388. *The Dissociation Constants of Organic Acids. Part XIII. The Primary and Secondary Constants of Some Cyclic* 1 : 1-*Dicarboxylic Acids.*

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THE present series of investigations was started by one of us early in 1926 with the objects, *inter alia,* (i) of determining the distances between the carboxyl groups of dibasic acids from measurements of the primary and secondary dissociation constants by application of Bjerrum's expression (*Z. physikal. Chem.*, 1923, **106**, 219), and thus of extending Spiers and Thorpe's work on the glutaric acids (J., 1925, **127**, 538), and (ii) of providing accurate values of the " true " or thermodynamic dissociation constants. It was realised that potentiometric methods alone were suitable for the determination of *both* dissociation constants, but these were not employed at the time owing to lack of reproducibility in the results and to the different values obtained by calculating according to Auerbach and Smolczyk (*Z. physikal. Chem.*, 1924, **110**, 83) or to Britton (J., 1925, **127**, 1896). No trustworthy conductivity data were then available for comparative purposes, and most of the previous papers of this series are concerned with filling this gap. The first values of the thermodynamic primary dissociation constants of normal dibasic acids are given in Part XI (this vol., p. 21), and these differ in some instances, *e.g.*, for malonic and succinic acid, considerably from the potentiometric determinations of Britton (*loc. cit.*), Gane and Ingold (J., 1928, 1598; 1931, 2156), and Ashton and Partington (*Trans. Faraday Soc.*, 1934, **30**, 598), although agreement with our own measurements with the hydrogen and the quinhydrone electrode is within 2—3%. This subject will be discussed elsewhere.

New conductivity data are now recorded for *cyclo*-propane-, -butane-, -pentane-, and -hexane-1 : 1-dicarboxylic acids and their sodium salts, the latter corrected for hydrolysis and for the carbonic acid present in the water used; these replace the approximate figures given in Part II (J., 1929, 1487), which were vitiated by arithmetical errors (see this vol.,

p. 30). The true primary dissociation constants have been calculated in every case, although the value for the relatively strong *cyclo*propane acid, which was calculated on assumptions valid only for weak acids, must be regarded as approximate (compare iodic acid; Davies, " The Conductivity of Solutions," 1933, p. 107).

Determinations have also been made of the primary and the secondary dissociation constants by potentiometric titration with the quinhydrone electrode. The thermodynamic dissociation constants of these acids have been calculated for the first time (contrast the empirical method of Gane and Ingold, J., 1931, 2154), and the values for the primary constants agree within 1—2% with those deduced by conductivity, except that constant values for K_1 could not be obtained for the *cyclo*propane acid.

The distances between the two carboxyl groups, r, have been calculated by Bjerrum's expression, $P_2 - P_1 - \log 4 = 3{\cdot}1 \times 10^{-8}/r$, where $P_2 = -\log K_2$ and $P_1 = -\log K_1$, and also by Gane and Ingold's method, which takes into account the change in properties of the solvent (see J., 1931, 2153, 2160, 2180). The results for r (in Å.), as well as the values of the true dissociation constants (potentiometric), are given in the following table. The value for K_1 (therm.) for *cyclo*propane-1 : 1-dicarboxylic acid is that determined by conductivity.

1 : 1-Dicarboxylic acid.	K_1 (therm.) × 10^4.	K_2 (therm.) × 10^6.	r (B.).	r (G. and I.).
(I) *cyclo*Propane	150·0	0·0371	0·62	2·65
(II) *cyclo*Butane	7·47	1·32	1·44	3·50
(III) *cyclo*Pentane	5·89	0·83	1·38	3·45
(IV) *cyclo*Hexane	3·54	0·78	1·51	3·54

Points of interest are : (i) the small value of r for the acid (I); (ii) the different figures given by the two methods of calculation; (iii) the value for the *cyclo*pentane acid is not greater than that for the corresponding *cyclo*hexane acid, as would be expected on calculation of the extracyclic angles based upon the planar nature of both rings (compare Becker and Thorpe, J., 1920, **117**, 1579), and this may be taken as evidence for the now accepted multiplanar character of the *cyclo*hexane ring.

