388. *The Dissociation Constants of Organic Acids. Part XVI.* The Thermodynamic Primary Dissociation Constants of some Alkylmalonic Acids.*

By George H. Jeffery and Arthur I. Vogel.

Part I (J., 1929, 1476) of this series records the results of some preliminary measurements of the "classical" dissociation constants of a number of substituted malonic acids. These values, as already pointed out (Part XI, J., 1935, 30; Part XIII, *ibid.*, p. 1624), are subject to a number of errors and are only approximate. New measurements have now been carried out with methyl-, ethyl-, *n*-propyl-, dimethyl-, methylethyl-, diethyl-, ethyl-*n*-propyl-, and di-*n*-propyl-malonic acids in silica Hartley cells and of the sodium salts in Pyrex Hartley cells at 25° over the concentration range 0·0001—0·01*N*. The data for the sodium salts have been corrected for hydrolysis and for the carbonic acid present in the water used (J., 1935, 24), and the limiting mobilities evaluated. The thermodynamic primary dissociation constants have been computed by a modification of MacInnes's method (cf. Part XI, *loc. cit.*). No trustworthy determinations of the true primary dissociation constants by conductivity have been published previously, the only data available for comparison being Gane and Ingold's potentiometric measurements (J., 1929, 1691). Those authors corrected the classical values to zero ionic strength by an empirical method (J., 1931, 2153), and stated that a modification of the method of calculation by a suitable application of Debye and Hückel's equation for the activities of electrolytes "involves practical difficulties" (see, however, Part XIII, p. 1629, and Part XIV, where a method is described in which these difficulties are overcome). Table I contains our true primary constants, Gane and Ingold's corrected values, and the limiting mobilities of the ions.

Table I.

Malonic acid.	$K_1 \times 10^4$ (G. & I.).	K_1, therm. (J. & V.).	$l_{0X''}$.	Malonic acid.	$K_1 \times 10^4$ (G. & I.).	K_1, therm. (J. & V.).	$l_{0X''}$.
Methyl-	8·92	8·47	61·4	Methylethyl- ...	13·8	15·43	53·1
Ethyl-	10·3	10·94	57·7	Diethyl-	61·5	70·80	52·5
n-Propyl-	10·1	10·26	53·7	Ethyl-*n*-propyl...	71·6	78·37	51·7
Dimethyl-	6·83	7·06	57·2	Di-*n*-propyl- ...	85·8	91·98	51·1

For some acids the differences between the two values are considerable. The acids employed by Gane and Ingold "were either purchased or prepared by known methods, and in all cases carefully purified by recrystallisation before use" (J., 1929, 1698); no record is given either of the melting points of the pure acids or of the solvents employed for recrystallisation. Our own acids were analytically pure, and all the relevant experimental details are given in the "Experimental" section. Gane and Ingold employed the saturated calomel half cell in their measurements, for which they found a value, after standardisation against Walpole's acetate buffers, of 0·2509 volt at 25° (Ingold and Mohrhenn, J., 1935, 951). German and Vogel (Part XII, J., 1935, 913) obtained the experimental figure of 0·2458 volt at 25°, in good agreement with those of Clark ("The Determination of Hydrogen Ions," 1928, 314, 672) and Britton ("Hydrogen Ions," 1932, 24). An error of 1 mv. will cause a variation of about 5% in the magnitude of the dissociation constants (see Part XIV, p. 1547). It is probable that both the difference of *ca.* 4·5 mv. and the empirical method of extrapolation to $\mu = 0$ contribute to the discrepancies between the two sets of values for K_1.

The limiting mobilities of isomeric ions are in Table II, which includes also the data for the normal dibasic acids previously recorded (J., 1935, 22). The mobility of the normal straight-chain acid ion is slightly lower than that of the substituted acid ion, the difference

* Two recent papers (*J. Amer. Chem. Soc.*, 1936, **58**, 1546; *Phil. Mag.*, 1936, **22**, 790) are regarded as Parts XIV and XV respectively.

TABLE II.

Mobilities of Isomeric Ions at 25°.

