**859.** *The Molecular Association of Some Carboxylic Acids in Aqueous Solution from e.m.f. Measurements.*

By G. R. NASH and C. B. MONK.

The standard electrode potentials of the silver–silver chloride electrode from 15° to 45° in aqueous acetic, propionic, and butyric acids have been calculated from potential measurements obtained with the cell $H_2|HCl$, aqueous HA|AgCl|Ag (A = carboxylate ion), small concentrations of hydrochloric acid and up to 0·6m-organic acid being used. Similar molalities of the latter have been used in the buffered type of cell whereby Harned has obtained the dissociation constants of weak acids from e.m.f. measurements, *i.e.*, $H_2|HA,NaA,NaCl|Ag|AgCl$, and by using the known dissociation constants of the acids and the derived standard electrode potentials, the dimerisation constants of these acids have been calculated. The results are of the same order as, but somewhat lower than, those obtained by other methods. There are several unknown factors involved and the effects of these are discussed.

ONE of the most widely used and precise ways of obtaining the dissociation constants of weak acids in solution is by means of the " buffered " e.m.f. cell developed by Harned, *i.e.*,

$$H_2|Pt|HA(m_1), MA(m_2), MX(m_3)|AgX|Ag \qquad \text{(cell I)}$$
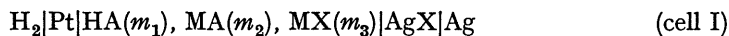
where HA is the weak acid, M a metal cation (usually Na^+), X^- a halide (usually Cl^-), A^- is the anion of the acid, and the quantities m are in molalities. This cell was first used by Harned and Ehlers[1] for the study of aqueous acetic acid, and has since been used with many weak electrolytes in a variety of solvents and over wide temperature ranges.[2,3]

[1] Harned and Ehlers, *J. Amer. Chem. Soc.*, 1932, **54**, 1350.
[2] Harned and Owen, " The Physical Chemistry of Electrolytic Solutions," Reinhold, New York, 1943, Ch. 15.
[3] Stokes and Robinson, " Electrolyte Solutions," Butterworths, London, 1955, Ch. 12.

The basic equations to obtain K, the thermodynamic dissociation constant of the acid HA, are

$$E = E_0 - k \log m_H m_X f_H f_X \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$K = m_H m_A f_H f_A / m_{HA} f_{HA} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

whence $\quad (E - E_0)/k + \log (m_{HA} m_X / m_A) = -\log K + \log (f_X f_{HA}/f_A) = -\log K'$. (3)

In these $k = 2 \cdot 303 RT/F$, f represents ion activity coefficients, E is the measured potential corrected to 1 atm. of hydrogen, and E_0 is the standard electrode potential of the $X^-|AgX|Ag$ electrode.

Since $m_{HA} = m_1 - m_H$, $m_X = m_2$, and $m_A = m_3 + m_H$, K' is easily found by a short series of approximations. Probably the most convenient way of calculating m_H is by means of eqn. (1), using an approximate form of the Debye–Hückel activity-coefficient expression such as that given by Davies,[4] which in a generalised form can be written

$$-\log f_i = A z_i^2 \{I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}}) - 0 \cdot 2 I\} = A \phi(I) \quad . \quad . \quad . \quad (4)$$

The factor A depends on T and D (dielectric constant), and the ionic strength I is $I = m_2 + m_3 + m_H$.

On theoretical grounds both f_{HA} and the ratio f_X/f_A should be very close to unity, and some experimental data which confirm this have been collected by Gimblett and Monk.[5] Further confirmation that the ratio $f_{Cl}/f_A = 1$ is given by the following activity coefficients for sodium salts in $0 \cdot 1$m-solution:[6] chloride $= 0 \cdot 778$, acetate $= 0 \cdot 791$, propionate $= 0 \cdot 800$, butyrate $= 0 \cdot 800$. Accordingly K', as calculated by eqn. (3), should not vary very much with increasing molalities of one or all of the cell constituents up to about $I = 0 \cdot 1$. In practice, marked variations are found, and three of the possible explanations for these are: (a) E_0 (at constant T) depends upon the solvent composition, particularly the concentration of HA, so that the values obtained from data for aqueous hydrochloric acid are not applicable, (b) a fraction of the organic acid is present as dimers, and (c) the dielectric constant of the medium decreases as the molality of HA increases.

