XCIV.—*Some Aspects of the Theory of Acids.*

By ARTHUR LAPWORTH.

ALTHOUGH it is now widely recognised that the phenomena which occur in solutions of acids are highly complex, it is still the custom to express the data in terms of the ionisation theory as Arrhenius first pronounced it. Whilst the theory in its original form gives a correct mathematical statement of certain quantitative relationships subsisting in highly dilute solutions in a single ionising medium, it is decidedly at variance with the properties of concentrated solutions, and breaks down altogether when solutions in different media are compared. The "hydrogen ion" in water and in alcohol respectively, for example, is not the same chemical individual, and it is probable that the same remark applies to the non-ionised part of any acid in these two media.

The phenomena become more intelligible when the theory is modified by the introduction of chemical hypotheses based on the idea of hydration and solvation. Nevertheless, such hypotheses remain somewhat tentative in character, and even if, as is the case, they can be shown to be advances on the right lines, they are almost necessarily inexact, because there are no means of ascertaining the precise extent of the solvation in any instance.

The activity of an acid in solution undergoes great variations, not only on the addition of substances having a basic character, but also on changing the medium, even when the degree of ionisation remains unaltered. Hitherto, no general method of estimating such changes in activity has been suggested, although the question is obviously one of great general interest. The author and his colleagues have repeatedly pointed out that, during some of the most remarkable changes which this activity undergoes, the parallelism between the catalytic activity and the power of forming salts with weak bases is complete (so far as the ionised part

of the acid is concerned), and two solutions may be regarded as being equal in "acidness" when they affect a given weak base under fixed conditions in precisely the same manner and to the same extent.

Change in Activity with Change in the Medium.

The justice of the preceding definition is not likely to be questioned when the two solutions are made with the same solvent. The author now ventures to suggest that it is the only definition capable of being logically extended to the comparison of solutions when the media are different. The need for some such criterion will be clear from the following considerations.

Small quantities of water greatly diminish the speed of reactions due to catalysis by ionised acids in alcoholic solutions, and this diminution has now been definitely associated with a fall in the activity of the cations ("hydrogen ions"*) of the catalyst. It is evident from the work of Kistiowski (*Zeitsch. physikal. Chem.*, 1898, **27**, 253) that the activity of the acid continues to fall over a very wide range as solvent alcohol is replaced by water, and Dawson (T., 1911, **99**, 1), who has studied the influence of such replacements throughout the whole range from absolute alcohol to water, found that the speed of isomerisation of acetone under the catalytic influence of sulphuric acid is more than one hundred times as great in the former solvent as in the latter.

The ratio of the speeds of the catalysed reactions in two media does not, however, afford a trustworthy measure of the relative activities of the catalyst, as not only the latter, but also all the other interacting compounds, may be profoundly modified, for example, by solvation, in passing from one solvent to another, and to very different extents, so that the ratio, *speed in alcohol*: *speed in water*, for example, is likely to vary considerably with the reaction which is catalytically promoted. Similar objections apply to any methods based on measurements of salt "hydrolysis" or of the depths of tints communicated to indicators, methods which are satisfactory enough when the medium is unchanged. It is clear, therefore, that any trustworthy mode of determining the relative activities must be based on considerations which are independent of the nature of any solutes other than the acid itself.

Let *A* and *B* be two solutions of any acid, and let *C* be a relatively minute quantity of a solution made with a very weak base dissolved in any solvent; also let *C* be contained in a small

* Throughout the present paper the cations present in any solution of an acid in a given solvent or in a mixture of alcohol and water are referred to as "hydrogen ions," which term is intended to include both free and solvated ions.

"test-vessel" which is pervious to the non-ionised, unsolvated acid only, and let this vessel be immersed successively in *A* and *B*, and in each case until equilibrium is attained; if the same proportion of base in *C* is converted into salt in both cases, *A* and *B* are equally "acidic" with respect to the non-ionised acid. This is evidently the case when the thermodynamic potential of the non-ionised acid is the same in the two solutions.