$(CH_2)_2(CO_2^-)_2$	60·9	$(CH_2)_3(CO_2^-)_2$	56·9	$(CH_2)_6(CO_2^-)_2$	47·4
$CHMe(CO_2^-)_2$	61·4	$CHEt(CO_2^-)_2$	57·7	$CEtPr^{\alpha}(CO_2^-)_2$	51·7
		$CMe_2(CO_2^-)_2$	57·2		
$(CH_2)_4(CO_2^-)_2$	52·9				
$CHPr^{\alpha}(CO_2^-)_2$	53·7	$(CH_2)_5(CO_2^-)_2$	50·1		
$CMeEt(CO_2^-)_2$	53·1	$CEt_2(CO_2^-)_2$	52·5		

being greatest for diethyl- and ethyl-*n*-propyl-malonates; this runs parallel with the large increase in dissociation constant observed in passing from methylethyl- to diethyl- and more highly substituted acids. The subject will be discussed further when more data have been accumulated.

EXPERIMENTAL.

Preparation of Materials.—Acids. The preparation and purification of all substances were carried out in Pyrex vessels, and all solvents for recrystallisation were of analytical reagent purity. The acids marked " B " were specially prepared and purified by Messrs. Boots.

(I) *Methylmalonic acid* (B). Recrystallised from benzene–ether–light petroleum (b.p. 40—60°); m. p. 132° (decomp.).

(II) *Ethylmalonic acid* (B). Recrystallised as for (I); m. p. 114·5° (decomp.).

(III) n-*Propylmalonic acid.* This was prepared as described in J., 1934, 337, and recrystallised successively from benzene and benzene–light petroleum (b. p. 40—60°); m. p. 96° (decomp.).

(IV) *Dimethylmalonic acid.* Kahlbaum's acid was recrystallised from benzene–ether–light petroleum (b. p. 60—80°); m. p. 193·5°.

(V) *Methylethylmalonic acid.* Kahlbaum's acid was recrystallised as for (I); m. p. 121°.

(VI) *Diethylmalonic acid* (B). Recrystallised as for (IV); m. p. 127°.

(VII) *Ethyl*-n-*propylmalonic acid.* This was prepared and purified as described in J., 1929, 1477; m. p. 116°.

(VIII) *Di*-n-*propylmalonic acid.* Kahlbaum's acid was recrystallised from chloroform and had m. p. 160°.

All the acids were dried in a vacuum desiccator over calcium chloride for several days before use.

Sodium salts. The methyl- and ethyl-malonates were prepared and purified by Messrs. Boots. The other salts were prepared by treating weighed quantities of the pure acids with the calculated volume of standardised sodium hydroxide solution, prepared from the AnalaR solid, and the resultant solutions were evaporated to dryness on the water-bath. All the salts were recrystallised from dilute alcohol; methyl-, ethyl-, dimethyl-, ethyl-*n*-propyl-, and di-*n*-propyl-malonates from ethyl alcohol, and *n*-propyl-, methylethyl- and diethyl-malonates from methyl alcohol, and then dried at 130°. In all cases the sodium content was determined by conversion into sulphate; the analytical data were as follows:

Substituent.		Me.	Et.	Pr^{α}.	Me_2.	MeEt.	Et_2.	$EtPr^{\alpha}$.	Pr^{α}_2.
Na, %	Found	28·31	26·18	24·17	26·10	24·23	22·61	21·12	19·85
	Calc.	28·29	26·15	24·22	26·15	24·22	22·55	21·10	19·84

General Technique and Apparatus for Conductivity Measurements.—This has been described in Part XI (*loc. cit.*). The same Hartley cells were employed, and their cell constants found to be unchanged. All measurements were carried out at 25° ± 0·01°.

For the sodium salts, the application of a " normal " solvent correction yielded the following results for the preliminary calculation of the mobilities required for the application of the combined solvent and hydrolysis correction (J., 1935, 24).