The first of these factors has already received some consideration by Harned and Owen [7] in a general survey of E_0 values in mixed aqueous organic solvents. They have calculated E_0 values at 25° in acetic acid solutions up to 60% of acid. There are very marked changes; thus in water at 25°, E_0 for the silver–silver chloride electrode is $0 \cdot 2224$ v, while in 10% acetic acid it is $0 \cdot 2105$ v. Their calculations are based on e.m.f. measurements obtained by Harned and Robinson [8] with the cell $H_2|HA(m_1)$, NaCl(m_3), water|AgCl|Ag, which was the first type used by Harned to obtain dissociation constants. In the present work hydrochloric acid has been used in preference to sodium chloride since it suppresses the dissociation of HA, and provides a bigger concentration of H^+ ions. By this means E_0 data for acetic, propionic, and n-butyric acid solutions up to $0 \cdot 6$m and from 15° to 45° have been obtained. It turns out, however, that if the correct E_0 values had been used to calculate K', then the variations with the HA molality would be even more marked.

The second point, namely, that dimerisation occurs, is supported by various experimental approaches which have been summarised elsewhere (some data are given in Table 4). To study this in detail we have obtained data by using Cell I, taking low concentrations of NaA and NaCl, and using high concentrations of HA.

The third point, concerning the dielectric constants of the media, is referred to later.

[4] Davies, *J.*, 1938, 2093.
[5] Gimblett and Monk, *Trans. Faraday Soc.*, 1954, **50**, 1965.
[6] Ref. 3, p. 477.
[7] Ref. 2, Ch. 15.
[8] Harned and Robinson, *J. Amer. Chem. Soc.*, 1928, **50**, 3157.

TABLE 1. *E_0 Values of the AgCl|Ag electrode in acetic, propionic, and* n-*butyric acid solution from 15° to 45° (cell* II).

Acetic acid.

$10^2 m_1 =$ (a) 10·00, (b) 20·00, (c) 40·00, (d) 60·00
$10^4 m_4 =$ (a) 43·70, (b) 42·05, (c) 48·45, (d) 56·31

	(a)	(b)	(c)	(d)	(a)	(b)	(c)	(d)
			15°				20°	
E (mv)	498·83	498·25	488·47	479·54	500·60	499·90	489·99	480·89
E_0 (mv)	227·82	227·23	225·78	224·55	224·76	224·17	222·72	221·41
			25°				30°	
E (mv)	502·21	501·41	491·36	482·10	503·59	502·80	492·57	483·16
E_0 (mv)	221·63	220·97	219·51	218·19	218·29	217·59	216·16	214·77
			35°				40°	
E (mv)	504·85	504·03	493·71	484·08	505·91	505·16	494·72	484·85
E_0 (mv)	214·77	214·04	212·59	211·17	211·05	210·41	208·96	207·40
			45°					
E (mv)	506·92	506·19	495·56	485·47				
E_0 (mv)	207·27	206·57	205·09	203·46				

Propionic acid.

