498. *The Dissociation Constants of Some Symmetrically Disubstituted Succinic Acids.*

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The thermodynamic dissociation constants of four diastereoisomeric pairs of 1 : 2-disubstituted succinic acids have been measured (in water at 25°) by a combination of conductometric and potentiometric procedures. The results do not confirm the apparent trend which could be observed in the earlier classical data, *viz.*, that the *meso*-acid is consistently weaker than the racemic acid.

THE strengths of dicarboxylic acids have been measured by numerous workers, but accurate thermodynamic data obtained by unambiguous techniques (from conductivity or e.m.f. measurements) are scarce. Methods for the calculation of $K_{1,\text{ therm.}}$ in a rational way from conductivity data have been known for some time[1,2] but there is still no wholly satisfactory way of calculating $K_{2,\text{ therm.}}$ from such data. K_1 values of six symmetrically disubstituted succinic acids, obtained conductometrically, are recorded here, together with

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[1] Davies, *J.*, **1939**, 1850.

[2] Darken, *J. Amer. Chem. Soc.*, 1941, **63**, 1007.

K_1 and K_2 values obtained by means of an approximate potentiometric method (although measurements on one pair of diastereoisomers were undertaken by the latter method only, see Table 1).

TABLE 1.

Acid	Conductometric method	Potentiometric method	
	$10^5K_{1,\text{ therm.}}$	$10^5K_{1,\text{ therm.}}$	$10^5K_{2,\text{ therm.}}$
D-Tartaric *	94·3	93	3·5
DL-Tartaric	93·0	—	—
*meso*Tartaric	60·2	51	1·21
DL-1 : 2-Dichlorosuccinic	2540	2100	66
meso-1 : 2-Dichlorosuccinic	2230	1810	57
DL-1 : 2-Dibromosuccinic †	3300	—	—
meso-1 : 2-Dibromosuccinic	3760	3800	108
DL-1 : 2-Dimethylsuccinic	—	11·9	0·10
meso-1 : 2-Dimethylsuccinic	—	17·1	0·44
Succinic	—	6·2	0·19

* *i.e.* The dextrorotatory acid, D according to Freudenberg, D_s = L_g by modern rules.

† All dihalogeno-succinic acids react gradually with water, yielding the corresponding hydrogen halides; with one exception, however, no significant drift in conductivity of these acids was observed at 25° during the period required for measurements (about 2 hr.), although an increase was noticeable over longer periods. DL-Dibromosuccinic acid showed the greatest reactivity; readings in this case had to be taken within 20 min. of wetting each sample of solid, and since reaction is even faster in alkaline solutions, the potentiometric titration method was omitted. It is noteworthy that most values in the literature for the strengths of these acids are higher than those recorded here, probably owing to the production of hydrogen halide.

Table 2 sets out the values of the published dissociation constants of 1 : 2-disubstituted succinic acids; none of the thermodynamic constants recorded (italicised) refers to a reasonably precise conductivity procedure.

TABLE 2.

