7. *The Dissociation Constants of Organic Acids. Part XI.* The Thermodynamic Primary Dissociation Constants of Some Normal Dibasic Acids.*

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In spite of numerous determinations of the dissociation constants of dibasic acids by conductivity methods during the last 45 years, neither the primary nor the secondary constant of any such acid is known with accuracy, as judged by modern physicochemical standards.

* The paper entitled " The Determination of the Thermodynamic Dissociation Constant of Benzoic Acid, at 25°, from Conductivity Measurements " (*Phil. Mag.*, 1934, **18**, 901) is regarded as Part X; this contains a review of our method for the determination of the true dissociation constants of monobasic acids.

The present communication describes the evaluation of the true primary dissociation constants of certain dibasic acids. The secondary dissociation constants cannot at present be satisfactorily calculated from conductivity data alone (compare Wegscheider, *Monatsh.*, 1902, **23**, 599; Luther, *Z. Elektrochem.*, 1907, **13**, 296; Chandler, *J. Amer. Chem. Soc.*, 1908, **30**, 709; Drucker, *Z. physikal. Chem.*, 1920, **96**, 405; Paul, *ibid.*, 1923, **110**, 434, for methods involving certain arbitrary assumptions); subsidiary transport-number data (compare Sherrill and Noyes, *J. Amer. Chem. Soc.*, 1926, **48**, 1861) or other data obtainable by potentiometric methods are necessary, and these, together with the method of computation, will be discussed in a later paper.

The chief difficulties in the evaluation of the primary dissociation constants are: (1) The determination of the limiting mobility of the acid ion, $l_{0\,HX'}$; direct determination from conductivity data of the acid salt, NaHX or KHX, is impossible owing to the secondary dissociation $HX' \rightleftharpoons H^{\cdot} + X''$; (2) the correction of the conductivity data relating to the disodium salt for hydrolysis. The latter difficulty has been completely overcome, and a method is described (see p. 24) for the application of a combined hydrolysis and solvent correction; μ_0 for the disodium salts can then be calculated by the "*n*" formula. A very close approximation to the limiting mobility of the acid ion can be obtained as follows: $l_{0\,HX'}$, which for normal dibasic acids is $l_{0\,CO_2H\cdot(CH_2)_x\cdot CO_2'}$, is assumed equal to that of the corresponding amic acid ion, $NH_2\cdot CO\cdot(CH_2)_x\cdot CO_2'$ (Part IX, J., 1934, 1101). The results for the limiting *equivalent* conductivities of the sodium amate and the derived dibasic acid salt, together with the corresponding limiting ionic mobilities, are collected in Table I ($l_{0\,Na^{\cdot}} = 49{\cdot}8$; Part IV, J., 1931, 1715).

TABLE I.

	Equivalent conductivity, Λ_0, for		Limiting ionic mobility, l_0, for		
x.	$NH_2\cdot CO\cdot(CH_2)_x\cdot CO_2Na$.	$CO_2Na\cdot(CH_2)_x\cdot CO_2Na$.	$NH_2\cdot CO\cdot(CH_2)_x\cdot CO_2'$, *A*.	$CO_2'\cdot(CH_2)_x\cdot CO_2'$, *B*.	$\frac{A}{B}$.
1	85·31	114·46	35·5	64·7	0·549
2	81·29	110·75	31·5	60·9	0·517
3	79·83	106·67	30·0	56·9	0·527
4	78·38	102·78	28·6	52·9	0·540
				Mean	0·533

It will be seen that there is a simple connexion between the mobility of the amic and hence of the acid ion and the corresponding neutral-salt ion; the relationship $l_{0\,HX'} = 0{\cdot}53 l_{0\,X''}$ may therefore be employed for the calculation of the limiting mobility of the acid ion from that of the derived bivalent ion * (compare Chandler, *J. Amer. Chem. Soc.*, 1908, **30**, 709; also Part IX, *loc. cit.*). Slight variations of this factor do not appreciably affect the value of the true dissociation constant, $K_{1,\,therm.}$ (compare p. 28 for malonic acid).

The true dissociation constant is computed in the usual manner (compare MacInnes, *J. Amer. Chem. Soc.*, 1926, **48**, 2068; MacInnes and Shedlovsky, *ibid.*, 1932, **54**, 1432; Parts VI and VII, J., 1932, 2829; 1933, 1637), Λ_e being given by the expression $\Lambda_e\,H_2A = \Lambda_{c''}\,HCl - \Lambda_{c''}\,NaCl + \Lambda_{c''}\,NaHA$, where c'' is the ionic concentration, and $\Lambda_{c''}\,NaHA$ is computed with the aid of the Debye–Hückel–Onsager equation (for details, see p. 26).

The final results for the thermodynamic dissociation constants and for Λ_0 are tabulated below.

Acid.	Λ_0.	$K_{1,\,therm.} \times 10^5$.	Acid.	Λ_0.	$K_{1,\,therm.} \times 10^5$.
Malonic	383·5	139·7	Adipic	376·6	3·715
Succinic	379·5	6·626	Pimelic	374·6	3·097
Glutaric	378·0	4·535	Suberic	373·1	2·994

* There is an error in the calculations of the mobility of the acid ion from the limiting conductivity of the disodium salt given in Parts I and II (J., 1929, 1476, 1487). The limiting *ionic* conductivity, *i.e.*, $l_{0\,X''}$, of the bivalent ion is derived from the limiting *equivalent* conductivity of the disodium salt by subtraction of the mobility of the sodium ion (compare Glasstone, "The Electrochemistry of Solutions," 1930, p. 68). The published figures for the limiting mobilities of the acid ions must therefore be halved, and the values of $K_{1,\,class.}$ appropriately corrected.

