336. *The Dissociation Constants of Organic Acids. Part XIX. Some Unsaturated Acids.*

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Conductivity measurements in silica or Pyrex cells at 25° over the concentration range 0·0001—0·01*N* of the following acids and their sodium salts have been made: acrylic, *trans*-crotonic, ββ-dimethylacrylic, tetrolic, furoic, and glutaconic acids. The results for the sodium salts have been corrected for hydrolysis and the carbonic acid in the water used.

The thermodynamic dissociation constants of the monobasic acids and the primary dissociation constant of glutaconic acid have been calculated by a modification of MacInnes's method.

The true dissociation constants of the acids have also been determined by potentiometric titration with the quinhydrone electrode.

It is shown that the ratio K_1/K_2 and also the titration curve for glutaconic acid, m. p. 138°, are similar to those for fumaric acid; independent evidence for the *trans*-configuration is thus obtained.

The present communication provides accurate conductivity data over the range 0·0001—0·01*N* for a number of unsaturated acids (and their sodium salts) of theoretical interest. These have been employed for the evaluation of the thermodynamic dissociation constants. Acrylic acid, *trans*-crotonic acid and ββ-dimethylacrylic acid give values for $K_{\text{therm.}}$ in agreement with those expected from the modern electronic theory and are in accord with the work of Ives, Linstead, and Riley (J., 1933, 561).

$CH_2{:}CH{\cdot}CO_2H$	$CHMe{:}CH{\cdot}CO_2H$	$CMe_2{:}CH{\cdot}CO_2H$	$CMe{:}C{\cdot}CO_2H$
$5{\cdot}501 \times 10^{-5}$	$2{\cdot}030 \times 10^{-5}$	$7{\cdot}569 \times 10^{-6}$	$2{\cdot}228 \times 10^{-3}$

The larger value for tetrolic acid as compared with *trans*-crotonic acid is noteworthy. Determination of the true dissociation constants have also been made by potentiometric titration with the quinhydrone electrode. The results agree with the conductivity values within 2—4%, showing that the quinhydrone electrode is trustworthy with these unsaturated acids.

Since the work was completed, independent determinations of $K_{\text{therm.}}$ for *trans*-crotonic acid (Saxton and Waters, *J. Amer. Chem. Soc.*, 1937, **59**, 1048) and acrylic acid (Dippy and Lewis, this vol., p. 1010) have been described. Saxton and Waters find $K_{\text{therm.}} = 1{\cdot}97_5 \times 10^{-5}$, which is about 3% lower than our figure. Their values of Λ for the acid agree well with our own, as do also the measurements of Ives, Linstead, and Riley (*loc. cit.*), but serious divergences (*ca.* 2 units) are apparent in the conductivity figures for the sodium salt. Saxton and Waters prepared their solutions of sodium crotonate from the acid and sodium carbonate—a not altogether satisfactory procedure—and corrected the conductivities for the effect of the excess of acid. Our measurements were made with solutions prepared from pure *solid* sodium crotonate, and corrections for hydrolysis and for the carbonic acid in the equilibrium water used were applied as described in Part XI (J., 1935, 24). The

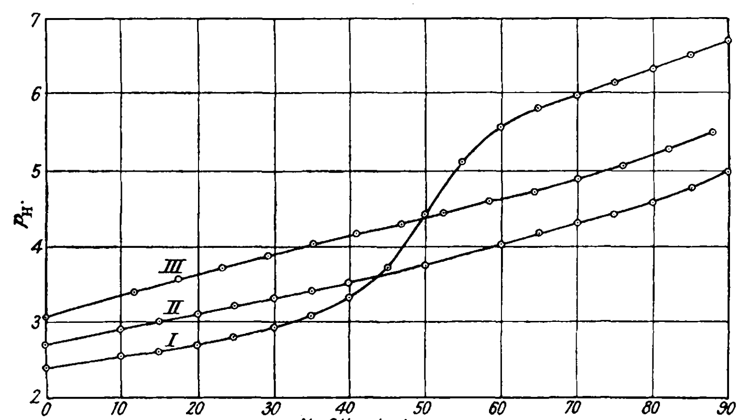
American authors give $\Lambda_0 = 83{\cdot}30$ (sodium salt) and $\Lambda_0 = 383{\cdot}11$ (acid; deduced from their own measurements upon hydrochloric acid and sodium chloride); our values are 84·35 and 381·84 respectively. The latter are in satisfactory agreement with the results of Ives, Linstead, and Riley (*loc. cit.*) (84·4 and 381·8 respectively).

Dippy and Lewis's conductivity figures for acrylic acid are in good agreement with our own, but they give $\Lambda_0 = 87{\cdot}5$ for sodium acrylate (prepared in solution from the acid and sodium hydroxide solution), whereas we find $\Lambda_0 = 90{\cdot}62$. No conductivity figures for the sodium salt are given by Dippy and Lewis, who employed a semi-empirical procedure for the determination of Λ_0 (J., 1934, 162, 1889). The difference between their value of $K_{\text{therm.}}$, $5{\cdot}56 \times 10^{-5}$ [$\Lambda_0 = 387{\cdot}1$, based on their own value for Λ_0 of the sodium salt and upon MacInnes, Shedlovsky, and Longsworth's figures (*J. Amer. Chem. Soc.*, 1932, **54**, 2758) for the limiting mobilities of the sodium (50·10) and hydrogen (349·72) ions], and that of the present authors, $5{\cdot}501 \times 10^{-5}$ ($\Lambda_0 = 388{\cdot}8$), is due largely to the different values of the mobilities employed in the calculations.