It is not possible, strictly speaking, to apply a test such as the above for equality in the acidity which is due to the "hydrogen ions," for if the test-vessel were pervious to these ions alone attainment of equilibrium in the above sense would be impossible, owing to the arrest of diffusion by electrostatic charges arising at the walls of the "test-vessel." Analogy suggests, however, that the same ultimate criterion as before may be adopted, and that *A* and *B* are equally "acidic" with respect to the "hydrogen ions" when the thermodynamic potentials of these ions are identical in the two solutions.*

In 1913 the author, with W. J. Jones, stated that "the thermodynamic potential of hydrogen chloride in absolute alcohol is depressed by the addition of water, and that to this depression may be traced" all the varied phenomena associated with the presence or absence of water in such solutions (T., 1913, 103, 253). It was shown that water caused a diminution in the partial pressure of the hydrogen chloride, thus proving that non-ionised hydrogen chloride tends to pass from dry to moist alcoholic solutions. That the same is independently true of the "hydrogen ions" was established by the work of Hardman and Lapworth (T., 1911, 99, 2242; 1912, 101, 2249), who found that the ionic solution pressure of hydrogen is smaller in moist than in dry alcoholic solutions having the same concentration of hydrogen chloride, and to just the extent calculated from measurements on the relative catalytic activities and acidities of such solutions. The anti-catalytic influence of water was thus successfully associated with changes which that substance causes in the thermodynamic potential of the catalyst and its cations.

The Functions of the Ionised and Non-ionised Acids.

Until very recently the views of the Arrhenius-Ostwald school, which attributed the whole catalytic action of an acid to the

* The author has previously used the function *P*, the "availability," to express the power of an acid in solution to form complex hydrions with a weak base (T., 1908, 93, 2203; compare also Lapworth and Partington, T., 1910, 97, 21). The values of *P* for two solutions therefore become identical when the "hydrogen ions" have the same thermodynamic potential.

"hydrogen ions," were almost universally accepted. Latterly, however, a broader point of view has been reached, and any treatment of this subject is necessarily disparate which deals with the ions alone. The author was conscious of this in 1908, when, pursuing the obvious parallelism between the catalytic activity of an acid and its power of forming salts with weak bases, he suggested for the first time in a definite manner that non-ionised as well as ionised complexes (salts) of the acid take part in the observed transformations. On this occasion, also, he pointed out that the much discussed effect of neutral salts of strong acids on their catalytic activities would receive a simple explanation on these lines (T., 1908, **93**, 2198 *et seq.*). Independently, and almost simultaneously, Goldschmidt made a similar suggestion (*Zeitsch. Elektrochem.*, 1909, **15**, 6),* and later, with Thuesen, was the first to provide an experimental proof of the correctness of this idea (*ibid.*, 1912, **81**, 39). Curiously enough, however, Goldschmidt (1909) supposed that the part played by the non-ionised acid would assume greatest importance with weak acid catalysts, whilst the expressions deduced by the present author showed that, in general, the opposite should be true, as has, in fact, been found to be the case by Bredig, Miller and Braune (*Zeitsch. Elektrochem.*, 1912, **18**, 535), Snethlage (*ibid.*, 539), and Taylor (*Medd. K. Vetenskapsakad. Nobelinst.*, **2**, Nos. 34, 35, and 37).