These values are being employed as standards for the investigation of the various potentiometric methods available for the determination of dissociation constants, and the results will be communicated later. The early work of Ostwald, Walden, Voermann, Smith, Bethmann, and others during 1889—1904 on the classical dissociation " constants " of these acids must now be regarded as of very little quantitative value and is not discussed further.

It is necessary to reply to the serious criticisms made by Ives, Riley, and Linstead (J., 1932, 1093) on the work on malonic acid and other dibasic acids described by one of us in Parts I and II (*loc. cit.*). First, referring to the hydrolysis of the disodium salts, they state that " the existence of this hydrolysis introduces a very difficult problem, for it is, at present, impossible to measure this, with anything like the same degree of accuracy as that which can be attained in the measurement of the conductivity of the solutions. Neither can it be calculated from the conductivity data without an accurate knowledge of the mobilities of acid and normal ions," but this criticism has little significance now in view of the methods described in this paper. Secondly, they employ the now generally discarded methods, such as those depending on the Ostwald dilution formula, Kraus's and also Derick's methods, for the evaluation of Λ_0 by the extrapolation of the acid conductivity results, since they hold the view that the high values (approximately 20 units) yielded by extrapolation of the disodium salt data are due to hydrolysis. Although we admit that hydrolysis is undoubtedly present, we do not consider that the discrepancy is to be attributed entirely to this cause. The largest error has been introduced in their calculation of the mobility $l_{0\,HX'}$. The correct relation is $l_{0\,HX'} = 0{\cdot}5 l_{0\,X''}$, which, for *cyclo*hexane-1 : 1-diacetic acid (*loc. cit.*, p. 1099), is $0{\cdot}5 \times 42{\cdot}5 = 21{\cdot}25$ or $\Lambda_0 = 349{\cdot}05 + 21{\cdot}25 = 370{\cdot}3$, if one employs Ives, Linstead, and Riley's figures, including Λ_0 for the disodium salt, the method of calculation of which is not described.

In view of the foregoing remarks and the fact that those authors have confined themselves to the primary Ostwald dissociation " constants," it would appear that, whilst their main theoretical conclusions may be correct, a determination of the *true* primary and secondary dissociation constants of these cyclic 1 : 1-diacetic acids is desirable.

EXPERIMENTAL.

Preparation of Materials.—Acids. The essential details have already been described (Vogel, J. 1934, 336). All operations were carried out in Pyrex vessels, and all solvents for recrystallisation, indicated in parentheses after the m. p., were of B.D.H. " A.R." purity.

Malonic acid. (I) Kahlbaum's acid. (II) Boots's acid. Both m. p. 136° (decomp.) [benzene–ether–light petroleum (b. p. 60—80°)].

Succinic acid. (I) Kahlbaum's acid. (II) *Ex* nitrile of m. p. 54°. Both m. p. 185—185·5° (acetone).

Glutaric acid. Two specimens, from two independent preparations of the nitrile (b. p. 149—150°/14 mm.), both had m. p. 97·5—98° (chloroform).

Adipic acid. (I) Ethyl succinate, b. p. 113°/22 mm., was reduced with sodium and ethyl alcohol (compare Bennett and Mosses, J., 1931, 1697) to tetramethylene glycol, b. p. 127—129°/12 mm., which was successively converted into the dibromide (b. p. 82—84°/12 mm.) by constant b. p. hydrobromic acid and sulphuric acid (compare Kamm and Marvel, *J. Amer. Chem. Soc.*, 1920, **42**, 307), the dinitrile (b. p. 180—182°/19 mm.) by aqueous-alcoholic potassium cyanide, and into the acid by 50% sulphuric acid; m. p. 151·5—152° (acetone). (II) A commercial specimen, m. p. 151—152° (acetone).

Pimelic acid. From two independent preparations of the dinitrile; b. p. 169—171°/15 mm., m. p. 106° (benzene–ether).

Suberic acid. From two independent preparations of the dinitrile; b. p. 178—180°/15 mm., m. p. 142° (acetone).

Disodium salts. With the exception of Boots's sodium malonate (specimen II), these were all prepared by adding the calculated quantity of sodium hydroxide solution, prepared from the A.R. solid and standardised against A.R. potassium hydrogen phthalate, to known weights of the pure acids, and were recrystallised from aqueous methyl (for the malonate and glutarate) or ethyl alcohol (for the other acids). Details of the preparations are tabulated below.

Disodium Salts.

	Na, %. Found.	Calc.		Na, %. Found.	Calc.
Malonate (Boots's)	31·02	31·08	Adipate, from acid (I)	24·16	24·21
„ from acid (I)	31·06		„ „ (II)	24·20	
Succinate, from acid (I)	28·45	28·38	Pimelate, from acid (I)	22·47	22·53
„ „ (II)	28·37		„ „ (II)	22·54	
Glutarate, from acid (I)	26·23	26·15	Suberate, from acid (I)	21·19	21·10
„ „ (II)	26·14		„ „ (II)	21·15	

Combined Hydrolysis and Solvent Correction for Disodium Salts.—In a solution of the disodium salt in "equilibrium" water, the most important equilibria are:

$$Na_2X \rightleftharpoons 2Na^{\bullet} + X'' \quad (1); \qquad H_2O \rightleftharpoons H^{\bullet} + OH' \quad (2);$$
$$H_2CO_3 \rightleftharpoons H^{\bullet} + HCO_3' \quad (3); \qquad X'' + H{\cdot}OH \rightleftharpoons HX' + OH' \quad (4).$$

