CCCXXXVII.—*Acid and Salt Effects in Catalysed Reactions. Part XXII. The Influence of Inert Salts on the Secondary Dissociation of Dibasic Acids.*

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It has been shown (Dawson and Lowson, this vol., p. 1217) that the changes produced in the ionisation of monobasic acids by the addition of chemically inert salts can be expressed by the relation

$$\log K_x - \log K_0 = a\sqrt{x} - bx \quad . \quad . \quad . \quad . \quad (1)$$

in which $K_0 = [H^\cdot][A']/[HA]$ is the ionisation constant of an acid HA in salt-free solution, K_x its value in a solution which contains x g.-mols. of a uni-univalent salt per litre, and a and b are coefficients which for a given inert salt are approximately independent of the nature of the acid HA. In accordance with the above equation, the ionisation constant reaches a maximum value given by $\log K_x - \log K_0 = a^2/4b$ when $x = a^2/4b^2$, and falls to the value for the salt-free solution when $x = a^2/b^2$.

Equation (1) is based on measurements of the velocity of a suitably chosen acid-catalysed reaction, and from these K_x can be derived with a fair degree of accuracy. This equation is of the same type as that which follows when the Debye–Hückel theory is applied to the consideration of the influence of electrical environment on the equilibrium $HA \rightleftarrows H^\cdot + A'$. The latter may be put in the form

$$\log K_\mu - \log K_a = A\sqrt{\mu} - B\mu \quad . \quad . \quad . \quad (2)$$

where K_a is the thermodynamic ionisation constant, and K_μ the ionisation constant for a solution of ionic strength μ. If the ions are univalent, and if the acid HA is sufficiently weak, then $\mu = x$, $K_\mu = K_x$, and $K_a = K_0$, and equation (2) may be written

$$\log K_x - \log K_0 = A\sqrt{x} - Bx \quad . \quad . \quad . \quad (3)$$

in which $A = 1{\cdot}01$ at 25°. Equation (3) would also be obtained if it were justifiable to assume that the interionic forces in salt-free solutions of the acid are negligibly small (see Dawson and Lowson, *loc. cit.*). From the catalytic data for a series of acids (acetic, glycollic, chloroacetic, and dichloroacetic) in solutions of sodium chloride, it has been found that $a = 0{\cdot}52$. The difference between this and the Debye–Hückel coefficient $A = 1{\cdot}01$ is considerable and suggests that the changes in the ionisation of monobasic acids which are produced by the addition of chemically inert salts are due in part to factors which do not find expression in the Debye–Hückel theory.

Since reaction-velocity measurements would appear to afford a trustworthy method for the determination of the concentration of the hydrogen ion when due consideration is given to the catalytic effects associated with other catalytically active entities and to the variations of the catalytic coefficients which accompany changes in the reaction medium, an attempt has been made to extend this method to the study of the influence of chemically and catalytically inert salts on the secondary dissociation of a dibasic acid represented by $HA' \rightleftharpoons H^{\cdot} + A''$.

For this investigation we have selected the second-stage dissociation of oxalic acid. The chief reason for this choice is to be found in the circumstance that the catalytic properties of oxalic acid have already been examined in some detail (Dawson, Hoskins, and Smith, this vol., p. 1884), but apart from this, oxalic acid offers certain advantages in the fact that the two stages of ionisation correspond to constants of widely different magnitude. The experiments to be described relate, therefore, to the catalytic effects which are produced by potassium hydrogen oxalate in solutions containing various quantities of potassium chloride as the inert salt. The acetone–iodine reaction was employed, and the reaction velocities were measured at 25° with $0{\cdot}04M$-potassium hydrogen oxalate as the catalyst.

In such solutions the catalytically active entities are the hydrogen ion, the binoxalate ion (HOx′), the oxalate ion (Ox″), and undissociated oxalic acid (H_2Ox), the catalytic effects of the potassium, chlorine, and hydroxyl ions and of undissociated water being negligibly small. The reaction velocity may therefore be represented by the equation

$$\begin{aligned} v &= v_h + v_{H_2Ox} + v_{HOx'} + v_{Ox''} \\ &= k_h[H^{\cdot}] + k_{H_2Ox}[H_2Ox] + k_{HOx'}[HOx'] + k_{Ox''}[Ox''] \quad (4) \end{aligned}$$

in which the values of the several catalytic coefficients are afforded by the results of previous experiments (*loc. cit.*). An equation of this type has already been applied with success in the determination of the ionisation constants of monobasic acids and of the constants which correspond to the primary ionisation of dibasic acids. The problem is, however, more complicated when the experimental data refer to the second-stage ionisation.