The result obtained by these workers is often regarded as a proof that the non-ionised acid is catalytically active as well as the hydrogen ions; but this is only one of several alternative interpretations of the fact that there are two simultaneous time reactions, the velocity of one of which is proportional to the concentration of the non-ionised acid. The original view propounded by the present author and by Goldschmidt appears more rational, and would also provide some explanation of what appears so remark-

* These suggestions, although they represent the first definite ones on such lines in connexion with the special case of catalysis by acids, were subsequent to and, certainly in the author's case, consequent on the discovery made by Senter that non-ionised water as well as hydroxylion is capable of hydrolysing chloroacetic acid (T., 1907, **91**, 467), and on the work and writings of Acree and his co-workers, who had opened a vigorous attack on the view which attributed special activity to ions (*Amer. Chem. J.*, 1907, **37**, 410; **38**, 258; 1908, **39**, 230, etc.) and who have since made very extensive and valuable experimental contributions in which the possibility of distinguishing between the simultaneous changes in the ionised and non-ionised constituents has been definitely proved (compare T., 1914, **105**, 2582). The services rendered by these pioneers have not, in the author's opinion, received due recognition; the extension of their work and views to the special case of acids was a fairly obvious move, although the practical results in this instance appealed with special force to chemists as a whole (compare Lapworth, P., 1909, **25**, 25; Arrhenius, T., 1914, **105**, 1424 *et seq.*).

able from the other point of view, namely, why the apparent catalytic activity of the non-ionised acid increases with the ionisation constant. It is easy to show, for example, that the ratio—*apparent activity of non-ionised acid: apparent activity of "hydrogen ions"*—is given by the expression $K_a \times k_1/k_2K_s$, where K_a is the ionisation constant of the acid, K_s is that of the salt-like complex of the acid with the reactive component, k_1 is the velocity coefficient of the reaction in which the non-ionised complexes take part, and k_2 is that of the corresponding change in which the complex cations are concerned.*

Whatever the explanation of the catalytic influence of acids may prove to be (compare Lamble and Lewis, T., 1914, **105**, 2330; 1915, **107**, 233), it is now clear that the activity of an acid, whether as catalyst or as salt-former, is twofold in the above sense, and it is permissible to represent its whole activity by the expression $P + aP'$ (compare p. 866). Here P is the "availability," and refers to the activity which may conventionally be associated with the "hydrogen ions," and aP' to that similarly connected with the non-ionised acid. It has already been shown that P is independent of the nature of the reaction in which the acid takes part; the magnitude of aP' , however, clearly varies with each acid and each reaction: but if the convention be adopted that P' bears to the thermodynamic potential of the non-ionised acid the same relation that P bears to that of the "hydrogen ions," then the expression $P + aP'$ may be said to be a measure of the "acidness" or "acidity" of a solution of a given acid, the value of a only being peculiar to the test used as a measure of the "acidness." The magnitude of aP' becomes negligible with very weak acids and in highly dilute solutions of all acids, when the acids and their salts are fully ionised, and the activity becomes sensibly equal to P .

Comparison of Thermodynamic Potentials of (a) Non-ionised and (b) "Hydrogen Ions" in Solutions of an Acid in Different Media.

In case (a), if the acid is appreciably volatile, the partial pressure of its vapour above the solutions may be ascertained; in most other instances, however, the comparison is hardly possible, and must await the development of the theory of concentrated solutions.

With two solutions in a single medium, the comparison of the thermodynamic potentials of the contained "hydrogen ions" (case b) is usually made by measuring the electromotive force of

* According to Taylor (*loc. cit.*), the ratio is roughly proportional to the square-root of K_a , suggesting a fairly definite relationship between k_1 , k_2 , and K_a .

a concentration cell with metallic electrodes saturated with hydrogen and immersed in the two solutions as cell liquids, a correction for the diffusion potential difference at the boundary being made by a formula based on Nernst's theory or by eliminating that difference by some recognised device.

When the media are different, the use of these methods involves assumptions very difficult to justify, although they have been applied to such problems by several workers, including Jones (*Zeitsch. physikal. Chem.*, 1894, **14**, 346), Jones and Smith (*Amer. Chem. J.*, 1900, **23**, 379), Kahlenberg (*J. Phys. Chem.*, 1899, **3**, 379), Wilson (*Amer. Chem. J.*, 1906, **35**, 78), and by Pearce and Farr (*J. Phys. Chem.*, 1914, **18**, 731). Thus Neustadt and Abegg (*Zeitsch. physikal. Chem.*, 1910, **69**, 486) measured the electromotive forces of a number of combinations each made up of several solutions in different media in series and in different orders, and obtained evidence, in certain instances, of boundary potentials amounting to several centivolts, showing that Nernst's views cannot at once be extended to contact potentials between different media.