The secondary dissociation of the carbonic acid is neglected, as is also the secondary hydrolysis $HX' + H{\cdot}OH \rightleftharpoons H_2X + OH'$. The ions present are $Na^{\bullet}$, $H^{\bullet}$, OH', HCO_3', HX', and X'', and since the solution is electrically neutral

$$[Na^{\bullet}] + [H^{\bullet}] = 2[X''] + [HX'] + [HCO_3'] + [OH'] \quad (5)$$

Now $$[H^{\bullet}][OH'] = K_w, \text{ and } [OH'] = K_w/[H^{\bullet}] \quad (6)$$

Also $$[X''][H^{\bullet}]/[HX'] = K_2 \quad (7)$$

and C = concn. of salt (g.-mols./l.) = $[X''] + [HX']$

or $$[HX'] = C - [X''] \quad (8)$$

Hence $$\frac{[X''][H^{\bullet}]}{(C - [X''])} = K_2 \text{ or } [X''] = \frac{K_2C}{[H^{\bullet}] + K_2} \quad (9)$$

Further, if m is the total concentration of carbonic acid (in g.-mols./l.),

$$K_c = \frac{[H^{\bullet}][HCO_3']}{m - [HCO_3']} \text{ or } [HCO_3'] = \frac{K_cm}{[H^{\bullet}] + K_c} \quad (10)$$

Substituting in (5), and remembering that $[Na^{\bullet}] = 2C$, one obtains

$$C + [H^{\bullet}] = \frac{K_2C}{[H^{\bullet}] + K_2} + \frac{K_w}{[H^{\bullet}]} + \frac{K_cm}{[H^{\bullet}] + K_c} \quad (11)$$

This expression is identical with equation (6) of Part VII (J., **1933**, 1639) except that K_2 is substituted for K_a.

The solution of this equation of the fourth degree for $[H^{\bullet}]$ is that given in our previous paper (*loc. cit.*); expression (7) is used for those cases where $K_2m > 10^{-10}$, and expression (9) where $K_2m < 10^{-10}$. Our thanks are due to Mr. H. V. Lowry, M.A., for this deduction.

Having calculated $[H^{\bullet}]$, we can readily compute the other ionic concentrations, and the correction to be *added* to the observed specific conductivity is given by

$$\Delta\kappa = 10^{-3}\{\Lambda_{X''}2(C - [X'']) - \Lambda_{H^{\bullet}}[H^{\bullet}] - \Lambda_{OH'}[OH'] - \Lambda_{HCO_3'}[HCO_3'] - \Lambda_{HX'}(C - [X''])\} \quad (12)$$

Sufficiently accurate values of K_2 for use in the application of the correction may be obtained directly, without any further calculation, from the potentiometric titration curve, determined with the hydrogen, quinhydrone, or glass electrode. For the actual calculations on the normal dibasic acids, K_2 was taken as 3×10^{-6} (compare Gane and Ingold, J., 1931, 2158), $K_c = 4{\cdot}54 \times 10^{-7}$, $\Lambda_{H^{\bullet}} = 348{\cdot}0$, $\Lambda_{OH'} = 210{\cdot}8$, $\Lambda_{HCO_3'} = 46{\cdot}9$, and $\Lambda_{X''}$ and $\Lambda_{HX'}$ were the preliminary values obtained by applying a normal solvent correction.

General Technique and Apparatus.—This was that described in earlier paper of this series. Four cells of the Hartley and Barrett type, two of silica, R ($0{\cdot}02586_3$) and Q ($0{\cdot}02674_8$), two of Pyrex, S ($0{\cdot}03422_8$) and V ($0{\cdot}02781_5$), and three Kohlrausch cells of Pyrex, J ($0{\cdot}2474_1$), V ($0{\cdot}2499_0$), and N ($0{\cdot}3330_4$), were employed; the figures in parentheses are the corresponding cell constants. All measurements were carried out at 25° ± 0·01°.

The experimental results for the disodium salts with equilibrium water are given in Table II; κ is the specific conductivity of the water used, μ, obs. is the molecular conductivity after application of a normal solvent correction, μ, corr. that corrected by means of equation (12), μ_0^n is the value of the limiting molecular conductivity calculated by the "n" formula, the constants of which, together with that of the limiting mobility of the anion, $l_{0\,X''}$, are given at the head of the table. Molecular weights are based on atomic weights given in J., 1933, 361.

TABLE II.

Disodium Salts of Normal Dibasic Acids at 25°.

Sodium malonate. $\mu_0^n = \mu_c + 403{\cdot}5C^{0{\cdot}491}$; $\mu_0^n = 228{\cdot}92$; $l_{0\,X''} = 64{\cdot}7$.

$C \times 10^4$.	μ, obs.	μ, corr.	μ_0^n.
Run 1. Cell V. $\kappa = 0{\cdot}615$. Specimen I.			
1·737	219·17	224·45	—
5·148	217·11	218·76	228·74
10·73	213·87	214·63	228·70
22·20	208·41	208·83	228·85
37·73	202·96	203·14	229·16
57·56	197·37	197·60	(229·62)
73·35	194·21	194·26	(213·17)
107·0	189·21	189·21	(232·63)
Run 2. Cell S. $\kappa = 0{\cdot}638$. Specimen II.			
3·471	217·97	220·22	—
8·308	215·50	216·51	228·86
16·02	211·32	211·76	228·84
26·88	206·78	207·09	229·11
31·70	204·88	205·19	229·06
48·73	199·66	200·21	(229·72)
81·01	192·82	192·92	—
92·48	191·14	191·20	—

Sodium succinate. $\mu_0^n = \mu_c + 648{\cdot}3C^{0{\cdot}635}$; $\mu_0^n = 221{\cdot}49$; $l_{0\,X''} = 60{\cdot}9$.

