* ions. This assumption is obviously in direct opposition to the space-lattice arrangement postulated in earlier articles, since the proximity of the oppositely-charged radicals in the pure melt would certainly involve a large proportion of bound ions. It is also incompatible with the experimental results of Goodwin and Mailey,[50] which show that the conductivity of a fused salt mixture, when the components contain a common ion, is *less* than that computed from the law of mixtures, while in a mixture containing no common ion, where metathesis is possible, the conductivity is *greater*.

The conductivity of silver iodide at its melting point is actually less in the *fused* than in the *crystalline* state.[51] Fused aluminum chloride and bromide are practically non-conductors.[52] It is rather difficult to understand why silver bromide is a salt, but not silver iodide, or why the halides of aluminum should not be classed with those of magnesium.

The Conductivity of Salts in Mixtures of Pyridine and Water.— The sixth and last paper of Ghosh[53] compares his own experimental figures for the molecular conductivity of potassium, sodium and barium chlorides in pyridine-water mixtures at 0° and 18° with those calculated from his equations. Satisfactory agreement is again claimed but, as in the case of the same salts in water, μ_v (obs.) and μ_v (calc.) are made identical at a point in the centre of the dilution range, and variations in μ_v throughout this range are in general small, so that the degree of concordance obtained is not unexpected. As the percentage of pyridine in the solvent is increased, and the proportion of free ions changes more rapidly with the dilution, significant deviations appear. In the case of the solvent containing 80% by weight of pyridine, these deviations range from 1

[49] Benrath and Wainoff [*Z. physik. Chem.*, **77**, 257 (1911)] reproduce their experimental data very satisfactorily by the simple empirical equation: $\log \mu = a + bT$.

[50] Goodwin and Mailey, *Phys. Rev.*, **25**, 469 (1907); **26**, 28 (1908).

[51] Tubandt and Lorenz, *Z. physik. Chem.*, **87**, 523 (1914).

[52] Isbekow and Plotnikow, *Z. anorg. Chem.*, **71**, 328 (1911).

[53] Ref. 47, p. 1390.

to 2 units, even although the extreme variation of μ_v from the fixed point in the center of the range is only from 2 to 5 units.

Much more striking agreement, however, is obtained by Ghosh from the data of Hartley, Thomas and Applebey[54] for lithium nitrate in the same mixed solvents. The dilutions tested range from $v = 16$ to $v = 1024$, and μ_v (obs.) is made identical with μ_v (calc.) at a point *outside* this interval (namely at $v = 8$). The concordance throughout the whole dilution range is exceedingly satisfactory. Even when the solvent contains from 80 to 96% by weight of pyridine, observed and calculated values agree within the limits of experimental error.

This peculiarity, remarked upon by Ghosh, is fully explained when reference is made to the original data of Hartley, Thomas and Applebey.[55] In only 2 cases out of a total of 32 are the values employed by Ghosh for μ_v (obs.) identical with the figures obtained by these authors. The values for μ_v (calc.) given by Ghosh in this table are also not derivable from his equations. The agreement arrived at is therefore entirely imaginary.

That the true experimental data of Hartley, Thomas and Applebey are not at all in accordance with the theory of Ghosh will be evident from the figures for a single pyridine–water mixture presented in Table IV below.

TABLE IV

MOLECULAR CONDUCTIVITY OF LITHIUM NITRATE IN A PYRIDINE-WATER MIXTURE CONTAINING 46.67 MOL. PER CENT. OF PYRIDINE $T = 25.08°$

v	16	32	64	128	256	512	1024
μ_v (obs.)	24.35	26.6	28.4	30.0	31.2	31.7	31.9
u_v (calc.)	25.1	28.3	31.2	33.6	35.7	37.5	39.0

The values for μ_v (calc.) are obtained from the Ghosh equation with the use of the observed value, 21.50, for μ_v at $v = 8$. For the dielectric constant of the solution the value 20.8, derived from Ghosh's own data,[56] is employed.

Similar discrepancies between μ_v (obs.) and μ_v (calc.) are found for all mixtures rich in pyridine.

The Ionization of Salts in Solvents of Low Dielectric Constant.— The Ghosh equation fails, indeed, to reproduce the ionization of salts not only in water-pyridine mixtures containing excess of pyridine, but in *all* solvents with a low dielectric constant. This will be obvious from a consideration of the following table, where the calculated proportions of free ions at various dilutions in solvents of various dielectric constants are shown.

[54] Hartley, Thomas and Applebey, *J. Chem. Soc.*, 93, 538 (1908).
[55] Ref. 54, p. 552.
[56] Ref. 47, p. 1392.

