CXXXVIII.—*The Velocity of the Hydrogen Ion, and a General Dissociation Formula for Acids.*

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WHILST the mobilities of most of the common ions have been definitely determined to an accuracy of one-tenth of a unit, the value for the velocity of the hydrogen ion, which is the most important from theoretical considerations, is not known more exactly than within several units. The experimental difficulties in the two methods available for the determination of ionic velocities are here much greater than is the case with other ions. In conductivity measurements the impurities contained in the water used have prevented the accurate determination of the equivalent

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conductivities of acids at very high dilutions, and no trustworthy correction for the influence of these impurities has yet been applied, as has been done for salts. The values obtained from the measurement of migration ratios are also less accurate, since the preponderating mobility of the hydrogen ion causes a small error in the ratio obtained to exert a comparatively large influence on the ionic velocity deduced from it. The results from both methods have proved very conflicting, as the following figures, which are the results of the chief researches on the mobility of the hydrogen ion, will serve to show. All values are expressed in terms of the reciprocal ohm.

Ostwald, from conductivity measurements with hydrochloric acid, obtained the value 342 at 25° (*Zeitsch. physikal. Chem.*, 1888, **2**, 842), and employed this figure in the calculation of the dissociation constants of all the weak acids subsequently examined (*Zeitsch. physikal. Chem.*, 1889, **3**, 172). The value was afterwards raised to 347 ("Lehrbuch der Allgemeinen Chemie," 1893, **2**, 675).

Kohlrausch ("Leitvermögen der Electrolyte," 1898, pp. 107-10, 200) deduced, by the application of an empirical formula to the results of conductivity measurements with dilute solutions of hydrochloric and nitric acids, the provisional value of 318 at 18°, or 352 at 25°. Until recently the above values of Ostwald and Kohlrausch have been adopted for the calculation of dissociation ratios.

The measurement of migration ratios was not of sufficient accuracy to be used for the purpose of determining the velocity of the hydrogen ion until an improved apparatus was devised by Noyes (*Zeitsch. physikal. Chem.*, 1901, **36**, 69). With this, a determination of the mobility by the method of migration ratios was attempted by Noyes and Sammet (*Zeitsch. physikal. Chem.*, 1903, **43**, 49), hydrochloric acid being used as the electrolyte. The unexpectedly high value of 365 was obtained.

It has been shown by Rothmund and Drucker (*Zeitsch. physikal. Chem.*, 1903, **46**, 827), in the course of an investigation on the dissociation of picric acid, that lower values for the velocity of the hydrogen ion give results for the degree of dissociation which are more satisfactory than those obtained with the use of Kohlrausch's figure, 352. A value as low as 338 is suggested, and tested with several strong acids. The subject is further developed by Drucker in a later paper (*Zeitsch. physikal. Chem.*, 1904, **49**, 563), where it is demonstrated that $H^+ = 312$ at 18° (that is, 345 at 25°) gives more satisfactory values for the dissociation constants of weak acids than does the higher figure of Kohlrausch.

The results of the investigations of several observers, both on

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conductivities and on migration ratios, are collected and compared by Drucker in a third paper (*Zeitsch. Elektrochem.*, 1907, **13**, 81). The measurements of the equivalent conductivities of dilute solutions of hydrochloric and nitric acids by Goodwin and Haskell (*Proc. Amer. Acad.*, 1904, **40**, 399), and of sulphuric acid by Whetham (*Zeitsch. physikal. Chem.*, 1906, **55**, 200), are combined with the migration ratios obtained with the same acids by Jahn and his pupils (*Zeitsch. physikal. Chem.*, 1901, **37**, 707) and Tower (*J. Amer. Chem. Soc.*, 1904, **26**, 1039) respectively. The mean value deduced for the velocity of the hydrogen ion is 313 at 18°, or 346 at 25°. From the results obtained it is inferred that the figure given by Kohlrausch is certainly too high.

Kohlrausch (*Zeitsch. Elektrochem.*, 1907, **13**, 333), whilst admitting that his former value was claimed to be merely an approximation, takes also into account further migration ratios recently determined by Jahn and his pupils (*Zeitsch. physikal. Chem.*, 1907, **58**, 641), and puts forward as the most probable value for the velocity of the hydrogen ion the figure 315 at 18°, or 348 at 25°.

Gorke (*Zeitsch. physikal. Chem.*, 1908, **61**, 495) obtained, by the measurement of the equivalent conductivities of dilute solutions of picric acid, the value 353 at 25°.

Noyes and Kato (*Zeitsch. physikal. Chem.*, 1908, **62**, 420), from the migration ratios obtained with dilute solutions of nitric and hydrochloric acids, were led to the conclusion that the velocity of the hydrogen ion varies considerably with the concentration. For solutions under one-thousandth normal its value may be taken as 315 at 18° (that is, 348 at 25°); for more concentrated solutions it is several per cent. higher. This theory of a change of mobility with the concentration had been previously advanced by Jahn (*Zeitsch. physikal. Chem.*, 1900, **33**, 545; **35**, 8) as applying to the ions of all strong electrolytes, and affording an explanation of the breakdown of the dilution law of Ostwald. The assumption of a varying mobility in dilute solution has, however, been vigorously criticised on many sides, and may be regarded as not yet confirmed (Wegscheider, *Zeitsch. physikal. Chem.*, 1909, **69**, 503).

From migration ratios obtained with dilute solutions of hydrochloric acid, Drucker and Krišnjavi (*Zeitsch. physikal. Chem.*, 1908, **62**, 731) have concluded that 313 at 18° (that is, 346 at 25°) is the maximum possible value for the velocity of the hydrogen ion.

In the above summary of investigations it will be seen that the values obtained range from a minimum of 338 to a maximum of 365; the general results of the more recent experiments are, however, within the much narrower limits of 345 to 348. The value must be determined more definitely than this before the problem

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regarding the dissociation of strong acids can be solved by the substantiation of any formula from the figures of experiment.

