CCCLXXV.—*Acid and Salt Effects in Catalysed Reactions. Part XVII. The Variation of the Catalytic Activity of an Acid with its Concentration, and the Determination of Ionisation Constants.*

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The facts established by various workers in the investigation of the dependence of the catalysing power of an acid on its concentration (Goldschmidt, *Z. physikal. Chem.*, 1910, **70**, 627; Goldschmidt and Thuesen, *Z. Elektrochem.*, 1911, **17**, 684; Bredig, Millar, and Braune, *ibid.*, 1912, **18**, 535; Snethlage, *ibid.*, p. 539; Dawson and Powis, J., 1913, **103**, 2135; Taylor, *Medd. K. Vetenskapsakad. Nobel-Inst.*, **2**, 34, 35, 37) led to the view that the catalytic effects are jointly due to the action of the hydrogen ion and of the undissociated acid. The sum total of the evidence for this joint action was such as to afford a very substantial basis for what became generally known as the dual theory of acid catalysis. In particular, it may be recalled that observations on the acetone–iodine reaction with acetic, chloroacetic, αβ-dichlorobutyric, dichloroacetic, and hydrochloric acids gave in all cases the same value for the catalytic activity of the hydrogen ion, whilst the coefficients for the undissociated acid molecules varied very largely according to the nature of the acid.

The dual theory marks a well-defined stage in the development of the modern view, according to which catalytic effects are to be attributed to positively charged " hydrogen " and similar complex kations, to neutral molecules, and also to negatively charged anions —in short, to all those molecular entities which may act either as proton donators or proton acceptors (compare Lowry, J., 1927, 2554; Brönsted, *J. Physical Chem.*, 1926, **30**, 777). For an aqueous solution which contains an acid HA and the corresponding anion A^-, the equation for the catalytic effect may be written

$$v = k_h[H^+] + k_a[A^-] + k_m[HA] + k_{OH}[OH^-] + k_w[H_2O] \quad . \quad (1)$$

in which the relative values of the respective catalytic coefficients vary widely with the nature of the catalysed reaction. It is possible, for instance, that k_{OH} may be of the same order of magnitude or millions of times greater than k_h, and that the action of the undissociated water molecules as measured by k_w may be negligibly small or may represent a very important part of the observed catalytic effect. In such circumstances, it is apparent that all acid-catalysed reactions do not lend themselves to the quantitative investigation of the individual catalytic effects which are produced by the undissociated acid HA and the corresponding anion A^-. Generally speaking, favourable conditions will not be attained if the ratios k_m/k_h and k_a/k_h are very much less than about 0·01.

For a given reaction, the magnitude of these ratios depends on the ionisation constant of the catalysing acid. As the ionisation constant increases, the value of k_m increases, whilst that of k_a diminishes. For very weak acids it may therefore be possible to determine k_a, but not k_m, whilst the converse may be true for relatively strong acids. The fact that the acetone–iodine reaction affords k_m/k_h and k_a/k_h ratios of suitable magnitude in the case of moderately weak acids is largely responsible for the discovery of those simple relations which have found expression in the generalised form of the catalytic catenary.

The results to be described are concerned with the catalytic activity of a series of acids of varying strength, and it will be shown that the change in the catalysing power with the concentration affords a measure of k_m and also a value for the ionisation constant of the acid. The measurements relate to the acetone–iodine reaction at 25°, and it may be noted at the outset that the maximum value of k_a/k_h is about 0·01. On account of the autocatalytic action of the hydriodic acid which is produced in the reaction, it is not possible to determine with the requisite accuracy the initial reaction velocity when the ionisation constant of the catalysing acid is much less than $K = 10^{-5}$.