We find $K_{1\text{therm.}}$ for glutaconic acid by conductivity $= 1{\cdot}711 \times 10^{-4}$. The values for $K_{1\text{therm.}}$ and $K_{2\text{therm.}}$, determined by potentiometric titration with the quinhydrone electrode, together with those for maleic and fumaric acids (*Phil. Mag.*, 1936, **22**, 790), are in the following table.

Acid.	$K_{1\text{therm.}}$	$K_{2\text{therm.}}$	K_1/K_2.
Maleic	$1{\cdot}20 \times 10^{-2}$	$5{\cdot}95 \times 10^{-7}$	$2{\cdot}02 \times 10^{-4}$
Fumaric	$9{\cdot}57 \times 10^{-4}$	$4{\cdot}13 \times 10^{-5}$	23·2
Glutaconic	$1{\cdot}70 \times 10^{-4}$	$8{\cdot}38 \times 10^{-6}$	20·3

The similarity between glutaconic and fumaric acids, indicated by the ratios K_1/K_2, is clearly shown by the titration curves (figure); the abscissæ have been displaced for the



I, *Maleic acid.* II, *Fumaric acid.* III, *Glutaconic acid.*

different acids to avoid overlapping. Very strong physical evidence is thus provided for the *trans*-structure of glutaconic acid, m. p. 138°. This view is rendered highly probable by the isolation of the unstable *cis*-glutaconic acid, m. p. 136·0—136·5°, by Malachowski (*Ber.*, 1929, **62**, 1323). This author found for the classical primary dissociation constants of *cis*- and *trans*-glutaconic acid at 0° the values $1{\cdot}43 \times 10^{-4}$ and $1{\cdot}74 \times 10^{-4}$ respectively. These approximate figures alone are insufficient to establish the *cis*- and *trans*-structures of these dibasic acids (compare maleic and fumaric acids); the small difference between them would appear to indicate that the unstable acid has been largely converted into the *trans*-form during the measurements. The original view of Feist as to the isomerism of the glutaconic acids and their derivatives, now accepted, but in slightly modified form, by Thorpe (J., 1931, 547, 1015) and supported by the recent work of Kon and his collaborators (J., 1931 *et seq.*)—ordinary *cis-trans* isomerism coupled with three-carbon tautomerism—is thus confirmed by an independent method.

The dissociation constant of furoic acid found by conductivity is $6{\cdot}776 \times 10^{-4}$ and by potentiometric titration $6{\cdot}99 \times 10^{-4}$. This constant was required in connexion with the new buffer mixtures incorporating furoic acid (*Analyst*, 1937, **62**, 271); the value calculated from the buffer mixtures was $6{\cdot}70 \times 10^{-4}$.

EXPERIMENTAL.

Preparation of Materials.—All the acids (with the exception of acrylic acid) were kept over calcium chloride in vacuum desiccators for several days before use. All solvents were of analytical reagent purity and sodium-dried.

Acrylic acid. 50 G. of Schuchardt's " Acid acrylic crystallis " were distilled from a fractionating Claisen flask in an all Pyrex glass apparatus; the fraction, b. p. 140°/753 mm., m. p. 13°, was used in the determinations (Biilmann, *J. pr. Chem.*, 1900, **61**, 494, gives b. p. 140·8—141°).

trans-*Crotonic acid.* A commercial sample, m. p. 72—73°, was recrystallised from light petroleum (b. p. 40—60°) and then twice from toluene. The feathery flat prisms, which tended to occlude some of the latter solvent, were powdered and left over calcium chloride in a vacuum desiccator for several days. One further recrystallisation from light petroleum (b. p. 60—80°) gave pure crotonic acid, m. p. 72·5°.

ββ-*Dimethylacrylic acid.* This was prepared by a modification of Kohn's method (*Monatsh.*, 1903, **24**, 771)—oxidation of mesityl oxide, b. p. 126—130°, with sodium hypobromite solution at 0°. The acid was recrystallised twice from hot water; m. p. 70°.

Tetrolic aicd. An adaptation of Feist's method (*Annalen*, 1906, **345**, 104) was employed. In the final purification the oily acid was extracted with 15% potassium hydroxide solution, the aqueous extract cautiously acidified with hydrochloric acid, and the separated oil extracted three times with ether after saturation with ammonium sulphate. The oil left after removal of the ether crystallised partly on keeping; it was distilled under diminished pressure. The fraction, b. p. 90—95°/5 mm., solidified completely on cooling. The solid crystallised from carbon tetrachloride in thin prisms, m. p. 78°.