These results will be fully discussed when the experiments on the corresponding substituted glutaric acids have been completed.

EXPERIMENTAL.

Preparation of Materials.—Acids. The details have already been described (Vogel, J., 1934, 337; compare J., 1929, 1488). All operations were carried out in Pyrex vessels, and all solvents for recrystallisation were of AnalaR purity. The acids were all dried over calcium chloride in a vacuum desiccator for several days before use and had the following m. p.'s : (I) 136—137°, (II) 157°, (III) 187°, (IV) 178°.

Sodium salts. These were prepared by adding the calculated quantity of sodium hydroxide solution, prepared from the AnalaR solid and standardised against AnalaR potassium hydrogen phthalate, to known weights of the pure acids; the solutions were evaporated to dryness on the water-bath, and the solids recrystallised from dilute ethyl alcohol and dried at 130°. Their purity was confirmed by analysis [Found, for sodium salts of (I), (II), (III), and (IV) respectively : Na, 26·48, 24·43, 22·74, 21·26. Calc. : 26·45, 24·46, 22·76, 21·30%].

General Technique and Apparatus for Conductivity Measurements.—This was identical with that described in Part XI (*loc. cit.*). The same Hartley cells were employed, and their constants were found to be unchanged. Kohlrausch cells were used for the higher concentrations of acids (III) and (IV) owing to their smaller solubility, and are indicated by the letters following the conductivity figures. The symbols in the following tables have the same significance as before.

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 (Part XI, *loc. cit.*).

Na salt of (I) : $\mu_0^n = \mu_c + 790{\cdot}4C^{0{\cdot}654} = 211{\cdot}9$; $l_{0_{X''}} = 56{\cdot}2$

,, (II) : $\mu_0^n = \mu_c + 708{\cdot}8C^{0{\cdot}668} = 200{\cdot}8$; $l_{0_{X''}} = 50{\cdot}6$

,, (III) : $\mu_0^n = \mu_c + 794{\cdot}5C^{0{\cdot}682} = 199{\cdot}0$; $l_{0_{X''}} = 49{\cdot}7$

,, (IV) : $\mu_0^n = \mu_c + 527{\cdot}1C^{0{\cdot}578} = 197{\cdot}4$; $l_{0_{X''}} = 48{\cdot}9$

The mobilities of the acid ions, $l_{0_{\mathrm{HX}'}}$, were computed from the relation, $l_{0_{\mathrm{HX}'}} = 0{\cdot}53 l_{0_{\mathrm{X}''}}$ (Part XI, *loc. cit.*), and were respectively 30·2, 27·0, 26·3, and 25·9. The approximate secondary dissociation constants, determined from the potentiometric titration curve, employed in the computations were: acid (I) 5·0 × 10^{-8}, (II) 1·5 × 10^{-6}, (III) 1·0 × 10^{-6}, (IV) 1·0 × 10^{-6}.

The corrected results for the sodium salts at 25° are in Table I.

TABLE I.

Sodium cyclo*propane*-1 : 1-*dicarboxylate* (M = 174·03).

$\mu_0^n = \mu_c + 385{\cdot}6C^{0{\cdot}463}$; $\mu_0^n = 219{\cdot}12$; $l_{0_{\mathrm{X}''}} = 59{\cdot}8$; $l_{0_{\mathrm{HX}'}} = 31{\cdot}9$.

$C \times 10^4$.	μ, obs.	μ, corr.	μ_0^n.	$C \times 10^4$.	μ, obs.	μ, corr.	μ_0^n.
Run 1. Cell V. $\kappa = 0{\cdot}768$.							
1·295	209·75	213·23	—	37·92	191·01	190·29	219·47
6·646	205·47	206·21	219·24	58·60	185·74	185·30	(221·00)
11·46	202·23	202·31	219·08	73·19	182·77	182·39	—
19·52	197·84	197·39	218·85	95·97	179·05	178·64	—
Run 2. Cell S. $\kappa = 0{\cdot}774$.							
3·991	207·58	208·85	—	47·98	188·17	187·65	(220·71)
9·310	203·85	203·86	218·87	62·41	184·77	184·43	—
16·02	199·82	199·46	219·04	77·31	181·91	181·62	—
28·24	194·46	193·82	219·25	92·01	179·51	179·19	—

Sodium cyclo*butane*-1 : 1-*dicarboxylate* (M = 188·05).