For a solution which contains c mols. of HA per litre, the equation for the reaction velocity may be written

$$\begin{aligned} v &= k_h[\mathrm{H^+}] + k_a[\mathrm{A^-}] + k_m[\mathrm{HA}] \\ &= (k_h + k_a - k_m)[\mathrm{H^+}] + k_m c \quad . \quad . \quad . \quad . \quad (2) \end{aligned}$$

If the acid is sufficiently weak, the hydrogen-ion concentration for the range of solutions $c = 0{\cdot}01$ to $c = 0{\cdot}5$ is given with close approximation by $[\mathrm{H^+}] = \sqrt{Kc}$, and equation (2) may be written

$$v/\sqrt{c} = (k_h + k_a - k_m)\sqrt{K} + k_m\sqrt{c} \quad . \quad . \quad . \quad (3)$$

according to which $v/\sqrt{c}$ is a linear function of $\sqrt{c}$. The slope of this line gives k_m, and its intercept on the zero ordinate yields $(k_h + k_a - k_m)\sqrt{K}$. As already indicated, k_a can be neglected without serious error, but if required its value can be determined by methods which have been previously described. Since k_h is known, it follows that the intercept affords a measure of the ionisation constant K. The accuracy of the value is obviously limited by the degree of approximation which is involved in the substitution of $\sqrt{Kc}$ for [H⁺], and the error thereby introduced increases with the magnitude of K. The value of K derived from equation (3) may, however, be used as a preliminary value in proceeding to the next step in the process of evaluation.

In this further step, the value of $[\mathrm{H^+}]$ in equation (2) is assumed to be given by the mass-law expression $[\mathrm{H^+}] = c\alpha = \sqrt{Kc(1 - \alpha)}$, where α is the degree of ionisation of the acid and K the ionisation constant derived from equation (3). From equation (2), which may be put in the form

$$v = (k_h + k_a)[\mathrm{H^+}] + k_m[\mathrm{HA}],$$

we then obtain by substitution for $[\mathrm{H^+}]$

$$v/\sqrt{c(1 - \alpha)} = (k_h + k_a)\sqrt{K} + k_m\sqrt{c(1 - \alpha)} \quad . \quad . \quad (4)$$

which yields a straight line when $v/\sqrt{c(1 - \alpha)}$ is plotted against $\sqrt{c(1 - \alpha)}$. The intercept of this line on the zero ordinate obviously leads to a value of K which is greater than that derived from the graph corresponding with equation (3), and at the same time the increased value of the intercept implies a smaller value of k_m.

If necessary, the second value of K may be used to derive a new series of values of $\sqrt{c(1 - \alpha)}$, and the procedure followed in the second stage may be repeated. When the strength of the acid is such that the relation $[H^+] = \sqrt{Kc}$ is not even approximately true, the first step in the process may be omitted and the catalytic data applied directly to equation (4) with values of $\sqrt{c(1-\alpha)}$ derived from an approximate ionisation constant afforded by conductivity or other measurements. It should be noted that equation (4) may be written in the alternative form

$$v/c\alpha = k_h + k_a + k_m c\alpha/K \quad . \quad . \quad . \quad . \quad (5)$$

according to which $v/c\alpha$ is a linear function of $c\alpha$. This form affords a convenient method for the determination of one of the quantities K or k_m if the other is known, but is not so suitable for the evaluation of both K and k_m.

The results which have been obtained in the application of the above method are shown in the following tables, of which the order is determined by the magnitude of K. The first line of figures gives the concentration of the acid in mols. per litre, the second gives the observed initial reaction velocity with an acetone concentration of 20 c.c. per litre, the third gives the values of $v/\sqrt{c}$ or $v/\sqrt{c(1-\alpha)}$, and the fourth the corresponding values calculated from equation (3) or (4).