Glutaconic acid. The method of Conrad and Gutzeit (*Ber.*, 1882, **15**, 284; *Annalen*, 1883, **222**, 249: compare Gutzeit and Bolam, *J. pr. Chem.*, 1896, **54**, 359; Heinrich, *Monatsh.*, 1899, **20**, 551; Ingold and Perren, J., 1921, **119**, 1591), modified in certain details, was employed. The hydrolysis of the ethyl dicarbethoxyglutaconate was conducted as follows. 66 G. of the oil were treated with 70 c.c. of concentrated hydrochloric acid and 140 c.c. of water. The mixture was refluxed for 7 hours, evaporated to a small bulk on the water-bath, and extracted six times with ether. The dried extract (anhydrous sodium sulphate) was evaporated, and the residue spread on a porous tile. The sticky residue was triturated on the tile with light petroleum (b. p. 40—60°); this treatment removed oily matter and various impurities and led to a clean product. The residue (6·5 g.), m. p. 134—136°, was recrystallised twice from ether–light petroleum (b. p. 40—60°) and melted sharply at 138° (compare Conrad and Gutzeit, *loc. cit.*, m. p. 133°; Gutzeit and Bolam, *loc. cit.*, m. p. 137—138°; Birch, J., 1930, 310, m. p. 132°; Malachowski, *loc. cit.*, m. p. 138·0—138·5°).

Furoic acid. The commercial product, m. p. 131—133°, was crystallised from boiling water (charcoal) and then had m. p. 132—133°. 100 G. of this acid, 200 g. of absolute alcohol, 200 g. of sodium-dried AnalaR benzene, and 20 g. of concentrated sulphuric acid were refluxed for 20 hours. After the usual working-up, including washing with sodium hydroxide solution to remove unchanged acid, 75 g. of pure ethyl furoate, b. p. 192°/746 mm., m. p. 38°, were obtained. A mixture of 60 g. of this ester in 120 g. of rectified spirit and 52 g. (2 mols.) of potassium hydroxide in 104 g. of water was refluxed for 16 hours, and then evaporated to dryness on the water-bath. The residue was triturated with ether, acidified with a large excess of dilute sulphuric acid at 0°, and extracted four times with ether. 49 G. of acid obtained on evaporation of the dried (anhydrous sodium sulphate) ethereal solution were recrystallised from chloroform and dried in a vacuum over calcium chloride; the product melted sharply at 132°.

Sodium salts. These were prepared by the sodium ethoxide method as employed for sodium malonamate (Part IX, J., 1934, 1102). Sodium ββ-dimethylacrylate did not separate from the absolute alcoholic solution and was precipitated by the addition of pure ether; it was purified by dissolution in absolute alcohol and precipitation with ether (Found: Na, 18·8. Calc., 18·9%). The other salts were purified by solution in a small volume of water and precipitation with absolute methyl or ethyl alcohol: sodium crotonate (ethyl alcohol) (Found: Na, 21·3. Calc., 21·3%); sodium tetrolate (ethyl alcohol) (Found: Na, 28·7. Calc., 28·8%); sodium acrylate (methyl alcohol) (Found : Na, 24·4. Calc., 24·5%); sodium glutaconate (methyl alcohol) (Found : Na, 26·3. Calc., 26·4%); sodium furoate (ethyl alcohol) (Found : Na, 17·2. Calc., 17·2%).

General Technique and Apparatus.—This has already been described in the earlier papers of the series; the symbols have the same significance. All measurements were carried out at 25° ± 0·01°.

Conductivity Measurements.—The same Pyrex and silica glass cells as used in previous work were employed and the constants were found to be unchanged. No solvent correction was applied to the acids. For the sodium salts of the monobasic acids, a normal solvent correction was first applied (*i.e.*, the specific conductivity of the water used was subtracted from the observed conductivity), from which a preliminary value of Λ_0 and thence of $l_{0_{X'}}$ and of $K_{class.}$ was obtained. These figures were employed in the computation of the combined solvent and hydrolysis correction (J., 1933, 1642; 1934, 167; *Phil. Mag.*, 1934, 18, 904). These preliminary figures are collected below.

Acid.		$l_{0_{X'}}$.	$K_{class.}$.
Acrylic	$\Lambda_0^n = \Lambda_c + 224{\cdot}2C^{0{\cdot}560} = 88{\cdot}4$	38·6	$5{\cdot}8 \times 10^{-5}$
Crotonic	$\Lambda_0^n = \Lambda_c + 310{\cdot}4C^{0{\cdot}896} = 83{\cdot}9$	34·1	$2{\cdot}1 \times 10^{-5}$
ββ-Dimethylacrylic	$\Lambda_0^n = \Lambda_c + 357{\cdot}7C^{0{\cdot}894} = 80{\cdot}4$	30·6	$7{\cdot}9 \times 10^{-6}$
Tetrolic	$\Lambda_0^n = \Lambda_c + 397{\cdot}9C^{0{\cdot}900} = 88{\cdot}5$	38·7	$2{\cdot}5 \times 10^{-3}$
Furoic	$\Lambda_0^n = \Lambda_c + 239{\cdot}3C^{0{\cdot}771} = 84{\cdot}1$	34·3	$7{\cdot}3 \times 10^{-4}$

The method described in Part XI (J., 1935, 24) was employed for sodium glutaconate. The preliminary values, a "normal" solvent correction being used, were : $\mu_0 = \mu_c + 501C^{0{\cdot}552} = 207{\cdot}3$, whence $l_{0_{X''}} = 53{\cdot}6$ and $l_{0_{HX'}} = 28{\cdot}4$; K_2 (approx.), from the potentiometric titration curve, was taken as 1×10^{-5}. For the sodium hydrogen salt data required in the evaluation of $K_{1therm.}$, $\Lambda_0 = 80{\cdot}0$ and "x" = 78·04.