Acid	10^5K_1	10^5K_2
Succinic	8·71,[3] 6·86,[4] 6·8,[5] 6·65,[6, 7, 8] *6·63*,[9] 6·52,[10] *6·41*,[11] 6·37,[12] *6·0*[13]	0·48,[3] 0·43,[14] 0·40,[4] *0·33*,[11] 0·27,[8] *0·25*,[12] *0·21*[13]
DL-1 : 2-Dichlorosuccinic	3700,[15] *3600*,[16] 3500[17]	180,[15] *150*[16]
meso-1 : 2-Dichlorosuccinic	3600,[15] *3100*,[16] 3000[17]	*ca.* 80,[17] *113*[16]
DL-1 : 2-Dibromosuccinic	*3800*,[16] 3700[15, 17]	81·7,[15] *58·0*,[16] 43[17]
meso-1 : 2-Dibromosuccinic	3700,[17] 3600,[15] 3400,[8] 2900[16]	240,[15] *200*,[16] 140[17]
D-Tartaric	127,[21] 117,[15] *104*,[20] 102,[17, 22] 97,[6, 7, 18, 23] *96*,[24] *92·5*,[25] 90[26]	7·5,[4] 5·9,[7, 15] 4·5,[19, 20] *4·3*,[25] 4·1,[16] 4·0,[17] 3·4,[14] 2·9,[27] 2·8[23]
*meso*Tartaric	*69*,[16] 65,[15] 63,[17] 61,[18] 60,[19] 60[20]	1·6,[15] 1·4,[17] *1·26*[16]
DL-1 : 2-Dimethoxysuccinic	*172*[16]	*2·0*[16]
meso-1 : 2-Dimethoxysuccinic	*110*[16]	5·5[16]
DL-1 : 2-Dimethylsuccinic	13·8,[5] 13·2,[22] 12·3,[7, 29] 12·2,[18] *11·2*[11]	*0·064*[11]
meso-1 : 2-Dimethylsuccinic	20·8,[5] 20·4,[28] 19·6,[29] 19·4,[22] 19·1,[7, 18] *17·0*[11]	*0·12*[11]
DL-1 : 2-Diethylsuccinic	34·7,[5] 34·3,[18, 30] *31·1*,[11] 20·1[29]	*0·025*[11]
meso-1 : 2-Diethylsuccinic	24·5,[18, 29] 23·5,[5] *23·3*,[11] 23·2[30]	*0·035*[11]
DL-1 : 2-Di-*n*-propylsuccinic	49[29]	—
meso-1 : 2-Di-*n*-propylsuccinic	25[29]	—
DL-1 : 2-Diphenylsuccinic	26·5,[30] 26[18]	—
meso-1 : 2-Diphenylsuccinic	33·0,[30] 23·5[18]	

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[3] Partington, *Trans. Faraday Soc.*, 1934, **30**, 598.
[4] Auerbach and Smolczyk, *Z. phys. chem.*, 1924, **110**, 65.
[5] Crum-Brown and Walker, *Annalen*, 1893, **274**, 47.
[6] Ostwald, *Z. phys. Chem.*, 1889, **3**, 282.
[7] Smith, *ibid.*, 1898, **25**, 193.
[8] Chandler, *J. Amer. Chem. Soc.*, 1908, **30**, 694.
[9] Vogel, *J.*, 1935, 21.
[10] Voermann, *Rec. Trav. chim.*, 1904, **23**, 277.
[11] Gane and Ingold, *J.*, 1931, 2158.
[12] Vogel, *J. Amer. Chem. Soc.*, 1936, **58**, 1546.
[13] Speakman, *J.*, 1940, 855.
[14] McCay, *J. Amer. Chem. Soc.*, 1908, **30**, 688.
[15] Kuhn, *Ber.*, 1934, **61**, 520.
[16] Bode, *Ber.*, 1938, **71**, 871.
[17] Holmberg, *J. prakt. Chem.*, 1911, **84**, 166.

In discussions of chemical constitution and the strengths of dicarboxylic acids the main interest has usually centred around the relative magnitudes of the primary and secondary dissociation constants. It is considered that deviation of the ratio K_1/K_2 from the statistical factor of 4 is a measure of the electrostatic influence of the carboxylate group on the carboxyl group, which in turn is determined by the intercarboxylic distance (r), according to the equation (see Bjerrum,[31] Kirkwood and Westheimer [32]):

$$K_1/K_2 = 4e^{-Ne^2/\boldsymbol{R}TDr}$$

(where D is the dielectric constant and other symbols have the usual meaning).

Values of K_1/K_2 (potentiometric) obtained in this work are shown in Table 3, together with the ratio of these values for the *meso*- and racemic acids. It is seen that there is no regularity in these results, which confirms an earlier observation made by Bode.[16]

TABLE 3.

Acid	K_1/K_2	$\dfrac{K_1/K_2\ (meso)}{K_1/K_2\ \text{(racemic)}}$
D-Tartaric	27	1·56
*meso*Tartaric	42	
DL-1 : 2-Dichlorosuccinic	33	1·0
meso-1 : 2-Dichlorosuccinic	32	
DL-1 : 2-Dibromosuccinic	—	—
meso-1 : 2-Dibromosuccinic	35	
DL-1 : 2-Dimethylsuccinic	119	0·32
meso-1 : 2-Dimethylsuccinic	38	
Succinic	33	

However, it is the relative magnitudes of $K_{1,\ \text{therm.}}$ for the *meso*- and racemic acids which are of main interest in this work. Since diastereoisomers contain the same selection of atoms and bonds, the internal electronic displacements must be the same. It is reasonable, therefore, to suggest that the observed differences in strengths arise from the interactions of the constituent groups and atoms in space.