For a solution which contains x_0 mols. of potassium binoxalate per litre, we may write on the basis of stoicheiometric and electroneutrality considerations

$$[H_2Ox] + [HOx'] + [Ox''] = x_0 \quad . \quad . \quad . \quad (5)$$

and $$[HOx'] + 2[Ox''] = [K^{\cdot}] + [H^{\cdot}] = x_0 + [H^{\cdot}] \quad . \quad (6)$$

and from these we obtain

$$[\mathrm{Ox''}] = [\mathrm{H^{\cdot}}] + [\mathrm{H_2Ox}] \quad . \quad . \quad . \quad . \quad (7)$$

and

$$[\mathrm{HOx'}] = x_0 - [\mathrm{H^{\cdot}}] - 2[\mathrm{H_2Ox}] \quad . \quad . \quad . \quad (8)$$

When these values for [Ox''] and [HOx'] are substituted in equation (4), this becomes

$$v = k_h[\mathrm{H^{\cdot}}] + k_{\mathrm{H_2Ox}}[\mathrm{H_2Ox}] + k_{\mathrm{HOx'}}\{x_0 - [\mathrm{H^{\cdot}}] - 2[\mathrm{H_2Ox}]\} + k_{\mathrm{Ox''}}\{[\mathrm{H^{\cdot}}] + [\mathrm{H_2Ox}]\}$$

or

$$v = (k_h + k_{\mathrm{Ox''}} - k_{\mathrm{HOx'}})[\mathrm{H^{\cdot}}] + k_{\mathrm{HOx'}}x_0 + (k_{\mathrm{H_2Ox}} + k_{\mathrm{Ox''}} - 2k_{\mathrm{HOx'}})[\mathrm{H_2Ox}] \quad (9)$$

$$= k'[\mathrm{H^{\cdot}}] + k_{\mathrm{HOx'}}x_0 + k''[\mathrm{H_2Ox}] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9a)$$

In accordance with the mass-law expression for the primary ionisation, we have, further,

$$[\mathrm{H_2Ox}] = [\mathrm{H^{\cdot}}][\mathrm{HOx'}]/K_1 \quad . \quad . \quad . \quad . \quad (10)$$

and by combination of equations (9*a*) and (10) we obtain

$$[\mathrm{H^{\cdot}}] = (v - k_{\mathrm{HOx'}}x_0)/(k' + k''[\mathrm{HOx'}]/K_1) \quad . \quad . \quad (11)$$

from which the hydrogen-ion concentration of the binoxalate solution may be derived.

In reference to the application of equation (11), it should be noted that k' is essentially determined by the magnitude of k_h, and k'' for the most part by the magnitude of $k_{\mathrm{H_2Ox}}$, for these coefficients are very much larger than the coefficients $k_{\mathrm{HOx'}}$ and $k_{\mathrm{Ox''}}$. The coefficient k_h increases very considerably with the salt content of the solution, and the required values for the various solutions of potassium chloride are afforded by reaction-velocity data with 0·01*N*-hydrochloric acid as catalyst. Such evidence as is available indicates that, on the other hand, $k_{\mathrm{H_2Ox}}$ varies but little with the salt concentration. Experiments have been made with various concentrations of free oxalic acid in 1*N*-potassium chloride, and it appears that the results can be interpreted in terms of $k_{\mathrm{H_2Ox}} = 210 \times 10^{-6}$ (the value of the coefficient in salt-free solution) provided that due allowance be made for the influence of the inert salt on k_h and on K_1. The variation of K_1 with the concentration of the potassium chloride has already been determined (this vol., p. 1884). The results show that the connexion between K_1 and x can be represented by

$$\log (K_1)_x - \log (K_1)_0 = 0{\cdot}42\sqrt{x} - 0{\cdot}275x,$$

where $(K_1)_0$ is the ionisation constant in salt-free solution.

