

LIII.—*The Abnormality of Strong Electrolytes. Part II. The Electrical Conductivity of Non-aqueous Solutions.*

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IN a previous paper it has been shown that in aqueous solutions of strong electrolytes, the increase in molecular conductivity with dilution can be accounted for quantitatively on the basis of the following simple assumptions:

(a) Only ions exist in solution, the force of attraction between oppositely charged ions being governed by the law of inverse squares.

(b) In solutions of binary electrolytes, the arrangement of ions is analogous to the marshalling of atoms in a simple cubic crystal, whilst that of the ions in solutions of ternary electrolytes corresponds with the fluorspar lattice.

(c) The oppositely charged ions of a molecule form electrically saturated neutral doublets.

(d) It has been shown that, on the above hypothesis, the work necessary to separate the constituent ions of a gram-molecule of univalent binary electrolytes to an infinite distance,

$$A = \frac{NE^2 \sqrt[3]{2N}}{D^3 V}$$

where N is Avogadro's number, E the charge on an ion, D the dielectric constant of the solvent, and V the molecular dilution. For a ternary electrolyte like barium chloride,

$$A = \frac{3NE^2 \cdot 2 \cdot \sqrt[3]{2N}}{D \cdot \sqrt{3} \cdot \sqrt[3]{V}}$$

(e) From Maxwell's equation of the distribution of velocities, it can be easily proved that the number of free ions in a solution containing a gram-molecule

$$= nN \cdot e^{-\frac{A}{n \cdot RT}}$$

where n is the number of ions into which a molecule dissociates.

(f) Since molecular conductivity is proportional to the number of free ions, and since $A=0$ at infinite dilution,

$$\frac{\mu_v}{\mu_\infty} = \frac{n \cdot N \cdot e^{-\frac{A}{nRT}}}{nN} = e^{-\frac{A}{nRT}}$$

In this paper it will be shown that the above equation, which gives very good results in the case of aqueous solutions, can be applied with equal success to non-aqueous solutions of strong electrolytes.

The organic ionising solvents have been arranged by Walden in the following order: (1) alcohols, (2) aldehydes, (3) acids, (4) acid anhydrides, (5) acid chlorides, (6) esters, (7) acid amides and amines, (8) nitriles, (9) thiocyanates, (10) thiocarbimides, (11) nitro-compounds, (12) dimethylnitrosoamine, (13) ketones, (14) *epichlorohydrin* (*Zeitsch. physikal. Chem.*, 1906, **54**, 130). This system of classification will be adhered to in the following pages.

1. Alcohols.

(a) *Methyl Alcohol*.—One of the most trustworthy investigations on the conductivity of electrolytes in methyl-alcoholic solutions is that of Carrara (*Gazzetta*, 1896, **26**, i, 119). The observed values of μ_v in tables I and II are taken from his work. The dielectric constant of methyl alcohol at 20° is 32.5. At 25° it is somewhat less; in the calculations, D has been taken as equal to 31. The solutes in tables I and II are all binary electrolytes, and μ_∞ is obtained from any particular value of μ_v by applying the equation

$$\frac{N \cdot E^2 \sqrt[3]{2N}}{D \cdot \sqrt[3]{V}} = 2RT \log_e \frac{\mu_\infty}{\mu_v} \dots \dots (1)$$

This particular value of μ_∞ is afterwards utilised to calculate the molecular conductivity at other dilutions. It will be seen

from tables I and II that the agreement between the calculated and observed values of μ_v is very good, both in the case of the binary salts and the acids.

Carrara (*loc. cit.*) has also determined the molecular conductivities of strontium iodide in methyl alcohol at various dilutions. Here we expect the equation for ternary electrolytes:

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

to hold good. Table III shows how well the calculated values agree with those observed.

TABLE I.

Solvent: Methyl alcohol. $T = 25^\circ$.