The results for the sodium salts are as follows :

Sodium acrylate (M = 94·02).

$\Lambda_0^n = \Lambda_c + 197{\cdot}6C^{0{\cdot}497}$. $\Lambda_0^n = 90{\cdot}62$. $l_{X'} = 40{\cdot}8$.

$C \times 10^4$.	$\Lambda_{obs.}$.	$[H^{\cdot}] \times 10^7$.	$\Lambda_{corr.}$.	Λ_0^n.	$C \times 10^4$.	$\Lambda_{obs.}$.	$[H^{\cdot}] \times 10^7$.	$\Lambda_{corr.}$.	Λ_0^n.
	Run 1.	Cell V.	$\kappa = 0{\cdot}789$.			Run 2.	Cell S.	$\kappa = 0{\cdot}791$.	
1·559	86·93	10·01	89·40	—	5·214	85·09	7·80	86·01	—
10·04	83·62	5·18	84·37	90·77	12·69	82·85	3·52	83·35	90·51
15·88	82·16	1·97	82·52	90·56	20·09	81·18	1·23	81·49	90·54
26·85	80·17	0·83	80·46	90·96	35·71	79·14	0·59	79·36	90·39
45·26	78·25	0·46	78·42	(91·42)	52·20	77·71	0·43	77·78	(91·48)
59·61	77·30	0·38	77·46	—	69·35	76·69	0·36	76·74	—
81·89	76·11	0·28	76·17	—	92·75	75·74	0·23	75·74	—
107·5	75·20	0·17	75·20	—					

Sodium crotonate (M = 108·04).

$\Lambda_0^n = \Lambda_c + 225{\cdot}2C^{0{\cdot}812}$. $\Lambda_0^n = 84{\cdot}35$. $l_{0_{X'}} = 34{\cdot}6$.

	Run 1.	Cell V.	$\kappa = 0{\cdot}819$.			Run 2.	Cell S.	$\kappa = 0{\cdot}821$.	
1·365	82·67	6·11	85·38	—	9·221	82·82	2·57	83·51	82·46
6·003	82·68	3·19	83·81	84·36	18·44	82·69	1·51	82·95	84·30
12·33	82·78	2·21	83·46	84·44	33·01	81·96	0·83	82·15	84·33
23·01	82·46	1·27	82·67	82·49	47·82	81·32	0·48	81·42	84·34
39·11	81·68	0·66	81·82	84·31	57·25	80·88	0·42	80·97	84·37
48·85	81·25	0·46	81·34	84·34	73·33	80·24	0·37	80·33	84·50
64·30	80·55	0·40	80·60	84·34	97·24	79·33	0·27	79·40	84·63
84·94	79·80	0·31	79·88	84·58					

Sodium ββ-dimethylacrylate (M = 122·05).

$\Lambda_0^n = \Lambda_c + 43{\cdot}83C^{0{\cdot}346}$. $\Lambda_0^n = 84{\cdot}44$. $l_{0_{X'}} = 34{\cdot}6$.

	Run 1.	Cell V.	$\kappa = 0{\cdot}850$.			Run 2.	Cell S.	$\kappa = 0{\cdot}821$.	
1·708	78·50	3·35	81·92	—	9·221	82·82	2·57	83·51	82·46
7·423	79·87	1·09	80·65	84·27	18·44	82·69	1·51	82·95	84·30
11·89	79·58	0·73	80·17	84·43	33·01	81·96	0·83	82·15	84·33
21·48	78·96	0·43	79·19	84·52	47·82	81·32	0·48	81·42	84·34
39·07	77·94	0·24	78·08	84·51	57·25	80·88	0·42	80·97	84·37
52·47	77·23	0·18	77·31	84·44	73·33	80·24	0·37	80·33	84·50
74·62	76·40	0·13	76·46	(84·81)	97·24	79·33	0·27	79·40	84·63
98·09	75·65	0·10	75·69	(84·94)					

Sodium tetrolate (M = 106·02).

$\Lambda_0^n = \Lambda_c + 254{\cdot}4C^{0{\cdot}801}$. Λ_0^n = 88·96. $l_{0X'}$ = 39·2.

$C \times 10^4$.	$\Lambda_{obs.}$.	$[H^\cdot] \times 10^7$.	$\Lambda_{corr.}$.	Λ_0^n.	$C \times 10^4$.	$\Lambda_{obs.}$.	$[H^\cdot] \times 10^7$.	$\Lambda_{corr.}$.	Λ_0^n.
	Run 1.	Cell *V*.	κ = 0·795.			Run 2.	Cell *S*.	κ = 0·791.	
1·310	88·45	19·66	88·62	—	4·251	88·17	18·71	88·40	—
6·429	87·98	17·79	88·17	88·88	9·492	87·78	17·23	87·96	88·92
10·65	87·73	16·59	87·85	88·91	16·46	87·32	15·52	87·41	88·91
20·99	87·01	14·36	87·09	88·91	26·41	86·66	13·68	86·88	88·87
37·75	86·01	12·02	86·07	89·01	42·70	85·71	11·55	85·76	89·05
46·84	85·55	11·12	85·59	89·05	57·31	84·94	10·44	84·96	89·04
68·17	84·52	9·55	84·54	(89·23)	78·44	84·16	9·01	84·17	—
87·06	83·82	8·41	83·83	(89·96)	99·72	83·59	7·59	83·59	—

Sodium furoate (M = 134·02).