Finally, it is to be observed that an approximate value of [H˙] is first obtained from equation (11) by assuming that $[\mathrm{HOx'}] = x_0$. From this value of [H˙] an approximate value of [H₂Ox] is similarly derived from equation (10), and these are then employed to obtain [HOx′] from equation (8). The substitution of this value of [HOx′], which is very large compared with [H˙] and [H_2Ox], in equations (11) and (10) then yields new values of [H˙] and [H_2Ox] which are not appreciably affected by a further stage of approximation, and these may therefore be used to obtain the required values of [Ox″] and [HOx′] by means of equations (7) and (8). Having thus derived the values of [H˙], [Ox″], and [HOx′], the second-stage ionisation constant is given by

$$K_2 = [\mathrm{H}^{\cdot}][\mathrm{Ox}'']/[\mathrm{HOx}'] \quad . \quad . \quad . \quad . \quad (12)$$

In order to illustrate numerically the details of the calculation, the data for 0·04·KHC_2O_4 + 1·0·KCl may be recorded. For this solution the total salt concentration $x = 1{\cdot}04$, $k' = 575 \times 10^{-6}$, $k'' = 185 \times 10^{-6}$, and $K_1 = 0{\cdot}079$. The observed initial reaction velocity is $v = 1{\cdot}96 \times 10^{-6}$. When the value [HOx′] = 0·04 is inserted, equation (11) gives a preliminary value of [H˙] = 0·00214, and from equation (10), [H_2Ox] = 0·001085, whence [HOx′] = 0·0357. Substituting the last value in equation (11), we obtain [H˙] = 0·002173, and from equation (10), [H_2Ox] = 0·000981, whence [Ox″] = 0·003155 and [HOx′] = 0·03586, which lead to $K_2 = 19{\cdot}1 \times 10^{-5}$.

Table I records the results for the entire series of potassium chloride solutions. The total salt concentrations (x) are shown in the first column, the observed reaction velocities (v) in the second, the values of $k' = (k_h + k_{\mathrm{Ox}''} - k_{\mathrm{HOx}'})$ in the third, and of K_1 in the fourth. The calculated concentrations [H˙], [H_2Ox], [Ox″] and [HOx′] are given in the fifth, sixth, seventh, and eighth columns, and the value of the second-stage ionisation constant K_2 is in the last column. The constants used in the calculations are $k_{\mathrm{H_2Ox}} = 210 \times 10^{-6}$, $k_{\mathrm{HOx}'} = 13{\cdot}2 \times 10^{-6}$, and $k_{\mathrm{Ox}''} = 1{\cdot}0 \times 10^{-6}$. On account of the relatively small part played by the oxalate ion in the reaction-velocity measurements, a precise knowledge of the value of $k_{\mathrm{Ox}''}$ is not required.

From the preceding results it is apparent that K_2 increases to a maximum and then decreases. The general form of the curve obtained by plotting K_2 against x is very similar to that which has already been obtained in the investigation of the influence of inert salts on the primary ionisation of acids. There is, however, an important difference between the two series of experiments in that the salt concentration can be reduced to zero in the case of the primary ionisation, whereas the concentration of the acid salt itself (x_0) sets a lower limit to the salt concentration at which it is possible to investigate the second-stage ionisation. Since the ionisation

TABLE I.

Influence of Potassium Chloride on the Second-stage Ionisation of Oxalic Acid.