Na salt of		$l_{0X''}$	$l_{0HX'}$	Na salt of		$l_{0X''}$	$l_{0HX'}$
(I)	$\mu_0^n=\mu_c+1236{\cdot}0\ C^{0{\cdot}736}=214{\cdot}7$	57·6	28·8	(V)	$\mu_0^n=\mu_c+791{\cdot}4\ C^{0{\cdot}664}=196{\cdot}8$	48·6	24·3
(II)	$\mu_0^n=\mu_c+1142{\cdot}4\ C^{0{\cdot}740}=205{\cdot}2$	52·8	26·4	(VI)	$\mu_0^n=\mu_c+874{\cdot}3\ C^{0{\cdot}675}=195{\cdot}0$	47·7	23·9
(III)	$\mu_0^n=\mu_c+1050{\cdot}7\ C^{0{\cdot}718}=197{\cdot}5$	48·9	24·5	(VII)	$\mu_0^n=\mu_c+771{\cdot}5\ C^{0{\cdot}652}=193{\cdot}4$	46·9	23·5
(IV)	$\mu_0^n=\mu_c+\ 886{\cdot}5\ C^{0{\cdot}680}=204{\cdot}5$	52·5	26·3	(VIII)	$\mu_0^n=\mu_c+971{\cdot}0\ C^{0{\cdot}684}=190{\cdot}6$	45·5	22·8

The limiting mobilities of the acid ions were calculated from the relation $l_{0HX'} = 0{\cdot}53 l_{0X''}$ (Part XI, *loc. cit.*). The approximate values for the secondary dissociation constants employed were: 1·5 × 10^{-6} for acids (I), (II), and (III); 1·0 × 10^{-6} for (IV); 0·5 × 10^{-6} for (V); 0·5 × 10^{-7} for (VI), (VII), and (VIII). The corrected results for the sodium salts at 25° are in Table III.

TABLE III.

Sodium methylmalonate (M = 162·03).

$\mu_0^n = \mu_c + 315{\cdot}3C^{0{\cdot}445}$; $\mu_0^n = 222{\cdot}46$; $l_{0_{X''}} = 61{\cdot}4$; $l_{0_{HX'}} = 32{\cdot}5$.

$C \times 10^4$. Run 1.	μ, obs.	[H˙]×10^8. Cell V.	μ, corr. κ = 0·670	μ_0^n.	$C \times 10^4$.	μ, obs. Run 2.	[H˙]×10^8. Cell S.	μ, corr. κ = 0·675.	μ_0^n.
1·710	212·33	7·63	218·18	—	3·512	210·95	2·99	213·72	—
5·993	209·40	2·19	210·93	222·57	9·951	206·90	1·44	207·84	222·39
12·36	205·82	1·11	206·47	222·43	17·54	203·05	0·83	203·52	222·28
22·41	201·04	0·65	201·34	222·21	30·17	198·33	0·51	198·57	222·38
37·78	196·26	0·42	196·36	222·58	45·46	194·12	0·33	194·21	222·69
57·81	191·86	0·30	191·95	(223·73)	61·72	190·89	0·29	190·96	(224·02)
75·73	188·69	0·25	188·76	—	82·53	187·68	0·24	187·73	—
97·07	185·64	0·20	185·71	—	94·07	186·16	0·21	186·20	—

Sodium ethyimalonate (M = 176·04).

$\mu_0^n = \mu_c + 274{\cdot}9C^{0{\cdot}414}$; $\mu_0^n = 214{\cdot}97$; $l_{0_{X''}} = 57{\cdot}7$; $l_{0_{HX'}} = 30{\cdot}6$.

Run 1.		Cell V.	κ = 0·666.		Run 2		Cell S.	κ = 0·671.	
1·024	204·46	13·00	213·80	—	3·142	202·41	3·21	205·17	—
5·264	201·47	2·19	202·93	214·99	7·618	199·69	1·78	200·91	215·10
11·37	197·58	1·27	198·14	214·79	15·16	195·77	0·97	196·39	215·07
23·60	192·16	0·64	192·58	215·05	25·47	191·38	0·58	191·75	214·96
35·60	188·17	0·43	188·30	214·91	38·76	187·06	0·42	187·30	214·84
51·98	184·20	0·31	184·28	(215·48)	54·45	183·19	0·30	183·30	215·03
67·59	180·71	0·27	180·73	—	71·19	180·12	0·26	180·19	(215·67)
85·89	177·75	0·22	177·76	—	99·80	176·08	0·19	176·09	—

Sodium n-*propylmalonate* (M = 190·06).