$10^2 m_1 =$ (a) 10·00,* (b) 20·00, (c) 40·00, (d) 60·00
$10^4 m_4 =$ (a) — , (b) 45·83, (c) 47·14, (d) 50·56

	(a)	(b)	(c)	(d)	(a)	(b)	(c)	(d)
			15°				20°	
E (mv)	—	494·79	490·25	484·28	—	496·49	491·74	485·78
E_0 (mv)	227·60 *	226·68	225·44	223·85	224·65 *	223·70	222·29	220·82
			25°				30°	
E (mv)	—	498·05	393·25	487·10	—	499·37	494·52	488·34
E_0 (mv)	221·45 *	220·56	219·16	217·59	218·10 *	217·18	215·80	214·24
			35°				40°	
E (mv)	—	500·58	495·64	489·36	—	501·58	496·62	490·34
E_0 (mv)	214·65 *	213·70	212·26	210·70	210·95 *	209·92	208·46	206·95
			45°					
E (mv)	—	502·52	497·56	491·16				
E_0 (mv)	207·30 *	206·11	204·69	203·12				

n-Butyric acid.

$10^2 m_1 =$ (a) 20·00,* (b) 30·00, (c) 40·00, (d) 50·00, (e) 60·00
$10^4 m_4 =$ (a) — , (b) 28·16, (c) 29·10, (d) 28·83, (e) 18·44

	(a)	(b)	(c)	(d)	(e)	(a)	(b)	(c)	(d)	(e)
			15°					20°		
E (mv)	—	511·28	507·45	505·79	518·72	—	513·39	509·31	507·59	520·72
E_0 (mv)	226·70 *	225·74	224·83	224·27	223·84	223·70 *	222·78	221·66	221·05	220·55
			25°					30°		
E (mv)	—	515·24	511·20	509·16	522·71	—	517·00	512·93	510·97	524·64
E_0 (mv)	220·47 *	219·54	218·50	217·58	217·25	217·15 *	216·21	215·16	214·32	213·83
			35°					40°		
E (mv)	—	518·60	514·54	512·56	526·60	—	520·08	516·07	514·20	528·63
E_0 (mv)	213·65 *	212·64	211·64	210·79	210·37	210·05 *	208·94	208·04	207·30	206·96
			45°							
E (mv)	—	521·48	517·44	515·49	530·36					
E_0 (mv)	206·20 *	205·13	204·22	203·39	203·19					

* Interpolated from the values in water and the lowest molalities of *m*.

Determination of E_o Values in Aqueous Organic Acids.—For the cell

$$H_2|Pt|HA(m_1), HCl(m_4)|AgCl|Ag \qquad \text{(cell II)}$$

from eqns. (1), (2), and (4),

$$\log m' = \log K + 2A\phi(I) + \log (m_1 - m' - 2x) - \log (m_4 + m')$$
$$E_o = E + k \log (m_4 + m')m_4 - 2A\phi(I)$$

where m' is the molality of H^+ ions resulting from the dissociation of the organic acid, x is the concentration of dimers, K is taken as the value in water, and $I = m_4 + m'$. Since x is unknown, it has been ignored in the calculations. The consequences of this are discussed later. The resulting E_o values are given in Table 1. In calculating these, the values of k and A were taken from the tables of Harned and Robinson [9] except that 0·009 was subtracted from A at each temperature (since Davies [4] takes $A = 0·500$ at 25° instead of 0·509). The conventional corrections of the measured potentials to 1 atm. of hydrogen