x.	$v.10^6$.	$k'.10^6$.	$K_1.10^2$.	$[H^{\cdot}].10^3$.	$[H_2Ox].10^3$.	$[Ox''].10^3$.	$[HOx'].10^3$.	$K_2.10^5$.
0·04	1·37	458	6·7	1·50	0·825	2·32	36·85	9·5
0·08	1·39	462	7·1	1·55	0·80	2·34	36·85	9·9
0·10	1·43	465	7·3	1·62	0·81	2·43	36·76	10·7
0·14	1·485	469	7·5	1·71	0·835	2·55	36·62	11·9
0·20	1·57	476	7·75	1·85	0·865	2·72	36·41	13·8
0·24	1·60	481	7·9	1·895	0·87	2·76	36·37	14·4
0·30	1·67	488	8·05	2·00	0·895	2·90	36·21	16·0
0·38	1·72	497	8·1	2·06	0·915	2·97	36·11	16·9
0·54	1·79	516	8·3	2·12	0·915	3·02	36·05	17·8
0·79	1·89	546	8·2	2·17	0·95	3·12	35·93	18·9
1·04	1·96	574	7·9	2·17	0·98	3·15	35·86	19·1
1·29	2·00	604	7·5	2·13	1·01	3·14	35·85	18·6
1·54	2·05	633	7·1	2·10	1·05	3·15	35·80	18·5
2·04	2·07	692	6·2	1·93	1·11	3·04	35·85	16·4
2·54	2·08	750	5·55	1·785	1·15	2·94	35·91	14·6
3·04	2·04	823	4·65	1·565	1·20	2·77	36·02	12·0
3·54	1·95	882	3·75	1·34	1·28	2·63	36·09	9·8

constant increases very rapidly at low salt concentrations, it is evident that the value of K_2 which would be obtained in the absence of measurable salt effects (*i.e.*, when $x = 0$) must be considerably less than its value ($9·5 \times 10^{-5}$) when $x = 0·04$.

In order to test the assumption that the connexion between K_x and K_0 for the second-stage ionisation is represented by the same type of equation as that which applies to the primary [compare equation (1)], it is therefore necessary to find the connexion between the ionisation constants K_x and K_{x_0} for the salt concentrations x and x_0. We may write

$$K_x/K_0 = K_x/K_{x_0} \,.\, K_{x_0}/K_0$$

and by applying equation (1) successively to $\log K_x$ and $\log K_{x_0}$ and taking the difference, we have

$$\log K_x - \log K_{x_0} = a(\sqrt{x} - \sqrt{x_0}) - b(x - x_0) \quad . \quad (13)$$

According to equation (13), $K_x = K_{x_0}$ when $a(\sqrt{x} - \sqrt{x_0}) = b(x - x_0)$, *i.e.*, when $x = x_0$ and also when $x = x_1 = \left(\frac{a}{b} - \sqrt{x_0}\right)^2$.

The salt concentrations x_0 and x_1 thus correspond to the same value of the ionisation constant, and the relation between the concentrations of these " conjugate " solutions is given by

$$\sqrt{x_0} + \sqrt{x_1} = a/b \quad . \quad . \quad . \quad . \quad . \quad (14)$$

Furthermore, it follows from equation (13) that K_x passes through a maximum when $d \log K_x/dx = 0$ or $a/2\sqrt{x} - b = 0$. In other words the salt concentration corresponding to the maximum value of the ionisation constant K_m is given by

$$x = x_m = a^2/4b^2 \quad . \quad . \quad . \quad . \quad . \quad (15)$$

Substitution of this value of x in equation (13) gives

$$\log K_m - \log K_{x_0} = a^2/4b - a\sqrt{x_0} + bx_0 \quad . \quad . \quad (16)$$

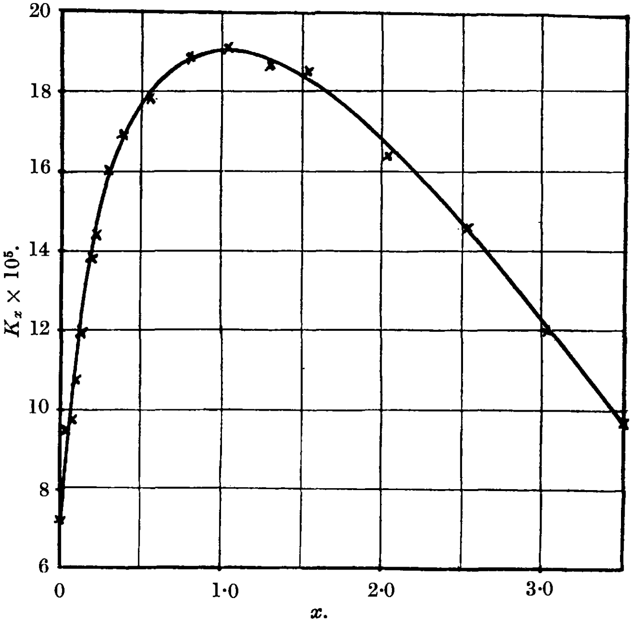
The constants a and b are then derived by combining equations (14) and (16), and we obtain