$C \times 10^4$.	μ, obs.	μ, corr.	μ_0^n.
Run 1. Cell V. $\kappa = 0{\cdot}633$. Specimen I.			
1·106	215·99	224·43	—
5·674	214·09	215·36	221·40
13·64	210·98	211·40	221·24
33·92	203·65	204·00	221·54
50·27	199·04	199·21	221·73
63·06	196·30	196·37	(222·38)
84·82	191·64	191·65	(222·75)
95·32	189·93	189·95	—
Run 2. Cell S. $\kappa = 0{\cdot}652$. Specimen II.			
2·542	215·33	218·56	—
7·141	213·51	214·28	221·60
18·53	208·94	209·40	221·35
33·62	203·89	204·16	221·46
43·57	200·91	201·03	221·59
58·22	197·34	197·45	(221·17)
76·83	291·32	193·35	—
80·00	192·67	192·70	—

Sodium glutarate. $\mu_0^n = \mu_c + 246{\cdot}8C^{0{\cdot}393}$; $\mu_0^n = 213{\cdot}34$; $l_{0\,X''} = 56{\cdot}9$.

$C \times 10^4$.	μ, obs.	μ, corr.	μ_0^n.
Run 1. Cell V. $\kappa = 0{\cdot}630$. Specimen I.			
0·782	203·07	209·01	—
5·491	198·79	199·94	213·35
9·777	195·94	196·98	213·17
18·55	191·73	192·20	213·03
41·84	184·43	184·55	213·23
60·87	180·33	180·49	213·72
79·34	177·22	177·27	(214·15)
96·78	174·73	174·75	(214·63)
Run 2. Cell S. $\kappa = 0{\cdot}658$. Specimen II.			
3·370	200·19	202·27	—
7·000	197·81	198·96	213·16
13·08	194·27	195·16	213·32
26·86	188·81	189·23	213·46
43·48	184·19	184·38	213·65
61·99	180·21	180·33	(214·82)
77·25	177·46	177·56	—

Sodium adipate. $\mu_0^n = \mu_c + 207{\cdot}7C^{0{\cdot}365}$; $\mu_0^n = 205{\cdot}36$; $l_{0\,X''} = 52{\cdot}9$.

$C \times 10^4$.	μ, obs.	μ, corr.	μ_0^n.
Run 1. Cell V. $\kappa = 0{\cdot}623$. Specimen I.			
1·087	194·35	199·23	—
5·140	191·03	192·27	205·34
11·23	187·00	187·98	205·37
26·84	180·93	181·25	205·15
43·95	176·67	176·79	205·41
66·88	172·36	172·49	(205·85)
86·37	169·43	169·46	(206·09)
108·3	166·73	166·74	—
Run 2. Cell S. $\kappa = 0{\cdot}654$. Specimen II.			
2·995	192·55	195·15	—
7·012	189·21	190·01	205·34
17·72	184·19	184·59	205·13
35·51	178·65	178·95	205·43
57·89	174·02	174·09	205·74
75·01	171·01	171·04	—
92·23	168·58	168·61	—
100·2	167·76	167·77	—

Sodium pimelate. $\mu_0^n = \mu_c + 205{\cdot}7C^{0{\cdot}370}$; $\mu_0^n = 199{\cdot}69$; $l_{0\,X''} = 50{\cdot}1$.

$C \times 10^4$.	μ, obs.	μ, corr.	μ_0^n.
Run 1. Cell V. $\kappa = 0{\cdot}640$. Specimen I.			
1·873	189·61	193·18	—
5·951	185·61	186·58	199·72
12·17	181·93	182·42	199·64
23·56	177·59	177·96	199·83
42·36	172·48	172·65	199·66
63·17	168·46	168·54	(199·97)
82·95	165·54	165·57	(200·41)
100·7	163·32	163·12	—
Run 2. Cell S. $\kappa = 0{\cdot}658$. Specimen II.			
2·781	188·30	191·01	—
7·001	184·55	185·38	199·33
11·12	182·59	183·26	199·82
16·81	180·07	180·48	199·78
32·14	175·05	175·10	199·64
51·06	170·65	170·69	199·82
75·12	166·48	166·50	—
97·57	162·69	162·69	—

Sodium suberate. $\mu_0^n = \mu_c + 213{\cdot}5C^{0{\cdot}403}$; $\mu_0^n = 194{\cdot}34$; $l_{0\,X''} = 47{\cdot}4$.

$C \times 10^4$.	μ, obs.	μ, corr.	μ_0^n.
Run 1. Cell V. $\kappa = 0{\cdot}640$. Specimen I.			
1·416	187·20	191·14	—
5·959	182·37	183·64	194·34
11·95	179·36	180·04	194·21
21·85	175·84	176·19	194·26
47·84	169·19	169·25	194·03
70·95	165·17	165·21	194·51
87·65	162·95	162·97	194·60
99·49	161·64	161·64	(194·93)
Run 2. Cell S. $\kappa = 0{\cdot}621$. Specimen II.			
3·712	184·64	186·64	—
9·013	181·14	181·68	194·33
19·01	176·99	177·29	194·38
30·65	173·17	173·35	194·07
40·39	170·51	170·72	(193·87)
80·01	164·10	164·19	194·69
97·51	162·08	162·09	(195·33)

The influence of various values of K_2 on the corrected values of the conductivity is shown in Table III for one run (No. 1) with sodium malonate. These results show clearly that only a very approximate value of K_2 is necessary.

TABLE III.

$C \times 10^4$.	μ, obs.	$10^6 K_2 = 2$.	μ, corr. $10^6 K_2 = 3$.	$10^6 K_2 = 4$.	$C \times 10^4$.	μ, obs.	$10^6 K_2 = 2$.	μ, corr. $10^6 K_2 = 3$.	$10^6 K_2 = 4$.
1·737	219·17	225·57	224·45	224·14	37·73	202·96	203·16	203·14	203·12
5·148	217·11	218·90	218·76	218·69	57·56	197·37	197·61	197·60	197·59
10·73	213·87	214·69	214·63	214·57	73·35	194·21	194·26	194·26	194·26
22·20	208·41	208·87	208·83	208·77	107·0	189·21	189·21	189·21	189·21

The values at round concentrations, obtained with the aid of a flexible spline, are collected in Table IV for convenience of reference and for comparison with other published data. The concentrations, somewhat extended, used by Kohlrausch and others, have been employed.