When steric interactions within substituted ethane molecules, such as the acids discussed here, are considered, it is necessary to examine the energetically preferred conformations of each diastereoisomer. A study of the molecular models of the three staggered conformations of the optically active and *meso*-forms of symmetrically disubstituted succinic acids shows that only the *meso*-form is capable of taking up an entirely symmetrical conformation with *all* the pairs of substituents at their positions of maximum separation, *i.e.*, the *trans*-configuration; in the optically active forms this is not possible, maximum separation being achieved on the ethane model by one pair of substituents at a time. It is expected, therefore, that the *meso*-form will exist predominantly in the completely *trans*-form, whereas for the D- and the L-form there is no obviously preferred conformation, although the two stable staggered forms will have either the carboxyl groups or the substituent groups in the *trans*-position. Thus in the absence of other factors, such as internal hydrogen-bonding, the carboxyl groups will, on the average, approach each other more closely in the optically active forms than in the *meso*-form. Now, it is well known

[18] Ostwald, *Z. phys. Chem.*, 1888, **2**, 840.
[19] Wegscheider, *Monatsh.*, 1902, **23**, 599.
[20] Jones and Soper, *J.*, 1934, 1836.
[21] Britton, *J.*, 1925, **127**, 1896.
[22] Böeseken, *Rec. Trav. chim.*, 1918, **37**, 181.
[23] Paul, *Z. phys. Chem.*, 1924, **110**, 417.
[24] Kolthoff and Bosch, *Rec. Trav. chim.*, 1928, **47**, 861.
[25] Bates, *J. Res. Nat. Bur. Stand.*, 1951, **47**, 343.
[26] Ives, Linstead, and Riley, *J.*, 1932, 1093.
[27] Drucker, *Z. phys. Chem.*, 1920, **96**, 381.
[28] Bethman, *ibid.*, 1890, **5**, 385.
[29] Bone and Sprankling, *J.*, 1900, **77**, 1298.
[30] Hartman, *Rec. Trav. chim.*, 1938, **57**, 679.
[31] Bjerrum, *Z. phys. Chem.*, 1923, **106**, 219.
[32] Kirkwood and Westheimer, *Chem. Reviews*, 1942, **30**, 159.

that in ethylenedicarboxylic acids, where molecular rigidity is ensured by a double bond, the *cis*-acid (with the smaller intercarboxylic separation) is always stronger than the *trans*-acid (see Branch and Calvin,[33] who suggested internal hydrogen-bonding, and Crawford,[34] who suggested steric inhibition of mesomerism); thus, by analogy with the *cis*-olefinic acids, the optically active form of a disubstituted succinic acid (or the racemic acid, which has an identical value of K_1) might be stronger than the *meso*-acid.

The same conclusion can be reached by considering the relative stabilities of the molecules of *meso*- and racemic acids, and of the univalent ions [35] from the point of view of steric repulsions: the fully *trans-meso*-acid molecule is more stable than the mixture of *gauche*-conformations of the racemic acid. However, internal hydrogen-bonding, likely to occur in the univalent anion between the carboxylate and carboxyl groups which are forced into a *cis*- (staggered) conformation, would stabilise the racemic ion (with the substituents *trans*) with respect to the *meso*-ion (with the substituents *cis*). Thus it would be expected that $K_{1,\ \mathrm{racemic}} > K_{1,\ \mathrm{meso}}$.

The present data, as shown in Table 1, clearly fail to confirm such a regularity (although shown as a trend in the earlier literature), and the apparent deviation of dimethyl- and dibromo-substituted acids is difficult to explain. From the K_1 data in Table 2 it is seen that 1 : 2-dimethoxysuccinic acids appear to repeat the behaviour of tartaric acids, whilst 1 : 2-diphenylsuccinic acids might be analogous to the methyl- and bromo-acids, as regards the relative magnitudes of K_1 of the *meso*- and racemic isomerides. It is significant that all substituents, even the electron-repelling alkyl groups, increase the strength (K_1) of succinic acid, and that dibromo-substituted acids are stronger than dichloro-acids, although the operation of their $-I$ effects alone should produce the opposite result. It is noteworthy that *trans*-2-methylcyclohexanecarboxylic acid was found [36] to be stronger than the parent acid and twice as strong as its *cis*-2-methyl isomer, although the distance separating

TABLE 4.