$$a = 4(\log K_m - \log K_{x_0})(\sqrt{x_1} + \sqrt{x_0})/(\sqrt{x_1} - \sqrt{x_0})^2 \quad (17)$$

$$b = 4(\log K_m - \log K_{x_0})/(\sqrt{x_1} - \sqrt{x_0})^2 \quad . \quad . \quad . \quad . \quad (18)$$

in which K_m, K_{x_0}, x_1, and x_0 are experimental quantities.

FIG. 1.



Curve showing the influence of an inert electrolyte (potassium chloride) on the second-stage ionisation constant of oxalic acid.

In regard to the above relations, it should be noted that no distinction is made between the chloride and the binoxalate so far as the constants a and b are concerned. Since the actual concentration of the binoxalate is small ($x_0 = 0{\cdot}04$), any difference in the respective values of b is not of much importance. The very small quantity of potassium iodide (0·004 mol. per litre) which was introduced into the solutions with the iodine can also be left out of account for the range of salt concentrations used in the experiments.

Fig. 1 shows the curve which is obtained when the experimental values of K_x (K_2 in Table I) are plotted against the total salt concentration (x). In so far as this curve conforms to the requirements of equation (13), it may be pointed out that any horizontal line should intersect the curve at points which are " conjugate " in the sense of equation (14). The rising branch of the curve corresponds to x_0 and the falling branch to x_1.

In order to test the applicability of the above relations, the " conjugate " salt concentrations for a series of K_x values may be read off from the smooth curve and examined with reference to the constancy of $(\sqrt{x_0} + \sqrt{x_1})$. Table II shows the results of this test. The first column gives a series of integral values of $K_x \,.\, 10^5$ covering the entire range of the observations; the corresponding values of x_0 and x_1 are shown in the second and third columns, and the fourth gives the sum of the square roots of the " conjugate " concentrations.

TABLE II.

$K_x \,.\, 10^5$.	x_0.	x_1.	$\sqrt{x_0} + \sqrt{x_1}$.	$K_x \,.\, 10^5$.	x_0.	x_1.	$\sqrt{x_0} + \sqrt{x_1}$.
10·0	0·07	3·47	2·12	15·0	0·26	2·43	2·07
11·0	0·10	3·27	2·12	16·0	0·32	2·20	2·05
12·0	0·14	3·06	2·12	17·0	0·42	1·96	2·05
13·0	0·17	2·86	2·10	18·0	0·55	1·67	2·04
14·0	0·20	2·65	2·08				

The above table shows that $\sqrt{x_0} + \sqrt{x_1}$ is very nearly constant, and it would therefore seem that the experimental results approximate closely to the requirements of equation (13). With regard to the individual values of $(\sqrt{x_0} + \sqrt{x_1})$ it may be noted that the estimation of x_0 from the smooth curve becomes increasingly difficult as x_0 diminishes, and that the probable error of $\sqrt{x_0}$ increases rapidly at the small salt concentrations. For this and other reasons it is not possible to say whether the slight trend in the values of $\sqrt{x_0} + \sqrt{x_1}$ has any real significance. In accordance with equation (14) the mean value 2·08 may be taken as the measure of a/b. Combining this ratio with equation (18), the coefficients a and b may be evaluated. It may be observed, however, that $(\log K_m - \log K_x)$ and $(\sqrt{x_1} - \sqrt{x_0})^2$ diminish as K_x increases and therefore the probable error attaching to the value of b given by equation (18) increases with K_x. On the other hand, the accuracy of $\sqrt{x_1} - \sqrt{x_0}$ is adversely affected by the difficulty of estimating x_0 for the smaller values of K_x. For these reasons it is probable that equation (18) affords the best results when it is applied to the middle portion of the experimental K_x–x curve. For $10^5 \,.\, K_x = 13·0$, 14·0, and 15·0, the values obtained for b are respectively 0·408, 0·387, and 0·382; the mean of the values ($b = 0·39$) gives $a = 2·08 \times 0·39 = 0·81$.

