The Conductometric Evaluation of the Ionisation Functions of the Monohalogenoacetic Acids.

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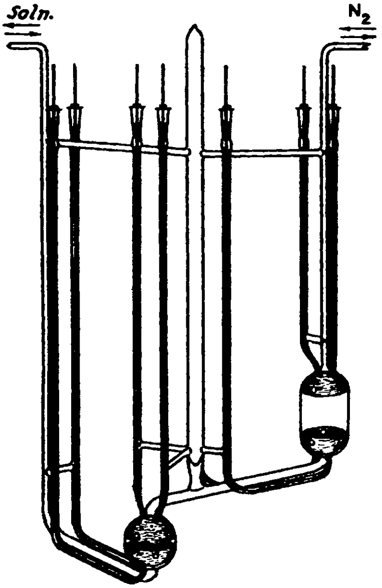
Conductance measurements of high accuracy on aqueous solutions of fluoro-, chloro-, bromo-, and iodo-acetic acids at 5° intervals between 15° and 35° are reported. Changes in Gibbs free energy, enthalpy, entropy, and heat capacity accompanying the dissociation of these acids have been calculated. The results are discussed in terms of the factors which determine acid strength.

Comparatively few dissociation constants of weak electrolytes have been determined as functions of temperature accurately enough for the changes in enthalpy, entropy, and heat capacity accompanying dissociation to be evaluated. All the data so far available have been obtained by the well-known E.M.F. method of Harned *et al.*, and none (except for the classical work of Schaller, *Z. physikal. Chem.*, 1898, **25**, 497) has been determined by conductance measurements. The conductance method, however, has the advantages that it approaches more closely to a purely physical method, and that it is economic of material, expeditious, and accurate. These points are illustrated in the present paper.

It is surprising that there are no satisfactory dissociation-constant data covering a range of temperatures for the four monohalogenoacetic acids, since such data would be of particular interest in studying the effects of polar substituents on acid strength. No doubt this is due to the limited availability and high toxicity of fluoroacetic acid (Saunders and Stacey, *J.*, 1948, 1773) on the one hand, and, on the other, to the tendency of the other three acids to hydrolyse, with elimination of halogen, in aqueous solution. This reaction is catalysed by silver ions and occurs rapidly at the surface of solid silver halides (Cowdrey, Hughes, and Ingold, *J.*, 1937, 1243). Use of Harned's method, involving silver–silver chloride electrodes, is therefore precluded and, very probably, an analogous method using calomel electrodes would also be unsuitable for a similar reason. It therefore seemed desirable to devise and apply a conductance method to the investigation of these acids.

It was foreseen that very accurate measurements would be necessary. The tendency to hydrolysis is enhanced in solutions of the sodium salts, and this excluded the normal procedure of obtaining ionic mobilities. Measurements on solutions of pure acids alone, therefore, had to be relied upon to provide both dissociation constants and equivalent conductances at zero concentration. All the methods designed for this purpose involve extrapolation to zero concentration and are consequently highly sensitive to systematic experimental errors. At the same time the determination of ΔH, since it is a function of the first derivative of $\ln K$ with respect to temperature, is more sensitive to errors of measurement than $\ln K$ itself. Taking these factors into account, it was judged that a limit of error of $\pm 0{\cdot}01\%$ must be set for the conductance measurements, with similarly stringent requirements for purity of materials and accuracy in the measurement of concentration and temperature.

Since the development of the conductance method to the necessary standards of accuracy forms an important part of the contribution made by the present paper, an outline is given of the essentials of the technique by which this was achieved. Whilst the main factors in the design of conductance cells and of A.C. bridges necessary to avoid systematic errors have been well understood for over 20 years, some unsatisfactory features remain, and these required special attention. Thus, although the frequency dependence of conductance measurements has been reduced to limits judged by various authors as adequate for their purposes, there is no satisfactory evidence that it has ever been entirely eliminated. Excluding gross sources of error such as the "Parker effect," the main difficulty is associated with so-called "polarisation effects" at the electrodes of the conductance cells. There can be no doubt that the essential electrical analogue of a conductance cell is a large condenser in series with an ohmic resistance, the small sinusoidal



current being carried across each interface, not by reversible ion-discharge processes, but by the very large capacity provided by the ionic double layer which resides at the interface. For high accuracy of measurement, these capacities should offer negligibly small reactance compared with the ohmic resistance of the electrolytic conductor, a condition which cannot be completely satisfied experimentally. This view is supported by the very marked effect of black platinisation of the electrodes in reducing frequency dependence; this device, however, cannot be tolerated for other reasons. The difficulty has been obviated in the present work by designing the cell shown in the Figure; this is discussed in detail in the Experimental section. It will be seen that the cell is a double one, the two parts being as nearly identical as possible, except for the distance between the electrodes, which are made from grey-platinised platinum spherical cups. All significant conductance measurements were derived from ***differences*** between the apparent resistances of the two parts of the cell when filled with the same solution, so that polarisation effects should be cancelled completely. Because of the difficulty of preparing two grey-platinised platinum electrodes of absolutely identical properties, this cancellation was not in fact complete, and these resistance differences retained a very small frequency dependence. The residual effect, however, seldom exceeded 0·01% within the frequency range 1150—3880 c./sec. and it was eliminated by a simple extrapolation to infinite frequency. The eminently satisfactory results of this procedure are apparent from the cell constants recorded in Table 1, in which " constants " calculated from the apparent resistances at infinite frequency of the two parts of the double cell and from the difference between these resistances are shown. Potassium chloride solutions at 25° were used for these calibrations, the extended Onsager equation (Shedlovsky, Brown, and MacInnes, *Trans. Electrochem. Soc.*, 1934, **66**, 165), with values of coefficients supplied by Gunning and Gordon (*J. Chem. Physics*, 1942, **10**, 126), being used to interpolate conductance values appropriate to the concentrations used. The equation was

$$(\Lambda + 60{\cdot}18\sqrt{C})/(1 - 0{\cdot}2289\sqrt{C}) = 149{\cdot}88 + 153{\cdot}7C + 32{\cdot}1C \log C \quad . \quad (1)$$

TABLE 1.