Acid	M. p.	Heat of combustion ($-\Delta H_v$) (kcal./mole)	Dipole moment (D) (benzene solution)
Tartaric			
DL	206° (anhyd.)	273·9,[40, 41] 276·7 [42] 275·7 [43]	Et_2 ester 3·12 [44] (at 22°)
meso	143 (anhyd.), 159 (anhyd.)	276·6,[40, 41] 280·7 [42] 280·2 [43]	Et_2 ester 3·66 [44] (at 22°)
1 : 2-Dimethoxysuccinic			
DL	171	Me_2 ester 965·3 [43]	Me_2 ester 2·8 [43]
meso	161	Me_2 ester 954·9 [43]	Me_2 ester 3·1 [43]
1 : 2-Dichlorosuccinic			
DL	175	—	Me_2 ester 2·93 [45]
meso	220 (sealed tube)	—	Me_2 ester (2·47 [45] (at 20°)
1 : 2-Dibromosuccinic			
DL	171	—	—
meso	257 (sealed tube)	—	—
1 : 2-Dimethylsuccinic			
DL	127	671·2 [46]	—
meso	209	672·7 [46]	—
1 : 2-Diethylsuccinic			
DL	132	985·3 [46]	—
meso	192	987·0 [46]	—
1 : 2-Di-*n*-propylsuccinic			
DL	121	—	—
meso	183	—	—
1 : 2-Diphenylsuccinic			
DL	183	1807·0 [46]	—
meso	252	1808·2 [46]	—

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[33] Branch and Calvin, " The Theory of Organic Chemistry," Prentice-Hall, Inc., 1947.

[34] Crawford, *Chem. and Ind.*, 1953, 797.

[35] Elving, Rosenthal, and Martin, *J. Amer. Chem. Soc.*, 1955, **77**, 5218.

[36] Dippy, Hughes, and Laxton, *J.*, 1954, 4102.

methyl and carboxyl groups in the two isomers is the same. This feature has since been discussed in terms of steric hindrance to solvation (notably of the anion [37]); the acid with both the groups in the more accessible *eq–eq* conformation, in this case the *trans*-acid, is stronger than the *eq–ax* or *cis*-acid. It certainly appears that the magnitude of the steric effects of substituents, whether in the cyclohexane molecule or the ethane molecule is regulated not only by intramolecular distances but also by the conformational relationship of the substituents to the rest of the molecule.

The dissociation constants are not alone in failing to reveal any regularity amongst the diastereoisomeric disubstituted succinic acids; a selection of other physical data (Table 4) is scarcely more conclusive. The Auwers–Skita rules for olefins being recalled, it is true that the melting points are higher and solubilities in water lower for the *meso*-acids (" *trans* ") than for the racemic acids (" *cis* ") (except for the tartaric and dimethoxysuccinic acids). From the study of equilibria and reaction rates (see Barton [38]), it has been concluded that the *meso*-form is invariably the more stable (see also Linstead [39]), although heat of combustion data (Table 4) lend no support on this point. The scarce dipole-moment data (for esters) indicate a more symmetrical conformation for dimethyl *meso*-dichlorosuccinate than for the racemic ester, although the reverse is true for the tartaric and dimethoxysuccinic esters (Table 4).

It is noteworthy, however, that Elving, Rosenthal, and Martin [35] have been able to explain some electrode reactions of dibromosuccinic acids (involving elimination of bromine) by assuming that the diastereoisomers exist in the preferred conformations.

EXPERIMENTAL

Preparation and Purification of Acids.—D- and DL-Tartaric acids were purchased, and repeatedly recrystallised from conductivity water. *meso*Tartaric acid was obtained by refluxing D-tartaric acid with aqueous potassium hydroxide, isolated according to Coops and Verkade's procedure,[40] and finally purified by recrystallisations from conductivity water.