Substituting these values of a and b in equation (15), we obtain $x_m = a^2/4b^2 = 1·08$ for the concentration of the salt solution at which the ionisation constant has a maximum value. If this is combined with the observed maximum $K_m = 19{\cdot}1 \times 10^{-5}$, it is possible to derive the limiting value of the ionisation constant (K_0) in salt-free solution from equation (1). This gives $K_0 = 7{\cdot}2 \times 10^{-5}$, and the equation from which the ionisation constant for any given concentration of potassium chloride can be calculated takes the form

$$\log K_x = \bar{5}{\cdot}857 + 0{\cdot}81\sqrt{x} - 0{\cdot}39x \quad . \quad . \quad . \quad (19)$$

Table III affords a comparison of the values of K_2 derived from the experimental observations (see Table I) with those calculated from equation (19).

TABLE III.

Comparison of Observed and Calculated Ionisation Constants.

x.	$K_x . 10^5$, obs.	$K_x . 10^5$, calc.	x.	$K_x . 10^5$, obs.	$K_x . 10^5$, calc.
0·04	9·5	10·1	0·79	18·9	18·6
0·08	9·9	11·3	1·04	19·1	19·0
0·10	10·7	11·8	1·29	18·6	18·8
0·14	11·9	12·7	1·54	18·5	18·3
0·20	13·8	13·8	2·04	16·4	16·6
0·24	14·4	14·4	2·54	14·6	14·4
0·30	16·0	15·3	3·04	12·0	12·1
0·38	16·9	16·1	3·54	9·8	10·0
0·54	17·8	17·5			

The preceding results lead to the conclusion that the influence of inert salts on the second-stage ionisation of oxalic acid can be represented by an equation of the same type as that which has already been found to express the influence of such salts on the primary ionisation of acids. It may readily be shown that the form of this equation is the same as that which is obtained when the Debye–Hückel theory is applied to the second-stage ionisation. According to this, the relation between K_0 and K_x is given by

$$K_0 = a_{H^{\cdot}} . a_{A''} / a_{HA'} = [H^{\cdot}][A''] . f_+'f_-'' / [HA'] . f_-' = K_x . f_+'f_-'' / f_-'$$

and if, in accordance with the usual assumption, we may equate f_+' to f_-', then $K_x = K_0 / f_-''$.

According to the Debye–Hückel theory, $-\log f'' = A'z^2\sqrt{\mu} - B\mu$, in which $A' = 0{\cdot}505$, $z = 2$, and for uni-univalent electrolytes $\mu = x$, and therefore $-\log f'' = 2{\cdot}02\sqrt{x} - Bx$,

whence $$\log K_x - \log K_0 = 2{\cdot}02\sqrt{x} - Bx \quad . \quad . \quad . \quad (20)$$

Apart from the coefficient B, which is composite in character and varies with the nature of the dissolved electrolyte, this equation is supposed to define in general terms the influence of the electrical field on the secondary ionisation which has been investigated in our experiments. There is, however, a very large difference between the coefficient $A = 2{\cdot}02$ in equation (20) and the coefficient $a = 0{\cdot}81$ which is indicated by our experimental data. It may be noted that equation (20) represents a group of curves which are distinguished solely by differences in the value of the coefficient B. To illustrate the difference between these curves and the experimental curve, particular values may be assigned to B. If we take the Debye–Hückel curve for which K_x has the same maximum value as that found by experiment, then B is given by $\log (19{\cdot}1 \times 10^{-5}) = \bar{5}{\cdot}857 + (2{\cdot}02)^2/4B$, or $B = 2{\cdot}40$ and $x_m = (2{\cdot}02)^2/4B^2 = 0{\cdot}177$, as compared with the actual value of $x_m = 1{\cdot}08$. On the other hand, if we take the Debye–Hückel curve for which x_m has the same value as that indicated by the experimental curve ($x_m = 1{\cdot}08$), then from $x_m = (2{\cdot}02)^2/4B^2$ we obtain $B = 0{\cdot}97$, and from $\log K_m = \bar{5}{\cdot}857 + (2{\cdot}02)^2/4B$ we derive $K_m = 81 \times 10^{-5}$ as compared with the experimental value $K_m = 19{\cdot}1 \times 10^{-5}$. In connexion with these very large differences, it should be recalled that the experimental data are concerned with a state of equilibrium which involves the hydrogen ion and that there is other evidence to show that the interionic forces associated with this ion are relatively very small. The present results add further weight to the opinion that these interionic forces are much smaller than would be anticipated according to the Debye–Hückel formula $\log 1/f = 0{\cdot}5z^2\sqrt{\mu}$.