$C \times 10^4$	Λ	" Constant " of large cell	" Constant " of small cell	Ratio : large/small	Constant of double cell
106·299	141·08	0·46429	0·11680	3·9751	0·34749
74·5656	142·34	0·46422	0·11677	3·9755	0·34745
49·1596	143·64	0·46426	0·11678	3·9755	0·34748
36·6060	144·44	0·46433	0·11683	3·9744	0·34750
14·9472	146·32	0·46427	0·11683	3·9739	0·34744
13·0958	146·54	0·46430	0·11683	3·9742	0·34747
5·85475	147·62	0·46432	0·11687	3·9730	0·34745
4·31205	147·94	0·46435	0·11687	3·9732	0·34748
				Mean :	0·34747 ± 0·00002

The final constants, over a wide range of concentrations, show a variance of only ±0·005%, with no perceptible systematic trend. Since these constants are, in effect, referred to conductance standards obtained by a high-precision direct-current method, there can be no doubt that frequency effects and all other systematic errors have been eliminated from our measurements. It can readily be shown that no significant alteration of cell constant with temperature occurred within the range of temperature used in our measurements; the cell constant also showed no change with time.

Other points relevant in characterising the method, described in detail in the Experimental section, may be mentioned. The need to set up a bridge of high precision for the conductance measurements suggested the advantage of platinum-resistance thermometry to establish the absolute temperature scale required. A thermometer for this purpose was constructed and calibrated against ice, steam, and the transition point of sodium sulphate. The readings of this thermometer were subsequently checked against N.P.L.-calibrated mercury-in-glass thermometers, with agreement consistent with errors in temperature of less than 0·002°. The " four-leads " connection system, used in modern resistance thermometry, was applied to the conductance measurements with very great advantage, since all leads and contact resistances were completely eliminated, thus allowing distribution switches of the normal type to be used for selecting cells or inserting shunts.

All solutions were prepared with water of average specific conductance $0{\cdot}1 \times 10^{-6}$ ohm^{-1} and were manipulated by pressure of highly purified nitrogen in a totally enclosed, all-glass apparatus. Each solution examined was prepared from independently weighed amounts of solute and solvent, all weighings being corrected to vacuum and to recent N.P.L. standards of mass. Each solute was rigorously purified by repeated crystallisation and fractional vacuum sublimation. Two samples were taken at different stages of the purification procedure and an equal number of solutions was prepared from each. In no case could the slightest discrimination be made between these samples within the limits of accuracy of the conductance measurements. For each solute, particular attention was paid to the rate of hydrolysis in solution. Measurements were made in order of increasing temperature and, periodically, the lowest temperature measurement was repeated. No significant change occurred during the period of the measurements, namely, 5 hours. In view of the labour involved in making large numbers of measurements at different temperatures, the measurements were restricted to four solutions of each solute, two from each sample, suitably spaced in concentration, at 5° intervals between 15° and 35°. A preliminary set of determinations with chloroacetic acid, and a general assessment of accuracy, indicated that this would be adequate.

Calculations of dissociation constants and of equivalent conductances at zero concentration were made by the method of Ives (*J.*, 1933, **731**), based upon the Ostwald dilution law, the Onsager equation, and the Debye–Hückel limiting law.

The method is summarised in the equation

$$\Lambda + a\sqrt{C_i} = \Lambda_0 - \Lambda^2 C \,.\, 10^{-2A\sqrt{C_i}}/K(\Lambda_0 - a\sqrt{C_i}) \quad . \quad . \quad . \quad (2)$$

where a is the " Onsager slope," A the Debye-Hückel coefficient, and the other symbols have their usual significance. The method consists in finding by successive approximation the value of Λ_0 which, when incorporated in the quantity $x = \Lambda^2 C \,.\, 10^{-2A\sqrt{C_i}}/K(\Lambda_0 - a\sqrt{C_i})$ (with appropriate adjustments of the values of a and C_i), gives, on linear extrapolation to zero concentration, a limiting value of $y = \Lambda + a\sqrt{C_i}$ which is identical with the same value of Λ_0. Each successive extrapolation until this end is secured is carried out by the method of least squares. Values of the Onsager slopes and Debye–Hückel constants for the various temperatures used were calculated from Birge's fundamental constants (*Rev. Mod. Phys.*, 1941, **13**, 233), Wyman's dielectric constant data (*Phys. Rev.*, 1930, **35**, 623), and Bingham and Jackson's viscosity data (*Bull. Bur. Stand.*, 1918, **14**, 75), and these are shown in Table 2. Large-scale graphical plots of equation (2) showed no deviations from strict linearity, and this is confirmed by the satisfactory constancy of the dissociation constants subsequently calculated for each concentration. The experimental equivalent conductances, Λ_0 values, and dissociation constants (in units mole l.$^{-1}$) are shown in

TABLE 2.