Solute.	μ_{∞} calc. from μ_{128}	$v =$	32.	64.	128.	256.	512.
1. NaI.....	94.0	$\left\{ \begin{array}{l} \mu_v \text{ calc.} \\ \mu_v \text{ obs.} \end{array} \right.$	68.9 68.8	73.5 73.1	77.3 77.3	80.5 79.9	83.0 82.2
2. NaBr....	91.8	$\left\{ \begin{array}{l} \mu_v \text{ calc.} \\ \mu_v \text{ obs.} \end{array} \right.$	67.3 65.8	71.8 71.0	75.5 75.5	78.6 79.9	81.1 82.8
3. NaCl ...	90.4	$\left\{ \begin{array}{l} \mu_v \text{ calc.} \\ \mu_v \text{ obs.} \end{array} \right.$	— —	70.6 69.6	74.3 74.3	77.4 78.1	79.8 81.8
4. KI	102.8	$\left\{ \begin{array}{l} \mu_v \text{ calc.} \\ \mu_v \text{ obs.} \end{array} \right.$	75.3 73.8	80.3 79.5	84.5 84.5	88.0 88.5	90.8 91.0

TABLE II.

Solvent: Methyl alcohol. $T = 25^\circ$

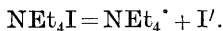
Solute.	μ_{∞} calc. from	$v =$	18.9	37.7.	150.9.
HCl...	$\mu_{37.7} = 157.0$	$\left\{ \begin{array}{l} \mu_v \text{ calc.} \\ \mu_v \text{ obs.} \end{array} \right.$	108.4 106.4	117.0 117.0	130.4 128.0
HBr...	μ_{∞} calc. from $\mu_{26.8} = 142.0$	$\left\{ \begin{array}{l} \mu_v \text{ calc.} \\ \mu_v \text{ obs.} \end{array} \right.$	$v =$ 6.7.	26.8.	107.4.
			84.0 88.0	101.9 101.9	115.0 113.1
HI ...	μ_{∞} calc. from $\mu_{71.4} = 152.2$	$\left\{ \begin{array}{l} \mu_v \text{ calc.} \\ \mu_v \text{ obs.} \end{array} \right.$	$v =$ 17.9.	71.4.	245.7.
			104.4 104.6	120.0 120.0	130.0 130.5

TABLE III.

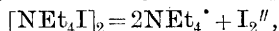
Solvent: Methyl alcohol. $T = 25^\circ$

Solute.	μ_{∞} calc. from	$v =$	64.	128.	256.	512.
SrI ₂ ...	$\mu_{128} = 200.4$	$\left\{ \begin{array}{l} \mu_v \text{ calc.} \\ \mu_v \text{ obs.} \end{array} \right.$	114.6 115.3	128.6 128.6	141.0 141.4	151.2 153.5

The most complete investigation in the field of non-aqueous solutions is that of Walden on solutions of tetraethylammonium iodide in various solvents. It is natural to expect that tetraethylammonium iodide would dissociate according to the following equation:



Except in the case of aldehydes, the variation of equivalent conductivity with dilution calculated from the equation for binary electrolytes (1) does not agree with the observed values. If, however, we assume that tetraethylammonium iodide at first undergoes polymerisation and then the double molecule $[\text{NEt}_4\text{I}]_2$ dissociates as a ternary electrolyte according to the equation:



the calculated values of equivalent conductivities agree extremely well with the observed ones. Indeed, a cursory examination of the data on the variation of equivalent conductivity with dilution will at once lead to the conviction that the electrolytic dissociation of potassium iodide and tetraethylammonium iodide is not of the same type. If it were so, the variation of λ_v (equivalent conductivity) with dilution would have been of the same order. As a matter of fact, whilst λ_v for potassium iodide varies from 80.3 to 84.5 as the dilution increases from 64 to 128, the value for tetraethylammonium iodide increases by 8 units from 83.1 to 91.1 for the same change in dilution. Iodine has a great tendency to form complex ions. We are already acquainted with I_3' , I_5' ions, etc. It is therefore not at all unreasonable to assume that in tetraethylammonium iodide solutions there exists a complex iodine ion of the type I_2'' . Again, the consensus of opinion among electrochemists is generally in favour of complex molecules in non-aqueous solutions. The exact coincidence between the observed and calculated values of equivalent conductivity for tetraethylammonium iodide solutions, as shown in table IV, leaves no room for doubt as to the mode of dissociation of this salt in methyl-alcoholic solution. Of course, the above equation is equally applicable if the salt dissociates, thus:



TABLE IV.

Solvent: Methyl alcohol. T = 25°.

Solute.	λ_x calc. from	V' =	64.	127.	256.	512.	1024.
			$\lambda_{128} = 130$	$\left\{ \begin{array}{l} \lambda_v \text{ calc.} \\ \lambda_v \text{ obs.} \end{array} \right.$	83.1	91.1	97.7
$\text{NEt}_4\text{I} \dots$			82.1	91.1	98.0	103.6	108.6

In the above table V' is the equivalent dilution.

(b) *Ethyl Alcohol and Propyl Alcohol*.—The dielectric constant of ethyl alcohol at 20° is 21.7 (Walden, *loc. cit.*). In table V the observed values of molecular conductivity are taken from the work of Jones and Lindsay (*Amer. Chem. J.*, 1902, **28**, 341) (*loc. cit.*).

The conductivity of sodium iodide in propyl alcohol has been determined by Schlamp (*Zeitsch. physikal. Chem.*, 1894, **14**, 280). The dielectric constant of propyl alcohol, according to Rudolph, is 13.8.

TABLE V.

Solvent: Ethyl alcohol. $T = 25^\circ$.

Solute.	μ_∞ calc. (equation 1) from	$\mu_{256} = 44.9$	$v =$					
			μ_v calc.	μ_v obs.	64.	128.	256.	512.
KI.			31.6	29.6	33.9	33.0	36.0	38.5
							36.0	38.5

TABLE VI.

Solvent: Propyl alcohol. $T = 25^\circ$.

Solute.	μ_∞ calc. (equation 1) from	$\mu_{166.3} = 176.0$	$v =$					
			μ_v calc.	μ_v obs.	19.8.	55.4.	166.3.	500.
NaI.			79.0	77.0	99.5	97.1	118.7	135.0
							118.7	138.0

2. Aldehydes.

Acetaldehyde, Propaldehyde, and Furfuraldehyde.—The dielectric constant of acetaldehyde is 21.2, according to Walden, and 18.6 according to Thwing. It is quite probable that the great reactivity of the solvent and its tendency towards polymerisation will completely prevent the formation of complexes in the solute. It is therefore to be expected that here at least tetraethylammonium iodide will dissociate normally as a binary electrolyte. The dielectric constant of propaldehyde is 14, whilst that of furfuraldehyde is 39.4.

TABLE VII.

Solvent: Acetaldehyde. $T = 0^\circ$.

Solute.	μ_∞ calc. (equation 1) from	$\mu_{1000} = 178$	$v =$				
			μ_v calc.	μ_v obs.	100.	1000.	4000.
NEt ₄ I.			124.0	122.0	151.0	151.0	160.0
							158.0

TABLE VIII.

Solvent: Propaldehyde. T = 25°.

Solute.	μ_{∞} calc. (equation 1)		$v =$				
	from		100.	200.	400.	700.	
NEt ₄ I.	$\mu_{200} = 127.6$	{	μ_v calc.	81.0	89.0	95.8	101.8
			μ_v obs.	79.8	89.0	94.5	103.9

TABLE IX.

Solvent: Furfuraldehyde. T = 25°.

