The Acidity Function H_0 for Solutions of Trifluoroacetic Acid and Trichloroacetic Acid in Water.

By J. E. B. Randles and J. M. Tedder.

[Reprint Order No. 5799.]

The acidity function H_0 has been determined for solutions of trifluoroacetic and trichloroacetic acid in water. The readings show that, although in very dilute aqueous solution both acids are barely distinguishable from strong acids, in more concentrated solutions they are appreciably associated. In concentrations greater than 25%, the dielectric constant of the solution appears to have an appreciable effect on the acidity, as measured by H_0, the effect being more marked with trichloroacetic than with trifluoroacetic acid solutions.

The acidity function H_0, introduced by Hammett and Deyrup (*J. Amer. Chem. Soc.*, 1932, **54**, 2721), measures the tendency of a solution to donate a proton to a neutral base.

$$H_0 = \mathrm{p}K + \log([\mathrm{B}]/[\mathrm{BH}^+]) \qquad (1)$$

This function has proved of considerable value in studies of the mechanism of acid-catalysed reactions, and its use has recently received considerable attention. In searching for a tool with which to study the mechanism of the synthetic reactions of trifluoroacetic anhydride, it was thought that the determination of the acidity function of various solutions of trifluoroacetic acid might prove of value, particularly in view of Mackenzie and Winter's studies (*Trans. Faraday Soc.*, 1948, **44**, 159) of the acidity function in acetic anhydride solutions. Previous work on the acidity of trifluoroacetic acid has been confined to conductometric measurements in dilute solution and the determination of the classical aqueous dissociation constant (Swarts, *Bull. Acad. roy. Belg.*, 1922, **6**, 352; Henne and Fox, *J. Amer. Chem. Soc.*, 1951, **73**, 2323). The only carboxylic acids for which the values of H_0 have been determined are pure and very concentrated formic acid (Hammett and Deyrup, *J. Amer. Chem. Soc.*, 1932, **54**, 4239) and trichloroacetic acid in relatively dilute solution (Hammett and Paul, *J. Amer. Chem Soc.*, 1934, **56**, 827).

Before describing the results of the present work, a very brief consideration of the properties of H_0 itself will greatly help to clarify subsequent discussion. In a system consisting of an acid HA in a solvent S with a neutral base B, the following equilibria are present:

$$\mathrm{HA} + \mathrm{S} \rightleftharpoons \mathrm{HS}^+ + \mathrm{A}^- \qquad (2)$$

$$\mathrm{HS}^+ + \mathrm{B} \rightleftharpoons \mathrm{HB}^+ + \mathrm{S} \qquad (3)$$

$$\mathrm{HA} + \mathrm{B} \rightleftharpoons \mathrm{HB}^+ + \mathrm{A}^- \qquad (4)$$

Equation (4) is contained in equations (2) and (3). Since $K = a_{\mathrm{B}}a_{\mathrm{H}^+}/a_{\mathrm{BH}^+}$ (cf. Hammett and Deyrup, *loc. cit.*), equation (1) can be rearranged to

$$H_0 = -\log a_{\mathrm{H}^+} - \log(f_{\mathrm{B}}/f_{\mathrm{HB}^+}) \qquad (5)$$

Throughout this discussion, dissociation constants and activity coefficients are to be referred to the standard state of infinitely dilute aqueous solution. Two extreme types of acid solution can be envisaged. When HA is a strong acid completely dissociated the following approximate equation can be written for dilute solutions :

$$H_0 \approx -\log [\text{Total Acid}] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

and when HA is a weak acid completely associated :

$$H_0 \approx -\tfrac{1}{2}\log [\text{Total Acid}] - \tfrac{1}{2}\log K_{\text{HA}} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

In these equations we neglect the activity of the solvent, and take the activity coefficients of all other constituents to be unity; they can therefore only be expected to apply in very dilute aqueous solution. Under such conditions and for small changes in concentration, H_0 plotted against the logarithm of the total acid concentration may be expected to give a curve whose maximum slope should approach unity when the acid is completely dissociated, and should diminish to a minimum of a half if the acid becomes largely associated while the solution is still relatively dilute. In concentrated solutions, the activity coefficients are changing rapidly so that these predictions will no longer hold.