$\mu_0^n = \mu_c + 338{\cdot}4C^{0{\cdot}478}$; $\mu_0^n = 206{\cdot}87$; $l_{0_{\mathrm{X}''}} = 53{\cdot}6$; $l_{0_{\mathrm{HX}'}} = 28{\cdot}4$.

$C \times 10^4$.	μ, obs.	μ, corr.	μ_0^n.	$C \times 10^4$.	μ, obs.	μ, corr.	μ_0^n.
Run 1. Cell S. $\kappa = 0{\cdot}672$.							
1·001	199·61	206·42	—	39·99	182·99	183·11	207·24
4·998	196·59	198·14	207·10	58·77	179·37	179·43	(208·42)
10·07	193·33	194·10	206·60	73·31	177·32	177·36	—
18·99	189·41	189·62	206·55	93·98	175·13	175·16	—
Run 2. Cell V. $\kappa = 0{\cdot}678$.							
2·992	197·54	200·65	—	34·99	184·17	184·29	206·95
8·611	194·16	195·39	207·00	52·61	180·33	180·39	(207·93)
15·26	191·01	191·44	206·69	72·18	177·55	177·59	—
26·08	186·92	187·06	206·76	89·31	175·53	175·56	—

Sodium cyclo*pentane*-1 : 1-*dicarboxylate* (M = 202·06).

$\mu_0^n = \mu_c + 345{\cdot}9C^{0{\cdot}488}$; $\mu_0^n = 204{\cdot}27$; $l_{0_{\mathrm{X}''}} = 52{\cdot}4$; $l_{0_{\mathrm{HX}'}} = 27{\cdot}7$.

$C \times 10^4$.	μ, obs.	μ, corr.	μ_0^n.	$C \times 10^4$.	μ, obs.	μ, corr.	μ_0^n.
Run 1. Cell V. $\kappa = 0{\cdot}582$.							
1·612	196·98	200·72	—	40·06	181·11	181·10	204·52
4·506	194·62	196·02	204·07	58·75	177·55	177·53	(205·77)
10·04	191·51	192·12	204·01	71·82	175·46	175·42	—
22·41	186·32	186·65	204·26	98·12	172·22	172·16	—
Run 2. Cell S. $\kappa = 0{\cdot}575$.							
3·611	195·58	197·08	—	44·99	180·18	180·17	(204·98)
8·607	192·63	193·17	204·23	61·97	176·98	176·96	—
15·62	189·17	189·48	204·28	76·49	174·88	174·84	—
26·68	185·13	185·34	204·51	91·50	173·01	172·95	—

Sodium cyclo*hexane*-1 : 1-*dicarboxylate* (M = 216·08).

$\mu_0^n = \mu_c + 349{\cdot}5C^{0{\cdot}492}$; $\mu_0^n = 199{\cdot}91$; $l_{0_{\mathrm{X}''}} = 50{\cdot}2$; $l_{0_{\mathrm{HX}'}} = 26{\cdot}6$.

$C \times 10^4$.	μ, obs.	μ, corr.	μ_0^n.	$C \times 10^4$.	μ, obs.	μ, corr.	μ_0^n.
Run 1. Cell V. $\kappa = 0{\cdot}582$.							
0·604	194·89	204·80	—	37·46	178·00	177·99	200·35
5·251	190·38	191·21	199·71	62·38	173·82	173·80	(202·55)
9·502	187·81	188·34	199·74	79·75	171·67	171·63	—
24·99	181·43	181·72	200·07	97·42	169·84	169·77	—
Run 2. Cell S. $\kappa = 0{\cdot}567$.							
3·612	192·03	192·95	—	39·84	177·56	177·55	200·58
8·499	188·68	189·25	200·03	57·26	174·49	174·47	(202·03)
15·51	185·01	185·16	199·66	73·11	172·53	172·49	—
27·12	180·79	181·08	200·18	87·68	170·81	170·74	—

The values at round concentrations, obtained with a flexible spline, are given in Table II for convenience of reference and comparison with other published data.