TABLE IV.

$C \times 10^4$.	Malonate.	Succinate.	Glutarate.	Adipate.	Pimelate.	Suberate.
5·0	219·10	216·35	210·30	192·40	187·25	184·65
10·0	215·30	213·59	196·90	184·48	183·84	181·30
20·0	209·92	208·90	191·65	183·72	178·18	176·75
30·0	205·81	205·19	187·85	180·30	175·75	173·57
40·0	202·39	202·10	185·06	177·65	173·10	170·98
50·0	199·55	199·31	182·65	175·50	170·90	168·85
60·0	197·12	196·84	180·50	173·70	168·99	167·00
70·0	194·93	194·58	178·70	172·03	167·33	165·40
80·0	193·06	192·55	177·03	170·35	166·02	164·05
90·0	191·35	190·90	175·62	168·90	166·64	162·83
100·0	190·00	189·40	174·38	167·66	163·42	161·65

The True Primary Dissociation Constants.—Λ_e has been deduced from the relation $\Lambda_e\,H_2A = \Lambda_{c''}\,HCl - \Lambda_{c''}\,NaCl + \Lambda_{c''}\,NaHA$, where c'' is the ionic concentration, for the calculation of which two approximations were sufficient (compare Part VI, J., 1932, 2837) except for malonic acid where three were required. This expression reduces, after substitution of our experimental values for NaCl and HCl (Parts IV and V, J., 1931, 1715; 1932, 400), to $\Lambda_e\,H_2A = 297{\cdot}49 + 117{\cdot}4c''^{0\cdot551} - 1380c''^{0\cdot929} + \Lambda_0\,NaHA - xc''^{0\cdot5}$. The last two terms of this expression refer to the acid salt, $\Lambda_0\,NaHA = \Lambda_{c''}\,NaHA + xc''^{0\cdot5}$; $\Lambda_0\,NaHA = l_{0\,Na^{\cdot}} + l_{0\,HA'}$, and for malonic, succinic, glutaric, and adipic acids $l_{0\,HA'}$ was assumed to be equal to that of the corresponding amic acid ion, whilst for pimelic and suberic acids it was calculated from the relation $l_{0\,HA'} = 0{\cdot}53 l_{0\,A''}$. The value of x was derived from the Debye–Hückel–Onsager equation which at 25° reduces to $\Lambda_0 = \Lambda_{c''} - (0{\cdot}228\Lambda_0 + 59{\cdot}8)c''^{0\cdot5}$ (compare Hartley, *Ann. Reports*, 1930, **27**, 331; J., 1932, 406). This expression applies to all the normal acids, where c'' is below 1×10^{-3}. For malonic acid, c'' is *ca.* 0·0035*N* at the highest concentration, which is somewhat outside the range of its valid applicability, and this doubtless accounts for the slight decrease of $K_{1,\,therm.}$ at the highest concentrations. The values deduced for Λ_0 and x are collected in Table V.

TABLE V.

Sodium Hydrogen Salts.

Acid	Malonic.	Succinic.	Glutaric.	Adipic.	Pimelic.	Suberic.
Λ_0	85·3	81·3	79·8	78·4	76·4	74·9
x	79·25	78·35	77·99	77·68	77·22	76·88

In the tabulated results for the acids (Table VI, in which cl. and th. = class. and therm. respectively), C is the concentration in g.-mols./l., μ, obs. is the molecular conductivity to which no solvent correction has been applied (compare Part VI, J., 1932, 2834), $K_{1,\,class.}$ is the Ostwald ionisation constant, c'' is the ionic concentration, and $K_{1,\,therm.}$ is the true dissociation constant deduced from the equation $\log K_{1,\,therm.} = \log K_1' - 1{\cdot}010\,c''^{0\cdot5}$, where K_1' is the dissociation constant computed from the degree of dissociation $\alpha = \Lambda_{c''}/\Lambda_e$. The values of $K_{1,\,class.}$, although having little significance according to modern electrochemical views since they should, and do, vary with concentration, are included for comparison with old data, and average values have been computed over the higher concentration range where the variation is least. The choice of the values of $K_{1,\,therm.}$ collected for the calculation of the mean has been influenced by the following considerations. Theory requires that for a monobasic acid $K_{1,\,class.}$ should increase with rising concentration, but in the present instance, owing to the attendant secondary ionisation, $K_{1,\,class.}$ falls rapidly at first and then commences to rise at a concentration of *ca.* 0·003—0·004*N*, whereat it may be assumed that the effect of secondary ionisation is negligible. Hence the values of $K_{1,\,class.}$ and consequently of $K_{1,\,therm.}$ possess significance from our viewpoint only after $K_{1,\,therm.}$ has passed the minimum.

TABLE VI.

True Primary Dissociation Constants.