Since both the primary and the secondary ionisation of oxalic acid have been examined in solutions of potassium chloride, it is possible to make a direct comparison between the coefficients of the $\sqrt{x}$ term in the general formula $\log K_x/K_0 = a\sqrt{x} - bx$. For the first-stage ionisation the value of a is $0{\cdot}42$ as compared with $0{\cdot}81$ for the second. Within the limits of error these are in the ratio 1 : 2, which is identical with that suggested by the Debye–Hückel theory, for the electrical field effect in the primary ionisation is determined by $(f')^2$ and in the secondary ionisation by f'', where f' and f'' represent the activity coefficients for uni- and bi-valent ions, respectively. In view of the fact that our experimental results lead to a relation between K_x and x which is of the same form as that derived from the Debye–Hückel theory, and that the dependence of the coefficient a on the valency is also in agreement with the latter, it is the more remarkable to find that the coefficients a and A of the $\sqrt{x}$ ($\sqrt{\mu}$) term are so widely divergent. The further investigation of this difference is obviously called for.

The Values of K_1 *and* K_2.—For the ionisation constants of oxalic acid in the absence of interionic forces the values obtained in this and the previous paper (*loc. cit.*) are $K_1 = 5{\cdot}7 \times 10^{-2}$ and $K_2 = 7{\cdot}2 \times 10^{-5}$. From conductivity data, Chandler (*J. Amer. Chem. Soc.*, 1908, **30**, 694) obtained $K_1 = 3{\cdot}8 \times 10^{-2}$ and $K_2 = 4{\cdot}9 \times 10^{-5}$. Enklaar (*Chem. Weekblad*, 1911, **8**, 375) derived $K_1 = 3{\cdot}4$—$3{\cdot}6 \times 10^{-2}$ at 18°, and later (*ibid.*, p. 824) gave $K_2 = 4{\cdot}7 \times 10^{-5}$ from potential measurements and $1{\cdot}3 \times 10^{-5}$ from conductivity data. The most complete examination of oxalic acid and oxalate solutions is, however, due to Drucker (*Z. physikal. Chem.*, 1920, **96**, 381), who from the combination of potential, freezing-point, and conductivity data obtained $K_1 = 5{\cdot}7 \times 10^{-2}$ and $K_2 = 6{\cdot}9 \times 10^{-5}$. These are in close agreement with our numbers. In the case of K_2, this is probably to some extent accidental, for Drucker's calculations are based on the classical form of the ionic theory. The difficulties attending the precise interpretation of conductivity data are well known, and on the evidence submitted in this and previous papers it seems permissible to conclude that catalytic data, properly interpreted, provide a more certain basis for the investigation of the ionisation of acids.

Summary.

The salt effects associated with the secondary ionisation of oxalic acid have been systematically investigated by catalytic measurements in solutions of potassium chloride.

In the derivation of the ionisation constant, due consideration has been given to the catalytic effects produced by the hydrogen ion, the undissociated oxalic acid, the binoxalate ion, and the oxalate ion. The variation of the ionisation constant K_x with the total salt concentration x can be expressed by the equation $\log K_x - \log K_0 = a\sqrt{x} - bx$, in which $a = 0{\cdot}81$, $b = 0{\cdot}39$, and K_0, the limiting value of the ionisation constant, $= 7{\cdot}2 \times 10^{-5}$.

When the primary and secondary stages of ionisation are compared, it is found that the ratio of the coefficients of the $\sqrt{x}$ term is very nearly 1 : 2.

In regard to the value of this ratio and the form of the equation connecting K_x and x, the experimental results show agreement with the Debye–Hückel theory, but in other respects the results diverge very considerably from the requirements of this theory, for the coefficient a of the $\sqrt{x}$ term is only 40% of the theoretical.

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