Temp.	Debye–Hückel constant, A	Onsager slope, a	Temp.	Debye–Hückel constant, A	Onsager slope, a
15°	0·50028	$0{\cdot}22485\ \Lambda_0 + 46{\cdot}942$	30°	0·51405	$0{\cdot}23104\ \Lambda_0 + 67{\cdot}466$
20	0·50456	$0{\cdot}22678\ \Lambda_0 + 53{\cdot}418$	35	0·51925	$0{\cdot}23338\ \Lambda_0 + 75{\cdot}019$
25	0·50908	$0{\cdot}22883\ \Lambda_0 + 60{\cdot}252$			

Table 3. Log Λ_0 was found to be a linear function of $1/T$, with deviations indicating a probable error in the Λ_0 values of about 0·2%.

TABLE 3.

	Equivalent conductance				Λ_0	$K \times 10^5$
Fluoroacetic acid						
$C \times 10^4$ (25°) =	15·8752	8·72730	4·06566	2·87610		
15°	240·10	268·61	296·76	305·92	335·88	278·93 ± 0·47
20	259·05	290·47	321·68	331·78	365·45	268·43 ± 0·41
25	277·43	311·49	345·74	357·00	394·20	259·59 ± 0·51
30	294·83	331·67	369·14	381·62	422·77	249·01 ± 0·43
35	311·10	350·80	391·56	405·29	450·70	237·86 ± 0·46
Chloroacetic acid						
$C \times 10^4$ (25°) =	27·8318	18·4848	11·4377	5·61169		
15°	171·04	193·83	220·40	257·10	334·30	142·98 ± 0·10
20	184·40	209·31	238·21	278·15	363·39	139·44 ± 0·11
25	197·32	224·04	255·32	298·65	392·01	135·94 ± 0·11
30	209·43	237·90	271·66	318·60	421·16	130·79 ± 0·01
35	220·73	251·03	287·15	337·48	449·34	125·94 ± 0·05
Bromoacetic acid						
$C \times 10^4$ (25°) =	28·0830	13·2823	10·2878	6·59113		
15°	165·24	206·45	220·47	243·72	331·44	133·31 ± 0·04
20	178·00	222·81	238·01	263·47	360·33	129·63 ± 0·04
25	190·06	238·33	254·87	282·47	389·03	125·30 ± 0·05
30	201·48	253·15	271·04	300·74	417·41	120·78 ± 0·07
35	212·08	267·18	286·17	318·15	445·42	115·88 ± 0·02
Iodoacetic acid						
$C \times 10^4$ (25°) =	20·8728	8·89308	6·02373	2·46310		
15°	148·02	194·62	216·36	261·81	332·45	71·90 ± 0·03
20	159·05	209·54	233·25	283·07	361·56	69·46 ± 0·02
25	169·41	223·74	249·32	303·62	390·41	66·80 ± 0·00
30	179·15	237·19	264·71	323·43	418·99	64·06 ± 0·01
35	188·19	249·78	279·24	342·37	447·10	61·26 ± 0·02

For the purpose of choosing the most representative values of the dissociation constants and of calculating the thermodynamic functions, the equation

$$\ln K = a + bT + cT^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

was fitted to the individual experimental results (*i.e.*, 20 values of ln K, from 4 solutions each at 5 temperatures) for each acid by the method of least squares. The choice of this equation was quite arbitrary and is justified solely by the fact that it fits the results within experimental error. It has been shown (Harned and Robinson, *Trans. Faraday Soc.*, 1940, **36**, 973) that several empirical formulæ fit such data equally well within the limits of accuracy in dissociation constant data yet attainable. Some of these formulæ imply that ΔC_p is independent of temperature (Everett and Wynne-Jones, *ibid.*, 1939, **35**, 1380; Briegleb and Bieber, *Z. Elektrochem.*, 1951, **55**, 250), but it is felt that this assumption can have no fundamental basis and that it might have to be discarded if sufficiently accurate measurements became available. It is hoped to explore this question in a later publication.

The results of these calculations are collected in Table 4, which shows the observed values of ln K, those calculated from the equations shown, the differences between these quantities, and the values of dissociation constants and Λ_0 finally selected. The fit of the equations was assessed in terms of the probable error in ln K, $\{\pm 0{\cdot}816\sqrt{[\Sigma q^2/(n-3)]}\}$, which had the values ±0·0024, ±0·0014, ±0·0005, and ±0·0004 for the acids in the order of Table 4. The higher error for the fluoroacetic acid results is no doubt associated with the greater difficulty in manipulating this intensely hygroscopic substance.

The thermodynamic functions of ionisation calculated from the interpolation equations are shown in Table 5. Since ΔH is derived from the temperature dependence of ln K, more uncertainty attaches to its value at the extremes of the temperature range; hence ΔH values are quoted only at 20—30°. A similar restriction applies to ΔC_p, which is thus

TABLE 4.