$\Lambda_0^n = \Lambda_c + 119{\cdot}7C^{0{\cdot}707}$. Λ_0^n = 84·80. $l_{0X'}$ = 35·0.

	Run 1.	Cell *V*.	κ = 0·760.			Run 2.	Cell *S*.	κ = 0·765.	
1·336	83·84	17·6	84·29	—	3·331	83·63	16·2	83·96	—
6·110	83·39	13·3	83·74	84·80	8·712	83·06	11·3	83·33	84·70
11·65	82·52	9·81	82·85	84·53	18·51	82·17	8·42	82·39	84·71
25·48	81·65	8·11	81·80	84·72	33·44	81·19	7·21	81·33	84·87
41·02	80·82	6·72	80·94	85·04	47·68	80·48	6·19	80·60	(85·15)
53·75	80·35	5·60	80·45	(85·44)	61·89	79·93	5·31	80·02	—
69·31	79·74	4·91	79·80	(85·74)	77·12	79·48	4·62	79·56	—
92·24	79·15	3·98	79·20	—	87·72	79·19	4·02	79·24	—

Sodium glutaconate (M = 174·03).

$\mu_0^n = \mu_c + 406{\cdot}8C^{0{\cdot}470}$. μ_0^n = 213·58. $l_{0X''}$ = 57·0. $l_{0HX'}$ = 30·2.

	Run 1.	Cell *V*.	κ = 0·638.			Run 2.	Cell *S*.	κ = 0·662.	
0·881	202·62	4·91	209·46	—	5·182	200·52	1·32	202·75	213·35
2·557	202·08	2·49	205·13	—	12·46	195·21	0·74	196·53	213·80
8·854	197·09	0·97	198·65	213·55	22·39	187·97	0·41	190·68	213·58
16·07	193·03	0·57	193·43	213·23	31·33	186·58	0·28	187·01	213·60
24·93	188·95	0·36	189·33	213·63	43·76	183·22	0·22	183·40	213·72
37·21	185·27	0·24	185·49	213·79	57·36	180·81	0·19	181·02	(216·92)
49·15	182·14	0·21	182·34	(215·74)	79·98	178·84	0·14	178·91	—
65·48	179·91	0·17	180·08	(214·38)	98·64	177·74	0·10	177·99	—

The results for the acids are in the following tables. c'' is the ionic concentration corresponding to the molecular concentration C, calculated as described in Part IX (J., 1934, 1104), two approximations being sufficient, except for tetrolic acid, where three were required. $K_{1\text{therm.}}$ is the thermodynamic or true dissociation constant, deduced from the equation $\log K_{1\text{therm.}} = \log K' - 1{\cdot}010c''^{0{\cdot}5}$, where K' is the dissociation constant computed from the corresponding degree of dissociation $\alpha' = \Lambda_c/\Lambda_e$. The values of $K_{1\text{class.}}$ are included for comparison with the data in the literature.

$C \times 10^4$.	Λ_c.	$K_{\text{class.}} \times 10^5$.	Λ_e.	$c'' \times 10^4$.	K'.	$K_{\text{therm.}} \times 10^5$.
			Acrylic acid (M = 72·03) (Λ_0 = 388·8).			
		Run 1. Cell *Q*. κ = 0·805.				
1·508	174·28	5·494	366·88	0·6793	5·571	5·465
7·740	91·38	5·575	386·11	1·8303	5·668	5·493
13·49	71·60	5·597	385·77	2·5038	5·696	5·494
27·66	51·69	5·638	385·01	3·7135	5·759	5·506
43·29	42·40	5·659	384·44	4·7855	5·797	5·509
59·76	36·08	5·673	384·16	5·4248	5·818	5·499
82·99	30·85	5·677	383·62	6·6739	5·838	5·497
107·8	27·22	5·681	383·22	7·6570	5·954	5·502
		Run 2. Cell *R*. κ = 0·817.				
4·292	117·01	5·561	386·57	1·2992	5·639	5·492
10·47	80·12	5·600	386·08	2·1726	5·689	5·502
20·02	59·98	5·633	385·47	3·1152	5·740	5·509
34·37	46·75	5·648	384·76	4·1763	5·776	5·508
51·93	38·61	5·686	384·18	5·2190	5·831	5·530
71·67	33·13	5·688	383·74	6·1876	5·847	5·518
92·30	29·32	5·703	383·38	7·0589	5·846	5·496
					Mean	5·501

trans-*Crotonic acid* (M = 86·05) (Λ_0 = 381·8).

$C \times 10^4$.	Λ_c.	$K_{class.} \times 10^5$.	Λ_e.	$c'' \times 10^4$.	K'.	$K_{therm.} \times 10^5$.
			Run 1. Cell Q. κ = 0·783.			
		($\times 10^5$).				($\times 10^5$).
1·375	122·19	2·061	382·30	0·4395	2·065	2·033
5·672	66·57	2·079	382·29	0·9877	2·083	2·035
11·32	48·55	2·088	382·28	1·4352	2·092	2·034
22·18	35·43	2·096	382·27	2·0558	2·100	2·031
41·97	26·18	2·110	382·25	2·8749	2·114	2·032
55·99	22·80	2·114	382·24	3·3393	2·118	2·030
76·23	19·64	2·117	382·19	3·9172	2·122	2·027
98·39	17·36	2·122	382·16	4·4700	2·127	2·026
			Run 2. Cell R. κ = 0·764.			
8·052	56·61	2·085	382·29	1·1966	2·089	2·036
20·29	36·89	2·091	382·28	2·0545	2·095	2·026
34·47	28·75	2·105	382·26	2·5923	2·109	2·031
59·60	22·10	2·111	382·24	3·4459	2·115	2·025
71·07	19·66	2·118	382·21	3·6557	2·122	2·030
93·30	17·82	2·123	382·17	4·3504	2·128	2·027
					Mean	2·030

$\beta\beta$-*Dimethylacrylic acid* (M = 100·06) (Λ_0 = 382·6).