Solute.	μ_{∞} calc. (equation 1)		$v =$				
	from		200.	400.	800.	1600.	
NEt ₄ I.	$\mu_{400} = 47.8$	{	μ_v calc.	42.2	43.4	44.3	45.0
			μ_v obs.	41.6	43.4	45.0	45.8

3. *Acids.*

TABLE X.

Solvent: Thioacetic acid. T = 0°. D = 17.3.

Solute.	λ_{∞} calc. (equation 2)		$V' =$			
	from		320.	640.	1280.	
NEt ₄ I.	$\lambda_{640} = 52.5$	{	λ_v calc.	33.2	36.6	39.5
			λ_v obs.	32.7	36.6	40.2

4. *Acid Anhydrides.*

The dielectric constant of citraconic anhydride is 39. The agreement in this case is perfect.

TABLE XI.

Solvent: Citraconic anhydride. T = 25°.

Solute.	λ_{∞} calc. (equation 2)		$V' =$				
	from		100.	200.	400.	800.	
NEt ₄ I	$\lambda_{200} = 24.9$	{	λ_v calc.	18.5	19.7	20.7	21.5
			λ_v obs.	18.5	19.7	20.6	21.1

5. *Acid Chlorides and Bromides.*

In these solvents the agreement between the observed and calculated values of equivalent conductivity is always within the limits of experimental error, which is somewhat large.

6. *Esters.*

(a) *Organic Esters.*—The dielectric constant of methyl cyanoacetate is 28, and that of the ethyl ester is 26.

(b) *Inorganic Esters.*—Walden's data on the equivalent con-

ductivities of solutions of tetraethylammonium iodide in methyl sulphate, ethyl sulphate, and trimethyl borate are the most trustworthy. The dielectric constants are 46, 38, and 8 respectively. The agreement is always very good.

TABLE XII.

Solute: Tetraethylammonium iodide. T = 25°.

Solvent.	λ_∞	calc. (equation 2) from	$V' =$	100.	200.	500.	1000.	2000.
Methyl cyano- acetate.	$\lambda_{500} = 30.8$		λ_v calc.	20.4	22.2	24.2	25.3	26.4
			λ_v obs.	20.3	22.1	24.2	25.3	26.1
Ethyl cyano- acetate	$\lambda_{500} = 28.1$		λ_v calc.	17.9	19.7	21.6	22.8	23.8
			λ_v obs.	17.7	19.6	21.6	22.8	23.6

TABLE XIII.

Solute: Methyl sulphate. T = 25°

Solute.	λ_∞	calc. (equation 2) from	$V' =$	200.	400.	800.	1600.	3200.
NEt ₄ I.	$\lambda_{400} = 44.3$		λ_v calc.	36.1	37.7	38.9	39.9	40.7
			λ_v obs.	35.5	37.7	38.7	39.6	40.4

TABLE XIV.

Solute: Ethyl sulphate. T = 25°.

Solute.	λ_∞	calc. (equation 2) from	$V' =$	200.	400.	800.	1600.
NEt ₄ I.	$\lambda_{400} = 40.5$		λ_v calc.	31.9	33.5	34.9	36.0
			λ_v obs.	30.3	33.5	35.6	36.7

TABLE XV.

Solute: Trimethyl borate. T = 25°.

Solute.	λ_∞	calc. (equation 2) from	$V' =$	200.	400.	800.
NEt ₄ I.	$\lambda_{400} = 32.5$		λ_v calc.	10.2	13.0	15.7
			λ_v obs.	10.2	13.0	16.5

7. Amides, Amines, etc.

Among amides, formamide is a solvent that most resembles water. The inorganic salts dissolve in it quite as readily as in water, and, like the latter, it has a high dielectric constant, namely, 84.

Pyridine.—Laszczyński and Gorski have determined the conductivity of potassium iodide in pyridine solutions (*Zeitsch. Elektro-*

chem., 1897, **4**, 290), whilst Walden has determined the equivalent conductivity of tetraethylammonium iodide at various dilutions (*Zeitsch. physikal. Chem.*, 1906, **55**, 334). According to Schlundt, the dielectric constant of pyridine is 12.4 (*J. Physical Chem.*, 1901, **5**, 157, 503).