Temp.	ln $K_{obs.}$	ln $K_{calc.}$	Δ	$K \times 10^5$	Λ_0
Fluoroacetic acid					
	$\ln K = -9{\cdot}4581 + 0{\cdot}0313701T - 0{\cdot}00006581T^2$				
15°	−5·8820	−5·8831	+0·0011	278·6	335·9
20	−5·9204	−5·9175	−0·0029	269·2	365·4
25	−5·9538	−5·9553	+0·0017	259·2	394·2
30	−5·9955	−5·9962	+0·0007	248·8	422·8
35	−6·0413	−6·0406	−0·0007	238·0	450·7
			Mean ±0·0014		
Chloroacetic acid					
	$\ln K = -14{\cdot}4918 + 0{\cdot}0592736T - 0{\cdot}00011006T^2$				
15°	−6·5502	−6·5505	+0·0003	143·0	334·3
20	−6·5753	−6·5741	−0·0012	139·6	363·4
25	−6·6007	−6·6031	+0·0024	135·6	392·0
30	−6·6393	−6·6376	−0·0017	131·0	421·2
35	−6·6771	−6·6776	+0·0005	125·9	449·3
			Mean ±0·0012		
Bromoacetic acid					
	$\ln K = -12{\cdot}0888 + 0{\cdot}0432874T - 0{\cdot}00008436T^2$				
15°	−6·6202	−6·6200	−0·0002	133·3	331·4
20	−6·6483	−6·6488	+0·0005	129·6	360·3
25	−6·6821	−6·6818	−0·0003	125·3	389·0
30	−6·7189	−6·7190	+0·0001	120·8	417·4
35	−6·7604	−6·7604	—	115·9	445·4
			Mean ±0·0002		
Iodoacetic acid					
	$\ln K = -10{\cdot}8078 + 0{\cdot}0314747T - 0{\cdot}00006623T^2$				
15°	−7·2377	−7·2376	−0·0001	71·91	332·4
20	−7·2720	−7·2727	+0·0007	69·42	361·6
25	−7·3112	−7·3111	−0·0001	66·80	390·4
30	−7·3531	−7·3528	−0·0003	64·08	419·0
35	−7·3977	−7·3980	+0·0003	61·25	447·1
			Mean ±0·0003		

TABLE 5.

Temp.	$CH_2F{\cdot}CO_2H$	$CH_2Cl{\cdot}CO_2H$	$CH_2Br{\cdot}CO_2H$	$CH_2I{\cdot}CO_2H$
Gibbs free-energy change, ΔG (cal.)				
15°	3368	3750	3789	4143
20	3446	3828	3872	4235
25	3527	3911	3958	4330
30	3611	3997	4046	4428
35	3698	4088	4138	4529
Enthalpy change, ΔH (cal.)				
20°	−1232	− 897	−1054	−1256
25	−1390	−1123	−1239	−1416
30	−1558	−1362	−1435	−1585
Entropy change, ΔS (cal. deg.$^{-1}$)				
20°	−16·0	−16·1	−16·8	−18·7
25	−16·5	−16·9	−17·4	−19·3
30	−17·1	−17·7	−18·1	−19·8
Heat capacity change, ΔC_p (cal. deg.$^{-1}$)				
25°	−32·6	−46·4	−38·1	−32·9

quoted for 25° only. For this reason, no statement can be made concerning the temperature dependence of ΔC_p for these acids. An independent check on these results was made by plotting the observed value of ln K against $1/T$, drawing the best representative curves, and estimating their slopes graphically. The results so obtained showed mean deviations from those in Table 5 of ±0·5 cal. in ΔG, ±10 cal. in ΔH, ±0·05 cal. deg.$^{-1}$ in ΔS, and ±1 cal. deg.$^{-1}$ in ΔC_p; these deviations provide an assessment of the reliability of the data.

Comparison with existing data can only usefully be made for chloroacetic acid, for which previous dissociation constant data at 25° are listed in Table 6. It is believed that the new, somewhat lower, value is to be preferred. Greater attention has been paid to purity of materials in the present work and also, for the first time, the importance has been realised of using only freshly-prepared solutions and conducting the measurements with the least possible delay. The stock-solution method formerly used is highly disadvantageous when applied to these acids and especially to their sodium salts. Sodium chloroacetate hydrolyses faster than chloroacetic acid in aqueous solution (Senter, *J.*, 1907, **91**, **460**) at a rate which increases with rising concentration (Kastle and Keiser, *Amer. Chem. J.*, 1893, **15**, **471**), and this can be understood in terms of the complex hydrolytic reactions established for the analogous bromoacetic acid system (Dawson and Dyson, *J.*, 1933, 49, 1133; Brooke and Dawson, *J.*, 1936, 497). Although these observations relate to conditions other than those of very dilute aqueous solutions at 25°, it is quite clear that hydrolytic decomposition is a danger which attends ostensibly accurate physical measurements involving aqueous solutions of these substances. No satisfactory evidence is given in the earlier work that this hazard was successfully avoided. In the present investigation, a long series of trial measurements was made by the stock-solution method; the results were erratic and, in all cases, high compared with those finally obtained. No such trouble was encountered when each solution was made up rapidly and independently, immediately before measurement.

TABLE 6. *Data for chloroacetic acid.*

$K \times 10^5$	Method	Reference
151	Catalytic	Dawson, Hall, and Key, *J.*, 1928, 2844
141	Catalytic	Grove, *J. Amer. Chem. Soc.*, 1930, **52**, 1404
139·7	Conductance	MacInnes, Shedlovsky, and Longsworth, *Chem. Rev.*, 1933, **13**, 29
139·6	Conductance	Saxton and Langer, *J. Amer. Chem. Soc.*, 1933, **55**, 3638
137·8	E.M.F.	Wright, *ibid.*, 1934, **56**, 314
135·6	Conductance	Present investigation

The value of the mobility of the chloroacetate ion derived from the present work (42·2) is appreciably higher than the value formerly assigned (39·8). This higher value is supported by the results from two independent extrapolations on other sets of chloroacetic acid measurements which each gave 42·0 for this mobility. Further, measurements made of the conductances of freshly-prepared solutions of sodium chloroacetate containing a trace of excess of acid gave, on extrapolation of Λ against $\sqrt{C}$, a value of 41·7. (The authors record their thanks to Mr. S. F. Feates for this result.) This agreement is reasonably satisfactory, for the remaining discrepancy is within the limit of accuracy of the Λ_0 determinations previously stated.