The failure to obtain satisfactory conductivity measurements with very dilute solutions of strong acids has been attributed to the influence of the impurities in the water used, namely, carbonic acid and ammonia from the atmosphere, and alkali from the glass vessels employed. No satisfactory correction can be applied, since the mutual influence of the substances in solution on their dissociation is quite uncertain (Kohlrausch, "Leitvermögen der Electrolyte," 1898, p. 92). The figures are, in general, given without any correction, and the degree of error is unknown. Any deductions from the results cannot, therefore, unless supported by other evidence, be regarded as conclusive; thus Kohlrausch (*Zeitsch. Elektrochem.*, 1907, **13**, 646) states, after a criticism of conclusions drawn by Bogdan from experiments with dilute solutions of hydrochloric and nitric acids (*Zeitsch. Elektrochem.*, 1907, **13**, 596): "The last word upon the subject of dilute acids and bases will certainly not be spoken until we have succeeded in investigating the solutions in pure water."

The water used in the following conductivity experiments was obtained by distillation, in the open air, from water to which a little Nessler's solution has been added. Jena-glass flasks and a bent tube of pure tin, fitted with a condenser, were used, and spiriting-over was prevented by a series of constrictions in the upright portion of the tube. The first distillation gave water with a specific conductivity of 1.20×10^{-6} at 25° ; by a second distillation this was reduced to 0.90×10^{-6} . This value did not increase appreciably on exposure to outside air. Water of specific conductivity 0.70×10^{-6} was obtained by distillation in silica vessels, but on transference to a glass cell the value quickly rose to 0.90×10^{-6} at 25° .

With the water available for use in conductivity measurements possessing a specific conductivity of at least 0.90×10^{-6} at 25° , it did not seem probable that the results obtained from dilute acid solutions could be of sufficient accuracy to prove of service in the determination of the velocity of the hydrogen ion. Nevertheless, it was found possible, by a modification of the method for determining the value of the equivalent conductivity at infinite dilution, to obtain with acids of a certain strength very satisfactory results.

It has been observed previously by Drucker (*Zeitsch. physikal. Chem.*, 1904, **49**, 563) that the dissociation constants obtained for weak acids are more or less satisfactory according to the value for the velocity of the hydrogen ion that is employed in the calculation of the equivalent conductivity at infinite dilution. The fact that

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lower values than Kohlrausch's figure of 352 give more satisfactory dissociation constants for weak acids than does the latter, was considered by Drucker as a strong argument for the assumption that the value of Kohlrausch was too high. The point, however, seems to have escaped observation that with acids of a certain strength a satisfactory dissociation constant at high dilutions is to be obtained with the use of one particular value for the velocity of the hydrogen ion, and not with the use of any other value.

As an illustration of this point, the results obtained from one series of conductivity measurements of cyanoacetic acid at 25° are given below in table I. The method of experiment is described in full subsequently; the water employed possessed a specific conductivity of 0.90×10^{-6} at 25°.

The first column gives the dilution v , the second the equivalent conductivity μ . The dissociation constants $100k_1$ and $100k_2$ are calculated with the use of the values of Ostwald and of Kohlrausch, $H^* = 347.0$ and $H^* = 352.0$ respectively. In the third column the percentage dissociation, using the value $H^* = 347.0$, is shown. The mobility of the anion is taken as 38.9 (see table IX below).

TABLE I.

Cyanoacetic Acid. Water, 0.9×10^{-6} .

v .	μ .	100 m .	100 k_1 ($H^* = 347.0$).	100 k_2 ($H^* = 352.0$).
20.80	96.2	24.93	0.398	0.386
41.60	127.1	32.93	0.389	0.376
83.20	164.5	42.63	0.381	0.368
166.4	207.3	53.71	0.375	0.360
332.8	252.4	65.40	0.372	0.354
665.6	294.9	76.40	0.372	0.348
1331.0	329.2	85.32	0.372	0.338
2662.0	353.2	91.52	0.371	0.318
5324.0	368.3	95.44	0.375	0.288

For the above series it is evident that the value $H^* = 347.0$ gives a far more satisfactory constant than the value $H^* = 352.0$. Indeed, a satisfactory dissociation constant for the dilute solutions of the series can be obtained only within a very limited region about $H^* = 347.0$. Values only a few tenths of a unit removed from this produce appreciable divergences in the constant.

With acids of this type it is possible, therefore, after the measurement of a number of conductivity series, carried to high dilutions, to obtain from each series that value for the velocity of the hydrogen ion that is required to give a satisfactory dissociation constant, and, by comparison of the values obtained, to ascertain to what degree of accuracy the determination can be carried. This has been done in the experiments described below.

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The acids that can be employed are of a very limited range of strength, namely, those which possess a dissociation constant between the limits of 0.001 and 0.01. Acids of this type pass from slight to almost complete dissociation within the ordinary range of dilutions. With acids possessing a smaller dissociation constant, the constant obtained is fairly satisfactory through a large variation in the value taken for the velocity of the hydrogen ion, and no definite value for the latter can be deduced. With stronger acids, dissociation is so nearly complete in dilute solution that the errors of experiment exert sufficient influence, since they are greatly magnified in the calculation of the dissociation constant, to prevent any value taken giving a satisfactory constant. In the more concentrated solutions of these stronger acids, where the degree of dissociation is not so great, the dilution law of Ostwald is not exactly obeyed, as will be shown later.

The above difficulties exist even within the narrow limits indicated, and acids possessing dissociation constants near the centre of the range were found to be far more useful than those having constants near the upper or lower limit. Suitable acids are, however, very few in number. Acids of as simple a constitution as possible must be chosen, in order to avoid the presence of any group likely to cause complications at high dilutions. The acids employed were all, in fact, simple substituted acetic and benzoic acids:

Cyanoacetic acid.....	$k=0.00368$
<i>o</i> -Nitrobenzoic acid	$k=0.00620$
<i>o</i> -Chlorobenzoic acid	$k=0.00128$
3 : 5-Dinitrobenzoic acid	$k=0.00157$

Of these, cyanoacetic acid was the most suitable. *o*-Nitrobenzoic acid, owing to its larger dissociation constant, gives results which are appreciably affected by the errors of experiment, whilst the remaining acids, which possess smaller constants, give results from which the value deduced is rather indeterminate.

It is obviously essential that the acids should be quite pure; they were therefore repeatedly crystallised until constant conductivity values at high dilutions were obtained. *o*-Chlorobenzoic and 3:5-dinitrobenzoic acids were specially prepared.

o-Chlorobenzoic acid was prepared by the distillation of salicylic acid with phosphorus pentachloride, as described by Hübner (*Annalen*, 1884, **222**, 192). The mixed chlorides obtained were decomposed by water, and steam was passed through the solution for several hours until all salicylic acid was removed. *o*-Chlorobenzoic acid was then obtained pure by recrystallisation from water.