DL-Dibromosuccinic was prepared by addition of bromine to maleic anhydride [48] and purified by recrystallisations from ethyl acetate–chloroform. *meso*Dibromosuccinic acid was purchased and recrystallised from conductivity water, care being taken not to raise the temperature above 70° (addition of silver nitrate–nitric acid to the filtrate did not produce turbidity under these conditions).

meso- and DL-Dichlorosuccinic acids were prepared by addition of chlorine to aqueous disodium fumarate (Timmermans [49]) and fractional crystallisation of the mixture of the diastereoisomeric acids from acetone–chloroform.

DL-Dimethylsuccinic acid was derived from a mixture of 1 : 2-dimethylsuccinonitriles (a gift from Imperial Chemical Industries Ltd., Dyestuffs Division) by hydrolysis with concentrated hydrochloric acid; on cooling, the impure *meso*-acid separated as crystals and the DL-acid was extracted with ether from the solution. The residue from the ethereal extract was recrystallised from benzene. *meso*Dimethylsuccinic acid (a gift from Imperial Chemical Industries Ltd., Dyestuffs Division) was purified by recrystallisation from conductivity water.

All the acids were stored in desiccators over silica gel for at least 2 weeks. The m. p.s (shown in Table 5; cf. also best values from the literature, in Table 4) and equivalent weights (by alkalimetry) of all acids were determined.

Measurement of Conductivities.—The conductivities of all solutions were measured by the

[37] Baddeley, *Ann. Reports*, 1955, **52**, 140.
[38] Barton, *Quart. Rev.*, 1956, **10**, 47.
[39] Linstead, *J.*, 1954, 3722.
[40] Coops and Verkade, *Rec. Trav. chim.*, 1925, **44**, 998.
[41] Wasserman, *Z. phys. Chem.*, 1930, *A*, **146**, 418.
[42] Blanck and Wolf, *Z. phys. Chem.*, 1936, *B*, **32**, 139.
[43] Wolf, *Z. phys. Chem.*, 1938, *B*, **38**, 441.
[44] Wolf, *Trans. Faraday Soc.*, 1930, **26**, 315.
[45] Hassel, *Tidskr. Kjemi Bergvesen Met.*, 1930, **10**, 128.
[46] Hartman, *Rec. Trav. chim.*, 1933, **52**, 945.
[47] Duncanson, *J.*, 1952, 1753.
[48] Michael, *J. prakt. Chem.*, 1895, **52**, 293.
[49] Timmermans, *Bull. Soc. chim. belges*, 1939, **48**, 33.

TABLE 5.

Acid	M. p.	Acid	M. p.
D-Tartaric	169·5—170°	DL-1 : 2-Dibromosuccinic...	172°
DL-Tartaric	208	*meso*-1 : 2-Dibromosuccinic	257·5 (sealed tube)
*meso*Tartaric	151·5—152	DL-1 : 2-Dimethylsuccinic	121·5—122
DL-1 : 2-Dichlorosuccinic ...	171·2	*meso*-1 : 2-Dimethylsuccinic	211
meso-1 : 2-Dichlorosuccinic	223·5 (sealed tube)	Succinic	185

TABLE 6. *Table of conductivities and* K_1 *values.*

(*a*) Davies's method of calculating Λ°.

(N.B. Λ denotes the conductivity of the dicarboxylic acid for the range where it behaves as a monobasic one, and its equiv. wt. = mol. wt.)

D-Tartaric acid

10^3M	Λ	$10^5K_{1,\ \text{therm.}}$
7·970	115·3	93·0
7·441	118·5	93·0
6·766	123·4	93·7
6·634	124·6	94·0
6·306	127·0	94·1
5·593	133·6	94·7
5·413	134·8	93·9
4·497	145·6	95·5
4·437	146·3	95·4
3·869	154·4	96·1

($\Lambda^{0}_{(\mathrm{H}^{+}\frac{1}{2}\mathrm{A}^{2-})}$ = 413·0 from the conductivity of disodium salt; $\Lambda^{0}_{(\mathrm{H}^{+}\mathrm{HA}^{-})}$ = 388·7 from the conductivity of monosodium salt by Davies's method.)