$C \times 10^4$.	μ, obs.	$K_{1,\,cl.} \times 10^3$.	Λ_e.	$c'' \times 10^4$.	$K_{1,\,th.} \times 10^3$.	$C \times 10^4$.	μ, obs.	$K_{1,\,cl.} \times 10^3$.	Λ_e.	$c'' \times 10^4$.	$K_{1,\,th.} \times 10^3$.
Malonic acid (M = 104·03; Λ_0 = 383·5).											
Run 1. Cell R. κ = 0·691. Specimen I.											
1·626	357·04	(2·047)	372·34	1·5180	(2·081)	58·79	153·21	1·506	378·15	23·4922	1·397
7·541	282·37	(1·550)	382·06	2·8604	(1·514)	84·72	131·24	1·510	377·08	29·4873	1·391
22·28	211·44	(1·513)	380·20	12·3861	(1·430)	107·0	119·63	1·514	376·27	34·0201	1·385
33·93	184·62	(1·502)	379·30	16·4614	(1·412)	122·4	113·45	1·521	375·77	36·8767	1·385
Run 2. Cell Q. κ = 0·680. Specimen II.											
3·206	327·67	(1·607)	382·07	2·8070	(1·593)	29·94	191·95	(1·488)	379·60	15·4945	(1·414)
5·262	301·96	(1·534)	381·77	4·2586	(1·501)	46·03	165·58	1·507	378·72	20·5962	1·407
10·43	260·56	(1·502)	381·18	7·2958	(1·414)	55·19	155·10	1·516	378·21	23·1634	1·407
15·40	235·21	(1·498)	380·70	9·7385	(1·413)	65·86	145·24	1·518	377·71	25·9147	1·405
Run 3. Cell V. κ = 0·615. Specimen I.											
2·550	338·19	(1·663)	382·19	2·2562	(1·675)	15·03	239·81	(1·568)	380·75	9·4680	(1·500)
5·163	305·04	(1·597)	381·79	4·1250	(1·564)	42·50	170·25	1·506	378·95	19·0912	1·407
8·702	274·71	(1·574)	381·37	6·2680	(1·523)	70·96	141·91	1·507	377·56	26·6715	1·392
							Mean	1·513		Mean	1·397
Succinic acid (M = 118·06; Λ_0 = 379·5).											
Run 1. Cell Q. κ = 0·615. Specimen I.											
1·375	191·85	(7·107)	378·55	0·6967	(7·130)	51·95	41·25	6·888	377·50	5·6773	6·590
6·019	107·85	(6·791)	378·31	1·7159	(6·637)	63·81	37·49	6·909	377·38	6·3384	6·593
12·38	79·03	(6·779)	378·13	2·5865	(6·584)	82·39	33·31	6·957	377·21	7·2748	6·618
24·09	58·65	(6·806)	377·90	3·7386	(6·566)	102·1	30·10	6·973	377·04	8·1859	6·613
Run 2. Cell R. κ = 0·624. Specimen II.											
3·443	137·53	(7·092)	378·41	1·2514	(6·961)	46·49	43·73	6·897	377·59	5·2617	6·639
9·942	87·68	(6·900)	378·19	2·3048	(6·714)	77·27	34·46	6·996	377·25	7·0530	6·650
17·71	67·67	(6·852)	378·01	3·1701	(6·632)	95·76	31·10	7·004	377·10	7·8968	6·648
34·45	49·79	(6·824)	377·73	4·5406	(6·560)						
Run 3. Cell S. κ = 0·626. Specimen I.											
1·890	174·35	(7·242)	378·51	0·8708	(7·278)	18·95	65·77	(6·885)	377·99	3·2972	(6·659)
7·440	100·02	(7·017)	378·27	1·9670	(6·843)	37·90	47·76	6·866	377·66	4·8702	6·622
10·34	86·16	(6·895)	378·19	2·3558	(6·706)	64·48	37·47	6·975	377·35	6·4922	6·653
							Mean	6·941		Mean	6·626
Glutaric acid (M = 132·06; Λ_0 = 378·0).											
Run 1. Cell Q. κ = 0·500. Specimen I.											
1·056	194·04	(5·718)	377·12	0·5434	(5·671)	46·46	36·31	4·721	376·28	4·4936	4·530
5·268	99·65	(4·972)	376·92	1·3927	(4·870)	61·89	31·66	4·740	376·17	5·2095	4·538
11·18	71·07	(4·867)	376·77	2·1089	(4·740)	81·04	27·84	4·747	375·95	6·1420	4·531
21·54	52·47	(4·816)	376·59	2·9994	(4·666)	100·5	25·13	4·756	375·85	6·6709	4·533
Run 2. Cell R. κ = 0·615. Specimen II.											
3·952	114·81	(5·229)	376·96	1·2029	(5·131)	34·75	41·74	(4·763)	376·39	3·9793	(4·587)
10·10	74·52	(4·887)	376·78	2·0622	(4·761)	47·23	35·98	4·728	376·24	4·6633	4·541
18·16	56·70	(4·864)	376·62	2·8234	(4·658)	79·17	25·28	4·771	375·84	6·8036	4·535
							Mean	4·745		Mean	4·535
Adipic acid (M = 146·08; Λ_0 = 376·6).											
Run 1. Cell Q. κ = 0·600. Specimen I.											
0·983	187·05	(4·819)	375·71	0·4894	(4·786)	42·44	34·35	3·860	374·98	3·8757	3·720
5·912	87·32	(4·138)	375·50	1·3746	(4·148)	60·01	29·05	3·869	374·83	4·6502	3·716
11·00	64·87	(3·943)	375·38	1·9007	(3·854)	77·69	25·69	3·879	374·69	5·3259	3·715
21·47	47·38	(3·887)	375·22	2·7105	(3·771)	96·66	23·14	3·888	374·57	5·9715	3·715
Run 2. Cell R. κ = 0·612. Specimen II.											
2·501	127·02	(4·317)	375·61	0·8456	(4·228)	50·68	31·48	3·864	374·90	4·2557	3·718
8·188	74·62	(4·010)	375·45	1·6275	(3·946)	69·68	27·05	3·873	373·74	5·0297	3·714
15·33	55·81	(3·952)	375·31	2·2795	(3·844)	90·95	23·89	3·882	374·62	5·8000	3·710
33·23	38·62	(3·894)	375·08	3·4212	(3·762)		Mean	3·873		Mean	3·715

TABLE VI (*contd.*).