3:5-Dinitrobenzoic acid was prepared by the nitration of benzoic

acid, as described by Shukoff (*Ber.*, 1895, **28**, 1800), and purified by several crystallisations from water.

Cyanoacetic acid, being extremely soluble in water, was recrystallised from benzene until pure. Owing to the deliquescent nature of the acid, all solutions were made up volumetrically. *o*-Nitrobenzoic acid was obtained pure by repeated crystallisations from water.

The conductivity measurements were carried out with the greatest possible accuracy. The cells used were of the type described by Cantor (*Zeitsch. Elektrochem.*, 1903, **9**, 922). The cell constants were determined by means of *N*/50- and *N*/100-potassium chloride (Kahlbaum's 100.00 per cent.). With solutions made up independently, values were obtained all agreeing within 1 in 2000.

The dilutions were carried out in the cell itself by means of 30 c.c. and 60 c.c. graduations. The accuracy of these was tested by weighing the water run out at a known temperature. Correct volumes of 30 c.c. are not necessary; all that is required for accurate dilution is that the two volumes shall be equal. The correct graduations for doubling the volume were determined for each cell within an error of 0.01 c.c. in 30 c.c.

The conductivities of the solutions were measured by means of a rotating commutator and a galvanometer. By this method the results obtained at high dilutions are much more accurate than with the usual induction coil and telephone. The bridge employed was a three-metre platinum wire, divided into one thousand parts; readings could easily be obtained within one-tenth of a division, the galvanometer being used as a zero instrument, at all dilutions.

The cells were immersed in a small thermostat, heated beneath, and regulated to 25°. The copper sides of the bath were not protected in any way, and convection was sufficient, without any stirring at all, to keep the temperature constant. The cells were suspended away from the sides, and the temperature in their neighbourhood was never found to vary more than 0.03° from 25°.

The acid solutions used were standardised either volumetrically or gravimetrically. In the former case a known volume was titrated with barium hydroxide solution, phenolphthalein (except where otherwise stated) being used as indicator. The barium hydroxide solution (approximately *N*/100) was standardised against *N*/10-hydrochloric acid, and also against certain of the acids used—the results obtained were in agreement within 1 in 1000.

In the latter case a weighed quantity of acid was dissolved in water and made up to a known volume. All weights were reduced, with sufficient accuracy, to true weights in vacuum by addition of one-thousandth part. This is the correction for substances with a

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specific gravity slightly greater than unity, and is accurate for the acids used well within the limits of error in weighing. All volumes were reduced to volumes occupied at 25°.

The results obtained by the above methods were, on comparison, usually in agreement within 1 in 1000; the greatest divergence was 1 in 600. This may be taken as the maximum degree of error in the estimation of the concentration of a solution.

The graduation of the cells is accurate within 0.01 c.c. of 30 c.c., as described above; the various dilutions in a conductivity series were not carried out, however, within a greater accuracy than 0.03 c.c. in 30 c.c. This is due to considerations of time, since for more exact dilutions it is necessary to allow the cell to remain for a long period, in order to drain completely, before each reading. A series must be completed as quickly as possible, and with the above apparatus the measurements are already protracted, since the large glass surface of the cell is slow in attaining the true temperature of the thermostat, from which the cell must be removed during the mixing of the solutions. Greater accuracy than the above (1 in 1000) was therefore not aimed at in the dilutions. The error is not so important as may at first sight appear, since it is not (as is the initial error in the graduation) doubled at each step, but is equally likely to be positive or negative at each dilution. Indeed, as has often been pointed out, the most important error incurred in conductivity determinations is in the estimation of the initial concentration of a solution. Two series, differing slightly in their first values, will usually run parallel throughout their whole length.

There remains the question of the influence of the impurities in the water on the values of the equivalent conductivity obtained for very dilute solutions. In the series for cyanoacetic acid given above, no correction has been made for this. From the figures obtained it seems that the impurities in the water used do not affect the value appreciably until a high dilution is reached. Here a small increase is observable, still, however, within the limits of experimental error. A small difference in the value taken for the velocity of the hydrogen ion produces a much greater effect on the dissociation constant; the influence of the water impurities cannot therefore be directly measured.

We can determine, however, to what dilutions the experiments can be carried without taking the influence of the water into account, by examination of the results obtained with dilute solutions of a much weaker acid. In such solutions any small error in the value taken for the velocity of the hydrogen ion does not influence the dissociation constant, owing to the less complete dissociation;

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at the same time the specific conductivity of the solutions is small, and the influence of the water on the value obtained is more readily perceived.

With this object preliminary experiments were carried out with acetic acid. Two series of conductivity measurements were performed; the water used for dilution possessed a specific conductivity of 0.90×10^{-6} in the first series, and of 1.20×10^{-6} in the second. The results obtained are given in tables II and III; the value of the equivalent conductivity at infinite dilution is taken as 387.7 ($H' = 347.0$; $Ac' = 40.7$) (Bredig, *Zeitsch. physikal. Chem.*, 1894, 13, 218).

TABLE II.

Acetic Acid. Water, 0.90×10^{-6} .

v .	μ .	100m.	100k.
13.57	6.086	1.570	0.001845
27.14	8.591	2.216	0.001851
54.28	12.09	3.118	0.001849
108.56	16.98	4.380	0.001849
217.1	23.81	6.141	0.001851
434.2	33.22	8.568	0.001849
868.4	46.13	11.90	0.001850
1737.0	63.60	16.41	0.001854
3474.0	86.71	22.36	0.001855
6948.0	116.8	30.13	0.001870
∞	387.7	—	—

TABLE III.

Acetic Acid. Water, 1.20×10^{-6} .

v .	μ .	100m.	100k.
15.816	6.561	1.692	0.001842
31.63	9.260	2.388	0.001848
63.26	13.03	3.361	0.001847
126.52	18.30	4.721	0.001848
253.04	25.60	6.603	0.001846
506.1	35.67	9.200	0.001843
1012.2	49.50	12.77	0.001846
2024.4	68.22	17.60	0.001856
4049.0	93.5	24.12	0.001893
8098.0	125.8	32.45	0.001924
∞	387.7	—	—

In the first series a very satisfactory dissociation constant is obtained, without the application of any correction, up to $v = 3500$; with water of a slightly higher specific conductivity, in the second table, the constant has already begun to show an increase at $v = 2000$.