$\mu_0^n = \mu_c + 303{\cdot}8C^{0{\cdot}426}$; $\mu_0^n = 206{\cdot}98$; $l_{0_{X''}} = 53{\cdot}7$; $l_{0_{HX'}} = 28{\cdot}5$.

Run 1.		Cell V.	κ = 0·659.		Run 2.		Cell S.	κ = 0·676.	
1·004	196·05	13·2	206·43	—	3·512	193·91	3·52	196·88	—
4·695	193·89	2·51	195·52	207·13	7·527	191·50	1·77	192·62	206·76
11·73	188·72	1·25	189·54	206·97	16·44	186·60	0·91	186·99	206·77
22·44	184·38	0·67	184·78	207·39	27·23	182·02	0·56	182·38	206·88
31·71	180·84	0·47	181·01	207·18	36·91	179·51	0·42	179·84	(207·72)
47·75	176·47	0·32	176·60	(207·75)	57·48	174·06	0·30	174·21	—
61·63	173·46	0·29	173·54	—	72·56	171·76	0·28	171·90	—
82·05	170·81	0·22	170·84	—	98·61	169·42	0·19	169·45	—

Sodium dimethylmalonate (M = 176·04).

$\mu_0^n = \mu_c + 264{\cdot}9C^{0{\cdot}398}$; $\mu_0^n = 214{\cdot}01$; $l_{0_{X''}} = 57{\cdot}2$; $l_{0_{HX'}} = 30{\cdot}3$.

Run 1.		Cell V.	κ = 0·555.		Run 2.		Cell S.	κ = 0·571.	
1·241	202·29	5·04	208·07	—	2·712	200·97	2·12	203·44	—
5·409	199·56	1·25	200·71	213·97	7·598	197·81	1·01	198·62	213·81
10·64	196·09	0·69	196·60	213·96	14·99	193·50	0·52	194·01	213·90
23·14	190·18	0·37	190·23	213·88	28·17	188·23	0·33	188·35	213·93
42·53	184·10	0·21	184·12	214·29	38·24	185·08	0·23	185·18	214·08
63·37	179·39	0·19	179·39	(214·68)	53·41	181·22	0·20	181·24	214·26
82·11	176·30	0·16	176·28	—	72·65	177·58	0·18	177·58	(214·85)
103·2	173·02	0·13	172·98	—	91·61	174·49	0·14	174·46	—

Sodium methylethylmalonate (M = 190·06).

$\mu_0^n = \mu_c + 278{\cdot}3C^{0{\cdot}408}$; $\mu_0^n = 205{\cdot}88$; $l_{0_{X''}} = 53{\cdot}1$; $l_{0_{HX'}} = 28{\cdot}1$.

Run 1.		Cell V.	κ = 0·688.		Run 2.		Cell S.	κ = 0·657.	
1·210	195·07	3·92	203·00	—	2·712	193·11	1·71	195·82	—
5·584	191·78	0·88	193·29	(206·47)	8·699	189·52	0·66	190·18	205·87
11·30	187·67	0·48	188·32	205·79	16·24	185·01	0·33	185·81	206·05
22·46	182·39	0·27	182·77	205·88	28·99	180·09	0·27	180·24	205·84
33·58	178·49	0·25	178·61	205·85	42·61	175·68	0·23	175·79	205·83
53·12	173·64	0·21	173·64	(206·46)	60·53	171·67	0·20	171·67	(206·32)
67·92	170·68	0·17	170·67	(206·85)	77·78	168·82	0·15	168·80	(207·13)
86·63	167·60	0·11	167·56	—	99·71	166·23	0·09	166·17	—

Sodium diethylmalonate (M = 204·07).

$\mu_0^{*} = \mu_c + 243{\cdot}0C^{0{\cdot}376}$; $\mu_0^{*} = 204{\cdot}53$; $l_{0X''} = 52{\cdot}5$; $l_{0HX'} = 27{\cdot}8$.