TABLE XVI.

Solvent: Formamide. T = 25°.

Solute.	λ_{∞} calc. (equation 2) from	$V' =$	$V' =$			
			100.	200.	400.	800.
NEt ₄ I.	$\lambda_{200} = 29.0$	$\left\{ \begin{array}{l} \lambda_v \text{ calc.} \\ \lambda_v \text{ obs.} \end{array} \right.$	25.2	26.0	26.5	27.0
			25.0	26.0	26.6	27.2

TABLE XVII.

Solvent: Pyridine. T = 25°.

Solute.	λ_{∞} calc. (equation 2) from	$V' =$	$V' =$			
			100.	200.	400.	800.
NEt ₄ I.	$\lambda_{400} = 71.0$	$\left\{ \begin{array}{l} \lambda_v \text{ calc.} \\ \lambda_v \text{ obs.} \end{array} \right.$	26.9	32.9	39.5	43.7
			27.0	33.0	39.5	46.0
KI.	$\lambda_{714} = 50.0$	$\left\{ \begin{array}{l} \lambda_v \text{ calc.} \\ \lambda_v \text{ obs.} \end{array} \right.$	178.5.	357.0.	714.0.	
			22.8	26.9	30.7	
			22.0	26.2	30.7	

8. Nitriles.

The nitriles are excellent ionisers, and their dielectric constants are high. Thus glycollonitrile has a dielectric constant as high as 68, whilst the dielectric constants of acetonitrile, propionitrile, and benzonitrile are 37, 27, and 26 respectively.

TABLE XVIII.

Solvent: Acetonitrile. T = 25°.

Solute.	λ_{∞} calc. (equation 2) from	$V' =$	$V' =$					
			200.	500.	1000.	2000.	4000.	8000.
NaI.	$\lambda_{500} = 199.3$	$\left\{ \begin{array}{l} \lambda_v \text{ calc.} \\ \lambda_v \text{ obs.} \end{array} \right.$	155.0	165.9	172.3	177.4	182.0	185.4
			151.0	165.9	171.0	176.7	181.0	183.5

TABLE XIX.

Solvent: Propionitrile. T = 25°.

Solute.	λ_{∞} calc. (equation 2) from	$V' =$	$V' =$				
			64.	128.	256.	512.	1024.
NEt ₄ I.	$\lambda_{128} = 169$	$\left\{ \begin{array}{l} \lambda_v \text{ calc.} \\ \lambda_v \text{ obs.} \end{array} \right.$	102.6	113.7	123.5	131.6	138.6
			102.0	113.7	123.4	131.5	139.4

TABLE XX.

Solvent: Benzonitrile. T = 25°.

Solute.	λ_{∞} calc. (equation 2) from	$V' =$				
			200.	400.	800.	1600.
NEt ₄ I.	$\lambda_{400} = 55.6$	$\left\{ \begin{array}{l} \lambda_v \text{ calc.} \\ \lambda_v \text{ obs.} \end{array} \right.$	39.0	42.0	44.5	46.6
			37.7	42.0	45.0	47.6

TABLE XXI.

Solvent: Glycollonitrile. T = 25°.

Solute.	λ_{∞} calc. (equation 2) from	$V' =$			
			100.	200.	800.
NEt ₄ I.	$\lambda_{200} = 79.5$	$\left\{ \begin{array}{l} \lambda_v \text{ calc.} \\ \lambda_v \text{ obs.} \end{array} \right.$	67.0	69.4	73.0
			66.8	69.4	71.0

TABLE XXII.

Solvent: Acetonitrile. T = 25°.