TABLE II.

Molecular Conductivities of Sodium Salts of 1 : 1-*Dicarboxylic Acids at* 25°.

$C \times 10^4$.	*cyclo*-Propane.	*cyclo*-Butane.	*cyclo*-Pentane.	*cyclo*-Hexane.
5·0	207·66	198·25	195·83	191·62
10·0	203·38	194·40	192·25	188·03
20·0	197·74	189·22	187·63	183·19
30·0	192·98	185·74	184·17	179·84
40·0	189·68	183·05	181·28	177·52
50·0	187·07	180·99	179·07	175·66
60·0	184·93	179·20	177·26	174·15
70·0	182·92	177·78	175·75	172·80
80·0	181·10	176·55	174·40	171·62
90·0	179·49	175·47	173·18	170·62
100·0	178·07	174·52	172·08	169·78

The True Primary Dissociation Constants.—These were calculated exactly as described in Part XI (*loc. cit.*, p. 26); three approximations were, however, necessary for the calculation of the ionic concentration c''' owing to the strength of the acids (see J., **1932**, 2837; this vol., p. 26). The data employed for the sodium hydrogen salts were :

Acid.	Propane.	Butane.	Pentane.	Hexane.
Λ_0	81·7	78·2	77·5	76·4
x	78·43	77·63	77·47	77·22

The values of K_1 (therm.) were not calculated for some of the results in dilute solution, for experience showed that they are of little value in its final evaluation (see this vol., p. 26).

The collected results are in Table III; the symbols have their customary significance.

TABLE III.

Primary Dissociation Constants at 25°.

cyclo*Propane*-1 : 1-*dicarboxylic Acid* (M = 130·05; Λ_0 = 379·9).

Run 1. Cell R. $\kappa = 0·684$.

$C \times 10^4$.	μ, obs.	K_1 (class.) $\times 10^2$.	Λ_e.	$c''' \times 10^4$.	K_1 (therm.) $\times 10^2$.
0·925	367·42	0·26	378·94	0·8969	(0·28)
5·189	359·01	0·84	378·19	4·9258	(0·88)
8·338	352·74	1·00	377·70	7·7774	(1·03)
17·19	340·06	1·31	376·07	15·5440	(1·36)
27·78	324·95	1·41	374·59	24·0987	(1·41)
38·04	313·23	1·47	373·43	31·9077	1·48
51·85	300·52	1·52	372·09	41·8769	1·48
76·41	280·02	1·58	370·06	60·5358	1·50

Run 2. Cell Q. $\kappa = 0·672$.

$C \times 10^4$.	μ, obs.	K_1 (class.) $\times 10^2$.	Λ_e.	$c''' \times 10^4$.	K_1 (therm.) $\times 10^2$.
3·511	361·75	0·67	378·49	3·3557	(0·70)
7·102	354·98	0·94	377·88	6·6716	(0·97)
11·67	346·65	1·11	377·10	10·7274	(1·13)
23·21	330·03	1·33	375·12	20·4201	(1·35)
33·39	318·00	1·44	373·93	28·3957	(1·43)
47·69	303·61	1·52	372·47	38·8724	1·48
73·29	281·61	1·56	370·54	55·7004	1·48
96·29	267·07	1·60	369·24	69·6462	1·50
					Mean 1·5

cyclo*Butane*-1 : 1-*dicarboxylic Acid* (M = 144·06; Λ_0 = 376·4).

Run 1. Cell Q. $\kappa = 0·677$.

$C \times 10^4$.	μ, obs.	K_1 (class.) $\times 10^4$.	Λ_e.	$c''' \times 10^4$.	K_1 (therm.) $\times 10^4$.
1·399	330·42	8·828	375·39	1·2344	(8·881)
6·412	250·41	8·479	374·83	4·2837	(8·215)
15·14	193·52	8·236	374·19	7·8299	(7·859)
25·99	159·20	8·058	373·55	11·0764	(7·614)
39·10	136·49	8·047	372·87	14·3127	7·572
48·76	125·18	8·080	372·41	16·3899	7·553
63·12	112·87	8·108	371·88	19·1577	7·541
87·06	98·86	8·145	371·26	23·1826	7·557

Run 2. Cell R. $\kappa = 0·701$.