Run 1.	Cell V.	$\kappa = 0{\cdot}748$.			Run 2.	Cell S.	$\kappa = 0{\cdot}740$.		
1·414	193·11	0·552	199·68	—	2·997	191·17	0·214	192·22	—
6·223	189·19	0·138	189·18	204·32	9·992	186·32	0·171	186·32	204·41
12·78	185·07	0·086	184·62	204·46	16·23	182·98	0·075	182·89	204·57
23·54	180·07	0·056	179·53	204·50	26·98	178·65	0·053	178·42	204·68
43·91	173·60	0·040	173·05	204·61	39·81	174·91	0·047	174·21	204·65
63·63	169·33	0·032	168·82	(205·13)	53·64	171·16	0 030	170 76	(204 80)
85·32	166·01	0·028	165·51	—	74·52	167·43	0·029	166·89	—
102·9	163·29	0·025	162·80	—	90·33	165·09	0·026	164·43	—

*Sodium ethyl-*n*-propylmalonate* (M = 218·09).

$\mu_0^{*} = \mu_c + 229{\cdot}6C^{0{\cdot}366}$; $\mu_0^{*} = 203{\cdot}05$; $l_{0X''} = 51{\cdot}7$; $l_{0HX'} = 27{\cdot}4$.

Run. 1.	Cell V.	$\kappa = 0{\cdot}741$.			Run 2.	Cell S.	$\kappa = 0{\cdot}743$.		
0·918	190·22	0·779	199·46	—	3·312	189·11	0·212	191·91	—
6·536	187·22	0·137	187·51	203·36	10·24	184·62	0·100	184·54	203·01
11·62	183·93	0·095	183·68	203·01	17·11	181·33	0·072	180·71	203·02
19·04	180·14	0·058	179·29	202·88	29·29	180·36	0·049	175·74	202·91
31·26	175·62	0·046	174·96	202·77	42·14	172·41	0·036	171·90	202·93
47·72	171·40	0·033	170·85	203·32	56·28	169·18	0·031	168·78	203·25
60·93	168·53	0·030	168·02	(203·52)	74·99	165·92	0·028	165·51	(203·83)
78·59	165·45	0·028	164·98	—	97·82	163·08	0·026	162·48	—

*Sodium di-*n*-propylmalonate* (M = 232·11).

$\mu_0^{*} = \mu_c + 218{\cdot}3C^{0{\cdot}347}$; $\mu_0^{*} = 201{\cdot}73$; $l_{0X''} = 51{\cdot}1$; $l_{0HX'} = 27{\cdot}1$.

Run 1.	Cell V.	$\kappa = 0{\cdot}751$.			Run 2.	Cell S.	$\kappa = 0{\cdot}755$.		
5·416	185·98	0·159	186·26	(202·36)	2 751	187·70	0·22	190·85	—
10·60	181·86	0·104	181·54	201·79	7·342	183·91	0·13	183·90	201·75
16·86	178·05	0·073	177·51	201·61	13·72	179·93	0·082	179·58	202·08
31·30	172·48	0·056	172·13	201·65	23·84	175·36	0·056	174·82	201·65
51·12	167·83	0·031	167·20	(202·23)	38·28	170·42	0·048	169·95	201·58
62·34	164·99	0·030	164·36	(202·88)	59·57	165·48	0·030	164·89	201·77
86·18	161·00	0·027	160·37	—	77·72	162·19	0·028	161·68	(203·17)
					100·6	158·85	0·024	158·45	—

The values at round concentrations, obtained with a flexible spline, are in Table IV.

TABLE IV.

Molecular Conductivities of Sodium Salts of Alkylmalonic Acids at 25°.