$C \times 10^4$.	Λ_c.	$K_{class.}$	Λ_e.	$c'' \times 10^4$.	K'.	$K_{therm.}$
			Run 1. Cell R. κ = 0·822.			
		($\times 10^6$).				($\times 10^6$).
1·001	93·89	(7·984)	381·13	0·2465	8·057	(7·965)
4·914	44·87	7·633	380·85	0·5861	7·738	7·601
13·82	27·51	7·697	380·64	0·9964	7·780	7·601
26·54	20·06	7·699	380·49	1·3991	7·787	7·576
46·20	15·32	7·715	380·34	1·8608	7·810	7·560
60·42	13·44	7·721	380·24	2·1348	7·823	7·561
77·52	11·88	7·728	380·16	2·4247	7·830	7·551
98·44	10·58	7·735	380·07	2·7392	7·840	7·561
			Run 2. Cell Q. κ = 0·818.			
2·319	63·41	7·636	380·98	0·3878	7·708	7·597
7·517	36·75	7·673	380·76	0·7255	7·751	7·598
18·74	23·74	7·693	380·58	1·1690	7·777	7·584
34·78	17·59	7·706	380·41	1·6082	7·798	7·571
55·42	14·01	7·713	380·28	2·0417	7·810	7·557
73·73	12·18	7·717	380·17	2·3622	7·818	7·543
85·68	11·32	7·729	380·13	2·5515	7·825	7·539
95·03	10·76	7·733	380·08	2·6903	7·838	7·544
					Mean	7·569

Furoic acid (M = 112·03) (Λ_0 = 383·0).

$C \times 10^4$.	Λ_c.	$K_{class.}$	Λ_e.	$c'' \times 10^4$.	K'.	$K_{therm.}$
			Run 1. Cell Q. κ = 0·845.			
1·386	326·61	6·849	382·51	1·1304	6·918	6·748
5·908	247·79	7·005	382·26	3·8292	7·056	6·742
11·99	202·25	7·084	381·90	6·3486	7·148	6·741
24·43	158·87	7·185	381·27	10·1790	7·272	6·751
40·94	130·96	7·274	380·50	15·0917	7·430	6·809
53·83	117·74	7·344	379·86	16·6844	7·495	6·806
78·17	100·96	7·391	379·19	20·9267	7·568	6·805
99·25	91·46	7·436	378·71	24·2483	7·615	6·807
			Run 2. Cell R. κ = 0·840.			
3·243	284·81	6·997	382·27	2·4162	7·062	6·811
8·262	226·34	7·055	382·12	4·8938	7·110	6·754
15·71	184·45	7·141	381·71	7·6325	7·213	6·764
26·15	155·18	7·217	381·19	10·6455	7·310	6·776
38·29	134·25	7·243	380·65	13·5044	7·353	6·751
50·12	120·97	7·309	380·19	15·9474	7·442	6·767
71·79	104·56	7·360	379·37	19·9864	7·528	6·787
90·45	95·13	7·424	378·75	23·9539	7·620	6·801
					Mean	6·776

Tetrolic acid (M = 84·03) (Λ_0 = 387·2).

$C \times 10^4$.	Λ_c.	$K_{class.} \times 10^5$. ($\times 10^3$).	Λ_e.	$c'' \times 10^4$. $c''' \times 10^4$.	K'.	$K_{therm.} \times 10^5$. ($\times 10^3$).
		Run 1. Cell R. κ = 0·845.				
1·265	360·16	(1·566)	386·77	1·1782	1·592	(1·552)
9·577	295·13	2·340	386·38	6·9861	2·367	2·226
12·20	281·08	2·346	386·19	8·4802	2·374	2·219
25·44	234·21	2·356	385·02	15·4761	2·437	2·194
40·96	204·30	2·412	383·99	21·7931	2·479	2·223
61·76	178·78	2·446	382·93	29·5089	2·526	2·236
74·72	167·33	2·452	382·26	33·7025	2·546	2·224
94·21	154·08	2·478	381·62	39·5615	2·577	2·246
		Run 2. Cell Q. κ = 0·821.				
3·926	337·45	2·321	386·75	3·4414	2·344	2·245
15·21	267·59	2·352	385·87	10·5477	2·387	2·213
22·15	244·06	2·380	385·27	14·0315	2·425	2·223
33·46	217·37	2·414	384·35	18·9234	2·464	2·226
54·56	186·65	2·448	383·30	26·5683	2·522	2·237
67·67	173·31	2·454	382·73	30·6427	2·536	2·230
84·50	160·55	2·482	382·07	35·5078	2·574	2·240
100·1	150·99	2·495	381·56	39·6114	2·594	2·241
						Mean 2·228

trans-*Glutaconic acid* (M = 130·05) (Λ_0 = 378·2).