It seems reasonable to suppose, therefore, that with the use of water of a specific conductivity 0.90×10^{-6} at 25° , the measurements with stronger acids can be relied on, without any correction, up to

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high dilutions, as in table I. To test this further, however, and to find by experiment what effect the specific conductivity of the water used has on the value for the velocity of the hydrogen ion deduced from the measurements with these acids, the following plan was adopted. A conductivity series of each acid was carried out with four different samples of water, possessing the following specific conductivities at 25°:

- (a) 0.90×10^{-6} ; (b) 1.20×10^{-6} ; (c) 1.80×10^{-6} ;
(d) 2.50×10^{-6} .

The first two samples were obtained as described above; (c) is an earlier fraction of the first distillation; (d) is the ordinary distilled water of the laboratory.

The conductivity results obtained are expressed in tables V to XII. It is necessary, however, first of all to determine the equivalent conductivities of dilute solutions of the sodium salts of the acids employed, in order to obtain accurate values for the velocities of their respective anions.

The measurement of these conductivities was carried out as has been already described. The solutions were made up to known concentration by the exact neutralisation of known solutions of the acid and of sodium hydroxide. The latter was freshly made up from metallic sodium, and standardised with *N*/10-hydrochloric acid, using methyl-orange as indicator. In certain cases the results obtained were checked by preparing a small sample of the salt, and making up a solution gravimetrically.

The dilutions were made with water of a specific conductivity 1.20×10^{-6} at 25°; this value is subtracted from the conductivity obtained at each dilution (Kohlrausch, "Leitvermögen der Electrolyte," 1898, p. 91). The value of the equivalent conductivity at infinite dilution is obtained by graphical extrapolation, according to the empirical formula of Kohlrausch (*Zeitsch. Elektrochem.*, 1907, **13**, 337). From this value the velocity of the anion of each acid is found by subtracting 51.0, the value for the sodium ion.

The figures obtained agree closely, where comparison is available, with the results of Ostwald (*Zeitsch. physikal. Chem.*, 1888, **2**, 847); the greatest divergence obtained with independent series of the same salt was 0.3. Results are shown in table IV below, interpolated to the ordinary dilutions.

TABLE IV.

Equivalent Conductivity of Sodium Salts.

<i>v.</i>	Cyanoacetate.	<i>o</i> -Nitrobenzoate.	<i>o</i> -Chloro-benzoate.	3:5-Dinitro-benzoate.
16	73·6	66·9	—	—
32	77·3	70·6	71·5	68·8
64	80·3	73·6	74·3	71·3
128	82·7	76·0	76·6	73·2
256	84·4	77·9	78·4	75·0
512	85·8	79·3	79·8	76·3
1024	87·0	80·4*	80·9	77·3
2048	87·9	81·2	81·8	78·1
∞	89·9	83·2	83·8	80·1
Mobility of anion	38·9	32·2	32·8	29·1

The conductivity measurements with the acids themselves are given in tables V to XI; the columns are arranged as in table I. The dissociation constant $100k_1$ is calculated with the use of that value for the equivalent conductivity at infinite dilution that gives the most satisfactory constant at high dilutions; $100m$ is the percentage dissociation obtained with this value. The constant $100k_2$ is calculated with the use of the mean value $347·2$ finally taken (see p. 1293) for the velocity of the hydrogen ion.

The results obtained with each sample of water are shown in full only for cyanoacetic acid; for the other acids the figures for one sample are given in full, and the values obtained in the other cases are summarised in table XII. The effect of the different samples of water on the results was found to be the same for all the acids used, and is discussed later.

TABLE V.

Cyanoacetic Acid. Water, $0·9 \times 10^{-6}$.

<i>v.</i>	μ .	$100m$.	$100k_1$, ($H' = 347·1$).	$100k_2$, ($H' = 347·2$).
16·82	88·0	22·80	0·400	0·400
33·64	117·0	30·31	0·392	0·392
67·28	152·5	39·50	0·383	0·383
134·56	193·9	50·23	0·378	0·378
269·1	238·7	61·84	0·372	0·372
538·2	282·6	73·20	0·372	0·371
1076·4	320·0	82·89	0·373	0·372
2153·0	347·1	89·90	0·373	0·371
4306·0	364·8	94·52	0·378	0·376
∞	386·0	—	—	—

TABLE VI.

Cyanoacetic Acid. Water, 1.2×10^{-6} .

<i>v.</i>	μ .	100 <i>m.</i>	$100k_1$ ($H' = 347.0$).	$100k_2$ ($H' = 347.2$).
17.404	89.4	23.16	0.401	0.401
34.81	118.8	30.79	0.393	0.393
69.62	154.8	40.12	0.386	0.386
139.24	196.3	50.86	0.378	0.378
278.5	241.4	62.54	0.375	0.375
557.0	285.0	73.83	0.374	0.373
1114.0	321.6	83.34	0.374	0.373
2228.0	348.1	90.20	0.372	0.371
4456.0	365.3	94.67	0.377	0.373
∞	385.9	—	—	—

TABLE VII.

Cyanoacetic Acid. Water, 1.8×10^{-6} .

<i>v.</i>	μ .	100 <i>m.</i>	$100k_1$ ($H' = 346.8$).	$100k_2$ ($H' = 347.2$).
17.350	89.3	23.15	0.402	0.401
34.70	118.8	30.80	0.395	0.394
69.40	154.7	40.11	0.387	0.386
138.8	196.1	50.83	0.379	0.378
277.6	241.2	62.53	0.376	0.375
555.2	284.8	73.82	0.375	0.373
1110.4	321.5	83.85	0.376	0.373
2221.0	347.9	90.19	0.374	0.369
∞	385.7	—	—	—

TABLE VIII.

Cyanoacetic Acid. Water, 2.5×10^{-6} .

<i>v.</i>	μ .	100 <i>m.</i>	$100k_1$ ($H' = 347.0$).	$100k_2$ ($H' = 347.2$).
21.05	96.5	25.00	0.396	0.396
42.10	127.7	33.09	0.389	0.388
84.20	165.2	42.81	0.381	0.380
168.4	208.0	53.90	0.374	0.374
336.8	253.0	65.56	0.370	0.370
673.6	295.6	76.60	0.372	0.371
1347.0	330.4	85.60	0.378	0.377
2694.0	354.8	91.94	0.389	0.387
∞	385.9	—	—	—

TABLE IX.

c-Nitrobenzoic Acid. Water, 0.9×10^{-6} .

