380. *Ionic Equilibria in Acid Salts of Dibasic Acids.*

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When the acid salt of a weak dibasic acid is dissolved in water the primary dissociation, *e.g.*, $NaHA \longrightarrow Na^{\cdot} + HA'$, is succeeded by the interaction $2HA' \rightleftharpoons H_2A + A''$. This reaction may proceed very extensively, being usually much more important than the simple acid dissociation of the intermediate ion; as much as one-half of the acid radical may be present as uncharged acid or doubly charged anion. Equations are derived from which the relative concentrations of HA', A'', and H_2A can be calculated if the two dissociation constants of the acid are known. Two consequences of importance in the use of buffer solutions are that the ionic strength of an acid salt solution is greater than its molar concentration, and that buffers containing polybasic acids must not be used in conjunction with solutions containing multivalent cations.

The equations enable the mobility of an intermediate ion to be derived from conductivity measurements. The results of such calculations fail to confirm the empirical rules hitherto used for estimating these mobilities.

It is often assumed that when the acid salt of a weak dibasic acid is dissolved in water it dissociates according to the equations: $NaHA \longrightarrow Na^{\cdot} + HA'$; $HA' \rightleftharpoons H^{\cdot} + A''$. This is incorrect, for it overlooks a third process, *viz.*, $HA' + HA' \rightleftharpoons H_2A + A''$, which is considerably more important than the second (simple dissociation of the intermediate ion), since the ion HA' is usually a much stronger base than water. The presence in the solution of uncharged acid molecules was recognised by McCoy and Chandler (*J. Amer. Chem. Soc.*, 1908, **30**, 688, 694), but their treatment has been rendered inadequate by the acceptance of the interionic attraction theory.

The composition of the solution can be calculated as follows, in which it is assumed throughout that the solution has an acid reaction, so that the concentration of hydroxyl ion is negligibly small. The first and second dissociation constants of the acid are $K_1 = f_{H^{\cdot}}f_{HA'}[H^{\cdot}][HA']/[H_2A]$, $K_2 = f_{H^{\cdot}}f_{A''}[H^{\cdot}][A'']/f_{HA'}[HA']$, and by division, $K_2/K_1 = f_{A''}[A''][H_2A]/f_{HA'}{}^2[HA']^2$; in the approximate treatment that follows, the activity coefficient ratio is neglected. Now $[A''] = [H_2A] + [H^{\cdot}]$, from the equations given above, and so long as $[H^{\cdot}]$ is small compared with the other two concentrations, as it usually will be in all but the most dilute solutions, we may write $[A''] = [H_2A]$, approximately, and therefore $[A'']/[HA'] = \sqrt{K_2/K_1} = x$, say; further, $[HA'] = m - [A''] - [H_2A] = m - 2[A'']$, where m is the molar concentration; from these simultaneous equations we obtain: $[HA'] = m/(1 + 2x)$; $[H_2A] = [A''] = xm/(1 + 2x)$. These equations determine the composition of the solution, and it will be noticed that the *proportions* of H_2A, HA', and A'' are independent of the concentration.

The conditions under which the approximation is justified, *viz.*, that $[H^{\cdot}]$ is small compared with $[A'']$ or $[H_2A]$, may be estimated by substituting the above values in the equation for the second-stage dissociation of the acid, whereupon we obtain as a first approximation $[H^{\cdot}] = K_2/x$; for $[H^{\cdot}]$ to be small compared with $[H_2A]$, therefore, K_2/x must be small compared with $mx/(1 + 2x)$; and since the maximum possible value of x is 0·5 (see later), this reduces to the condition that $2K_1$ should be small compared with m.

The ratio K_1/K_2 cannot be less than 4, on account of statistical considerations (Bjerrum, *Z. physikal. Chem.*, 1923, **106**, 210), and if the acid is unsymmetrical, or if the ionisation of one acid group hinders that of the second, the ratio will be correspondingly increased. The maximum possible value of x is therefore 0·5, and for this theoretical limiting case the formulæ given show that in the acid salt solution 25% of the acid radical is in the form of uncharged acid, 25% in the form of doubly charged anions, and only 50% in the form of acid anions, HA'. A number of common acids, *e.g.*, those of the malonic acid homologous series, approach this limiting case fairly closely. The figures, obtained by a second approximation, for 0·1M-solutions of the acid sodium salts of some acids are given in Table I.

A consequence of the high concentration of doubly charged anions, which will be important, for instance, where a dibasic acid is a constituent of a buffer solution, is that the

TABLE I.