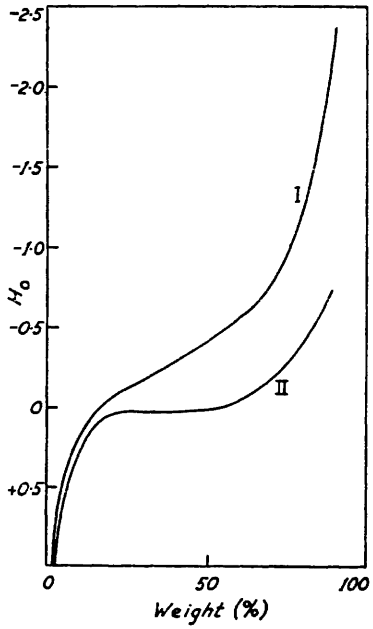
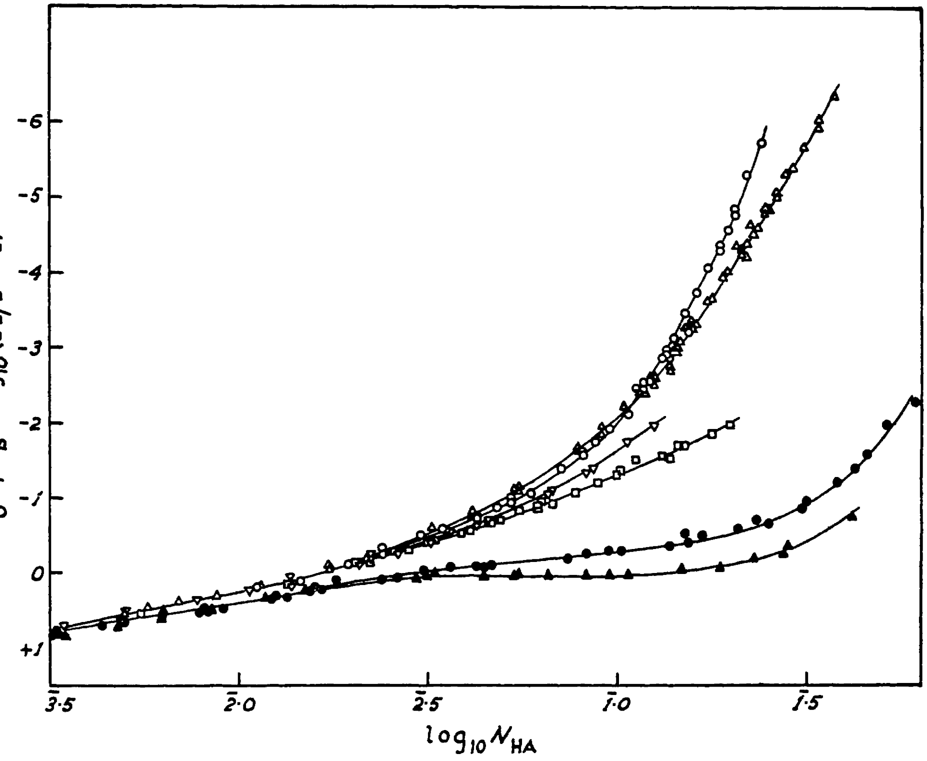


FIG. 1.

I, $CF_3{\cdot}CO_2H$. II, $CCl_3{\cdot}CO_2H$.