$C \times 10^4$.	Λ_c.	$K_{1class.} \times 10^4$.	Λ_e.	$c'' \times 10^4$.	K'.	$K_{2therm.} \times 10^4$.
		Run 1. Cell Q. κ = 0·615.				
1·220	285·05	2·809	—	—	—	—
8·516	141·13	1·891	—	—	—	—
13·61	116·32	1·856	—	—	—	—
21·39	95·09	1·805	376·41	5·4036	1·826	(1·730)
56·19	62·00	1·806	375·67	9·2737	1·833	1·706
71·46	55·75	1·819	375·43	10·6113	1·848	1·713
99·67	47·91	1·832	374·99	12·7342	1·865	1·717
		Run 2. Cell R. κ = 0·632.				
3·980	202·54	2·458	—	—	—	—
14·75	110·92	1·795	—	—	—	—
30·12	81·77	1·796	376·19	6·5470	1·818	1·713
48·05	66·45	1·800	375·82	8·4959	1·825	1·705
64·18	58·39	1·809	375·53	9·9791	1·837	1·706
77·12	53·81	1·820	375·36	11·0556	1·850	1·712
87·48	50·87	1·829	375·21	11·8604	1·860	1·717
						Mean 1·711

The values of the equivalent conductivities at round concentrations were interpolated from the conductivity–concentration graph drawn with a flexible spline.

Conductivities at Round Concentrations.
Acids.

$C \times 10^4$.	Acrylic.	*trans*-Crotonic.	ββ-Dimethyl-acrylic.	Tetrolic.	Furoic.	*trans*-Glutaconic (μ).
1	—	—	90·0	376·0	335·0	290·0
2	155·0	86·1	—	—	—	—
5	108·3	67·2	$43{\cdot}3_5$	322·0	267·0	170·5
10	81·6	52·2	31·8	289·6	212·0	129·0
20	60·5	36·8	22·8	249·7	171·3	98·31
30	49·8	31·0	19·0	224·5	147·3	81·78
40	43·8	26·9	16·5	206·6	131·4	71·62
50	39·7	23·8	14·7	192·4	119·8	65·03
60	35·7	21·7	$13{\cdot}2_5$	180·6	111·4	60·52
70	32·8	20·4	12·2	272·3	104·9	56·62
80	30·4	19·2	11·3	163·2	99·7	53·34
90	28·8	18·4	10·8	257·1	95·3	50·58
100	27·9	17·5	10·6	151·6	92·3	47·97

Sodium salts.

$C \times 10^4$.	Acrylate.	*trans*-Crotonate.	ββ-Dimethyl-acrylate.	Tetrolate.	Furoate.	*trans*-Glutaconate (μ).
5	86·18	83·86	81·23	88·32	83·83	202·70
10	84·17	83·53	80·42	87·88	83·26	198·33
20	81·66	82·86	79·20	87·23	82·27	191·75
30	80·04	82·30	78·53	86·46	81·52	186·60
40	78·87	81·78	77·96	85·85	80·94	184·50
50	77·96	81·30	77·45	85·33	80·48	182·30
60	77·27	80·83	76·95	84·86	80·07	180·75
70	76·71	80·41	76·54	84·46	79·78	179·80
80	76·26	80·02	76·19	84·14	79·48	179·05
90	75·75	79·64	75·87	83·83	79·23	178·40
100	75·19	79·27	75·59	83·30	79·02	177·90

Potentiometric Measurements.—The experimental details have already been described (for references, see this vol., p. 1108). Measurements were conducted in an electrically-controlled oil thermostat maintained at 25° ± 0·01° with the quinhydrone electrode. The results for monobasic acids were computed as described for phenylacetic acid (J., 1935, 913), and for glutaconic acid as detailed for fumaric acid (*Phil. Mag.*, 1936, **22**, 797) (the potentiometric titration figures are incorporated in the table).

Acrylic acid.

Potentiometric titration of 100·00 *c.c. of* 0·01M-*acid with* 0·01037*M*-NaOH at 25°.

NaOH, c.c.	p_H.	$\mu \times 10^3$.	$K_{therm.} \times 10^5$.
0·00	3·105	—	—
10·00	3·457	—	—
20·00	3·710	1·923	5·56
25·00	3·819	2·225	5·55
30·00	3·915	2·515	5·57
35·00	4·013	2·785	5·50
40·00	4·105	3·042	5·47
45·00	4·19	3·283	5·54
50·00	4·274	3·509	5·53
55·00	4·358	3·724	5·57
60·00	4·453	3·924	5·53
65·00	4·548	4·111	5·55
70·00	4·663	4·291	5·42
75·00	4·783	4·459	5·42
80·00	4·959	—	—
90·00	5·589	—	—
		Mean	5·52

trans-*Crotonic acid.*

Potentiometric titration of 100·00 *c.c. of* 0·01M-*acid with* 0·00990*M*-NaOH *at* 25°.