Plot of E_o values at 25° against total HA molality.
O = Acetic, ◒ = propionic, ◑ = n-butyric acid.
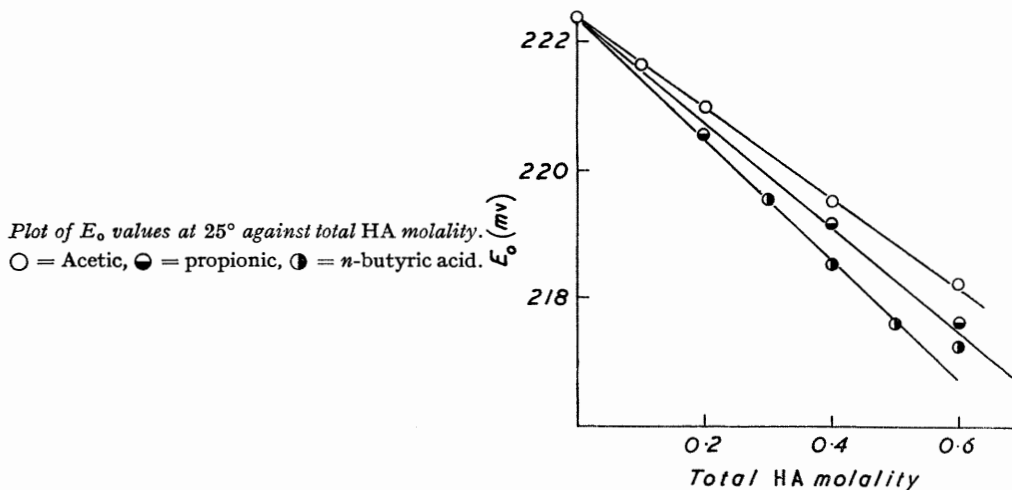
were based on the vapour pressures of water since the vapour pressures of the solutions are almost identical with these.[10] The K values used are those obtained by Harned and his associates [11] by extrapolating K' data for dilute solutions against I, which, although it is a somewhat empirical procedure, removes errors due to various causes.

The E_o values at any one temperature decrease almost linearly with the molality of HA, the change being most marked with butyric acid. These effects are illustrated by the Figure.

Estimation of the Dimerisation Constants from e.m.f. Data.—By using cell I with molalities of HA ranging from 0·1 to 0·6, and using the E_o values of Table 1, values of m_H were calculated by eqn. (1). To minimise errors resulting from the use of a general type of activity coefficient expression (eqn. 4), and to ensure as much as possible that $f_{Cl}/f_A = 1$, low concentrations of $NaA = m_2$ and of $NaCl = m_3$ were taken. The concentrations of single HA molecules were then calculated from

$$\log m_{HA} = \log m_H m_A - \log K - 2A\phi(I)$$

where $m_A = m_2 + m_H$, and the K values are those obtained by Harned and his associates. Then, the dimers being represented by $(HA)_2$, and the equilibrium constant for the process $(HA)_2 = 2HA$ by L, i.e., $L = (m_{HA})^2/m_{(HA)_2}$, where $m_{(HA)_2} = 0·5(m_1 - m_{HA} - m_H)$, the results shown in Table 2 were obtained.

[9] Ref. 3, pp. 456, 491.
[10] " International Critical Tables," McGraw-Hill, New York, 1928, III, pp. 306, 290, 291.
[11] Ref. 2, p. 580.

TABLE 2. *Dimerisation constants of acetic, propionic, and* n-*butyric acids in aqueous solution from e.m.f. data* (15—45° c) (*cell* I).

Acetic acid. $10^2 m_1 =$ (a) 10·00, (b) 20·00, (c) 40·00, (d) 60·00
$10^4 m_2 =$ (a) 72·13, (b) 79·07, (c) 84·37, (d) 100·10
$10^4 m_3 =$ (a) 82·62, (b) 99·05, (c) 100·06, (d) 116·60

	(a)	(b)	(c)	(d)	(a)	(b)	(c)	(d)
		15°					20°	
E (mv)	555·00	535·84	519·95	509·63	557·52	537·93	521·88	511·48
$-\log m_H$	3·533	3·280	3·029	2·929	3·531	3·276	3·029	2·928
L	17·3	17·7	17·1	20·6	16·7	21·7	17·2	18·3
		25°					30°	
E (mv)	560·02	540·25	523·78	513·20	526·45	542·28	525·29	514·85
$-\log m_H$	3·529	3·277	3·025	2·927	3·529	3·277	3·027	2·927
L	19·5	15·3	19·8	17·5	17·0	15·5	17·1	17·5
		35°					40°	
E (mv)	564·90	544·42	527·41	516·53	567·30	546·50	529·20	518·09
$-\log m_H$	3·533	3·282	3·030	2·932	3·539	3·286	3·035	2·937
L	18·8	15·0	17·6	17·2	15·6	15·6	18·3	17·0
		45°						
E (mv)	569·73	548·52	530·88	519·69				
$-\log m_H$	3·546	3·292	3·040	2·944				
L	15·6	16·4	19·7	16·3				