Fig. 1 represents H_0 plotted against percentage composition for the systems $CF_3{\cdot}CO_2H$–H_2O, and $CCl_3{\cdot}CO_2H$–H_2O. Comparison of Fig. 1 with the curves previously reported for perchloric and sulphuric acid (Hammett and Deyrup, *loc. cit.*) and for phosphoric acid (Heilbronner and Weber, *Helv. Chim. Acta*, 1949, **32**, 1513) gives the impression that trifluoroacetic acid behaves very similarly to the strong acids, while trichloroacetic acid behaves anomalously. However the similarity between the curve for trifluoroacetic acid and that of the mineral acids is somewhat superficial as can be seen from Fig. 2, where H_0 is plotted against the logarithm of the acid concentration expressed in mole fractions. It will be seen that, in the dilute solutions, the values for the acidity functions of the mineral acids coincide, forming a linear plot, the slope of which is nearly unity, as predicted by the above discussion. At greater concentrations the activity coefficients are changing rapidly and the curves slope upwards steeply. In dilute solutions of the carboxylic acids the curve of the acidity function approaches that of the mineral acids both in the slope of the curve and in actual value. As the solutions become more concentrated, however, the slopes of their acidity curves become less, clearly indicating that the acids are appreciably associated. This is fully in accord with expectations since the classical dissociation constants of both these acids are known and are less then unity. The slope of the trifluoroacetic acid curve decreases, until between the concentrations 0·03 mole fraction and 0·15 mole fraction it is approximately linear with a slope of nearly a half. This, according to the above discussion, would indicate that the acid is almost completely associated in this region. Assuming this to be so, an approximate value of 0·7 for the dissociation constant of trifluoroacetic acid can be calculated from equation (7). This is in reasonable agreement with value of 0·59 obtained by Henne and Fox (*loc. cit.*) using a much more precise method. Though it appears, on a preliminary inspection, that the behaviour of the acidity function for solutions of trifluoroacetic acid is in accord with the initial discussion, this is not the case with trichloroacetic acid. Between the concentration 0·03 mole fraction and 0·1 mole fraction, Fig. 2 (25—50%, Fig. 1), the acidity function remains constant instead of increasing along a line parallel to that of trifluoroacetic acid as would be expected from equation (7). This exceptional behaviour of trichloroacetic acid was first observed by Hammett and Paul (*loc. cit.*) who offered no comment (the actual value of H_0 when constant, reported by these workers, is considerably higher, *i.e.*, the acidity less, then that reported here). Experiments have been made to ensure that the observed concentrations of the indicator, by which H_0 was determined, were real concentrations and that medium effects were not altering the validity of the optical measurements (see p. 1222). Hammett has drawn attention to the fact that H_0 becomes more dependent on the medium than on the intrinsic acidity of the solute acid when the dielectric constant is low. Clearly the work required for donation of a proton to a neutral base, thus creating a positive and a negative ion, is greatly increased by a decrease in dielectric constant. This problem has been discussed by James and Knox (*Trans. Faraday Soc.*, 1950, **46**, 254) but a somewhat different approach will be made here. The dielectric constant of trichloroacetic acid is very low ($\epsilon_{60} = 4{\cdot}55$; Walden, *Z. physikal. Chem.*, 1910, **70**, 569). Thus it seems reasonable to suggest that the abnormal behaviour of the acidity function H_0 in moderately concentrated trichloroacetic acid may be explained by the rapid decrease of the dielectric constant of these solutions. If so, then the acidity function measuring the tendency of a solution to transfer a proton to a base with a negative charge, called H_- by Hammett (cf. " Physical Organic Chemistry," McGraw Hill, New York, 1940, p. 269), should be affected in the opposite manner since this process results in a neutralisation of charges. This hypothesis has been tested

FIG. 2.



○ $HClO_4$ and △ H_2SO_4 (from Hammett and Deyrup). ▽ HCl and □ HNO_3 (from Hammett and Paul). ● $CF_3{\cdot}CO_2H$ and ▲ $CCl_3{\cdot}CO_2H$ (present investigation). (For density tables see " International Critical Tables," McGraw-Hill, New York, 1928, Vol. III, pp. 54, 58.)

experimentally by using picric acid as indicator, and the results are shown in Fig. 3. It will be seen that in dilute solution the slopes of the H_0 and H_- curves for trichloroacetic acid are identical. In the more concentrated solutions, where the slope of the H_0 curve flattens off, the slope of the H_- curve increases and seems to confirm the above hypothesis. The slope of the H_- curve of trifluoroacetic acid also becomes greater than that of the corresponding H_0 curve, but the difference between the two is less than that between the two trichloroacetic acid curves. This is in conformity with, and probably due to, the fact that the dielectric constant of trifluoroacetic acid, though fairly low ($\varepsilon_{25} = 8{\cdot}2$; Dannhauser and Cole, *J. Amer. Chem. Soc.*, 1952, **74**, 6105; cf. also Tedder, *J.*, 1954, 2646), is higher than that of trichloroacetic acid.

In conclusion it can be said that neither of these carboxylic acids is as strong as is frequently suggested. Although in very dilute aqueous solution they become almost indistinguishable from strong acids, they are appreciably associated in moderate concentrations. These findings are in accord with their classical dissociation constants (trifluoroacetic acid, $K = 5{\cdot}88 \times 10^{-1}$, Henne and Fox, *loc. cit.*; trichloroacetic acid, $K = 2{\cdot}5 \times 10^{-1}$, Drucker, *Z. physikal. Chem.*, 1904, **49**, 563; 1920, **96**, 381). A recent suggestion that trifluoroacetic acid is nearly as strong as or stronger than nitric acid (Emeléus, Haszeldine, and Paul, *J.*, 1954, 881) is clearly misleading. Finally, it can be said that in concentrations greater than 25% in water, the low dielectric constants of these acids appear to have a considerable effect on their acidity as determined by acidity functions, and therefore this effect may also be expected to make itself felt in the catalytic properties of these solutions.