A more direct method of attacking the problem is that of measuring the single potential differences between the hydrogen electrode and the solutions the acidities of which are to be compared. As is well known, however, there is no general agreement on the question whether either the dropping electrode or the capillary electrometer is a trustworthy instrument for ascertaining the null-point for such determinations. At the author's request, Mr. Newbery undertook a series of experiments with the dropping electrode as applied to alcoholic solutions (T., 1914, **105**, 2553), and found it useless for the purpose; his investigation of the behaviour of the capillary electrode (this vol., p. 852), however, has given results which appear to indicate that this device may be applied successfully to such determinations. The following were the considerations which determined the lines of this investigation:

A concentration cell with mercury electrodes is imagined to be constructed to hold two solutions in the same or in different media. The solutions are each saturated with respect to mercurous chloride and to sodium chloride, and are separated by a diaphragm which is permeable to mercurous ions only. In such a cell, the passage of a current leads to solution of metallic mercury in one compartment, with the separation of an equal quantity of mercury from solution in the other compartment, whilst an equal quantity of mercury, as ions, passes from the first to the second solution. On the whole, therefore, the only change which has taken place is

that metallic mercury has passed from one place to another, and, neglecting any influence of gravity, no change in free energy has taken place, so that the electromotive force of the cell must be zero.

It does not follow that the single potential difference between the mercury and the solution is necessarily the same in each case: were the above considerations the only ones available, the conclusion to be drawn is that electromotive force at the boundary opposes and exactly balances any discrepancy between the single potential differences at the electrodes. When mercury is in contact with a saturated solution of mercurous chloride, the single potential difference depends on the thermodynamic potential of the mercurous ions in the solution, and this varies with that of the chloridions. When the solution is saturated with respect both to mercurous chloride and to sodium chloride, the thermodynamic potentials of the non-ionised salts in solution are equal to those of the two solid salts respectively, and thus will be the same in all solvents at a given temperature; the thermodynamic potentials of the separate ions, however, will vary with their relative affinities for the solvent. Thus, if one solvent has a great affinity for chloridion, but not for sodion, then the thermodynamic potential of chloridion in that solution will be much smaller, and that of the sodion correspondingly greater, than in the similar solution with a solvent which has no special affinity for chloridion; consequently, in contact with a solution prepared with the former solvent saturated with respect both to mercurous and sodium chlorides, mercury will have a higher "absolute potential" than in a solution similarly prepared with the latter.

Hydron has a considerably greater affinity for alcohol than for water, but is the only ion for which such a character can be demonstrated. The exceptional behaviour of hydron as compared with Na^+ , NH_4^+ , K^+ , Ag^+ , NO_3^- , Cl^- , and possibly others, is exhibited, not only in its chemical character, but also in its transport numbers, which change completely when alcohol is used as a solvent instead of water (T., 1911, 99, 1418). The transport numbers of ions in salts, however, or at least those containing the above radicles, are the same, or very nearly so, in alcohol and water, and this suggests either (1) that these ions, unlike hydron, have no affinity for either solvent, or (2) that all these ions have approximately the same affinity for water and also for alcohol; the latter view would appear wholly rational if these "affinities" are due solely to the electric charges on the ions.

If this interpretation of the data on transport numbers is correct, then the single potential differences between metallic

mercury and solutions saturated with both mercurous and sodium chlorides must be nearly the same in alcoholic as in aqueous solutions. Mr. Newbery's experiments appear to confirm this idea in a most striking manner, the agreement found being even closer than was anticipated; both in this instance and in the case in which ammonium chloride was used instead of sodium chloride, the single potential difference, as estimated by the capillary electrometer, appeared to be the same, within the limits of experimental error, whether the solvent was water or alcohol.