$C \times 10^4$.	Me.	Et.	Pr^a.	Me$_2$.	MeEt.	Et$_2$.	EtPr^a.	Pr$^a{}_2$.
5·0	212·00	203·10	195·30	200·80	193·18	190·10	188·15	186·50
10·0	207·85	199·08	190·85	197·00	189·25	186·46	183·85	181·92
20·0	202·45	194·02	185·30	191·62	183·90	181·05	178·18	176·25
30·0	198·62	190·15	181·32	187·72	179·92	177·20	174·48	172·55
40·0	195·65	187·00	178·20	184·62	176·68	174·15	171·52	169·55
50·0	193·25	184·35	175·68	182·08	174·02	171·62	169·12	166·98
60·0	191·28	182·22	173·72	179·92	171·82	169·50	167·10	164·83
70·0	189·52	180·32	172·20	178·02	169·96	167·65	165·35	162·96
80·0	188·00	178·68	170·95	176·35	168·40	166·05	163·83	161·35
90·0	186·65	177·28	170·05	174·85	167·05	164·55	162·50	159·90
100·0	185·38	176·00	169·38	173·43	165·80	163·20	161·25	158·62

The True Primary Dissociation Constants.—These were computed exactly as detailed in Part XI (*loc. cit.*). The data employed for the sodium hydrogen salts were :

Acid.	(I)	(II)	(III)	(IV)	(V)	(VI)	(VII)	(VIII)
Λ_0	82·3	80·4	78·3	80·1	77·9	77·6	77·2	76·9
x	78·56	78·13	77·65	78·06	77·56	77·49	77·40	77·34

The values for K_1, therm., were not calculated for some of the results at low concentrations, for experience has shown that they are of little value in its final evaluation. The collected

TABLE V.

Primary Dissociation Constants at 25°.