<i>v.</i>	μ .	100 <i>m.</i>	$100k_1$ ($H' = 347.0$).	$100k_2$ ($H' = 347.2$).
32	139.7	36.85	0.672	0.671
64	179.0	47.22	0.660	0.659
128	221.9	58.52	0.645	0.644
256	265.0	69.88	0.633	0.632
512	303.6	80.07	0.628	0.626
1024	333.5	87.94	0.627	0.623
2048	353.6	93.26	0.629	0.624
4096	365.3	96.36	0.618	0.609
∞	379.2	—	—	—

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TABLE X.

o-Chlorobenzoic Acid. Water, 0.9×10^{-6} .

<i>v.</i>	$\mu.$	100 <i>m.</i>	100 <i>k</i> ₁ . (<i>H</i> '=347.4).	100 <i>k</i> ₂ . (<i>H</i> '=347.2).
150.1	134.6	35.41	0.1293	0.1294
300.2	174.0	45.76	0.1286	0.1288
600.4	218.0	57.34	0.1284	0.1286
1201.0	262.6	69.08	0.1284	0.1287
2402.0	302.1	79.45	0.1279	0.1283
4804.0	333.0	87.58	0.1286	0.1292
9608.0	353.7	93.05	0.1288	0.1298
∞	380.2	—	—	—

TABLE XI.

3:5-Dinitrobenzoic Acid. Water, 0.9×10^{-6} .

<i>v.</i>	$\mu.$	100 <i>m.</i>	100 <i>k</i> ₁ . (<i>H</i> '=346.7).	100 <i>k</i> ₂ . (<i>H</i> '=347.2).
254.5	175.7	46.76	0.1614	0.1607
509.0	219.0	58.28	0.1599	0.1591
1018.0	262.7	69.90	0.1594	0.1585
2036.0	301.5	80.23	0.1599	0.1586
4072.0	330.9	88.06	0.1594	0.1574
8144.0	350.7	93.34	0.1602	0.1569
∞	375.8	—	—	—

The results of the above tables, together with those obtained from the remaining experiments for *o*-nitrobenzoic acid, *o*-chlorobenzoic acid, and 3:5-dinitrobenzoic acid, are summarised in table XII. The figures shown are those values for the velocity of the hydrogen ion that give, for each particular series, the most satisfactory dissociation constant at high dilutions, as found under 100*k*₁ in the above tables.

TABLE XII.

Velocity of the Hydrogen Ion.

	Water, 0.9×10^{-6} .	Water, 1.2×10^{-6} .	Water, 1.8×10^{-6} .
Cyanoacetic acid	347.1	347.0	346.8
<i>o</i> -Nitrobenzoic acid	347.0	346.7	346.6
<i>o</i> -Chlorobenzoic acid	347.4	347.4	347.2
3:5-Dinitrobenzoic acid	346.7	346.9	346.7
Mean value..	347.0	347.0	346.8

It will be seen that the values in the above table are all in agreement within a unit; the mean value obtained from all experiments is *H*'=347.0. A modification in this figure; however, to the slightly higher value *H*'=347.2 will be shown to be necessary in a later section of the paper.

The variation in the values obtained with the use of the three different samples of water given in the table is negligible. With

the first sample, which is the purest, the results obtained are more trustworthy than in the other cases, since the agreement of the values of the dissociation constant at high dilutions was here found to be more satisfactory. With the second and third samples the agreement is still good, but with the fourth sample, the ordinary distilled water of the laboratory, no agreement at all could be obtained, as will be seen in table VIII for cyanoacetic acid. The influence of the impurities in the water on the conductivity measurements is here appreciably affecting the results; the use of the fourth sample was therefore discontinued. The constant $100k_1$ in table VIII is calculated with the use of the mean value obtained from other experiments with the same acid.

From the above results it would appear that the influence of the water on the conductivity measurements obtained may be neglected, up to very high dilutions, if its specific conductivity is not greater than 1.8×10^{-6} at 25° . Such a general conclusion, however, cannot be drawn, for it was found that with a sample of specific conductivity only 1.1×10^{-6} at 25° (obtained by "rushing" a current of outside air for some time through the laboratory distilled water) no satisfactory results could be obtained in the above experiments, since the dissociation constant showed an appreciable increase at high dilutions. It seems that the nature of the impurities in the water is of importance, as well as the amount. The amount is so small that we can only, in most cases, speculate as to its nature.

We cannot be certain that the measurements obtained with dilute acid solutions are the true values unless, as stated by Kohlrausch, the water used is absolutely pure. Nevertheless, it is possible that in certain cases water with a fairly large specific conductivity will not affect the values obtained, and this would appear to be so with the water obtained by distillation from water containing Nessler's solution.

Whilst, owing to the uncertainty as to the nature of the minute trace of impurities present, we are unable to assume this with certainty, yet the satisfactory results obtained at high dilutions support the view that such is here the case.

Limits of Ostwald's Dilution Law.

It will be found on an examination of tables VI to XI that the dissociation constant $100k_1$ obtained in each case is not a true constant at the higher concentrations. The value falls steadily with dilution, and only at very high dilutions does it approach a limit. The acids employed belong, therefore, to the class of transi-

tion acids, which obey the dilution law of Ostwald only in very dilute solution.

The divergence from the law is seen to be greater as the strength of the acid increases. The difference with *o*-nitrobenzoic acid is greater than with cyanoacetic acid at the same dilution; *o*-chlorobenzoic acid and 3:5-dinitrobenzoic acid give very small divergences, and acetic acid (table II) obeys the law exactly.

The dilution law of Ostwald, which is not applicable at all to solutions of strong electrolytes, is thus applicable for weak electrolytes only within certain limits. These limits have been fully discussed by Wegscheider (*Zeitsch. physikal. Chem.*, 1909, **69**, 603); the conclusions there drawn are summarised below.

In the first place, the law holds exactly only for dilute solutions; as solutions become more concentrated the dissociation constant obtained decreases, owing to the diminished fluidity of the solution. This effect begins to be appreciable, for the majority of organic acids, between $v=16$ and $v=32$; more dilute solutions obey the dilution law exactly.