$C \times 10^4$.	μ, obs.	K_1 (class.) $\times 10^4$.	Λ_e.	$c''' \times 10^4$.	K_1 (therm.) $\times 10^4$.
4·312	276·42	8·756	—	—	—
9·377	225·24	8·361	—	—	—
18·31	181·51	8·223	—	—	—
28·88	153·08	8·051	373·40	11·8397	(7·595)
47·07	126·93	8·076	372·49	16·0396	7·554
61·20	114·32	8·100	371·89	18·8709	7·549
81·07	101·74	8·117	371·37	22·2782	7·527
93·89	95·79	8·158	371·05	24·3133	7·523
					Mean 7·547

TABLE III (*Contd.*).

Primary Dissociation Constants at 25°.

cyclo*Pentane*-1 : 1-*dicarboxylic Acid* (M = 158·08; Λ_0 = 375·7).

$C \times 10^4$.	μ, obs.	K_1 (class.) $\times 10^4$.	Δ_e.	$c''' \times 10^4$.	K_1 (therm.) $\times 10^4$.
		Run 1. Cell R. $\kappa = 0{\cdot}712$.			
2·041	302·11	6·737	—	—	—
5·644	242·46	6·625	—	—	—
9·769	201·21	5·978	—	—	—
18·22	165·04	6·271	373·45	8·0520	5·969
28·90	139·42	6·327	372·90	10·8538	5·976
45·57	116·06	6·373	372·21	14·2093	5·973
66·63J	99·68	6·384	371·36	17·8855	5·947
89·96V	87·89	6·427	370·85	21·2254	5·950
		Run 2. Cell Q. $\kappa = 0{\cdot}723$.			
3·631	270·31	6·701	—	—	—
7·992	220·16	6·629	—	—	—
14·61	180·07	6·446	—	—	—
24·19	149·42	6·353	373·12	9·6872	5·964
38·34	125·11	6·374	372·48	12·8778	5·964
58·80	105·00	6·375	371·56	16·6164	5·940
76·74J	93·84	6·382	371·14	19·4031	5·954
91·90V	87·15	6·439	370·81	21·5989	5·956
					Mean **5·959**

cyclo*Hexane*-1 : 1-*dicarboxylic Acid* (M = 172·10; Λ_0 = 374·6).

$C \times 10^4$.	μ, obs.	K_1 (class.) $\times 10^4$.	Δ_e.	$c''' \times 10^4$.	K_1 (therm.) $\times 10^4$.
		Run 1. Cell Q. $\kappa = 0{\cdot}745$.			
0·985	277·12	4·176	—	—	—
4·721	219·33	3·905	—	—	—
7·032	170·98	3·879	—	—	—
13·07	152·88	3·674	—	—	—
23·44	122·33	3·721	372·41	7·6996	3·531
35·61	103·39	3·747	372·00	9·8971	3·544
54·33	86·52	3·769	371·46	12·6545	3·546
69·24J	78·14	3·807	371·07	14·5806	3·559
		Run 2. Cell R. $\kappa = 0{\cdot}738$.			
2·908	252·43	4·049	—	—	—
7·174	192·91	3·923	—	—	—
12·50	158·49	3·879	—	—	—
19·18	133·55	3·788	—	—	—
32·51	107·38	3·745	372·07	7·3824	3·545
47·81	91·33	3·758	371·62	11·7499	3·544
73·22J	76·03	3·785	370·94	15·0076	3·536
95·73V	67·53	3·795	370·32	17·4569	3·540
					Mean **3·543**

The values for μ at round concentrations for the acids are in Table IV.

TABLE IV.