Propionic acid. $10^2 m_1 =$ (a) 10·00, (b) 20·00, (c) 40·00, (d) 60·00
$10^4 m_2 =$ (a) 77·69, (b) 67·89, (c) 69·66, (d) 66·51
$10^4 m_3 =$ (a) 92·18, (b) 104·73, (c) 89·83, (d) 82·63

	(a)	(b)	(c)	(d)	(a)	(b)	(c)	(d)
		15°					20°	
E (mv)	560·37	537·17	525·02	516·22	563·15	539·57	527·22	518·30
$-\log m_H$	3·674	3·339	3·084	2·924	3·673	3·338	3·086	2·923
L	10·9	9·9	10·9	11·5	10·9	9·7	9·6	11·1
		25°					30°	
E (mv)	565·78	541·85	529·35	520·34	568·43	544·09	531·35	522·28
$-\log m_H$	3·673	3·337	3·084	2·925	3·675	3·340	3·087	2·928
L	10·7	9·8	10·2	10·2	9·7	9·3	8·7	10·1
		35°					40°	
E (mv)	571·06	546·33	533·37	524·29	573·76	548·50	535·41	526·17
$-\log m_H$	3·679	3·344	3·092	2·935	3·688	3·352	3·101	2·942
L	9·9	9·1	9·3	9·1	9·9	9·5	9·1	9·3
		45°						
E (mv)	576·23	550·74	537·36	528·07				
$-\log m_H$	3·695	3·361	3·107	2·951				
L	9·5	8·1	8·9	8·6				

n-Butyric acid. $10^2 m_1 =$ (a) 20·00, (b) 30·00, (c) 40·00, (d) 50·00, (e) 60·00
$10^4 m_2 =$ (a) 44·99, (b) 48·04, (c) 44·18, (d) 50·40, (e) 87·22
$10^4 m_3 =$ (a) 47·43, (b) 66·57, (c) 44·80, (d) 58·58, (e) 98·92

	(a)	(b)	(c)	(d)	(e)	(a)	(b)	(c)	(d)	(e)
			15°					20°		
E (mv)	545·08	528·73	530·28	521·75	514·62	547·95	531·31	532·94	532·82	516·94
$-\log m_H$	3·158	3·027	2·906	2·876	2·964	3·163	3·031	2·914	2·877	2·973
L	6·5	6·6	8·1	5·9	6·7	6·8	7·0	7·4	6·5	6·3
			25°					30°		
E (mv)	550·71	533·73	535·49	525·88	519·18	553·43	536·12	537·84	528·33	521·46
$-\log m_H$	3·170	3·037	2·921	2·882	2·980	3·177	3·043	2·926	2·890	2·990
L	6·5	7·1	7·3	6·6	6·1	6·4	7·1	7·6	6·3	5·8
			35°					40°		
E (mv)	556·11	538·65	540·30	530·49	523·74	558·79	540·91	542·66	532·92	525·80
$-\log m_H$	3·187	3·055	2·936	2·898	2·999	3·198	3·066	2·945	2·909	2·004
L	6·8	6·9	7·7	6·8	6·1	7·0	6·9	8·1	6·7	6·8
			45°							
E (mv)	561·36	543·15	545·02	535·01	528·38					
$-\log m_H$	3·210	3·076	2·957	2·920	2·023					
L	7·1	7·3	7·9	6·8	6·0					

DISCUSSION

As Table 3 shows, there are no marked changes in L with temperature. This agrees with the conclusions of Davies and Griffiths,[12,13] who used freezing-point and distribution methods for studying dimerisation in aqueous acetic and butyric acids, and also with Trayhard's[14] observations which were based on Raman spectra studies of aqueous acetic acid.