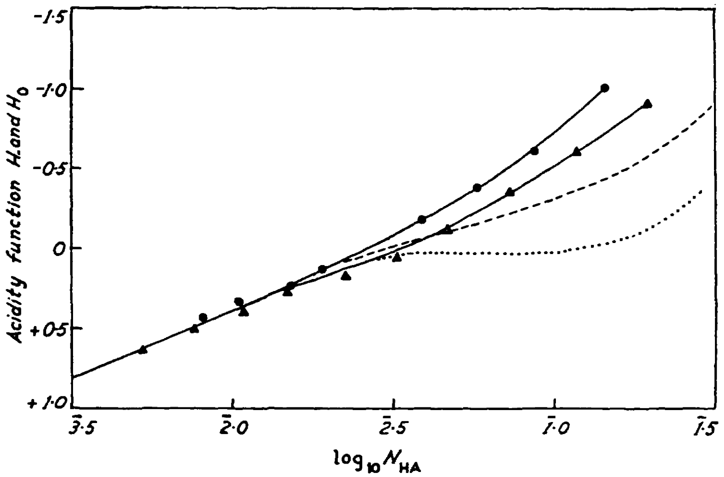


FIG. 3.

● H_- in $CF_3{\cdot}CO_2H$.
▲ H_- in $CCl_3{\cdot}CO_2H$.
--- H_0 in $CF_3{\cdot}CO_2H$.
.... H_0 in $CCl_3{\cdot}CO_2H$.

EXPERIMENTAL

H_0 was calculated from equation (1), the ratio $[B]/[BH^+]$ being determined by colorimetric measurements, and the pK of *p*-nitroaniline was taken to be 1·11 (Hammett and Paul, *loc. cit.*), while the pK of the other indicators was determined by comparison (Hammett and Deyrup, *loc. cit.*).

Preparation of the Solutions.—The appropriate indicator was first dissolved in water (*ca.* 0·02 g./l.). Two portions (10 c.c.) of this solution were placed into two graduated flasks (100 c.c.), one of which was made up to the mark with distilled water, the other with trifluoroacetic acid (or very concentrated trichloroacetic acid). A portion of the acid solution was placed in a ground-stoppered flask, to which measured portions of the aqueous solution were added from a burette. After the mixture had been shaken, a sample was withdrawn and run into a tared cell from the spectrophotometer. After the colorimetric measurements had been made, the whole cell was weighed and the solution quantitatively washed out and titrated with alkali. This served to determine the concentration of the acid in the solution, the small concentration of indicator being neglected.

Purity of the Reagents.—Commercial trifluoroacetic acid was redistilled and the centre fraction (b. p. 38·7—39·0°) was used for the acidity measurements. " AnalaR " trichloroacetic acid was used without further purification. The basic indicators were recrystallised three times from aqueous acetone; *p*-nitroaniline had m. p. 148°, *o*-nitroaniline, m. p. 71—72°, and 4-chloro-2-nitroaniline, m. p. 116—117°. Picric acid was recrystallised from hot water, and had m. p. 122—123°.

Colorimetric Measurements.—For each solution prepared as above, a solution with identical acid concentration, but without indicator, was also prepared. By using the two solutions in conjunction the extinction coefficient of the indicator solutions was obtained directly by means of a Cambridge " SP 500 Unicam " spectrophotometer ($\varepsilon = \log I/I_0$; I = transmission coefficient of the acid solution with indicator; I_0 = transmission coefficient of the same solution without indicator). Readings were taken at a fixed wave-length for any one indicator. From these readings the ratios [B]/[BH$^+$] were calculated by applying Beer's law. If ε_B, ε_{BH^+}, and ε_x are the extinction coefficients of the solution of the un-ionised base, the completely ionised base, and the unknown solution, respectively, then the indicator ratio for the unknown solution can be expressed as: $[BH^+]/[B] = (\varepsilon_B - \varepsilon_x)/(\varepsilon_x - \varepsilon_{BH^+})$ (in practice ε_{BH^+} was always negligible).