The history of the problem of determining single potential differences offers forcible proof of the danger of regarding any apparently reasonable solution of the question as a final one, and none is likely to be generally accepted until it has withstood a long series of stringent tests. Mr. Newbery's results, however, show a striking agreement with the *a priori* considerations which led to them, and inspire further confidence by their general harmony, not only among themselves, but with the most acceptable results obtained by previous workers. Assuming the correctness of the principle, it becomes possible, by measuring the electromotive forces of galvanic combinations involving no contacts between different media, to compare single potential differences at ("absolute potentials" of) electrodes in solutions made with two different solvents.

From the data obtained, Mr. Newbery calculates that the single potential difference at the hydrogen electrode in contact with a decinormal solution of hydrogen chloride in anhydrous alcohol at 25° is about 0.299 volt, that at the electrode in contact with a decinormal aqueous solution of hydrogen chloride at this temperature being about 0.186* volt. Thus the difference in the electrical potential of the electrode in the two cases (when there is no difference between the electrical potentials of the two solutions) is roughly 0.113 volt, hence the difference in the thermodynamic potentials of the "hydrogen ions" in the two solutions is about 2625 cal., or 11×10^{11} ergs per gram-equivalent. The thermodynamic potential of the "hydrogen ions" in the *N/10*-alcoholic solution is therefore about the same as that in an aqueous solution having a concentration of "hydrogen ions" eighty-two times as great as in the *N/10*-aqueous solution. Considerable uncertainty exists as to the degrees of ionisation of strong electrolytes, but adopting 0.5 as representing the maximum possible fraction of hydrogen chloride ionised in *N/10*-alcoholic solution, and 0.8 as the minimum ionised in *N/10*-aqueous solution, it may

* This number is the one deduced from Palmaer's results with the dropping electrode with which Mr. Newbery's measurements, made with the capillary electrometer, are in close agreement.

be concluded that the "acidness" of an alcoholic solution of fully ionised hydrogen chloride is at least 130 times as great as that of an aqueous solution having the same volume-concentration.

Dawson (*loc. cit.*) found that the speed of isomerisation of acetone by sulphuric acid is rather more than 100 times as great in alcohol as in water, and although for several reasons no precise comparison between the two cases is possible, it is at least significant that the magnitude of the apparent change in "acidness" due to change in the medium is of the same order as that deduced by the electrical method.

Chemical Interpretation of the Anticatalytic Action of Water on Alcoholic Hydrogen Chloride.

In previous papers the author, with his colleagues, has shown that, from a chemical point of view, the results obtained with ionised hydrogen chloride are best reconciled with the assumption that the water diminishes the concentration of the free hydrogen ions and any complexes of the latter with the solvent. It should, however, be made clear that the data already obtained furnish the basis for a theoretical proof of the validity of the writer's view. An outline of this proof may be given:

Hardman and Lapworth (T., 1911, **99**, 2242; 1912, **101**, 2249) found that the electromotive force of a concentration cell, with hydrogen electrodes and with alcoholic hydrogen chloride at the same concentration in both compartments, but with a little water in one compartment only, is given by the expression $\frac{RT}{F} \ln \frac{r}{r+w}$,* where R , T , and F have their usual significance, r is a constant for the alcohol at a given temperature, and w is the number of gram-molecules of water per litre in the moist alcohol. The formula given applies when the boundary *E.M.F.* has been eliminated, and it follows that the single potential difference at (absolute potential of) the electrode in alcohol containing water and hydrogen chloride at given concentrations is expressible in the form $\frac{RT}{F} \ln \frac{d}{r+w}$, where d is a constant, and that the thermodynamic potential, z , of the "hydrogen ions" has the form $RT \cdot \ln \frac{b}{r+w}$, where b is another constant which, like d , depends on the concentration of the acid (1)†

* In this and the following expressions the influence of external pressures on the values of thermodynamic potentials of solute is neglected, so that the expressions take the same form as those for the free energies.