TABLE 3. *Average L values from the e.m.f. data.*

Temp.	15°	20°	25°	30°	35°	40°	45°
Acetic acid ...	18·2 ± 1·2	18·5 ± 1·6	18·0 ± 1·6	16·8 ± 0·6	17·2 ± 1·1	16·6 ± 1·0	17·0 ± 1·4
Propionic acid	10·8 ± 0·5	10·3 ± 0·7	10·2 ± 0·2	9·5 ± 0·6	9·5 ± 0·4	9·5 ± 0·3	8·8 ± 0·5
n-Butyric acid	6·8 ± 0·6	6·8 ± 0·3	6·7 ± 0·4	6·6 ± 0·6	6·9 ± 0·4	7·1 ± 0·4	7·0 ± 0·5

A comparison of the dimerisation constants obtained by various methods (Table 4) reveals that the e.m.f. values, although of the same order as those obtained in other ways, are somewhat the smaller. The tendency to dimerise increases as the chain length grows. (The value for propionic acid by conductance–viscosity is not very reliable, being the mean of 22, 22·5, and 15, calculated from measurements with very dilute solutions.)

TABLE 4. *Values of L obtained by various methods.*

	Acetic acid	Propionic acid	*n*-Butyric acid
Freezing point [12,13] (0°)	28	—	11
F.p.–distribution [12,13] (25°)	28	—	10
Vapour pressure [12] (25°)	20 ± 3	—	—
Conductance–viscosity [15] (25°)	19 ± 2	20 ± 3	11 ± 0·6
E.m.f. (25°)	18 ± 1·6	10·2 ± 0·2	6·7 ± 0·4

There are several reasons which could account for the fact that the L values from the e.m.f. data are smaller than those obtained in other ways, and originate from the factors referred to earlier. Among these is one about which no precise information is available, namely, the dielectric constants (D) of the solutions. However, there is sufficient evidence to indicate that the presence of organic acids lowers the dielectric constant from that of water, since $D = 6·2$ and 2·9 for pure acetic acid[16] and butyric acid,[17] respectively, and Drude,[18] who studied concentrated propionic acid, reported that $D = 43·8$ for a 55% solution at 17° (D for water is 81·5). These figures suggest that the dielectric constants of the 0·6m-solutions are about three units lower than that of water at the corresponding temperature. This would influence both the value of K and the Debye–Hückel factor A in eqn. (4). Nevertheless, even if the dielectric constants were known exactly, as Stokes and Robinson have pointed out,[3] it is not possible to calculate the precise extent to which the values of K are altered from those in water. Born's equation,[19] which should predict this change, proves under test to be only an approximation. With mixed solvents such as alcohol–water and dioxan–water marked specific effects are found which no doubt are the result of ion–solvent interactions. Calculation shows that even the average change of log K with $1/D$ from known data for alcohols–water and dioxan–water[3] is excessive, since, if this is used together with the estimate that D changes by 3 units from water to 0·6m-acetic acid, the calculated molality of undissociated single molecules becomes greater than 0·6. However, on taking, *e.g.*, the results at 25°, if K (acetic acid) changes from $1·745 \times 10^{-5}$ in water[11] to $1·68 \times 10^{-5}$ in 0·6m-acid, L is raised from 18 to 28, and similarly if K (butyric acid)[11] changes from $1·515 \times 10^{-5}$ to $1·37 \times 10^{-5}$, L is raised from 6·7 to 11. (For both of these estimates it is assumed that D changes by 3 units, *i.e.*, the Debye factor A is raised from 0·50 to 0·55.) At the same time, the standard electrode potentials change

[12] Davies and Griffiths, *Z. phys. Chem. (Frankfurt)*, 1954, **2**, 353.
[13] *Idem, ibid.*, 1956, **6**, 143.
[14] Trayhard, *Compt. rend.*, 1945, **223**, 202.
[15] Cartwright and Monk, *J.*, 1955, 2500.
[16] Le Fèvre, *Trans. Faraday Soc.*, 1938, **34**, 1127.
[17] Ref. 10, VI, 87.
[18] Drude, *Z. phys. Chem.*, 1897, **23**, 267.
[19] Born, *Z. Physik*, 1920, **1**, 45.

slightly from those given in Table 1. The two concerned here for example become 0·6 mv and 1·1 mv lower, respectively.