H_0 for the System Trifluoroacetic Acid–Water.—See Table 1.

TABLE 1.

$N_{CF_3\cdot CO_2H}$ *	Log N	Log ([BH$^+$]/[B])	H_0	$N_{CF_3\cdot CO_2H}$ *	Log N	Log ([BH$^+$]/[B])	H_0
			(*a*) *p*-Nitroaniline. pK = 1·11.				
0·00071	$\bar{4}$·85	−0·44	+1·55	0·0063	$\bar{3}$·79	+0·54	+0·57
0·00081	$\bar{4}$·91	−0·39	+1·50	0·0082	$\bar{3}$·91	+0·66	+0·45
0·00100	$\bar{3}$·00	−0·22	+1·33	0·0083	$\bar{3}$·92	+0·62	+0·49
0·00104	$\bar{3}$·02	−0·18	+1·29	0·0092	$\bar{3}$·96	+0·65	+0·46
0·0014	$\bar{3}$·14	−0·07	+1·18	0·0122	$\bar{2}$·09	+0·78	+0·33
0·0016	$\bar{3}$·21	+0·05	+1·06	0·0135	$\bar{2}$·13	+0·79	+0·32
0·0023	$\bar{3}$·37	+0·20	+0·91	0·015	$\bar{2}$·19	+0·88	+0·23
0·0032	$\bar{3}$·51	+0·29	+0·82	0·016	$\bar{2}$·20	+0·90	+0·21
0·0033	$\bar{3}$·52	+0·34	+0·77	0·018	$\bar{2}$·26	+1·01	+0·09
0·0034	$\bar{3}$·53	+0·30	+0·81	0·024	$\bar{2}$·38	+1·02	+0·07
0·0044	$\bar{3}$·64	+0·43	+0·68	0·037	$\bar{2}$·56	+1·19	−0·08
0·0049	$\bar{3}$·69	+0·52	+0·59	0·074	$\bar{2}$·87	+1·31	−0·20
0·0050	$\bar{3}$·70	+0·44	+0·66	0·134	$\bar{1}$·14	+1·48	−0·37
			(*b*) *o*-Nitroaniline. pK = −0·13.				
0·0080	$\bar{3}$·90	−0·64	+0·51	0·042	$\bar{2}$·63	−0·03	−0·10
0·0125	$\bar{2}$·10	−0·42	+0·29	0·047	$\bar{2}$·67	−0·03	−0·10
0·016	$\bar{2}$·20	−0·31	+0·18	0·083	$\bar{2}$·92	−0·14	−0·27
0·026	$\bar{2}$·42	−0·18	+0·05	0·094	$\bar{2}$·98	−0·19	−0·32
0·031	$\bar{2}$·49	−0·08	−0·05	0·150	$\bar{1}$·18	−0·41	−0·54
			(*c*) 4-Chloro-2-nitroaniline. pK = − 0·94.				
0·045	$\bar{2}$·65	−0·85	−0·09	0·31	$\bar{1}$·49	−0·06	−0·88
0·102	$\bar{1}$·01	−0·64	−0·30	0·32	$\bar{1}$·50	+0·03	−0·97
0·155	$\bar{1}$·19	−0·51	−0·43	0·38	$\bar{1}$·58	+0·31	−1·25
0·17	$\bar{1}$·23	−0·46	−0·48	0·46	$\bar{2}$·66	+0·67	−1·61
0·21	$\bar{1}$·32	−0·33	−0·61	0·52	$\bar{1}$·71	+1·06	−2·00
0·25	$\bar{1}$·40	−0·27	−0·67	0·62	$\bar{1}$·79	+1·37	−2·31

* In this and other Tables, N = mole fraction.

H_0 for the System Trichloroacetic Acid–Water.—Several experiments were carried out to investigate the possibility that the flat portion of the trichloroacetic acid curve was due to changes in the absorption of light not directly associated with a change in the concentration of un-ionised indicator. The first possibility considered was a shift of the wave-length of the absorbing band. The absorption maximum was at 415 mμ for a solution of *p*-nitroaniline in water, in 50% trichloroacetic acid the band had shifted to 425 mμ, and in 90% acid to *ca.* 430 mμ. As the band is very broad and readings were taken at 418 mμ, this slight shift could not account for the apparent decrease in concentration of the pure base. The second possibility considered was a solvent effect causing a decrease in adsorption without any shift in the wave-length. Neutral trichloroacetate ion was found to have no effect on the absorption of the pure base. For results see Table 2.