† It has been shown that the "availability," P , is proportional to $1/r+w$

Let the cations in alcoholic hydrogen chloride be either free or solvated or both, say: $H^+, H(HOEt)^+, H(HOEt)_2^+, H(HOEt)_3^+$, etc., and let the numbers of these present in a given quantity of a solution be n_1, n_2, n_3 , etc.; also let the total number of all these be N , and the total number of molecules (acid, solvent, cations, and anions, etc.) be Σn . From the thermodynamic theory of dilute solutions it follows that the thermodynamic potential per gram-molecule, z , of each type of hydrion is the same as that of the cations ("hydrogen ions") as a whole, or

$$z = RT \cdot \ln k_1 \frac{n_1}{\Sigma n} = RT \cdot \ln k_2 \frac{n_2}{\Sigma n} = \dots = RT \cdot \ln K \frac{N}{\Sigma n} \dots \quad (11),$$

whence, of course, $k_1 n_1 = k_2 n_2 = k_3 n_3 = \dots = KN$ (k_1, k_2 , etc., being constants).

Comparing (1) and (11), we have, putting $c = \frac{n_1}{\Sigma n}$, etc. and $C = \frac{N}{\Sigma n}$,

$$k_1 c_1 = k_2 c_2 = \dots = KC = \frac{h}{r + w}.$$

It has been shown experimentally that at 0° the value of r is about 0.05, so that if we compare, at 0° , two alcoholic solutions containing the same quantity of ionised hydrogen chloride, one of which is anhydrous and the other contains, say, one gram-molecule of water per litre (about 2 per cent.), then, in the latter, $w = 1.00$, and the ratio $c(\text{dry})/c(\text{moist}) = \frac{r+w}{r} = \frac{1.05}{0.05} = 21$, that is, the addi-

tion of 2 per cent. of water has reduced the quantities $\frac{n_1}{\Sigma n}, \frac{n_2}{\Sigma n}, \dots, \frac{N}{\Sigma n}$ to about one-twentieth of their original values.

The supposition that the addition of one gram-molecule of water to one litre of the solution has increased Σn , the total number of gram-molecules, twenty-one times, is kinetically and thermodynamically absurd, for the above relations hold good in the presence of vanishingly small quantities of hydrogen chloride, and would require that the molecular weight of the alcohol had fallen to about one-twentieth of its original value. It is necessary to conclude, therefore, that the fall is due almost wholly to the decrease in the values of $n_1, n_2, n_3, \dots$, and N , and this was the writer's original proposition.

(T., 1910, 97, 22), so that the relation of P to z is given by: $P = ae^{z/RT}$, where a is a constant at a fixed temperature. Similarly, $P' = a'e^{z'/RT}$, where z' is the thermodynamic potential of the non-ionised acid and a' is another constant. The absolute magnitudes of z and z' depend on the zero adopted for thermodynamic potentials, but as a and a' are also wholly arbitrary we may define P and P' by putting them equal to $e^{z/RT}$ and $e^{z'/RT}$ respectively.

It may be noted that whilst the value of N decreases so very largely, the total number of ions present in the highly dilute solution does not greatly alter, so that about $N \times 20/21$ cations of a new type have appeared, replacing those which have vanished; these new cations cannot be supplied by ionisation of the water (T., 1908, 93, 2166, 2167) nor by new combinations of the hydrogen ions with the alcohol alone, and must therefore contain water with or without alcohol of solvation.

The effect of water on the "hydrogen ions" in alcoholic solutions must therefore be due to reactions, which are expressed by the equations:

or, generalised,

the former of which Goldschmidt and Udby were the first to use in their paper on esterification (*Zeitsch. physikal. Chem.*, 1907, 60, 728).