DL-Tartaric acid

10^3M	Λ	$10^5K_{1,\ \text{therm.}}$
8·364	112·4	91·8
6·717	122·9	92·1
5·781	130·7	92·7
4·979	139·2	93·9
4·383	146·2	94·4

($\Lambda^{0}_{(\mathrm{H}^{+}\frac{1}{2}\mathrm{A}^{2-})}$ = 413·0, assumed; $\Lambda^{0}_{(\mathrm{H}^{+}\mathrm{AH}^{-})}$ = 388·7, assumed.)

*meso*Tartaric acid

10^3M	Λ	$10^5K_{1,\ \text{therm.}}$
7·996	93·99	60·0
7·782	95·00	59·9
6·928	99·82	60·0
6·400	103·4	60·4
6·380	103·5	60·4
5·537	109·6	60·2
5·187	112·8	60·0
3·600	130·8	(61·0)

($\Lambda^{0}_{(\mathrm{H}^{+}\frac{1}{2}\mathrm{A}^{2-})}$ = 413·8 from the conductivity of disodium salt; $\Lambda^{0}_{(\mathrm{H}^{+}\mathrm{HA}^{-})}$ = 382·7 from the conductivity of monosodium salt by Davies's method.)

(*b*) Darken's graphical extrapolation for Λ^0 and $K_{1,\ \text{therm.}}$.

DL-1 : 2-Dichlorosuccinic acid

10^3M	Λ	$10^2K_{1,\ \text{therm.}}$
60·18	189·8	(2·39)
67·56	182·0	2·34
72·04	177·9	2·32
82·66	169·2	2·27
91·33	162·9	2·24
96·51	159·6	2·22
101·7	156·3	2·20
105·7	154·1	2·19
114·9	149·1	2·16

Extrapolated $10^2K_1{}^0{}_{,\ \text{therm.}}$ = 2·54; Λ_0 = 383·5.

meso-1 : 2-Dichlorosuccinic acid

10^3M	Λ	$10^2K_{1,\ \text{therm.}}$
71·93	171·1	2·09
72·86	170·7	2·09
78·93	165·1	2·06
88·45	158·1	2·02
93·23	154·9	2·01
102·2	149·6	1·98
113·3	143·4	1·94
122·5	139·0	1·92

Extrapolated $10^2K_1{}^0{}_{,\ \text{therm.}}$ = 2·23; Λ_0 = 382·5.

DL-1 : 2-Dibromosuccinic acid

10^3M	Λ	$10^2K_{1,\ \text{therm.}}$
76·78	188·6	3·00
77·57	187·9	3·00
82·46	184·1	2·97
85·16	182·0	2·95
91·55	177·4	2·92
93·76	175·9	2·92
101·6	170·9	2·88

Extrapolated $10^2K_1{}^0{}_{,\ \text{therm.}}$ = 3·30; Λ_0 = 380·0.

meso-1 : 2-Dibromosuccinic acid

10^3M	Λ	$10^2K_{1,\ \text{therm.}}$
75·64	194·5	3·26
80·87	189·7	3·20
81·48	189·0	3·19
85·35	185·9	3·16
90·72	181·8	3·11
91·09	181·4	3·10

Extrapolated $10^2K_1{}^0{}_{,\ \text{therm.}}$ = 3·76; Λ_0 = 380·0.

method and equipment described elsewhere,[50] and all solutions were prepared individually by weight.[50] A pipette-type cell (cell constant, *ca.* 25) was used for the stronger halogeno-succinic acids, and calibrated directly with 0·1D-potassium chloride solution (by using the specific conductance data of Jones and Bradshaw [51]).

Derivation of $K_{1,\ \text{therm.}}$.—For moderately strong acids, measurements were made on the free acid in the region above *ca.* 0·003 equiv./l. (where secondary dissociation is negligible) and on

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[50] Dippy, Hughes, and Laxton, *J.*, 1954, 1470.