TABLE 2.

$N_{\text{CCl}_3\cdot\text{CO}_2\text{H}}$	Log N	Log ([BH⁺]/[B])	H_0	$N_{\text{CCl}_3\cdot\text{CO}_2\text{H}}$	Log N	Log ([BH⁺]/[B])	H_0
(*a*) *p*-Nitroaniline. pK = 1·11.							
0·0025	$\bar{3}$·40	+0·13	+0·98	0·044	$\bar{2}$·65	+1·08	+0·03
0·0035	$\bar{3}$·54	+0·28	+0·83	0·053	$\bar{2}$·73	+1·08	+0·03
0·0047	$\bar{3}$·68	+0·40	+0·71	0·065	$\bar{2}$·82	+1·08	+0·03
0·0063	$\bar{3}$·80	+0·53	+0·58	0·083	$\bar{2}$·92	+1·08	+0·03
0·0085	$\bar{3}$·93	+0·64	+0·47	0·108	$\bar{1}$·03	+1·10	+0·01
0·012	$\bar{2}$·07	+0·81	+0·30	0·15	$\bar{1}$·17	+1·17	−0·06
0·015	$\bar{2}$·18	+0·89	+0·22	0·23	$\bar{1}$·36	+1·33	−0·22
0·031	$\bar{2}$·50	+1·08	+0·03	0·28	$\bar{1}$·45	+1·48	−0·37
(*b*) *o*-Nitroaniline. pK = − 0·24.							
0·0063	$\bar{3}$·80	−0·72	+0·48	0·096	$\bar{2}$·98	−0·27	+0·03
0·030	$\bar{2}$·47	−0·30	+0·06	0·19	$\bar{1}$·27	−0·15	−0·09
0·033	$\bar{2}$·52	−0·24	0·00	0·27	$\bar{1}$·44	+0·05	−0·29
0·055	$\bar{2}$·74	−0·27	+0·03	0·42	$\bar{1}$·62	+0·54	−0·78

H_- for the Systems Trifluoroacetic Acid–Water and Trichloroacetic Acid–Water.—For results see Table 3.

TABLE 3.

$N_{\text{CF}_3\cdot\text{CO}_2\text{H}}$	Log N	Log ([XH]/[X⁻])	H_-	$N_{\text{CF}_3\cdot\text{CO}_2\text{H}}$	Log N	Log ([XH]/[X⁻])	H_-
Picric acid. pK = 0·04.*							
0·0081	$\bar{3}$·91	−0·40	+0·44	0·039	$\bar{2}$·59	+0·22	−0·18
0·0106	$\bar{2}$·02	−0·29	+0·33	0·057	$\bar{2}$·76	+0·40	−0·38
0·015	$\bar{2}$·18	−0·20	+0·24	0·087	$\bar{2}$·94	+0·65	−0·61
0·019	$\bar{2}$·28	−0·09	+0·13	0·14	$\bar{1}$·16	+1·05	−1·01
$N_{\text{CCl}_3\cdot\text{CO}_2\text{H}}$	Log N	Log ([XH]/[X⁻])	H_-	$N_{\text{CCl}_3\cdot\text{CO}_2\text{H}}$	Log N	Log ([XH]/[X⁻])	H_-
0·0052	$\bar{3}$·72	−0·56	+0·64	0·032	$\bar{2}$·51	−0·02	+0·06
0·0076	$\bar{3}$·88	−0·47	+0·51	0·047	$\bar{2}$·67	+0·16	−0·12
0·0108	$\bar{2}$·03	−0·36	+0·40	0·073	$\bar{2}$·86	+0·40	−0·36
0·015	$\bar{2}$·17	−0·23	+0·27	0·12	$\bar{1}$·07	+0·65	−0·61
0·023	$\bar{2}$·35	−0·14	+0·18	0·20	$\bar{1}$·29	+0·95	−0·91

* This value was chosen so that the values of H_0 and H_- should coincide in the dilute region.

We thank Dr. J. C. Tatlow for his interest, and one of us (J. M. T.) is indebted to the University of Edinburgh for the award of an I.C.I. Fellowship.

DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF BIRMINGHAM.
DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF EDINBURGH. [*Received, October 12th,* 1954.]