Wright's E.M.F. method (*J. Amer. Chem. Soc.*, 1934, **56**, 314) is open to strong objection for reasons which have already been indicated. Reference to the literature (Euler, *Ber.*, 1906, **39**, 2726; Senter, *J.*, 1910, **97**, 346; Cowdrey, Hughes, and Ingold, *loc. cit.*) and experiments conducted in these laboratories on the effects of silver ion and solid silver halide on the rate of hydrolysis of chloroacetic acid solutions lead to the view that little weight can be given to these results.

DISCUSSION

To facilitate discussion, results and related data for acetic acid and the four monohalogenoacetic acids in aqueous solution at 25° are collected in Table 7.

Comment is first required on the anionic mobility values, which at first sight would seem to be anomalous. Evidence of freedom from considerable error in the conductance measurements has already been presented. The extrapolation method of treating these results is but one way of finding the unique values of Λ_0 and K for a given electrolyte consistent with the Ostwald, Onsager, and limiting Debye–Hückel laws, and its validity is not open to question any more than the fundamental laws on which it is based. The properties originally claimed for the method (Ives, *loc. cit.*) have been confirmed (Kilpatrick, *J. Chem. Phys.*, 1940, **8**, 306) and it has been tested successfully by application to some of the best available conductance data (Ives and Sames, *J.*, 1943, 511). When applied to Shedlovsky's data (*J. Amer. Chem. Soc.*, 1932, **54**, 1411) on acetic acid, it gives a value for Λ_0 of 391·0 (cf. Table 7), an agreement which is entirely satisfactory. Furthermore, the sensitivity of the method to error decreases with increasing strength of the electrolyte concerned (Belcher, *J. Amer. Chem. Soc.*, 1938, **60**, 2744). It is therefore felt that the effects of halogen substitution on the mobility of the acetate ion which are revealed by the present work are real and significant, even though their interpretation may be a matter of some difficulty. It may also be pointed out that reference to Landolt–Börnstein's " Tabellen " reveals many such " unexpected " ionic mobility relationships.

TABLE 7.

	$CH_3{\cdot}CO_2H$	$CH_2F{\cdot}CO_2H$	$CH_2Cl{\cdot}CO_2H$	$CH_2Br{\cdot}CO_2H$	$CH_2I{\cdot}CO_2H$
$K \times 10^5$	1·754 (*a*)	259·2	135·6	125·3	66·80
pK	4·7560 (*a*)	2·5864	2·8689	2·9021	3·1752
Λ_0	390·6 (*b*)	394·2	392·0	389·0	390·4
l_0	40·8	44·4	42·2	39·2	40·6
ΔG (cal.)	6487 (*a*)	3527	3911	3958	4330
ΔH (cal.)	−112 (*a*)	−1390	−1123	−1239	−1416
ΔS (cal. deg.$^{-1}$)	−22·1 (*a*)	−16·5	−16·9	−17·4	−19·3
ΔC_p (cal. deg.$^{-1}$)	−33·9 (*a*)	−32·6	−46·4	−38·1	−32·9
μ, CH_3X	—	1·81 (*c*)	1·87 (*d*)	1·80 (*d*)	1·64 (*d*)
Field strength, E	—	0·197 (*e*)	0·190 (*e*)	0·177 (*e*)	0·153 (*e*)
Bond refractivity, C–X (c.c.)	1·69 (*f*)	1·72 (*f*)	6·53 (*f*)	9·37 (*f*)	14·55 (*f*)
ΔpK/E	—	11·0	10·0	10·5	10·3

(*a*) Harned and Ehlers, *J. Amer. Chem. Soc.*, 1933, **55**, 652. (*b*) Shedlovsky, *ibid.*, 1932, **54**, 1411 (*c*) Smyth and McAlpine, *J. Chem. Physics*, 1934, **2**, 499. (*d*) Groves and Sugden, *J.*, 1937, 158. (*e*) Ives and Sames, *J.*, 1943, 513. (*f*) Syrkin and Dyatkina, " The Structure of Molecules," Butterworths, London, 1950, p. 201.

The K, pK, and ΔG values recorded show that the chloro- and bromo-acids resemble each other more closely than the other two members; this was already known from classical data and is paralleled by many other features of halogen chemistry. The other thermodynamic functions, however, show rather different relationships. Thus, $-\Delta H$ shows a minimum at the chloro-acid; $-\Delta S$, somewhat lower than for acetic acid, shows a smooth, almost asymptotic decrease from the iodo- to the fluoro-acid, whilst the $-\Delta C_p$ values show an entirely different trend, with a marked maximum at the chloro-acid. These relationships can at once be taken to indicate that the effect of polar substitution on acid strength is no simple function of purely energetic factors. Ives and Sames (*J.*, 1943, 513), using the best data then available, attempted to show that the change in acid strength (ΔpK) caused by polar substitution is directly related to the strength of the field (E) set up in the appropriate direction by the polar bond of the substituent at the position supposedly occupied by the ionising hydrogen atom of the carboxyl group. The approximate constancy of the ratio ΔpK/E which was found was taken to support the view that the substitutional influence on acid strength operates, in these cases, by a direct field effect. The new data, shown in Table 7, do not strengthen the evidence for this, the values of ΔpK/E at 25° being made somewhat less constant.