TABLE V

IONIZATION OF UNI-UNIVALENT ELECTROLYTES AT 18°, ACCORDING TO THE GHOSH THEORY

Dielectric Constant of Solvent	$v = 1$	$v = 10$	$v = 100$	$v = 1000$	$v = 10000$
1	0.81×10^{-13}	0.84×10^{-6}	0.00151	0.0491	0.2468
2	0.28×10^{-6}	0.00091	0.0389	0.2215	0.4967
5	0.0024	0.0610	0.2729	0.5472	0.7560
10	0.0491	0.2468	0.5222	0.7399	0.8694
20	0.2215	0.4967	0.7228	0.8601	0.9324
50	0.5472	0.7560	0.8782	0.9415	0.9724
100	0.7399	0.8694	0.9371	0.9703	0.9864

The most important point disclosed by the above figures is that, in solvents of low dielectric constant, the ionization of salts should, according to the Ghosh theory, increase *exceedingly rapidly* with the dilution. Where the dielectric constant is very low, the variation demanded is so extreme that even the *specific conductivity* should increase with the dilution. For example, in chloroform, with a dielectric constant of 5, the specific conductivity of a 0.01 N solution of a uni-univalent salt should exceed slightly that of a 1.0 N solution. In benzene, with a dielectric constant a little above 2, the specific conductivity of a 0.01 N solution should be several hundred times larger than that of a 1.0 N solution. Even this figure sinks into insignificance when compared with the wonderful results that should be obtained for the conductivity of air (with a dielectric constant very little in excess of 1) containing a small amount of vapor from a volatile salt.

In practice, of course, we do not find the specific conductivity of salts in solvents of low dielectric constant increasing in this remarkable way. Exactly the opposite behavior is exhibited; it is a general rule that the specific conductivity decreases so rapidly throughout the range 1.0 N to 0.01 N that even the *equivalent conductivity* decreases. That this abnormality is characteristic for salts in solvents of low dielectric constant, and that it is more marked the smaller the dielectric constant, has been conclusively shown by Sachanov.[57]

Another point may now be noted. The theory of Ghosh requires that salts of the same type should be ionized to the same extent in the same solvent at any given dilution. In an earlier section of this paper the validity of this rule for uni-univalent salts in aqueous solution was questioned, but no definite conclusion reached. For the same salts in non-aqueous solutions, however, the rule is obviously not valid. From the many cases found in the literature a single example, the lithium halides in pyridine,[58]

[57] Sachanov, Z. physik. Chem., **80**, 13 (1912); **83**, 129 (1913).

[58] Anderson, J. Phys. Chem., **19**, 753 (1915).

may be cited. At $25°$ and $v = 10$, the equivalent conductivities are as follows: lithium chloride, 0.322; lithium bromide, 5.34; lithium iodide, 23.35. The abnormal tendency of iodides towards polymerization[59] cannot be adduced to explain these figures, since it is the *iodide* which here behaves normally.

Before we sum up the results of our examination of the theory of Ghosh, two lines of evidence which have been brought forward in recent papers by other investigators in support of the hypothesis that strong electrolytes are completely dissociated in aqueous solution may be briefly discussed.

The Distribution of a Salt between an Ionizing and a Non-ionizing Solvent.—Silver perchlorate is a salt which is fairly soluble in benzene, giving a solution which is practically non-conducting. The extraction of the salt from its benzene solution by water is quantitatively complete. It follows that no molecular species is common to the two liquid layers, and the conclusion has been drawn that the salt, in the water layer, is entirely dissociated.[60]

If this conclusion is generally valid, then *any* strong electrolyte should be completely extracted from a non-ionizing solvent by water. Hantzsch[61] has found, indeed, that dimethyl-ammonium chloride is almost totally removed from its solution in chloroform by shaking with water. Opposite results, however, have been obtained by Wedekind and Paschke[62] with the system propylbenzylmethylphenyl-ammonium bromide: chloroform: water, and by Drucker[63] with 3 systems of the type tribenzylammonium bromide: bromoform: water. In all these cases it has been established that the distribution of the salt between the two solvents follows the laws formulated by Nernst on the basis of the Arrhenius ionization theory.

The bulk of the evidence in this field, therefore, is *against* the hypothesis of complete ionization. In both instances where practically complete extraction has been claimed, the solubility ratio is already overwhelmingly in favor of the water. Thus, in the experiments of Hill, the calculated distribution ratio of silver perchlorate between water and benzene is 406 to 1. While the ratio actually obtained was far in excess of this, yet it is obvious that more convincing proof would be afforded if a salt with a smaller solubility ratio could be similarly extracted.

The Vapor Pressure of the Hydrogen Halides in Aqueous Solution.— The fact that a normal solution of hydrochloric acid does not have an appreciable vapor pressure of hydrogen chloride, although according to

[59] Ghosh, Ref. 17, p. 630.

[60] Hill, THIS JOURNAL, **43**, 254 (1921).