Molecular Conductivities of 1 : 1-*Dicarboxylic Acids.*

$C \times 10^4$.	*cyclo*-Propane.	*cyclo*-Butane.	*cyclo*-Pentane.	*cyclo*-Hexane.	$C \times 10^4$.	*cyclo*-Propane.	*cyclo*-Butane.	*cyclo*-Pentane.	*cyclo*-Hexane.
1·0	366·71	340·12	310·42	277·00	50·0	302·40	123·50	111·50	89·30
5·0	358·75	270·14	241·00	214·85	60·0	294·30	114·50	103·30	83·70
10·0	349·80	217·80	201·30	168·80	70·0	286·80	107·20	96·70	78·50
20·0	334·70	174·80	161·50	131·00	80·0	280·00	101·60	91·70	74·00
30·0	321·80	151·60	138·00	110·50	90·0	273·70	97·50	87·40	70·70
40·0	311·30	135·30	122·20	97·80	100·0	267·50	94·00	83·50	65·50

General Technique and Apparatus for the Potentiometric Titrations.—Full details of these have already been described (German and Vogel, Part XII, this vol., p. 912). The measurements were carried out in an oil thermostat maintained electrically at 25° ± 0·01°. Stirring was effected in most cases with purified nitrogen. All titrations were accurate to 0·01 c.c

The quinhydrone electrode was used throughout. The cell employed was $Hg|Hg_2Cl_2,KCl$ (satd.) || Solution, quinhydrone | Pt, and the liquid-junction potential was assumed to be negligible. Before and after each titration, the saturated calomel electrode was standardised against at least two independent N/10-calomel cells, for which a value of 0·3376 volt was assumed. The cell system was further standardised against Walpole's standard acetate buffer.

Calculation of the Thermodynamic Primary and Secondary Dissociation Constants.—The values of K_1 (class.) and K_2 (class.) were computed by Britton's modification (*loc. cit.*) of Auerbach and Smolczyk's formulæ (*loc. cit.*). The true dissociation constants were then evaluated by correction for ionic strength, the simple Debye–Hückel equation for activities being used. It can be readily shown that, in dilute solution where the ionic strength μ is small,

$$p_{K_1\,(\text{therm.})} = p_{K_1\,(\text{class.})} + 0{\cdot}505\mu^{0{\cdot}5}$$

and

$$p_{K_2\,(\text{therm.})} = p_{K_2\,(\text{class.})} + 1{\cdot}515\mu^{0{\cdot}5}$$

The values of μ, the total ionic strength, were obtained as follows from the mean K_1 (class.) and K_2 (class.) values. The ions present in solution at any point of the titration are $Na^{\bullet}$, $H^{\bullet}$, HA', and A'', and it is necessary to find the relative amounts of HA' and A'' present at any point (compare Michaelis–Perlzweig, " Hydrogen Ion Concentration," 1926, p. 55; Glasstone, " The Electrochemistry of Solutions," 1930, p. 203).

The total acid concentration $C = [H_2A] + [HA'] + [A'']$. Let the fractions of HA' and A'' ions present be α_1 and α_2 respectively.

Then
$$\alpha_1 = \frac{[HA']}{[H_2A] + [HA'] + [A'']} = \frac{1}{[H^{\bullet}]/K_1 + 1 + K_2/[H^{\bullet}]}$$

and
$$\alpha_2 = \frac{1}{[H^{\bullet}]/K_2 + 1 + [H^{\bullet}]^2/K_1K_2}$$

(Glasstone's expression, *op. cit.*, requires correction.) If C is expressed in mols./l., then $\alpha_1C = [HA']$ and $\alpha_2C = [A'']$ approximately.

Now $\mu = 0{\cdot}5\Sigma cz^2$ (where c and z are respectively the concentration and valency of the ions)

$$= 0{\cdot}5\,([Na^{\bullet}] + [H^{\bullet}] + [HA'] + [A''] \times 2^2)$$
$$= 0{\cdot}5\,(a + h + \alpha_1C + 4\alpha_2C)$$
$$= 0{\cdot}5\left(a + h + C\left\{\frac{1}{(h/K_1 + 1 + K_2/h)} + \frac{4}{(h/K_2 + 1 + h^2/K_1K_2)}\right\}\right)$$

where a is the concentration of sodium hydroxide added and $h = [H^{\bullet}]$.

The essential titration results are in Table V.

TABLE V.

Potentiometric Titration of Cyclic 1 : 1-Dicarboxylic Acids with Sodium Hydroxide at 25°.