Solute.	μ_{∞} calc. (equation 2) from	$v =$			
			100.	200.	400.
CuBr ₂	$\mu_{200} = 73.9$	$\left\{ \begin{array}{l} \mu_v \text{ calc.} \\ \mu_v \text{ obs.} \end{array} \right.$	49.8	54.0	57.7
			48.6	54.0	58.0

9, 10. *Thiocyanates and Thiocarbimides.*

The calculated values of equivalent conductivity also agree well with Walden's data for these solvents.

11, 12. *Nitro-compounds and Dimethylnitrosoamine.*

The dielectric constants of nitromethane and dimethylnitrosoamine are 39 and 53.3 respectively.

TABLE XXIII.

Solvent: Nitromethane. T = 25°.

Solute.	λ_{∞} calc. (equation 2) from	$V' =$					
			100.	200.	400.	800.	1600.
NEt ₄ I.	$\lambda_{200} = 127.8$	$\left\{ \begin{array}{l} \lambda_v \text{ calc.} \\ \lambda_v \text{ obs.} \end{array} \right.$	94.5	100.5	105.4	109.6	113.0
			94.0	100.5	105.9	109.5	112.0

TABLE XXIV.

Solvent: Dimethylnitrosoamine. T = 25°.

Solute.	λ_{∞} calc. (equation 2) from	$V' =$				
			250.	500.	1000.	2000.
NEt ₄ I.	$\lambda_{500} = 92.0$	$\left\{ \begin{array}{l} \lambda_v \text{ calc.} \\ \lambda_v \text{ obs.} \end{array} \right.$	78.3	81.2	83.2	85.0
			77.5	81.2	84.2	86.4

C C*

13. *Ketones.*

The dielectric constant of acetone is 21, and that of acetylacetone is 22 at 25°.

TABLE XXV.

Solvent: Acetone. T = 25°

Solute.	μ_{∞} calc. (equation 1) from	$v =$	256.	512.	1024.
			$\mu_{512} = 158.5$	$\left\{ \begin{array}{l} \mu_v \text{ calc.} \\ \mu_v \text{ obs.} \end{array} \right.$	127.0 126.3

TABLE XXVI.

Solvent: Acetylacetone. T = 25°.

Solute.	λ_{∞} calc. (equation 2) from	$V' =$	200.	400.	800.	1600.
			$\lambda_{400} = 86.4$	$\left\{ \begin{array}{l} \lambda_v \text{ calc.} \\ \lambda_v \text{ obs.} \end{array} \right.$	56.9 56.7	62.0 62.0

14. *Epichlorohydrin.*

TABLE XXVII.

Solvent: *epi*Chlorohydrin. T = 25°. D = 26.

Solute.	λ_{∞} calc. (equation 2) from	$V' =$	100.	200.	400.	800.	1600.
			$\lambda_{400} = 65.7$	$\left\{ \begin{array}{l} \lambda_v \text{ calc.} \\ \lambda_v \text{ obs.} \end{array} \right.$	42.1 40.0	46.0 45.0	49.6 49.6

Conclusion.

It will be seen that equations 1 and 2 have been subjected to a very severe test, and that their validity has been completely confirmed by the mass of experimental data on the conductivity of salt solutions in some thirty solvents.

The term "degree of dissociation" thus loses all significance in the case of strong electrolytes. In his first paper on the conduction of electricity by electrolytes, Arrhenius (*Bihang. der. Stockholm. Akad.*, 1883, 8, Nos. 13, 14) used the term "activity coefficient" for the ratio μ_v/μ_{∞} , and this is, indeed, a very suitable term in view of the fact successfully demonstrated here, that in salt solutions there are only free and bound ions. Incidentally, there has also been obtained a valuable method of determining the mode of dissociation of a solute in any solvent. Walden's normal electrolyte, tetraethylammonium iodide, really dissociates