The second disturbing influence, of greater theoretical importance, is in the opposite direction, increasing the dissociation constant, and depends on the ionic concentration. The dilution law holds approximately only for solutions where the ionic concentration is less than $N/60$; if it exceeds this limit, an increasing constant is obtained; thus, for binary electrolytes, the law is approximately obeyed if $2v/m$ is greater than 120 (m being the degree of dissociation at the dilution v), and breaks down for more concentrated solutions.

In order to determine the particular point at which the law ceases to hold exactly, it is evident that accurate conductivity measurements must be made for a series of dilutions. Such experiments have been carried out by Wegscheider and Lux (*Monatsh.*, 1909, **30**, 411) in the cases of several sulphonic acids. The result obtained is that Ostwald's dilution law gives perfect agreement for solutions in which $2v/m$ exceeds 320, and approximate agreement for solutions up to $2v/m=120$.

In the conductivity measurements given above in tables I to XI, the point at which the law ceases to be applicable in each case is of interest, for comparison with the results of Wegscheider. Tables I and V to VIII (cyanoacetic acid) and table IX (*o*-nitrobenzoic acid) show clearly the divergence in the values obtained for the dissociation constant at the higher concentrations. With *o*-chlorobenzoic acid and 3:5-dinitrobenzoic acid a slight increase in the value obtained at the highest concentration is suggested, but the acids employed are so slightly soluble that solutions of a concentration at which the effect would be appreciable cannot be prepared.

The results from the above tables are given in table XIII below. v indicates the dilution at which the divergence from the law of Ostwald becomes inconsiderable, m is the degree of dissociation at that dilution, and $2v/m$ the ionic concentration.

TABLE XIII.

Limits of Ostwald's Dilution Law.

	Table.	v .	m .	$2v/m$.
1.	Cyanoacetic acid	166	0.537	618
5.	" "	135	0.502	538
6.	" "	139	0.509	546
7.	" "	139	0.508	547
8.	" "	168	0.539	623
9.	<i>o</i> -Nitrobenzoic acid	256	0.699	733

The limit is evidently higher than that obtained by Wegscheider, and the law is seen to be applicable only for solutions with an ionic concentration of less than $2v/m=600$ (approximately). This is one dilution further than the limit given by Wegscheider, but it is by no means certain that the law is exactly applicable for solutions still more dilute, although any divergence will naturally diminish with the concentration; for we have, in the above tables, arbitrarily fixed the value for the equivalent conductivity at infinite dilution so as to obtain a satisfactory dissociation constant at high dilutions. We have no proof that a value, higher by a few tenths of a unit, which would give at these dilutions a still slowly decreasing constant, may not be nearer to the truth.

A modification of Ostwald's dilution law, so that it will apply to the more concentrated solutions, would enable us to calculate what effect this second disturbing influence exerts on the constant at high dilutions. Such a formula is developed below.

The Dissociation of Transition Electrolytes.

In dilute solution (v greater than 16) very weak electrolytes are found to follow exactly the dilution law of Ostwald, $m^2/(1-m)v=k$, as will be seen for acetic acid in tables II to III. Strong electrolytes obey approximately the empirical formula of van't Hoff, $m^3/(1-m)^2v=C$, which may be written in the form $m^2/(1-m)v=c(1-m)/m$. It is therefore to be expected that the intermediate or transition electrolytes will obey an intermediate formula, for example,

$$m^2/(1-m)v=k+c(1-m)/m;$$

and the agreement of this with the experimental data is shown in the tables which follow.

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The values for $m^2/(1-m)v$ that are obtained for solutions of an acid by the above formula decrease with the concentration of the solution, and ultimately attain a limiting value k_∞ at infinite dilution. The value of k_∞ is found from the conductivity results of a series of dilutions by the use of that particular value for the velocity of the hydrogen ion that gives values, for $m^2/(1-m)v$, slowly falling as dilution increases, and ultimately approaching (so far as can be perceived within experimental error) a limiting value. The value of c is obtained by trial from the experimental results.

In the results shown previously in table XII, that velocity for the hydrogen ion was taken in each series that gave constant values for $m^2/(1-m)v$ at high dilutions. The mean value deduced was $H^*=347.0$. The value required to give slowly-falling figures for $m^2/(1-m)v$ at high dilutions is very slightly higher in each series; the mean value required is $H^*=347.2$. In the following tables, therefore, k_∞ is obtained with the use of this value, $H^*=347.2$.

Table XIV gives the results for cyanoacetic acid obtained from table V. The first column shows the dilution, the second the ratio of the non-ionised to the ionised part. In the third column the values calculated from the formula for the dissociation constant at each dilution are given. These are compared with the experimental values, $100m^2/(1-m)v$, obtained with the use of the two different values for the velocity of the hydrogen ion referred to above. These experimental figures are the same as were expressed by $100k_1$ and $100k_2$ in table V. Finally, the figures under $100k$ show the value obtained at each dilution from the experimental results in the preceding column ($H^*=347.2$) by subtracting the value of $c(1-m)/m$. The constancy of the values obtained in the last column therefore shows the agreement of the formula with the experimental results.

TABLE XIV.

Cyanoacetic Acid (see table V). $k_\infty = 0.00368$; $c = 0.00010$.

v .	$(1-m)/m$.	$100(k_\infty + c(1-m)/m)$.	$100m^2/(1-m)v$ ($H^*=347.1$).	$100m^2/(1-m)v$ ($H^*=347.2$).	$100k$.
16.82	3.39	0.402	0.400	0.400	0.366
33.64	2.30	0.391	0.392	0.392	0.369
67.28	1.53	0.383	0.383	0.383	0.368
134.56	0.99	0.378	0.378	0.378	0.368
269.1	0.62	0.374	0.372	0.372	0.366
538.2	0.37	0.372	0.372	0.371	0.367
1076.4	0.21	0.370	0.373	0.371	0.369
2153.0	0.11	0.369	0.373	0.371	0.370
4306.0	0.06	0.369	0.378	0.376	0.375
∞	0.00	0.368	—	—	—

The agreement between the calculated and experimental values is seen to be very satisfactory throughout the whole range of

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dilutions. Further examples of the agreement of the formula with the previous results are shown in its application to *o*-nitrobenzoic acid and 3:5-dinitrobenzoic acid in tables XV and XVI below.