Ultimately, a mode of directly comparing the ratio of free (unsolvated) hydrogen ions in alcohol and water, respectively, would have much interest. In considering the interpretation of the data available for the effect produced by change of solvent from alcohol to water, it is probable that for a highly dilute solution the thermodynamic potential of any single chemical individual (for example, H^+ , the free, hypothetical, unsolvated hydrogen ion) is given by the above expression, $RT \cdot \ln \frac{k_1 n_1}{\Sigma n}$, and that k_1 is practically independent of the nature of the solvent. The thermodynamic potential of the hydrogen ions would thus become identical in the two media when $\frac{n_1}{\Sigma n} = \frac{n'_1}{\Sigma n'} \left[\text{or } \frac{n_1}{n_0} = \frac{n'_1}{n'_0} \text{ in highly dilute solution} \right]$, where n_1 , n'_1 are the numbers of free hydrogen ions, Σn and $\Sigma n'$ are the total number of molecules present, and n_0 and n'_0 the total number of solvent molecules.

The imperfect state of our knowledge of the true association factors of liquids precludes any comparison being made between the numbers of free hydrogen ions present in any alcoholic and aqueous solutions.

ADDENDUM.

Direct Determination of Transport Number of Hydrion and Lithion in Alcoholic Solutions of Hydrogen and Lithium Chlorides.

This magnitude has repeatedly been discussed, but no experimental data on its direct determination have yet been published. Mr. R. T. Hardman has made a large number of determinations at

25° in the author's laboratory, using an apparatus similar to that figured in Ostwald-Luthers' "Physicochemische Messungen" (3rd edition, 1910, p. 504), but with the left-hand tube in U-form, detachable, and provided with a ground-glass plug at the junction. The following were the last series of numbers obtained, the last four representing the results of experiments with the most dilute solution of alcoholic hydrogen chloride it was found possible to deal with. The solution in the cathode compartment was removed at the end of each experiment, measured, then diluted to a definite alcohol-water concentration, and its strength carefully determined by titration with standard alkali free from carbonate. In all instances the composition of the solution in the middle of the cell was checked in similar manner at the end of the experiment, and found to be unaltered.

In the table, a was the total volume of cathode solution removed for analysis; b was the initial concentration of the alcoholic hydrogen chloride in gram-molecules per litre; c was its final concentration; d the increase in weight of the copper plates used as voltameter, and $(1-n)$ the value of the transport number of hydrion deduced from the data. In experiment (v), however, a hydrogen voltameter was used, and here the volume of moist hydrogen is given under d :

	a .	b .	c	d .	$(1-n)$.
(i)	60.2 c.c.	0.8360	0.797	0.230	0.32
(ii)	60.0 "	0.1110	0.0982	0.0746	0.31
(iii)	61.5 "	0.1110	0.0988	0.0783	0.30
(iv)	61.0 "	0.1110	0.0987	0.0691	0.29
(v)	60.0 "	0.1110	0.0982	$\left\{ \begin{array}{l} 29.7 \text{ c.c. moist} \\ \text{H}_2 \text{ at } 17^\circ \\ \text{and } 757 \text{ mm.} \end{array} \right.$	0.32
Average.....					= 0.31

A series of experiments was also made in which the concentration of the cathode mixed liquor was determined by comparing its conductivity with that of the initial solution. The results, which are certainly much less trustworthy than the above numbers, gave a mean value for $(1-n)=0.37$. In similar manner, Mr. J. I. Crabtree has very carefully determined the value of the migration ratio of lithion and chloridion in absolute alcohol; his numbers for $(1-n)$ varied from 0.63 in $N/5$ -solution to 0.65 in $N/25$ -solution, and thus confirm the conclusions formerly deduced from the results of Völlmer and others (compare T., 1911, **99**, 1417 *et seq.*).

CHEMICAL LABORATORIES,
THE UNIVERSITY,
MANCHESTER.

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