A more fundamental approach to the problem may be suggested on the basis of the equation defining ΔG as a function of temperature, namely,

$$\Delta G = \Delta H_0 + \int_0^T \Delta C_p \,.\, \mathrm{d}T - T\int_0^T \frac{\Delta C_p}{T} \,.\, \mathrm{d}T - T\Delta S_0 \quad . \quad . \quad . \quad . \quad (4)$$

in which the term ΔH_0 should properly include the electrostatic energy terms affecting the free energy of ionisation. Since, however, this term is not accessible, the next best procedure would seem to be to discuss such energy effects in terms of ΔH. If this is done for the four halogenoacetic acids on lines comparable with those just followed, the ratios of the terms ($\Delta H_{\text{unsubs.}} - \Delta H_{\text{subs.}}$) to the field strength at the site of ionisation must be examined. These are, absolute magnitudes being disregarded, 6·4, 5·3, 6·4, and 8·6 in the order fluoro- to iodo-acetic acid. This leaves no doubt that, whilst a direct field effect may, in these cases, be a major one, it is far from adequate to explain all the facts. No quantitative treatment of this problem on simple lines appears to be possible, but discussion of relative $-\Delta H$ values for the dissociation of weak acids may be profitable. The ionisation of all four halogenoacetic acids is more exothermic than that of acetic acid, in line with their greater ease of ionisation. The order of the $-\Delta H$ values, however, except for fluoroacetic acid, is the reverse of that to be expected from the field due to the substituent at the seat of ionisation. This suggests that the minimum in $-\Delta H$ which occurs at the chloro-acid is due to the joint effect of two factors, both tending to enhance acidity, one of which increases from iodo- to fluoro-acetic acid and the other in the opposite direction. The first of these must be the direct field effect, and the other is suggested by inspection of the bond refractivities shown in Table 7. For fluorine, the polarisability of the substituent is hardly greater than that of hydrogen, but it increases rapidly with the atomic number of the halogen. During ionisation, the carboxyl group in its normal or transition state will set up a field embracing the whole of the molecule, and any polarisable atom situated within the critical cone of semi-angle 55° with respect to the axis of the primary (carboxyl) dipole will develop an induced moment in such a direction as to enhance the field promoting ionisation. Similarly, for the anion, a polarisable residue will have an electrostatic effect tending to hinder the return of the proton. An analogy is to be found in the effect of a substituent olefinic or aromatic group on the strength of acetic acid (Ives, Linstead, and Riley, *J.*, **1933**, **561**; Baker, Dippy, and Page, *J.*, 1937, 1774), where the polarisability effect, if not the only one, is undoubted.

Attention may now be turned to the entropy and heat-capacity changes accompanying the ionisation of these acids. A tentative interpretation of the observed trend of these values may be based upon the assumption of the solvation of the undissociated acid molecules by virtue of the polar carbon–halogen bonds which they contain. Such dipole solvation, approaching zero for the carbon–iodine bond, is likely to increase from iodo- to fluoro-acetic acid at a rate faster than would appear from the bond moments. Such solvation will be controlled by the intensity of the field at the halogen atom, and this will be an inverse function of atomic size. In the corresponding ions, however, not only may the larger halogen atoms exercise a screening effect, sterically hindering the approach of solvent molecules to the site of the negative charge, but the presence of this charge may so modify the dipole solvation as to cause a general levelling of the effect. In other words, it seems reasonable to suppose that the molecules show a greater individuality in regard to solvation than the ions. The *increase* in the degree of solvation which accompanies ionisation may, by these arguments, be expected to be rather less for the substituted acids than for the unsubstituted acid and, in general, to run parallel with the observed values of $-\Delta S$.

TABLE 8.

Acid	M. p.	Equiv., obs.	Equiv., calc.	Acid	M. p.	Equiv., obs.	Equiv., calc.
$CH_2F{\cdot}CO_2H$	35·4—35·5°	78·03 ± 0·04	78·04	$CH_2Br{\cdot}CO_2H$	47·8—48·2°	138·95 ± 0·07	138·96
$CH_2Cl{\cdot}CO_2H$ (α-form)	62·3—62·7	94·46 ± 0·05	94·50	$CH_2I{\cdot}CO_2H$	81·6—81·9	186·00 ± 0·09	185·95

It seems evident that the endothermic desolvation process, and the new degrees of freedom of the solvent molecules which are liberated in this process, must make an important contribution to heat capacity (cf. Eigen and Wicke, *Z. Elektrochem.*, 1951, **55**, 354). Heat capacity may then be a function, *inter alia*, both of the extent and of the stability of solvation. For the anions of these acids, it has been found that the quantity ($d \ln l_0/dT - d \ln \phi/dT$), where ϕ is the fluidity of water, has values at 25° of 68, 196, 237, and 243×10^{-5} deg.$^{-1}$ for the fluoro-, chloro-, bromo- and iodo-acetate ions respectively. These figures, representing the increase of ionic mobility over and above that due to the increase of fluidity, possibly give some indication of the relative vulnerability of these ions to desolvation with rise of temperature. If, then, desolvation should contribute significantly to the heat capacity of the ionised system, ΔC_p for ionisation should decrease in its negative value in this order. This appears to be the case, except that the fluoro-compound, as is so often the case, is exceptional. But molecular dipole solvation has already been suggested as a factor significantly affecting the entropy of ionisation, and this is as likely to affect ΔC_p. If the heat capacity of the un-ionised system is influenced mainly by the extent of this, probably rather unstable, kind of solvation, this would again be consistent with the same trend of ΔC_p values. In this case, however, the exceptional behaviour of fluoroacetic acid finds a possible explanation in a special stability of the dipole solvation centred on the fluorine atom, for hydrogen bonding might well be involved. The fact that the lower alkyl fluorides " are somewhat unexpectedly soluble in water " (Dyson, " Manual of Organic Chemistry," Longmans, 1950, p. 231) may be relevant in this connection.