TABLE XV.

o-Nitrobenzoic Acid (see table IX). $k_{\infty} = 0.00620$; $c = 0.00032$.

v .	$(1-m)/m$.	$100(k_{\infty} + c(1-m)/m)$.	$100m^2/(1-m)v$ ($H' = 347.0$).	$100m^2/(1-m)v$ ($H' = 347.2$).	$100k$.
32	1.71	0.675	0.672	0.671	0.616
64	1.12	0.656	0.660	0.659	0.623
128	0.71	0.643	0.645	0.644	0.621
256	0.43	0.634	0.633	0.632	0.618
512	0.25	0.628	0.628	0.626	0.618
1024	0.14	0.624	0.627	0.623	0.619
2048	0.07	0.622	0.629	0.624	0.622
4096	0.04	0.621	0.618	0.609	0.608
∞	0.00	0.620	—	—	—

TABLE XVI.

3:5-Dinitrobenzoic Acid (see table XI). $k_{\infty} = 0.001570$;
 $c = 0.000030$.

v .	$(1-m)/m$.	$100(k_{\infty} + c(1-m)/m)$.	$100m^2/(1-m)v$ ($H' = 346.7$).	$100m^2/(1-m)v$ ($H' = 347.2$).	$100k$.
254.5	1.14	0.1604	0.1614	0.1607	0.1573
509.0	0.72	0.1592	0.1599	0.1591	0.1569
1018.0	0.43	0.1583	0.1594	0.1585	0.1572
2036.0	0.25	0.1577	0.1599	0.1586	0.1579
4072.0	0.14	0.1574	0.1594	0.1574	0.1570
8144.0	0.07	0.1572	0.1602	0.1569	0.1567
∞	0.00	0.1570	—	—	—

The agreement of the formula with the results of experiment is for both acids very satisfactory. With the very dilute solutions the values for $m^2/(1-m)v$ obtained with the use of $H' = 347.2$ are seen to be in better agreement with the formula than those given in the preceding column. The results obtained in tables XIV to XVI, therefore, lead us to the conclusion that the value for the velocity of the hydrogen ion is not that required to give constant values for $m^2/(1-m)v$ at high dilutions, but that which gives values slowly decreasing and ultimately reaching a limit.

The method employed in the first part of the paper to obtain the velocity of the hydrogen ion is thus found to give results a little below this required value. The mean value $H' = 347.0$ previously deduced has therefore been amended to the slightly higher figure of $H' = 347.2$.

The values for the velocity of the hydrogen ion obtained in table XII are all in agreement within a unit. If the two purest samples of water only are considered, the agreement is slightly

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better; results are concordant within 0.2 to 0.4 for each acid, whilst the greatest divergence between those for different acids is 0.7. The value for the velocity of the hydrogen ion, amended from the above results, can therefore be stated as 347.2 ± 0.4 at 25° . At 18° the value becomes, with the use of the temperature-coefficient given by Kohlrausch (*Zeitsch. Elektrochem.*, 1902, **8**, 290), $H' = 313.9$.

The General Application of the above Dissociation Formula.

It has been remarked that the divergence from the simple dilution law increases with the strength of the acid used, and in tables XIV to XVI it is seen that c does increase with k . With very weak acids, therefore, it will be impossible to notice any divergence from Ostwald's dilution law in dilute solutions; this is so in the case of acetic acid, as shown in table II. With stronger acids, however, the variation in the values of the dissociation constant with dilution will be much greater; an example—trichlorobutyric acid—is given in table XVII below.

The figures given in the table differ materially from those of Ostwald (*Zeitsch. physikal. Chem.*, 1888, **3**, 194). This is probably due to the removal of impurities in the method of purification adopted. The acid dissolves readily on treatment with a small quantity of water, but leaves a less soluble residue. This was collected, and the clear filtrate carefully evaporated to dryness. The acid was then dissolved in light petroleum, and recrystallised several times.

TABLE XVII.

Trichlorobutyric Acid. $k_\infty = 0.095$; $c = 0.35$.

v .	μ .	$(1-m)/m$.	$\frac{100(k_\infty + c(1-m)/m)}{100m^2/(1-m)v}$.	$100m^2/(1-m)v$.	$100k$.
38.63	326.4	0.152	14.8	14.8	9.5
53.98	336.0	0.119	13.7	13.9	9.7
77.26	343.9	0.093	12.7	12.7	9.5
107.96	350.4	0.073	12.1	11.8	9.2
154.5	357.0	0.054	11.4	11.5	9.6
215.9	361.2	0.041	10.9	10.9	9.5
309.0	365.1	0.030	10.5	10.5	9.5
431.8	368.2	0.021	10.2	10.7	10.0
618.0	370.9	0.014	10.0	11.6	11.1
∞	(376.0)	0.000	9.5	—	—

The value for the equivalent conductivity at infinite dilution is only approximate, being obtained from the number of atoms in the molecule by Ostwald's method (*Zeitsch. physikal. Chem.*, 1888, **2**, 840). In view of the proximity of the measurements to this uncertain value, the agreement throughout the series between the calculated and experimental figures is very satisfactory.

A complete series of measurements with a still stronger acid, namely, *p*-toluenesulphonic acid, has been carried out by Wegscheider and Lux (*Monatsh.*, 1909, **30**, 436); the agreement of the formula with their results is shown in the following table. In the calculation of the results from the experimental data the value $H^* = 347.2$ is employed.

TABLE XVIII.

p-Toluenesulphonic Acid. $k_\infty = 0.090$; $c = 5.6$.

v	25.00	32.66	44.44	51.02	59.17	69.44	82.64	100.0	123.4
$100(k_\infty + c(1-m)/m)$..	50.4	45.4	39.8	37.0	34.8	32.0	29.7	28.0	25.8
$100m^2/(1-m)v$	50.6	44.3	38.7	37.2	35.2	34.0	31.8	28.7	26.5
$100k$	9.2	7.9	7.9	9.2	9.4	11.0	11.1	9.7	9.7
v	156.3	204.1	277.7	330.6	400.0	493.8	625.0	816.8	1111
$100(k_\infty +$									∞
$c(1-m)/m) \dots$	24.1	21.9	19.6	18.5	17.4	16.2	15.2	14.0	12.9
$100m^2/(1-m)v$..	22.6	21.0	18.3	17.4	16.8	16.0	14.9	13.9	13.0
$100k$	7.5	8.1	7.7	7.9	8.4	8.8	8.7	8.9	9.1
									10.3

The acid is so highly dissociated that the differences between the calculated and experimental values are all within the limits of experimental error. The formula is found to hold throughout a five-fold change in the values obtained by experiment for $m^2/(1-m)v$.