[61] Hantzsch, *Zentr.*, [2] **1902**, p. 922; *Ber.*, **38**, 1046 (1906).

[62] Wedekind and Paschke, *Z. physik. Chem.*, **73**, 118 (1910).

[63] Drucker, *Z. Elektrochem.*, **18**, 562 (1912).

the Arrhenius theory 15% of the solute must be assumed to be in the un-ionized state, has been cited by Noyes and MacInnes[64] as another point in favor of the complete dissociation hypothesis.

An alternative explanation of this phenomenon, however, is available. The hydrogen halides, like all strong acids,[65] are very extensively hydrated in aqueous solution, and the lack of an appreciable vapor pressure may very well be due to the practically complete combination of volatile HCl mole-cules with the solvent to form non-volatile complexes of the type $HCl.x$-H_2O.

The consideration of an analogous case may assist in deciding the relative plausibilities of the two explanations. A normal solution of water in 100% sulfuric acid resembles exactly a normal solution of a hydrogen halide in water. It is a good conductor of electricity,[66] and possesses practically zero vapor pressure of the volatile solute. Are we to con-clude that water, dissolved in sulfuric acid, is entirely dissociated into H^+ and OH^-?

The Role of the Solvent in Ionization.—This brings us to the vital question of the part played by the solvent in ionization. Both the Ar-rhenius theory and the theory of complete ionization, as at present de-veloped, refer conductance in solution entirely to the solute. The sol-vent is either regarded as so much "dead space," in which the solute has opportunity to dissociate, or its activity is restricted to the formation of "ionic envelopes." Detailed arguments against this point of view have been presented in previous papers,[67] in which the essential equivalence of solvent and solute has been made the fundamental feature of a modi-fied ionization theory. Any hypothesis which neglects one component altogether is bound to give a distorted outlook upon the subject and to lead to inconsistent conclusions.

Such inconsistencies, indeed, are immediately evident when we try to extend the current hypotheses, which are based almost entirely upon the behavior of dilute aqueous solutions, to conducting solutions in general. Ethyl alcohol is held to be a typical non-electrolyte, not broken up at all into ions; formic acid a typical weak electrolyte, only slightly dis-sociated in solution; hydrogen chloride a typical strong electrolyte, extensively (or wholly) dissociated in solution. These distinctions have

[64] Noyes and MacInnes, Ref. 6, p. 245. MacInnes, THIS JOURNAL, **43**, 1225 (1921). The discussion of other points adduced in support of the theory of complete dissociation, particularly the interpretation of electromotive-force measurements and the vexing question of the abnormal activity of undissociated molecules, will be taken up in a subsequent article.

[65] See Kendall, Booge and Andrews, THIS JOURNAL, **39**, 2307 (1917).

[66] Walden, *Trans. Faraday Soc.*, **6**, 71 (1910).

[67] See, particularly, Kendall and Booge, THIS JOURNAL, **39**, 2323 (1917). Kendall and Gross, *ibid.*, **43**, 1416 (1921). Kendall, *Proc. Nat. Acad. Sci.*, **7**, 56 (1921).

no basis in fact, and have been drawn simply because we have allowed our aqueous environment to mislead us. If we worked in a world where formic acid was the standard reference liquid, ethyl alcohol, water and hydrogen chloride would all appear to be weak electrolytes. In a universe where trichloro-acetic acid was the common solvent, water would become a typical strong electrolyte and hydrogen chloride a practically non-ionized substance.

Our division of substances into strong, transition, weak and non-electrolytes (or into polar and non-polar compounds) is therefore in many cases purely arbitrary. This may be emphasized by attempting to fix definite limits for any particular class. Naphthalene-β-sulfonic acid, according to Ghosh,[68] resembles hydrogen chloride in being entirely dissociated in water solution; trichlorobutyric acid, however, is a "transition acid" and gives both undissociated molecules and ions. Where are we to draw the line between *transition* and *strong* electrolytes?[69] How long, also, will a strong electrolyte remain "completely ionized" as the dielectric constant of the solvent is gradually decreased? Hill considers silver perchlorate to be entirely non-ionized in benzene and entirely ionized in water; what would be its character in a solvent of intermediate type? Ghosh, on the other hand, regards the ionization of strong electrolytes in solvents of low dielectric constant to be still complete, but the limit must evidently be reached before the dielectric constant approximates to unity, since otherwise hydrogen chloride diluted with dry air should be an excellent conductor of electricity.[70]

The "strength of an electrolyte" or the "polarity of a compound" depends primarily, as has been shown experimentally in preceding articles,[71] upon its ability to form ionically unstable complexes with the solvent selected. The most serious objection, therefore, to the theory of Ghosh is that it ignores entirely the part played by the solvent in the ionization process.