Acid.	Tartaric.	*o*-Phthalic.	Carbonic.	Malonic.	Succinic.	Glutaric.
K_1	$1{\cdot}3 \times 10^{-3}$	$1{\cdot}2 \times 10^{-3}$	$4{\cdot}5 \times 10^{-7}$	$1{\cdot}4 \times 10^{-3}$	$6{\cdot}4 \times 10^{-5}$	$4{\cdot}5 \times 10^{-5}$
K_2	$9{\cdot}7 \times 10^{-5}$	$8{\cdot}0 \times 10^{-6}$	6×10^{-11}	$2{\cdot}2 \times 10^{-6}$	$2{\cdot}5 \times 10^{-6}$	$3{\cdot}8 \times 10^{-6}$
HA′, %	64·7	85·9	97·8	92·7	71·6	63·2
A″, %	19·4	7·1	1·1	3·7	14·2	18·4
H_2A, %	15·8	7·0	1·1	3·6	14·2	18·4

K_1 and K_2 for malonic, succinic, and glutaric acids are from German and Vogel (*J. Amer. Chem. Soc.*, 1936, **58**, 1546); other values are from Britton (" Hydrogen Ions," 1932, p. 152).

ionic strength of the acid salt solution is much greater than its molar concentration. In the limiting case the ionic strength is given by $I = \frac{1}{2}([\text{Na}^{\cdot}] + [\text{HA}'] + 4[\text{A}'']) = 1{\cdot}25m$, and for the 0·1M-sodium hydrogen succinate buffer considered in the table the ionic strength is 0·114.

If the acid salt is that of a multivalent cation, say $M^{\cdot\cdot}$, it is still more incorrect to regard the solute as existing substantially in the form of the ions $M^{\cdot\cdot}$ and HA′, because extensive interaction will occur between the ions $M^{\cdot\cdot}$ and A″ to give undissociated molecules, or ion-pairs, MA, and this will reduce still further the proportion of the acid radical present as intermediate ion. The case of copper hydrogen malonate has been considered in a previous paper (J., 1935, 911); in a 0·000625M-solution 73·2% of the malonate radical is present as HM′, 2·9% as M″, 2·8% as H_2M, and 21·1% as CuM.

This effect is one that deserves emphasis in connection with the choice of buffer solutions. It can be easily illustrated by adding 5 ml. of 0·025M-zinc nitrate to 50 ml. of a 0·025M-sodium hydrogen malonate buffer coloured with bromophenol-blue. The colour of the indicator changes, primarily as a result of the reaction $\text{Zn}^{\cdot\cdot} + \text{HMal}' \longrightarrow \text{ZnMal} + \text{H}^{\cdot}$, the p_H of the solution being reduced from 4·26 to 3·72; *i.e.*, the addition of the zinc salt more than trebles the hydrogen ion concentration, and, in fact, calculation shows that *the zinc salt solution causes a greater alteration of the* p_H *of the buffer than does a strong acid of the same molar concentration.* The two cases cited are rather exceptional, as copper and zinc malonates are both rather weak electrolytes, but such data as are available for calcium and barium salts indicate that even these will significantly affect the p_H values of acid salt solutions, and the general rule may be stated that buffers containing polybasic acids should not be used in conjunction with solutions containing multivalent cations.

The Determination of Primary Dissociation Constants.—When the primary dissociation constant of a dibasic acid is determined by the conductivity method a value must be assigned to the mobility of the intermediate ion. This cannot be measured directly, and various method of evaluating it have been proposed. Chandler (*loc. cit.*, p. 694) used the equation $\Lambda_{HA'} = 0{\cdot}6\ \Lambda_{A''}$, which he justified by showing that the value so obtained for the intermediate ion never differed greatly from the measured mobility of a monobasic acid anion of closely similar structure. More recently, Vogel (J., 1934, 1101) has determined the mobilities of a number of amic acid ions, and has assumed that the mobility of the intermediate ion $CO_2H{\cdot}R{\cdot}COO'$ will be the same as that of the corresponding ion $NH_2{\cdot}CO{\cdot}R{\cdot}COO'$. This leads to the relationship $\Lambda_{HA'} = 0{\cdot}53\ \Lambda_{A''}$ (Jeffery and Vogel, J., 1935, 21; 1936, 1756). The difference between these two methods is not inconsiderable; for the hydrosuccinate ion, for instance, Jeffery and Vogel adopt the value 31·5, whereas Chandler's equation would give 36·5.

It is now possible to test these equations, for the dissociation constants of several dibasic acids have been determined by potentiometric methods, and the relationships given at the beginning of this paper enable the composition of the acid salt solutions to be calculated; the measured conductivity of these solutions, corrected for the hydrogen ion and bivalent ion known to be present, then gives by difference the conductivity of the intermediate ion. These calculations have been carried out for sodium hydrogen malonate, succinate, and glutarate (Jeffery and Vogel, German and Vogel, *locc. cit.*); the results are summarised below, the detailed figures being given in Tables II—IV.