$C \times 10$.	μ, obs.	10^3K_1, class.	Λ_i.	$c''' \times 10^4$.	10^3K_1, therm.	$C \times 10$.	μ, obs.	10^3K_1, class.	Λ_i.	$c''' \times 10^4$.	10^3K_1, therm.
Methylmalonic Acid (M = 118·05; Λ_0 = 380·5).											
	Run 1.	Cell Q.		κ = 0·768.			Run 2.	Cell R.		κ = 0·751.	
1·096	347·17	(1·041)	—	—	—	3·985	299·51	(1·160)	—	—	—
5·383	267·02	(0·889)	—	—	—	8·187	242·75	(0·921)	—	—	—
10·88	222·14	0·891	378·52	6·3830	0·855	14·99	202·43	(0·907)	—	—	—
24·10	172·04	0·899	377·63	10·9668	0·851	27·07	165·01	0·899	377·93	9·3883	0·853
49·59	131·28	0·901	376·20	17·3462	0·842	38·37	144·98	0·900	376·84	14·7619	0·844
69·40	115·28	0·914	375·58	21·3005	0·847	58·31	123·47	0·909	375·64	20·7183	0·844
90·37	103·50	0·919	375·05	24·9390	0·846	81·88	107·82	0·918	375·25	23·5264	0·847
113·2	94·23	0·923	374·52	28·4880	0·846	101·7	98·49	0·920	374·78	26·7262	0·845
										Mean	0·847
Ethylmalonic Acid (M = 132·06; Λ_0 = 378·6).											
	Run 1.	Cell Q.		κ = 0·570.			Run 2.	Cell R.		κ = 0·562.	
0·942	434·03	—	—	—	—	3·512	312·51	(1·371)	—	—	—
5·719	289·63	(1·424)	—	—	—	7·219	272·01	(1·324)	—	—	—
9·760	250·74	(1·268)	—	—	—	17·01	212·49	(1·221)	—	—	—
23·21	191·14	(1·195)	—	—	—	30·75	173·25	1·187	375·09	14·2031	(1·117)
42·26	154·23	1·183	374·29	17·4128	(1·116)	45·74	149·35	1·176	374·18	18·2683	1·098
64·28	131·34	1·185	373·52	22·6024	1·097	57·75	136·72	1·179	373·73	21·1264	1·095
79·47	120·69	1·186	373·08	25·7065	1·090	72·64	125·19	1·187	373·24	24·3645	1·096
97·64	111·03	1·188	373·56	29·0991	1·088	91·11	114·46	1·194	372·71	27·9801	1·097
										Mean	1·094
n-*Propylmalonic Acid* (M = 146·08; Λ_0 = 376·5).											
	Run 1.	Cell Q.		κ = 0·768.			Run 2.	Cell R.		κ = 0·781.	
1·016	354·70	(1·558)	—	—	—	4·296	291·46	(1·140)	—	—	—
5·314	275·62	(1·063)	—	—	—	14·49	215·52	(1·110)	—	—	—
9·896	237·41	1·065	374·55	6·2724	1·024	25·18	178·81	1·082	373·43	12·0570	1·022
21·19	189·28	1·077	373·71	10·7337	1·021	34·95	159·36	1·086	372·83	14·9388	1·019
47·11	142·90	1·094	372·13	18·0915	1·022	53·59	136·41	1·103	371·88	19·6575	1·027
59·55	130·92	1·104	371·68	20·9758	1·025	65·72	126·25	1·112	371·44	22·3378	1·029
69·18	123·58	1·109	371·38	23·0197	1·027	84·37	114·39	1·119	370·93	26·0186	1·030
80·94	116·24	1·119	371·00	25·3596	1·029	103·0	105·47	1·123	370·43	29·3265	1·029
										Mean	1·026
Dimethylmalonic Acid (M = 132·05; Λ_0 = 378·3).											
	Run 1.	Cell Q.		κ = 0·585.			Run 2.	Cell R.		κ = 0·596.	
1·392	326·18	(0·751)	—	—	—	4·460	269·55	(0·788)	—	—	—
10·15	213·44	(0·741)	—	—	—	12·99	197·46	0·741	376·25	6·8173	0·709
17·77	178·27	0·746	375·95	8·4268	0·710	23·78	161·22	0·753	375·61	10·2069	0·713
34·19	140·77	0·754	375·95	12·8266	0·709	31·41	145·34	0·753	375·38	11·3496	0·709
50·61	120·44	0·753	374·31	16·2847	0·705	41·66	130·29	0·754	374·72	14·4852	0·707
68·44	106·60	0·757	373·67	19·5245	0·703	57·57	114·41	0·755	373·97	17·6126	0·704
88·45	96·23	0·768	373·22	22·4934	0·710	75·79	102·25	0·759	373·50	20·7484	0·704
						99·34	91·78	0·772	372·93	24·4481	0·711
										Mean	0·706
Methylethylmalonic Acid (M = 146·08; Λ_0 = 376·1).											
	Run 1.	Cell Q.		κ = 0·678.			Run 2.	Cell R.		κ = 0·674.	
0·985	409·21	—	—	—	—	4·171	325·31	(2·259)	—	—	—
4·952	311·57	(1·981)	—	—	—	19·19	223·88	(1·680)	—	—	—
15·76	236·72	(1·684)	—	—	—	28·44	197·24	1·645	372·42	15·0623	1·550
24·99	206·36	1·664	372·68	13·8294	(1·572)	34·48	184·76	1·636	371·88	17·1306	1·551
50·29	163·00	1·667	371·11	22·0863	1·551	45·01	169·51	1·665	371·34	20·5463	1·553
70·79	143·68	1·672	370·34	27·4670	1·541	58·85	153·88	1·668	370·76	24·4250	1·545
90·32	130·94	1·680	369·66	31·9920	1·538	77·15	139·00	1·672	370·10	28·9755	1·538
106·0	122·92	1·682	369·16	35·2970	1·532	98·60	126·33	1·675	369·42	33·7181	1·531
										Mean	1·543

Diethylmalonic Acid (M = 160·10; Λ_0 = 375·8).

Run 1.	Cell R.	κ = 0·793.			
1·033	409·73	—	—	—	—
5·786	358·23	(11·26)	—	—	—
13·27	327·47	(7·833	—	—	—
25·06	297·66	7·563	371·12	20·1005	7·173
50·74	257·55	7·573	368·37	35·3477	7·138
67·80	239·54	7·597	367·79	44·1592	7·067
92·00	220·57	7·672	366·55	55·3625	6·924
114·2	206·75	7·683	365·65	64·5563	6·967

Run 2.	Cell Q.	κ = 0·801.			
3·775	372·64	(43·17)	—	—	—
18·29	313·35	(7·651)	—	—	—
32·16	284·33	7·563	370·42	24·6856	7·264
41·39	269·76	7·558	369·50	30·9214	7·183
59·26	247·82	7·568	368·29	39·8757	7·083
70·90	236·61	7·586	367·63	45·6319	7·036
84·12	226 20	7·655	366·89	51·8553	7·052
104·7	212·19	7·666	366·02	60·6969	6·985
				Mean	7·080

*Ethyl-*n*-propylmalonic Acid* (M = 174·07; Λ_0 = 375·4).