NaOH, c.c.	p_H.	$\mu \times 10^3$.	$K_{therm.} \times 10^5$.
0·00	3·365	—	—
10·00	3·785	1·064	2·09
20·00	4·086	1·732	2·05
25·00	4·201	2·063	2·08
30·00	4·299	2·334	2·07
35·00	4·391	2·608	2·08
40·00	4·475	2·864	2·11
45·00	4·560	3·101	2·11
50·00	4·644	3·324	2·11
55·00	4·729	3·533	2·11
60·00	4·820	3·730	2·09
65·00	4·907	3·912	2·10
70·00	5·000	4·087	2·11
75·00	6·105	4·251	2·12
80·00	5·223	4·405	2·13
		Mean	2·10

ββ-Dimethylacrylic acid.

Potentiometric titration of 100·00 *c.c. of* 0·01M-*acid with* 0·00980*M*-NaOH *at* 25°.

NaOH, c.c.	p_H.	$\mu \times 10^3$.	$K_{therm.} \times 10^6$.
0·00	3·600	—	—
10·00	4·174	—	—
20·00	4·496	1·666	7·61
25·00	4·614	1·985	7·63
30·00	4·718	2·280	7·64
35·00	4·826	2·616	7·60
40·00	4·905	2·813	7·61
45·00	4·989	3·051	7·63
50·00	5·074	3·275	7·63
55·00	5·157	3·484	7·65
60·00	5·245	3·682	7·61
65·00	5·333	3·865	7·62
70·00	5·428	4·039	7·61
75·00	5·533	4·204	7·58
80·00	5·655	4·357	(7·48)
90·00	5·971	—	—
100·00	6·969	—	—
		Mean	7·62

Tetrolic acid.

Potentiometric titration of 100·00 *c.c. of* 0·01M-*acid with* 0·00989*M*-NaOH *at* 25°.

NaOH, c.c.	p_H.	$\mu \times 10^3$.	$K_{therm.} \times 10^3$.
0·00	2·408	—	—
10·00	2·508	—	—
20·00	2·605	4·131	(2·27)
25·00	2·660	4·166	2·21
30·00	2·708	4·241	2·23
35·00	2·760	4·302	2·23
40·00	2·813	4·364	2·24
45·00	2·870	4·418	2·23
50·00	2·929	4·476	2·23
55·00	2·990	4·534	2·24
60·00	3·057	4·586	2·23
65·00	3·132	4·633	2·22
70·00	3·213	4·684	2·22
75·00	3·308	4·732	2·19
80·00	3·416	4·779	2·19
90·00	3·756	—	—
100·00	5·337	—	—
		Mean	2·22

Furoic acid.

Potentiometric titration of 100·00 *c.c. of* 0·01M-*acid with* 0·00961*M*-NaOH *at* 25°.

NaOH, c.c.	p_H.	$\mu \times 10^3$.	$K_{therm.} \times 10^4$.
0·00	2·644	—	—
10·00	2·743	2·683	(7·13)
20·00	2·871	2·948	6·91
25·00	2·925	3·110	7·08
30·00	2·990	3·242	6·98
35·00	3·051	3·360	6·94
40·00	3·111	3·520	7·01
45·00	3·176	3·649	6·99
50·00	3·237	3·784	7·09
55·00	3·311	3·898	6·93
60·00	3·379	4·022	7·00
65·00	3·455	4·136	6·99
70·00	3·540	4·246	6·93
75·00	3·624	4·356	7·05
80·00	3·726	4·459	7·07
90·00	4·000	—	—
100·00	4·452	—	—
		Mean	7·00

trans-*Glutaconic acid.*

Potentiometric titration of 100·00 *c.c. of* 0·005M-*acid with* 0·01170*M*-NaOH *at* 25°. *Calculation of dissociation constants.*

Pairs of points used. NaOH, c.c.	p_H.	$\mu \times 10^3$.	$K_{1class.} \times 10^4$.	$K_{1therm.} \times 10^4$.	$K_{2class.} \times 10^6$.	$K_{2therm.} \times 10^6$.
0·00	3·406	—	—	—	—	—
45·00	4·425	—	—	—	—	—
10·00	3·377	—	—	—	—	—
50·00	4·575	—	—	—	—	—
15·00	3·548	1·825	1·82	1·73	—	—
55·00	4·724	5·146	—	—	11·42	8·67
17·50	3·623	2·015	1·83	1·74	—	—
57·50	4·807	5·400	—	—	11·27	8·64
20·00	3·712	2·232	1·76	1·66	—	—
62·50	4·978	6·026	—	—	10·92	8·33
22·50	3·775	2·390	1·81	1·71	—	—
65·00	5·052	·6·230	—	—	11·14	8·46
25·00	3·846	2·582	1·81	1·71	—	—
60·00	4·885	5·750	—	—	11·18	8·58
27·50	3·920	2·732	1·80	1·70	—	—
67·50	5·146	6·511	—	—	11·01	8·31
30·00	4·000	2·970	1·77	1·66	—	—
70·00	5·240	6·687	—	—	11·07	8·32
32·50	4·068	3·189	1·79	1·68	—	—
72·50	5·352	6·931	—	—	10·85	8·92
35·00	4·140	3·140	1·82	1·70	—	—
75·00	5·481	7·175	—	—	10·75	8·00
40·00	4·269	—	—	—	—	—
80·00	5·701	—	—	—	—	—
			Mean	1·70	Mean	8·38

The authors' thanks are due to the Royal Society and Imperial Chemical Industries for grants.

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[*Received, July 23rd,* 1937.]