Acid.	Λ_0 A″.	Λ_0 HA′.	Λ_0 HA′/Λ_0 A″.
Malonic	64·7	38·6	0·597
Succinic	60·9	35·8	0·588
Glutaric	56·9	29·7	0·522

The first column of figures shows the bivalent ions' mobilities given by Jeffery and Vogel, the second the newly calculated mobilities for the intermediate ions, and the third the ratio. The figures in this column fail to confirm either Chandler's or Vogel's relationship, and one must conclude that the conductivity method of determining primary dissociation constants will only be reliable where measurements on the acid, the acid salt, and the normal salt are available, and where the tedious calculations necessary to determine the mobility of the intermediate ion are carried out.

Calculation of the Mobility of the Intermediate Ion.—The composition of the acid salt solution is calculated from the equations $[\mathrm{A}''] = [\mathrm{H}^{\bullet}] + [\mathrm{H_2A}]$, $m = [\mathrm{H}^{\bullet}] + [\mathrm{HA}'] + 2[\mathrm{H_2A}]$, $f_1^2[\mathrm{H}^{\bullet}][\mathrm{HA}']/[\mathrm{H_2A}] = K_1$, and $f_2[\mathrm{H}^{\bullet}][\mathrm{A}'']/[\mathrm{HA}'] = K_2$. Here f_1 is the activity coefficient of a univalent ion and f_2 that of a bivalent ion, and these were calculated from the general equation recently proposed (J., 1938, 2093). Eliminating in turn $[\mathrm{A}'']$, $[\mathrm{H_2A}]$, and $[\mathrm{H}^{\bullet}]$ from these relationships, we have

$$\frac{2K_2[\mathrm{HA}'](2f_1^2[\mathrm{HA}'] + K_1)}{f_2K_1\{1 + K_1/(2f_1^2[\mathrm{HA}'] + K_1)\}} = (m - [\mathrm{HA}'])^2,$$

and this is solved for $[\mathrm{HA}']$ by successive approximations, starting from the value previously given, *viz.*, $[\mathrm{HA}'] = m/(1 + 2x)$. The hydrogen-ion concentration then follows from the relation $[\mathrm{H}^{\bullet}] = K_1(m - [\mathrm{HA}'])/(2f_1^2[\mathrm{HA}'] + K_1)$, and the other concentrations from the equations $2[\mathrm{A}''] = m + [\mathrm{H}^{\bullet}] - [\mathrm{HA}']$ and $[\mathrm{H_2A}] = [\mathrm{A}''] - [\mathrm{H}^{\bullet}]$. The ionic strength is given by $I = \frac{1}{2}(m + [\mathrm{H}^{\bullet}] + [\mathrm{HA}'] + 4[\mathrm{A}'']) = m + [\mathrm{H}^{\bullet}] + [\mathrm{A}'']$.

In treating the conductivity figures, the solution is regarded as a mixture of three electrolytes, $(\mathrm{Na}^{\bullet} + \mathrm{HA}')$, $(2\mathrm{Na}^{\bullet} + \mathrm{A}'')$, and $(2\mathrm{H}^{\bullet} + \mathrm{A}'')$, and these are assumed to contribute to the conductivity as if present singly in a uni-univalent or uni-bivalent solution of the given ionic strength. The conductivities of $\mathrm{Na_2A}$ and $\mathrm{H_2A}$ are calculated with the help of the Onsager equation, and subtraction from the measured conductivity gives the specific conductivity of the NaHA; Onsager's equation is again used to calculate the conductivity of this salt at infinite dilution, and the mobility of the intermediate ion is obtained by subtracting the mobility of the sodium ion.

The results of the calculations are in Tables II—IV. The only significant uncertainty

TABLE II.

Sodium hydrogen malonate.

$\Lambda_0\mathrm{Na}^{\bullet} = 50{\cdot}1$; $\Lambda_0\mathrm{H}^{\bullet} = 350{\cdot}0$; $\Lambda_0\mathrm{Mal}'' = 64{\cdot}7$.

$\Lambda\mathrm{Na_2Mal} = 114{\cdot}8—140{\cdot}3\sqrt{I}$; $\Lambda\mathrm{H_2Mal} = 414{\cdot}7—238{\cdot}1\sqrt{I}$; $\Lambda_0\mathrm{NaHMal} = \Lambda + 79{\cdot}4\sqrt{I}$.