Run 1.	Cell R.	κ = 0·781.			
1·319	380·31	—	—	—	—
6·607	349·30	(8·400)	—	—	—
12·35	331·43	(8·265)	—	—	—
28·79	294·75	8·263	370·31	22·9166	(7·995)
52·82	260·15	8·263	368·24	37·3174	7·790
76·25	238·39	8·425	366·75	49·5632	7·815
95·53	224·91	8·552	365·79	58·7341	7·844

Run 2.	Cell Q.	κ = 0·842.			
4·311	360·66	(10·13)	—	—	—
19·64	314·33	(8·464)	—	—	—
31·49	290·65	(8·364)	—	—	—
37·93	274·49	8·229	369·45	28·6942	7·871
46·18	268·31	8·269	368·74	33·6024	7·844
60·11	252·58	8·317	367·74	41·2864	7·798
72·18	242·18	8·465	367·01	47·6296	7·872
87·61	230·32	8·532	366·18	55·1050	7·861
				Mean	7·837

*Di-*n*-propylmalonic Acid* (M = 188·13; Λ_0 = 375·1).

Run 1.	Cell R.	κ = 0·741.			
2·524	365·12	(8·992)	—	—	—
6·892	348·21	(8·284)	—	—	—
10·09	337·30	8·094	372·09	10·3576	(8·154)
21·47	312·75	8·981	370·75	18·1113	(8·848)
40·73	283·84	9·585	368·76	31·3505	9·199
62·51	260·25	9·827	367·08	44·3178	9·249
84·16	242·13	9·892	365·82	55·7041	9·167
99·72	232·24	10·04	365·05	63·4405	9·218

Run 2.	Cell Q.	κ = 0·768.			
4·751	355·46	8·142	—	—	—
14·75	325·91	8·493	371·88	12·9267	(8·431)
23·61	310·12	9·317	370·48	19·7634	9·158
36·11	289·98	9·511	369·19	28·3526	9·197
50·62	272·01	9·686	367·93	37·4233	9·205
73·12	250·84	9·870	366·42	50·1557	9·215
78·16	246·72	9·878	366·13	52·6688	9·190
93·23	236·07	9·964	365·37	60·2370	9·182
				Mean	9·198

results are in Table V (the symbols have their customary significance), and the values of μ_c at round concentrations for the acids are in Table VI.

TABLE VI.

Molecular Conductivities of Alkylmalonic Acids at 25°.

$C \times 10^4$.	Me.	Et.	Pr^a.	Me$_2$.	MeEt.	Et$_2$.	EtPr^a.	Pr$_2{}^a$.
1·0	350·0	390·0	331·0	340·0	407·0	410·0	382·0	372·0
5·0	267·6	294·0	274·8	249·5	311·8	363·4	357·8	254·8
10·0	229·5	251·0	238·2	213·0	265·8	339·8	338·0	338·2
20·0	183·4	201·3	193·7	171·6	218·6	309·0	312·3	315·6
30·0	159·5	175·0	167·2	146·6	192·8	288·4	293·4	298·6
40·0	143·6	157·3	151·5	131·6	176·3	272·1	277·8	284·6
50·0	131·8	144·6	139·8	120·7	163·5	258·8	265·1	272·8
60·0	122·7	134·7	130·7	112·3	153·2	247·7	254·1	262·5
70·0	115·3	126·8	123·3	105·7	144·7	237·8	244·7	253·7
80·0	109·0	120·3	116·8	100·2	137·4	229·3	236·3	245·5
90·0	103·7	114·8	111·1	95·5	131·2	221·4	228·7	238·2
100·0	99·2	110·1	105·8	91·6	125·7	214·3	222·1	232·2

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