Conclusions.—The nature of the results obtained from our detailed examination of Ghosh's articles renders extended comment superfluous. It is clear that the equations employed by Ghosh are not, in general, in satisfactory agreement with the experimental facts. In certain cases they serve very well as interpolation equations over a restricted range, but confirmatory evidence as to their fundamental validity is totally lacking. It may be noted that the application of the corrections discussed in the earlier sections of this paper would not materially affect this conclusion.

[68] Ref. 17, p. 794.
[69] Compare Dawson, *Trans. Faraday Soc.*, 15, 152 (1919).
[70] See Table V, p. 733.
[71] See, particularly, Kendall and Gross, THIS JOURNAL, 43, 1426 (1921).

It has not, of course, been proved hereby that the whole theory of Ghosh is invalid. The abnormality of strong electrolytes cannot possibly be accounted for on a purely kinetic basis, and the necessity of taking into consideration the electrical forces exerted between the various species (molecular or ionic) existent in a conducting solution cannot be ignored. This idea, however, is not original with Ghosh; it has been brought forward by several previous investigators, notably by Noyes.[72] Ghosh carries it too far in one respect, namely, in regarding the electrical forces as all-important and neglecting all other factors entirely. In another respect he does not carry it far enough, namely, in restricting the electrical forces to solute particles and disregarding the polarity of the solvent.

In the absence of any evidence in its favor, Ghosh's second postulate— the space-lattice arrangement of the charged solute particles in definite mean positions in the solution—cannot be considered as more than an interesting possibility. While it cannot be definitely disproved, the behavior of salts in solvents of low dielectric constant argues very strongly against it. For the present, it is certain that no arguments have been adduced which would justify us in discarding entirely our present kinetic interpretation of the state of affairs in conducting solutions. The ionization theory of Arrhenius may be in need of modification, but no case has yet been made out for its abandonment.

Summary

A critical analysis of the ionization theory of Ghosh has led to the following conclusions.

1. The second and third postulates are inconsistent. If the particles of a salt in solution possess a definite space-lattice arrangement, as in the crystalline state, then the combination of 2 oppositely charged particles to form a salt-molecule or a completely saturated electrical doublet is impossible.

2. Ghosh's calculation of the electrical work required to separate the component radicals of a gram-molecule of dissolved salt is erroneous. The value actually derived, assuming a cubic space-lattice arrangement, exceeds that obtained by Ghosh by 75%.

3. The experimental conductivity data for potassium chloride solutions are not in agreement with the equation which Ghosh obtains from his postulates, or with various corrected forms of this equation.

4. The agreement claimed by Ghosh to exist between his equations and the experimental results of previous investigators is largely fictitious. The remarkable coincidence of calculated and observed values in many tables is due to far too frequent errors of calculation and transcription.

[72] Noyes, THIS JOURNAL, 30, 351 (1908).

In other cases, the only legitimate deduction is that the equations tested serve very well as interpolation equations over a restricted range.

5.   No confirmation of the theory of Ghosh is afforded by the experimental data for (a) the variation of equivalent conductivity with dilution for salts in aqueous solution, (b) the temperature coefficient of the ratio μ_v/μ_∞, (c) the electrical conductivity of non-aqueous solutions, (d) the molecular number i and the Clausius theorem, (e) the ionization of strong acids, (f) the ionization of weak acids, (g) the ionization of transition acids, (h) the electrical conductivity of pure salts in the solid and fused states, (i) the conductivity of salts in mixtures of pyridine and water, (j) the ionization of salts in solvents of low dielectric constant, (k) the distribution of a salt between an ionizing and a non-ionizing solvent, (l) the vapor pressure of the hydrogen halides in aqueous solution.

6.   The rôle of the solvent in ionization, which is ignored altogether by Ghosh, must be taken into account in any complete theory of conducting solutions.

7.   In its present form, the ionization hypothesis of Ghosh is unacceptable, and certain of the postulates upon which it is based must be either modified or rejected.

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THE PREFERENTIAL CATALYTIC COMBUSTION OF CARBON MONOXIDE IN HYDROGEN*

BY ARTHUR B. LAMB, CHARLES C. SCALIONE AND GRAHAM EDGAR

An important factor in the commercial success of the Haber process for the synthesis of ammonia is the cost of the pure hydrogen which it requires.   At present this hydrogen is usually obtained by "converting" mixed water- and producer- gas using a considerable excess of steam and a suitable catalyst, into a mixture relatively rich in hydrogen and carbon dioxide, and poor in carbon monoxide.   The carbon dioxide is then largely removed by a thorough water-scrubbing under moderate pressures.   The compositions of these gaseous mixtures are as follows, according to R. S. Tour.[1]

[1] Tour, J. Ind. Eng. Chem., 12, 844 (1920).