Although much of the above discussion is tentative and exploratory, it emphasises the probability that all the terms contained in equation (4) have their own physical significance as factors which determine acid strength.

EXPERIMENTAL

The Bridge.—An oscillator of the type used by Shedlovsky (*J. Amer. Chem. Soc.*, 1930, **52**, 1793), giving an output at eight frequencies from 1150 to 5250 c./sec., of very low harmonic content, was loosely inductively coupled to a feeder circuit consisting of two 1000-ohm potentiometers spanning the oscillator input. Between the moving contacts of these potentiometers there was available a signal of any desired phase and amplitude on either side of earth potential. This simple device has considerable advantages. The r.m.s. potential difference supplied to the bridge was measured by means of an instrument rectifier and a suitable micro-ammeter incorporated in the feeder unit; the latter supplied a Wagner earthing circuit of conventional design. The bridge ratio arms consisted of two 1000-ohm Cambridge Constantan non-inductive resistors connected together by means of a shunted potentiometer designed to adjust the ratio to equality within one part in 10^6. A Cambridge Constantan decade resistance box, adjustable to 0·0001 ohm, was used, and this was internally calibrated periodically during the course of this work and compared, by a D.C. method, with a standard box kindly lent by Dr. H. R. Nettleton. The Cambridge box was found to have zero temperature coefficient; its frequency dependence was also zero, except for the 1000-ohm decade, so that separate calibration at different frequencies was necessary only in this case. Frequent routine cleaning of the box contacts was found to be essential. Provision was made for shunting either bridge arm with mica or air condensers. The output from the bridge was fed to an amplifier (Ives and Pittman, *Trans. Faraday Soc.*, 1948, **44**, 644) of sensitivity adequate to allow bridge settings to one part in 10^6. The bridge was used alternatively for platinum thermometry, and all resistance measurements were made by the " four-leads " method (Smith, *Phil. Mag.*, 1912, **24**, 541; Mueller, *Bull. Bur. Stand.*, 1916/17, **13**, 547). The switch-gear for selecting either component of the double cell or the thermometer, for providing the shunts necessary for measuring very high resistances (*e.g.*, of cells containing conductance water), or for the reversals of connections involved in the " four-leads " method fell into two categories. The switches of which the contact resistances were cancelled by the " four-leads " method were of the ordinary multipole radio type; the others were mercury switches using conductors of very heavy cross-section. A residual correction of +0·0019 ohm for uncancelled leads resistance was applied where significant. The advantages of this system have already been mentioned and its success was checked by measurements of series–parallel resistance networks set up from individually-measured components; observed and calculated resistances invariably agreed to the highest order of accuracy. This device also provided a check on the accuracy of the box calibration.

Temperature Measurement.—No description could be found of a resistance thermometer of adequate sensitivity, and none was available commercially. A brief description of a thermometer made for the purpose, in accordance with the criteria given by Mueller (" Temperature, its Measurement and Control in Science and Industry," Reinhold, New York, 1941, p. 162) and by the National Physical Laboratory (" The International Temperature Scale of 1948," N.P.L., 1950, p. 6), may therefore be of interest. A non-inductive winding of 4 m. of 42 S.W.G. " thermopure " platinum wire was held by an octagonal mica former, each of the 64 turns resting in 1-mm. deep slots in the eight blades of the former. Close to the winding, each end of the wire was bifurcated by welding, and the four leads so produced were welded to 20-cm. lengths of gold wire, which were in turn welded to heavy silver output leads. The gold wires were threaded through 13 mica discs, fitting into a Pyrex tube which, flanged at its ends, confined the thermometer element in its Pyrex sheath. The annular space between this inner tube and the sheath was fitted with spaced mica rings. The upper end of the sheath was sealed to a B.24 cone, by which the thermometer could be fitted into an all-glass hypsometer, and was closed by a polystyrene plug which was sealed in with picein wax. The lower end of the sheath was attached to a high-vacuum system, and the thermometer was pumped out with the winding at bright red heat. Slow cooling was effected during several days, after which dry air was admitted, and the sheath sealed.

The thermometer was calibrated at the ice- and steam-points and at the transition point of sodium sulphate. The limit of accuracy was set by an irreducible uncertainty of ±0·002° in the steam-point, arising from the limitations of barometric readings. Local barometric readings were corrected by pressures ascertained from the Meteorological Office, Kingsway, and from Kew Observatory. The constants of the thermometer were: $R_{100} - R_0$, 12·8502 ohms; R_{100}/R_0, 1·3913; δ, 1·498; these are better than the criteria laid down by the N.P.L. (*loc. cit.*) for precise platinum thermometry. The final equation relating temperature to the resistance of this thermometer was

$$t = \frac{100(R_t - 32{\cdot}8423)}{12{\cdot}8502} + 1{\cdot}498\left(\frac{t}{100} - 1\right)\frac{t}{100} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Temperatures derived from this equation were checked against two points on a bomb-calorimeter thermometer certified by the N.P.L. to ±0·002°; agreement was within ±0·001°. Further checks at intervals against thermometers standardised at the N.P.L. to ±0·005° between 15° and 35° showed an agreement which averaged ±0·002° and in no case exceeded ±0·004°.