The agreement of the formula for an acid of another type—phosphoric acid—is shown in table XIX. The results are calculated with the use of the value $H^* = 347.2$ by interpolation from the figures given by Rothmund and Drucker for the experiments of Loomis (*Zeitsch. physikal. Chem.*, 1903, **46**, 850).

TABLE XIX.

Phosphoric Acid. $k_\infty = 0.0070$; $c = 0.0013$.

v	16	32	64	128	256	512	1024
$100(k_\infty + c(1-m)/m)$..	0.97	0.89	0.83	0.78	0.75	0.73	0.72
$100m^2/(1-m)v$	0.96	0.87	0.82	0.81	0.76	0.77	0.69
$100k$	0.69	0.68	0.69	0.73	0.71	0.74	0.67

The agreement between the calculated and observed figures is again satisfactory. The second and third dissociations of the acid are evidently too weak to affect the results, even at the highest dilutions given.

The stronger inorganic acids, such as hydrochloric acid, are of a different type. The values obtained for $m^2/(1-m)v$ certainly do fall away, as dilution is increased, to a limiting value k_∞ , but that limiting value is zero. The results for hydrochloric acid are given in table XX below. The measurements of Goodwin and Haskell at 18° (*Zeitsch. physikal. Chem.*, 1905, **52**, 630) are employed, the value $H^* = 313.9$ being used in the calculation of the degree of dissociation at each dilution.

TABLE XX.

Hydrochloric Acid. $k_{\infty}=0.00$; $c=13.4$.

v	20	33.3	50	100	200	500	667	1000
$100(k_{\infty} + c(1-m)/m)$	78.5	62.4	50.9	36.4	24.5	14.8	13.5	12.4
$100m^2/(1-m)v$	80.6	61.5	50.6	35.6	26.9	18.1	14.7	10.6
$100k$	+2.1	-0.9	-0.3	-0.8	+2.4	+3.3	+1.2	-1.8
v	1333			2000	4000		∞	
$100(k_{\infty} + c(1-m)/m)$	11.4			8.5	6.3		0.0	
$100m^2/(1-m)v$	8.7			7.8	5.2		—	
$100k$	-2.7			-0.7	-1.3		—	

The conductivity measurements are all so very near to the value at infinite dilution that the possible degree of error in the above calculations is considerable; the agreement in all cases is within the limits of experimental error.

In conclusion, the dissociation formulæ of a number of typical electrolytes, calculated from the available experimental data, are collected in table XXI.

TABLE XXI.

*Dissociation of Electrolytes.*Dissociation formula: $m^2/(1-m)v = k + c \cdot (1-m)/m$.

Acid.	Observer.	k .	c .
Acetic	Kendall	0.0000185	—
<i>o</i> -Bromobenzoic	Ostwald	0.00140	0.00004
<i>p</i> -Nitrophenylglycolic	"	0.00149	0.00004
3:5-Dinitrobenzoic	Kendall	0.00157	0.00003
Aniline- <i>o</i> -sulphonic	Ostwald	0.00310	0.00015
Cyanoacetic	Kendall	0.00368	0.00010
Trichloroacetic	Ostwald	0.00440	0.00020
<i>o</i> -Nitrobenzoic	Kendall	0.00620	0.00032
Phosphoric	Loomis	0.0070	0.0013
5-Bromo-2-nitrobenzoic	Ostwald	0.012	0.007
4:6-Dibromoaniline-3-sulphonic	"	0.019	0.030
Dichloroacetic	Walker	0.0316	0.080
β -Resorcylic	Ostwald	0.032	0.075
Trichlorobutyric	Kendall	0.095	0.35
<i>p</i> -Toluenesulphonic	Wegscheider and Lux	0.090	5.6
β -Naphthalenesulphonic	"	0.120	6.6
Hydrochloric	Goodwin and Haskell	—	13.4

It is evident from the above figures that c increases with k , and increases much more rapidly. Ostwald's dilution law is a limiting case of the formula, since with very weak electrolytes c is so nearly equal to zero that the dissociation constant is practically unaffected. Similarly, van't Hoff's empirical law for strong electrolytes is a special case of the above formula, where $k=0$. The dissociation formula given above is therefore applicable to all acids. For salts, however, the divergences from the simple van't Hoff formula are beyond the limits of experimental error, even in dilute solution.

It does not seem possible to establish a connexion between the constants k and c . In the above table c is roughly proportional to k^2 for the weaker acids, but this relation cannot be general, since for strong electrolytes c is large whilst k is zero. Finally, it may be noted that the dissociation of transition acids can in no way be expressed by a formula intermediate between Ostwald's dilution law and Rudolphi's formula for strong electrolytes.

Summary of Results.

The following method has been employed for the determination of the velocity of the hydrogen ion, and has been found to give concordant results. If conductivity measurements are carried out with a series of very dilute solutions of a weak acid, the values obtained for the dissociation constant vary greatly according to the value for the velocity of the hydrogen ion used in the calculation of the equivalent conductivity at infinite dilution. With acids of a certain range of strength (100% between 0.1 and 1.0) it has been found that a satisfactory dissociation constant at very high dilutions can only be obtained with the use of one particular value for the velocity of the hydrogen ion. The mean of the values deduced from a number of experiments with different acids was $H^* = 347.0$. A slight modification of this result was afterwards found necessary, the figure finally obtained being $H^* = 347.2$ at 25° (or 313.9 at 18°), with a maximum divergence of ± 0.4 .

It has been found that the dilution law of Ostwald is not exactly obeyed by the acids employed in the above determination, even in very dilute solution. A formula for the dissociation of these acids, $m^2/(1-m)v = k + c(1-m)/m$, where k and c are constants for each acid, has been developed, and found to be in perfect agreement with the experimental data. For the transition acids in general, c increases with k .

This formula has been extended to acids of all types. Ostwald's dilution law for weak electrolytes is a limiting case, since as k decreases c approaches zero; van't Hoff's formula for strong electrolytes is a special case, where k is zero. The above dissociation holds, therefore, within the limits of experimental error for all acids.

I desire to express my thanks to Professor Walker for the interest he has taken in this research, and for advice during its progress.

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