Finally, since the existence of dimers was ignored in calculating the E_0 values of Table 1, it has been implied that the dissociation constants of equilibria such as $(HA)_2 = H^+ + HA_2^-$ are twice as large as those of the single molecules. If the dimers do not dissociate, then both the E_0 and L values are different from those given in the Tables or when the effect of changing dielectric constant is considered. For instance, with 0·6m-acetic acid at 25°, if we take the lower K of $1·68 \times 10^{-5}$ suggested in the previous paragraph, and the higher Debye factor of 0·55, and also assume that the dimers do not dissociate, E_0 becomes 0·8 mv lower than the value given in Table 1, and L becomes 25, compared with the original estimate of 18 in Table 2, and the higher result of 28 when the dielectric constant effect and not the dimer dissociation is considered.

The general conclusion, therefore, is that the present interpretation of potential measurements can give some measure of the dimerisation process but the precision of the answers is markedly lowered by several unknown features.

EXPERIMENTAL

The conventional H-shaped cell was used for the e.m.f. measurements. It contained a tap with a wide bore in the tube connecting two electrode compartments, which was only opened when readings were being taken. The gas exits consisted of U-shaped capillary tubes, and the electrodes were fitted into the cell by means of standard ground-glass joints. The measuring apparatus consisted of a Tinsley potentiometer (type 4025), Tinsley Weston cells (type 1267), and Pye " Scalamp " galvanometer (No. 7904/5) with a sensitivity of 7·24 μv/mm. The potentiometer could be read to 0·1 mv, and the nearest 0·01 mv could be estimated from the galvanometer.

The cell and gas saturators were fixed in a water thermostat kept at the required temperatures to within ±0·03°, and the saturators were filled with the solution being studied to prevent concentration changes in the cell. Commercial B.O.C. nitrogen and hydrogen (purified by passage over palladium–abestos pellets) were passed through the silver–silver chloride and platinum-black electrode compartments, respectively, overnight before starting a " run." Several types of silver–silver chloride electrode were tried before final choice of the thermal-electrolytic type of Noyes and Ellis,[20] and Lewis.[21] The electrolytic type described by Brown [22] would not maintain a constant potential in the concentrated carboxylic acid solutions. The electrodes used remained constant during a " run " to within 0·05 mv, but to minimise errors due to the slight lack of reproducibility an electrode was used for a series of E_0 determinations in a particular HA molality, and then used for L determinations at the same HA molality. A fresh electrode was used for each such set of measurements.

" AnalaR " acetic acid, sodium hydroxide, sodium chloride, and hydrochloric acid were used. Stock solutions were prepared with conductivity water obtained by passing distilled water through a mixed-bed ion-exchange column. The propionic and *n*-butyric acids were purified by fractionation, the fractions of b. p. 140—140·7°/735 mm. and 163·0°, respectively, being collected. Solutions of the carboxylic acids were standardised by carbonate-free sodium hydroxide which was standardised by potassium hydrogen phthalate. The chloride stock solutions were standardised gravimetrically *via* silver chloride. The cell solutions were made up on a molality basis, *viz.*, per 1000 g. of water + carboxylic acid, by analogy with the conventional procedure with mixed solvents.

THE EDWARD DAVIES CHEMICAL LABORATORIES,
  UNIVERSITY COLLEGE OF WALES, ABERYSTWYTH.

[20] Noyes and Ellis, *J. Amer. Chem. Soc.*, 1917, **39**, 2532.
[21] Lewis, *ibid.*, 1906, **28**, 166.
[22] Brown, *ibid.*, 1934, **56**, 646.