$C \times 10^4$.	μ, obs.	$K_{1,\text{cl.}} \times 10^3$.	Λ_e.	$c'' \times 10^4$.	$K_{1,\text{th.}} \times 10^3$.	$C \times 10^4$.	μ, obs.	$K_{1,\text{cl.}} \times 10^3$.	Λ_e.	$c'' \times 10^4$.	$K_{1,\text{th.}} \times 10^3$.
					Pimelic acid (M = 160·10; Λ_0 = 374·6).						
					Run 1. Cell Q. κ = 0·540. Specimen I.						
1·249	171·72	(4·848)	373·69	0·5741	(4·797)	51·07	28·70	3·225	372·97	3·9305	3·130
6·495	78·03	(3·560)	373·50	1·3570	(3·488)	69·71	24·84	3·216	372·85	4·5483	3·083
12·54	56·82	(3·402)	373·39	1·9087	(3·318)	89·73	21·78	3·222	372·72	5·2443	3·087
25·00	40·65	(3·302)	373·23	2·7228	(3·202)	110·5	19·71	3·227	372·60	5·8416	3·084
					Run 2. Cell R. κ = 0·552. Specimen II.						
2·561	121·01	(3·947)	373·63	0·8294	(4·897)	20·20	45·03	(3·313)	373·29	2·4531	(3·219)
7·898	71·02	(3·501)	373·48	1·5014	(3·425)	36·95	33·65	(3·276)	373·10	3·3325	(3·167)
9·214	65·61	(3·424)	373·45	1·6185	(3·348)	45·71	30·25	3·229	373·03	3·6905	3·105
15·15	52·04	(3·389)	373·35	2·1101	(3·302)	79·12	23·17	3·227	372·78	4·9176	3·096
								Mean 3·225			Mean 3·097
					Suberic acid (M = 174·11; Λ_0 = 373·1).						
					Run 1. Cells R, J, V, N. κ = 0·595. Specimen I.						
1·502	156·16	(4·525)	372·14	0·6303	(4·473)	N 11·02	59·89	(3·382)	371·93	1·7745	(3·302)
4·160	98·20	(3·911)	372·07	1·0977	(3·842)	J 45·05	29·67	3·095	371·55	3·5975	2·987
6·714	76·71	(3·573)	372·00	1·3845	(3·500)	N 78·35	22·81	3·119	371·31	4·8131	2·987
8·602	67·64	(3·453)	371·96	1·5642	(3·377)	V 91·36	21·16	3·121	371·23	5·2046	2·990
11·62	57·98	(3·323)	371·93	1·8115	(3·242)	J 94·82	20·73	3·129	371·21	5·2951	2·996
					Run 2. Cells R, J, V, N. κ = 0·612. Specimen II.						
2·551	130·31	(4·753)	372·11	0·8790	(4·683)	N 28·89	38·00	(3·336)	371·66	3·0928	(3·229)
5·162	93·02	(4·272)	372·05	1·2903	(3·973)	J 51·41	27·91	3·109	371·49	3·8624	2·998
9·121	64·80	(3·330)	371·95	1·5854	(3·256)	J 69·26	24·21	3·118	371·36	4·5153	2·997
						V 93·24	21·01	3·133	371·22	5·2771	3·001
								Mean 3·117			Mean 2·994

The values of μ at round concentrations are given below:

$C \times 10^4$.	Malonic.	Succinic.	Glutaric.	Adipic.	Pimelic.	Suberic.
1·0	360·00	200·00	195·00	185·00	175·00	165·00
5·0	304·50	118·50	103·00	95·00	85·00	83·00
10·0	265·70	88·10	76·80	67·60	62·90	62·00
20·0	219·50	64·05	54·00	48·40	44·95	44·20
30·0	193·15	53·45	45·40	40·16	37·30	36·50
40·0	175·55	46·60	39·45	35·35	32·40	31·60
50·0	162·35	41·85	35·20	31·90	29·00	28·40
60·0	151·80	38·55	31·95	29·06	26·45	26·00
70·0	142·75	35·80	29·40	26·75	24·50	23·95
80·0	135·30	23·70	27·60	25·03	23·05	22·65
90·0	128·35	31·95	26·15	23·80	21·75	21·20
100·0	121·10	30·80	25·20	22·90	20·65	20·25

The influence of changing the factor from 0·55 to 0·50 in the calculation of the mobility of the acid ion for the extreme case of malonic acid is shown in Table VII; the effect is small, and will be much smaller for the other normal dibasic acids.

TABLE VII.

$l_{0\,\text{HX}'}$ = 0·50 × 64·7 = 32·4; Λ_0 = 380·4; Run 1.

$C \times 10^4$.	μ, obs.	$K_{1,\text{class.}} \times 10^3$.	Λ_e.	$c'' \times 10^4$.	$K_{1,\text{therm.}} \times 10^3$.*
1·626	357·04	(2·333)	—	—	—
7·541	282·37	(1·612)	—	—	—
22·28	211·44	(1·549)	—	—	—
33·93	184·62	1·539	376·29	16·5928	(1·445)
58·79	153·21	1·539	375·05	23·6858	1·427
84·72	131·24	1·545	373·97	29·7317	1·425
107·0	119·63	1·544	373·16	34·3829	1·413
122·4	113·45	1·552	372·65	37·1851	1·416
		Mean 1·544			Mean 1·420

* $K_{1,\text{therm.}}$ has been evaluated only over the range where the $K_{1,\text{class.}}$ figures are significant (see above, p. 26).

TABLE VIII.

Sodium Hydrogen Salts.