abnormally. It is, however, the peculiar characteristic of this solute that the same type of dissociation persists in all the solvents. To this property are due the many regularities that Walden observed in tetraethylammonium iodide solutions. Thus we have his empirical law that "if solutions of one and the same normal electrolyte, tetraethylammonium iodide, in various solvents have the same degree of dissociation (activity coefficient), then for all solvents, the product of the dielectric constant, and the cube root of the dilution of that solution has always a constant value. Thus $D\sqrt[3]{V} = D'\sqrt[3]{V'}$, etc. = k , where D , D' , etc., are the dielectric constants of the solvents, and V , V' , etc., are the respective dilutions at which the activity-coefficient of tetraethylammonium iodide is the same. The theoretical significance of this general empirical law is at once brought out by equation 2. Since the mode of dissociation of the salt is always the same, the equation:

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

is applicable to its solution in all solvents. For the same value of μ_v/μ_∞ it is obvious that

$$D \sqrt[3]{V} = k,$$

whatever be the nature of the solvent.

It was rightly suggested by Nernst and Thomson that the dielectric constant is the fundamental property which determines the dissociating power of a solvent. Walden's investigations proved conclusively that a direct parallelism exists between the dissociating power and the dielectric constants of solvents. The idea, however, never passed beyond the qualitative stage. In this paper, in the author's opinion, it has been proved beyond doubt that the exact quantitative relation between the activity-coefficient and the dielectric constant is given by equations 1 and 2.

Finally, it should be pointed out that the fundamental problem to be solved in this connexion is the work necessary to separate the constituent ions of a gram-molecule of a salt to an infinite distance at a given dilution. The assumption that the ions of a binary electrolyte are arranged according to a simple cubic lattice is necessarily arbitrary, although it is the simplest possible view. Some other views are possible, for example, we may have a face-centred cube lattice, a cube-centred lattice, etc. For ternary electrolytes good results have been obtained by assuming an arrangement corresponding with a fluorspar lattice. Here, also, it is possible that an ion, instead of occupying the centre of a cube, may be displaced diagonally towards an oppositely charged ion or towards an empty corner. Bragg has actually observed such dis

placement in crystals of iron pyrites. It is therefore not necessary that the above rigid forms of equation should always be applicable. It ought to be always possible, however, to express the relation between the activity-coefficient, the dilution, and the dielectric constant of the solvent by equations of the above type. The behaviour of acetone solutions of ammonium iodide is a case in point. Equation 2 does not hold good in this case. If, however, we assume that the NH_4^+ ions are displaced diagonally towards the oppositely charged $\text{I}_2^{''}$ ion by one-fourth the length of the diagonal we get the following equation:

$$\frac{3N \cdot E^2 \cdot 4 \sqrt[3]{2N}}{D \cdot \sqrt{3} \cdot \sqrt[3]{V}} = 3RT \log_e \frac{\mu_\infty}{\mu_v}$$

which holds good exactly as shown in table XXVIII.

TABLE XXVIII.

Solvent: Acetone.

Solute.	λ_∞ calc. from	$V' =$	128.	256.	512.	1024.	2048.
NH_4I .	$\lambda_{512} = 209$	λ_v calc.	69.0	86.9	104.1	120.2	135.0
		λ_v obs.	67.5	85.5	104.1	120.8	136.0

The above theory should not, therefore, be rejected in those cases where equations 1 and 2 do not hold good. We should rather proceed in the reverse direction, that is, calculate the total potential energy of the electrical doublets at a given dilution, from the observed value of the activity-coefficient at that dilution. An insight into the arrangement of ions in the interior of a solution will then be easily obtained, and the next problem will be to determine whether the equation based on this particular arrangement holds good at other dilutions. Theory demands that such should be the case, and it fails if the observed and the calculated activity-coefficients do not agree. In some cases, however, chemical action may interfere, as in the hydrolysis of salts, and these should be regarded as abnormal.

The fundamental hypothesis that only ions exist in salt solutions requires no elaborate justification in view of the fact conclusively established that even in a salt crystal there is no such thing as a molecule.

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