[51] Jones and Bradshaw, *J. Amer. Chem. Soc.*, 1933, **55**, 1780.

the mono- and di-sodium salts. $\Lambda^\circ_{(\mathrm{H}^+\mathrm{HA}^-)}$ was calculated by Davies's successive approximations method [1] from the conductivity of the above types of electrolyte; this is the only method (free from serious assumptions) for the derivation of $\Lambda^\circ_{(\mathrm{H}^+\mathrm{HA}^-)}$. Approximate values of K_1 and K_2 required for the calculation were obtained potentiometrically. $\Lambda^\circ_{(\mathrm{H}^+\frac{1}{2}\mathrm{A}^{2-})}$ was evaluated from data for the neutral sodium salt by the empirical method described by Dippy and Williams,[52] and $K_{1,\,\text{therm.}}$ calculated in the way described earlier, for monobasic acids.

For halogeno-succinic acids, secondary dissociation is significant in the range of concentrations where the Debye–Hückel limiting law is obeyed. An empirical extrapolation method described by Darken [2] was used in these cases to determine $K_{1,\,\text{therm.}}$ from the conductivity of the free acid at moderate concentrations, and it was found that his correction factor for secondary dissociation, as calculated from low-concentration data, was negligible. K_1 values calculated by Darken's method (which is limited to very soluble acids) are estimated to be accurate to within ±3%; whilst those calculated by Davies's method are within ±1%.

Measurement of pH.—A Cambridge pH-meter was used to measure the E.M.F. of solutions and this was calibrated by means of citric acid–Sörensen's salt buffers,[53] chosen because of their ease of preparation by mixing two stable stock solutions. No correction to paH scale was made, owing to the overall accuracy of the method, and good agreement was obtained with Speakman's results [13] for succinic acid (possibly owing to cancellation of errors, such as the unknown temperature specifications of the buffers).

The cell consisted of a sealed glass-electrode and a saturated potassium chloride dip-type calomel electrode (both supplied by the Cambridge Instrument Co.). All acid solutions were prepared in conductivity water by weight, and the sodium hydroxide solution (much more concentrated than the acid, to avoid large volume changes during titration) was run into the electrode vessel from a calibrated E-mil Green Line 2-ml. microburette. Several additions of gradually increasing amounts of the alkali solution were made between 25 and 75% neutralisation so as to obtain points at regular intervals on the graph. All measurements were conducted at 25°.

TABLE 7. *Potentiometric determination of* $K_{1,\,\text{therm.}}$ *and* $K_{2,\,\text{therm.}}$.

Total volume of acid titrated in each case = 75 ml. Sodium hydroxide solution, *ca.* 0·02N (except for halogeno-acids, when it was *ca.* 0·10N).

10^3M	$10^5K_{1,\,\text{therm.}}$	$10^5K_{2,\,\text{therm.}}$	10^3M	$10^5K_{1,\,\text{therm.}}$	$10^5K_{2,\,\text{therm.}}$	10^3M	$10^5K_{1,\,\text{therm.}}$	$10^5K_{2,\,\text{therm.}}$
D-Tartaric acid			*meso*-1 : 2-Dibromosuccinic acid			*meso*-1 : 2-Dimethylsuccinic acid		
0·599	90	3·2	5·01	3900	104	0·584	16·9	0·53
0·966	104	3·4	5·37	3900	105	1·053	17·0	0·38
1·223	83	3·9	5·63	3700	114	1·519	17·3	0·42
1·849	93	3·3						
			*meso*Tartaric acid			Succinic acid		
DL-1 : 2-Dichlorosuccinic acid			0·622	52	1·20	0·538	6·1	0·20
4·195	2120	67	0·782	50	1·22	0·722	6·2	0·18
4·32	2200	67	2·005	51	(0·82)			
5·06	2000	65						
			meso-1 : 2-Dichlorosuccinic acid					
DL-1 : 2-Dimethylsuccinic acid			4·53	1760	61			
0·538	12·1	0·11	5·89	1860	54			
0·913	11·8	0·09						
1·301	12·0	0·10						

Derivation of K_1 *and* K_2.—The method used for the determination of approximate values of K_1 and K_2, necessary for the evaluation of accurate value of K_1 from conductivity data by Davies's method, was that due to Speakman.[13] This gives average K_1 and K_2 values based on all the experimental values of pH at different points of neutralisation. The accuracy of the method is about ±5%.

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