Sodium hydrogen malonate (M = 126·02).

Run 1: Cell, Q; κ of water, 0·592; Specimen of acid, II; Specimen of salt, II.

$C \times 10^4$ ...	1·064	6·124	11·01	22·90	43·68	68·67	85·50	100·2
Λ_c	144·20	109·57	102·50	95·54	90·82	87·81	86·69	85·74

Run 2: Cell, R; κ of water, 0·604; Specimen of acid, II; Specimen of salt, II.

$C \times 10^4$ ...	3·654	9·473	18·12	33·34	53·53	63·47	92·54
Λ_c	118·68	104·75	98·26	93·39	89·00	88·60	86·50

Run 3: Cell, V; κ of water, 0·604; Specimen of acid, I; Specimen of salt, I.

$C \times 10^4$ ...	2·811	5·801	9·847	18·85	32·64	60·20
Λ_c	121·08	108·44	102·92	96·98	92·84	88·44

Sodium hydrogen succinate (M = 140·04).

Run 1: Cell, V; κ of water, 0·615; Specimen of acid, II; Specimen of salt, II.

$C \times 10^4$ ...	1·706	10·74	19·45	45·39	88·32	113·7
Λ_c	120·84	94·88	91·74	88·36	85·47	84·29

Run 2: Cell, Q; κ of water, 0·525; Specimen of acid, I; Specimen of salt, I.

$C \times 10^4$ ...	1·306	6·001	9·570	16·26	33·01	52·14	61·37	70·62
Λ_c	122·84	99·34	95·79	92·81	89·54	87·66	87·02	86·25

Sodium hydrogen glutarate (M = 154·04).

Run 1: Cell, Q; κ of water, 0·615; Specimen of acid, I; Specimen of salt, I.

$C \times 10^4$ ...	0·970	6·031	10·13	20·18	42·05	55·66	71·84	87·76
Λ_c	133·74	95·29	91·84	87·60	84·25	83·05	81·81	80·84

Run 2: Cell, R; κ of water, 0·666; Specimen of acid, II; Specimen of salt, II.

$C \times 10^4$ ...	3·608	10·40	18·46	36·69	72·91	86·23	107·8
Λ_c	103·34	92·20	88·40	84·50	81·74	80·89	79·63

Sodium hydrogen adipate (M = 168·07).

Run 1: Cell, Q; κ of water, 0·540; Specimen of acid, I; Specimen of salt, I.

$C \times 10^4$ ...	1·545	4·629	13·48	24·20	47·99	70·54	92·35	113·9
Λ_c	124·45	101·38	89·22	85·49	82·67	80·98	79·38	78·94

Run 2: Cell, R; κ of water, 0·593; Specimen of acid, II; Specimen of salt, II.

$C \times 10^4$ ...	1·544	7·369	14·59	25·74	52·79	71·93	106·3
Λ_c	125·24	95·31	88·65	85·82	82·17	80·89	79·04

Sodium hydrogen pimelate (M = 182·09).

Run 1: Cell, R; κ of water, 0·540; Specimen of acid, I; Specimen of salt, I.

$C \times 10^4$ ...	1·280	6·244	13·04	26·82	59·36	78·28	94·61	113·6
Λ_c	147·25	95·84	88·64	84·81	80·51	79·19	78·15	77·34

Run 2: Cell, Q; κ of water, 0·612; Specimen of acid, II; Specimen of salt, II.

$C \times 10^4$ ...	2·510	7·102	11·01	20·15	39·86	61·78	85·10
Λ_c	123·98	92·82	89·84	86·18	82·75	80·31	78·58

Sodium hydrogen suberate (M = 196·10).

Run 1: Cells, R, J, V, N; κ of water, 0·671; Specimen of acid, I; Specimen of salt, I.

$C \times 10^4$ ...	1·352	3·331	6·138	8·934	12·12	28·07	49·87	65·72
Λ_c	155·44	132·27	99·01	90·94	86·64	81·41 J	79·56 N	78·41 V
$C \times 10^4$ ...	66·13	86·38	110·8					
Λ_c	78·25 J	76·82 N	75·04 V					

Run 2: Cells, Q, J, V, N; κ of water, 0·652; Specimen of acid, II; Specimen of salt, II.

$C \times 10^4$ ...	2·501	7·342	10·09	13·14	21·12	35·51	54·98	77·61
Λ_c	137·34	96·01	97·15	86·00 J	82·94 V	80·57 N	79·05 J	77·52 V
$C \times 10^4$ ...	99·92							
Λ_c	71·88 N							

The *experimental* figures for the sodium hydrogen salts are collected in Table VIII; these were determined (*a*) to provide conductivity data for these substances, and (*b*) for the estimation of approximate values of K_2, but no satisfactory results were obtained. No solvent correction has been applied, but this will be discussed in a future communication. The stock solutions were prepared by weighing sufficient of the acid to give an approximately $N/10$-solution and then adding the calculated quantity of the disodium salt.

Correction.—The work described in Parts I and II (*loc. cit.*), which includes malonic acid, is subject to the following errors and criticisms: (1) Subtraction of the solvent correction for the acids—no solvent correction is necessary; (2) the density factor in the calculations was reversed; (3) the use of the normal solvent correction for the disodium salts—the correct method of application of a combined solvent hydrolysis correction is described in the present paper; (4) the values for Λ_0 of the acids are high for reasons given in footnote on p. 22; (5) values of $K_{1,\,\text{class.}}$ are given at round (interpolated) concentrations: the correct procedure is to use the actual experimental concentrations and to calculate the true dissociation constants, $K_{1,\,\text{therm.}}$.

The original results must therefore now be regarded as very approximate, and revised figures for all the acids, calculated in accordance with the methods described in this paper, will be published in the near future.

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