Temperature Control.—A 45-l. Perspex tank, thermally insulated with slag wool, was filled with Silvertown Lubricants transformer oil B.30, which was kept anhydrous by silica gel and circulated vigorously by two stirrers. A spiral toluene–mercury regulator operated a 300-w. Robertson lamp as heater through an electronic relay (Taylor, *J.*, 1951, 232). Cooling was provided by circulation of refrigerated glycol at a controlled rate through a copper cooling coil. Temperature fluctuation was negligible.

The Conductance Cell.—The double cell is illustrated in the Figure. The difficulty of maintaining a rigid electrode assembly whilst avoiding the leakages inseparable from massive platinum–Pyrex seals was met by using spherical-section platinum cups 2·5 cm. in diameter, 1 cm. deep, and 0·005 cm. thick as electrodes. These were drilled in the centre to allow free flow of solution, and near the edges to allow the insertion of Pyrex anchoring studs, subsequently fused to the inside of a Pyrex envelope. Electrical connection was made by welding on to each electrode two fine tags of platinum foil 0·001 cm. thick, at the edges of the central drilling. These were pinch-sealed into thin-walled Pyrex contact tubes, a procedure known to provide vacuum-tight seals (Campbell, *J. Amer. Chem. Soc.*, 1929, **51**, 2419; Hills and Ives, *J.*, 1951, 305). These tags were in turn welded to 28 S.W.G. platinum wires, which, at the upper ends of the contact tubes, were soldered to copper leads passing out through brass cones which were sealed into the contact tubes with sealing-wax. It may be noted that the resistance of the cell leads was about 2·5 ohms, but that this was cancelled out completely by the use of the " four-leads " method. The double cell, after grey-platinisation of the electrodes *in situ*, cleaning and steaming, was mounted permanently in the thermostat bath, and was not again subjected to any drastic cleaning procedure.

Conductance Water.—Water was prepared in a still of the Stuart and Wormwell type (*J.*, 1930, 85), in which steam from distilled water containing potassium hydroxide and permanganate was passed successively through a long packed column, a phosphoric acid scrubber, and steam traps into a vertical Vitreosil condenser, where it was mixed with a rapid stream of oxygen-free nitrogen which had passed through an efficient purification train. Water was not collected until a conductance cell attached to the still indicated a specific conductance less than $0{\cdot}08 \times 10^{-6}$ ohm^{-1}.

Potassium Chloride.—The very pure potassium chloride prepared by Hills and Ives (*J.*, 1951, 305) was used for the cell-constant determination. Comparison with pure silver by analysis had given an atomic ratio Cl/Ag = 0·99992.

Halogenoacetic Acids.—Fluoroacetic acid was supplied by Dr. B. C. Saunders of Cambridge University, to whom the authors express their thanks. This acid is intensely hygroscopic and liquefies completely on short exposure to air. The sample was dehydrated in a high-vacuum system, sublimed, and recrystallised five times from very pure anhydrous benzene in a totally enclosed, all-glass apparatus (Sample A). A second sample (B) was obtained by fractional sublimation *in vacuo* between temperatures of 30° and 0°. The other halogeno-acids were obtained from commercial sources and were purified by similar methods to yield samples A and B. M. p.s were determined in m. p. tubes attached to a high-vacuum apparatus and immersed in a large stirred water bath, the temperature of which was raised at a constant rate of 0·1° per min. Totally immersed N.P.L.-calibrated thermometers were used. It may be noted that, because of polymorphism and incipient decomposition in the melt, sharpness of m. p. cannot be taken as a criterion of purity, except for the fluoro-acid. Equivalents were determined by titration, very pure " Calorimetric Standard " benzoic acid, repeatedly crystallised from conductance water and dried over phosphoric oxide, being used as the primary standard. The results of these determinations are shown in Table 8; these m. p.s should be regarded as new data.

Procedure.—Solutions were prepared in 1-l., two-necked Pyrex flasks. These were steamed, washed with conductance water, oven-dried, cooled, filled with pure, dry nitrogen, and weighed. Solutes were weighed by difference directly into these flasks, by using an Oertling **141** semi-micro-balance and weights calibrated to 0·01 mg. against N.P.L. standards. Conductance water was introduced directly into the solution flask from the still against a counter-current of purified nitrogen. The flask was re-weighed, by use of an Oertling balance of maximum load 2 kg. and sensitivity ±1 mg., and the solution was thoroughly mixed, wetting of ground joints being carefully avoided. Appropriate buoyancy corrections were applied to all weighings, and concentrations in moles per litre were calculated at each temperature.

The conductance cell was kept permanently filled with conductance water, which was expelled by pressure of nitrogen before use. All-glass connections to the cell, except for short poly(vinyl chloride) connections with screw-clips, used as greaseless taps, enabled the cell to be filled with, and emptied of, solution by manipulating pressures of highly purified nitrogen. The cell was filled with solution and emptied again five times before the final filling on which, after temperature equilibration, readings of conductance were made. Measurements were made successively at 15°, 20°, 25°, 30°, and 35° with, when appropriate, a final return to 15° as a check. It was found advantageous to take each measurement at some arbitrary temperature within about 0·02° of the precise temperature desired, and then to apply an adjustment by means of a determined temperature coefficient of conductance.

The conductance of the water used in preparing the solutions was found by taking measurements on the section of the cell of lower constant, shunted by a standard resistance. Solvent correction was additive for potassium chloride solutions and zero for the acid solutions.

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