$C \times 10^3$	0·1064	0·2811	0·3654	0·5801	0·6124	0·9473	0·9847	1·101	1·812	1·885
$I \times 10^3$	0·1353	0·3306	0·4222	0·6529	0·6875	1·044	1·083	1·207	1·954	2·031
$[\mathrm{H}^{\bullet}] \times 10^5$...	1·40	2·28	2·56	3·10	3·17	3·75	3·80	3·96	4·65	4·70
$[\mathrm{A}''] \times 10^5$	1·49	2·67	3·12	4·18	4·34	5·87	6·04	6·55	9·58	9·90
$[\mathrm{H_2A}] \times 10^5$	0·09	0·39	0·56	1·08	1·17	2·12	2·24	2·59	4·93	5·20
$[\mathrm{HA}'] \times 10^5$	9·06	25·06	32·86	52·75	55·73	86·74	90·20	101·0	166·7	173·5
Λ, expt. ...	(144·20)	(121·08)	118·68	(108·44)	109·57	104·75	102·92	102·50	98·26	96·98
ΛNaHA ...	(85·97)	(84·80)	87·55	(84·14)	86·20	86·63	85·12	85·85	86·10	85·00
$\Lambda_0\mathrm{HA}'$	(36·79)	(36·14)	39·05	(36·07)	38·18	39·10	37·63	38·51	39·51	38·48

Mean 38·0, av. devn. 1·0; mean excluding values in parentheses 38·6, av. devn. 0·5.

TABLE III.

Sodium hydrogen succinate.

$\Lambda_0\mathrm{Na}^{\bullet} = 50{\cdot}1$; $\Lambda_0\mathrm{H}^{\bullet} = 350{\cdot}0$; $\Lambda_0\mathrm{Suc}'' = 60{\cdot}9$.

$\Lambda\mathrm{Na_2Suc} = 111{\cdot}0—138{\cdot}3\sqrt{I}$; $\Lambda\mathrm{H_2Suc} = 410{\cdot}9—236{\cdot}2\sqrt{I}$; $\Lambda_0\mathrm{NaHSuc} = \Lambda + 79{\cdot}1\sqrt{I}$.

$C \times 10^3$	0·1306	0·1706	0·6001	0·9570	1·074	1·626	1·945
$I \times 10^3$	0·1652	0·2117	0·7071	1·118	1·253	1·887	2·254
$[\mathrm{H}^{\bullet}] \times 10^5$	1·02	1·07	1·29	1·36	1·37	1·42	1·45
$[\mathrm{A}''] \times 10^5$	2·44	3·04	9·41	14·74	16·46	24·70	29·50
$[\mathrm{H_2A}] \times 10^5$	1·42	1·97	8·12	13·32	15·09	23·28	28·05
$[\mathrm{HA}'] \times 10^5$	9·20	12·05	42·49	67·64	75·86	114·59	136·90
Λ, expt.	(122·84)	(120·84)	99·34	95·79	94·88	92·81	91·74
ΛNaHA	(83·38)	(89·56)	83·78	83·30	82·90	82·75	82·23
$\Lambda_0\mathrm{HA}'$	(34·29)	(40·61)	35·78	35·84	35·60	36·09	35·89

Mean excluding values in parentheses 35·8, av. devn. 0·1.

TABLE IV.

Sodium hydrogen glutarate.

$\Delta_0\mathrm{Na}^{\cdot} = 50{\cdot}1$; $\Lambda_0\mathrm{H}^{\cdot} = 350{\cdot}0$; $\Lambda_0\mathrm{Glu}'' = 56{\cdot}9$.

$\Lambda\mathrm{Na_2Glu} = 107{\cdot}0 - 136{\cdot}1\sqrt{I}$; $\Lambda\mathrm{H_2Glu} = 406{\cdot}9 - 234{\cdot}2\sqrt{I}$; $\Lambda_0\mathrm{NaHGlu} = \Lambda + 77{\cdot}9\sqrt{I}$.

$C \times 10^3$	0·3608	0·6031	1·013	1·040	1·846	2·018
$I \times 10^3$	0·4474	0·7363	1·225	1·257	2·219	2·423
$[\mathrm{H}^{\cdot}] \times 10^5$	1·27	1·34	1·41	1·41	1·48	1·49
$[\mathrm{A}''] \times 10^5$	7·39	11·98	19·80	20·31	35·80	39·10
$[\mathrm{H_2A}] \times 10^5$	6·12	10·64	18·39	18·90	34·32	37·61
$[\mathrm{HA}'] \times 10^5$	22·58	37·68	63·10	64·80	114·5	125·1
Λ, expt.	103·34	95·29	91·84	92·20	88·40	87·60
$\Lambda\mathrm{NaHA}$	80·30	76·27	76·66	77·43	75·80	75·14
$\Lambda_0\mathrm{HA}'$	31·85	28·28	29·29	30·09	29·37	28·88

Mean 29·7, av. devn. 0·9.

in the calculation lies in the assumption that the ions contribute additively to the conductivity of the solution. Strictly, this is incorrect (J., 1938, 449), and might be expected to lead to mobility values that are slightly too low, the error being greatest in the most dilute solutions where the concentration of hydrogen ion is relatively high, and falling off rapidly with rising concentration of salt. The calculated results show no such trend, except possibly with the malonate, and it is believed that any error introduced by the assumption is insignificant when compared with the average deviation of the individual results from the mean value.

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