	Acid.	Concn. of acid, *M*.	Concn. of NaOH, *N*.
(I)	*cyclo*Propane	0·005	0·01085
(II)	*cyclo*Butane	0·010	0·00945
(III)	*cyclo*Pentane	0·005	0·00965
(IV)	*cyclo*Hexane	0·005	0·00942

100 C.c. of acid were used in all cases.

NaOH, c.c.	(I). p_H.	(II). p_H.	(III). p_H.	(IV). p_H.
0	2·435	2·614	2·839	2·956
5	2·492	—	2·919	3·061
10	2·560	2·736	3·023	3·162
15	2·634	—	3·122	3·267
17·5	2·675	—	3·208	—
20	2·719	2·851	3·254	3·856
22·5	2·763	—	3·294	3·447
25	2·814	—	3·362	3·504
27·5	2·864	—	3·426	3·568
30	2·922	2·969	3·492	3·639
32·5	2·986	—	3·563	3·727 *
35	3·057	3·020	3·641	3·787
37·5	3·176	—	3·729	3·870
40	3·243	3·083	3·827	3·971
42·5	—	—	3·937	4·066
45	3·541	3·142	4·089	4·232
50	4·952	3·210	4·496	4·570
55	6·533	3·271	4·978	4·946
60	6·919	3·340	5·318	5·257
62·5	7·057	—	5·419	5·382
65	7·196	3·411	5·524	5·491
67·5	7·267	—	5·624	5·589
70	7·369	3·491	5·712	5·680
72·5	7·457	—	5·797	5·768
75	7·541	—	5·883	5·851
77·5	7·622	—	5·958	5·934
80	7·700	3·673	6·049	6·015
82·5	—	—	6·130	6·100
85	—	—	6·198	6·188
90	—	3·907	6·396	6·377
100	—	4·245	6·848	6·976
110	—	4·685	—	—
120	—	5·020	—	—
130	—	5·260	—	—
140	—	5·450	—	—
145	—	5·529	—	—
150	—	5·616	—	—
155	—	5·697	—	—
160	—	5·778	—	—
165	—	5·856	—	—
175	—	6·012	—	—

* 33·0 C.c.

Table VI contains typical results of the calculation of the classical and the thermodynamic dissociation constant for one acid (III) in detail; only the final figures for the other three acids are given.

TABLE VI.

Dissociation Constants of Cyclic 1 : 1-Dicarboxylic Acids at 25° by Potentiometric Titration.

cyclo*Pentane*-1 : 1-*dicarboxylic acid.*

Pairs of points used.	K_1 (class.) $\times 10^4$.	K_2 (class.) $\times 10^6$.	μ.	K_1 (therm.) $\times 10^4$.	K_2 (therm.) $\times 10^7$.	Pairs of points used.	K_1 (class.) $\times 10^4$	K_2 (class.) $\times 10^6$	μ.	K_1 (therm.) $\times 10^4$.	K_2 (therm.) $\times 10^7$.
22·5	6·25		2·25	5·92		35·0	6·27		2·75	5·90	
72·5		1·05	5·15		8·16	70·0		1·07	4·95		8·35
25·0	6·23		2·32	5·86		37·5	6·24		2·80	5·87	
77·5		1·09	5·51		8·41	67·5		1·05	4·77		8·24
27·5	6·21		2·43	5·87		40·0	6·24		2·87	5·87	
80·0		1·08	5·74		8·28	65·0		1·05	4·54		8·31
30·0	6·24		2·54	5·89		42·5	6·27		2·97	5·89	
82·5		1·08	5·96		8·25	62·5		1·04	4·35		8·25
									Mean	5·88	8·28

	K_1 (therm.).	K_2 (therm.).
*cyclo*Propane-1 : 1-dicarboxylic acid	No constant value obtainable	$3·71 \times 10^{-8}$
*cyclo*Butane-1 : 1-dicarboxylic acid	$7·47 \times 10^{-4}$	$1·32 \times 10^{-6}$
*cyclo*Hexane-1 : 1-dicarboxylic acid	$3·54 \times 10^{-4}$	$7·78 \times 10^{-7}$

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