Propionic Acid.

c	0·01	0·02	0·05	0·1	0·2	0·4	0·5
$v \,.\, 10^6$	0·181	0·269	0·449	0·664	0·997	1·545	1·76
$v/\sqrt{c} \,.\, 10^6$	1·81	1·90	2·01	2·10	2·23	2·44	2·49
$v/\sqrt{c} \,.\, 10^6$ (calc.) ...	1·85	1·90	1·99	2·09	2·23	2·44	2·52

The slope of the line when $v/\sqrt{c}$ is plotted against $\sqrt{c}$ gives $k_m = 1{\cdot}10 \times 10^{-6}$, and the intercept on the zero ordinate $(k_h + k_a - k_m)\sqrt{K} = 1{\cdot}74 \times 10^{-6}$. Since $k_h = 465 \times 10^{-6}$ and $k_a = 4 \times 10^{-6}$, this gives $K = (1{\cdot}74/468)^2 = 1{\cdot}38 \times 10^{-5}$. The calculated values of $v/\sqrt{c}$ are those derived from $10^6 \times v/\sqrt{c} = 1{\cdot}74 + 1{\cdot}10\sqrt{c}$.

Acetic Acid.

c	0·01	0·02	0·05	0·1	0·2	0·4	0·8
$v \,.\, 10^6$	0·216	0·317	0·512	0·770	1·17	1·79	2·85
$v/\sqrt{c} \,.\, 10^6$	2·16	2·24	2·29	2·43	2·62	2·83	3·18
$v/\sqrt{c} \,.\, 10^6$ (calc.) ...	2·14	2·20	2·31	2·44	2·61	2·86	3·22

The slope of the $v/\sqrt{c}$ and $\sqrt{c}$ line gives $k_m = 1{\cdot}35 \times 10^{-6}$ and the intercept $= 2{\cdot}01 \times 10^{-6}$. Since $k_a = 4 \times 10^{-6}$, $K = (2{\cdot}01/467)^2 = 1{\cdot}85 \times 10^{-5}$. The calculated values of $v/\sqrt{c}$ are those given by $v/\sqrt{c} \,.\, 10^6 = 2{\cdot}01 + 1{\cdot}35\sqrt{c}$.

Succinic Acid.

c	0·01	0·02	0·05	0·1	0·2	0·4	0·5
$v\,.\,10^6$	0·388	0·588	1·030	1·60	2·47	4·02	4·74
$v/\sqrt{c(1-\alpha)}\,.\,10^6$	4·04	4·27	4·69	5·12	5·57	6·40	6·74
$v/\sqrt{c(1-\alpha)}\,.\,10^6$ (calc.)	4·11	4·29	4·65	5·04	5·60	6·40	6·72

The first-stage plot of $v/\sqrt{c}$ against $\sqrt{c}$ gives $k_m = 4{\cdot}35 \times 10^{-6}$ and $(k_h + k_a - k_m)\sqrt{K} = 3{\cdot}65 \times 10^{-6}$. Since k_a is approximately 1×10^{-6}, this gives a preliminary value of $K = (3{\cdot}65/462)^2 = 6{\cdot}24 \times 10^{-5}$. From this the values of $v/\sqrt{c(1-\alpha)}$ in the third line are derived, and the plot of these against $\sqrt{c(1-\alpha)}$ gives $k_m = 4{\cdot}30 \times 10^{-6}$ and the intercept $(k_h + k_a)\sqrt{K} = 3{\cdot}70 \times 10^{-6}$, from which $K = (3{\cdot}70/466)^2 = 6{\cdot}30 \times 10^{-5}$. The values in the last line are those calculated from $v/\sqrt{c(1-\alpha)}\,.\,10^6 = 3{\cdot}70 + 4{\cdot}30\sqrt{c(1-\alpha)}$.

β-*Chloropropionic Acid.*

c	0·01	0·02	0·05	0·1	0·2	0·5
$v\,.\,10^6$	0·473	0·710	1·20	1·81	2·79	5·02
$v/\sqrt{c(1-\alpha)}\,.\,10^6$	4·96	5·20	5·49	5·81	6·31	7·15
$v/\sqrt{c(1-\alpha)}\,.\,10^6$ (calc.)	5·03	5·19	5·49	5·83	6·31	7·28

The preliminary plot gives $k_m = 3{\cdot}85 \times 10^{-6}$ and $(k_h + k_a - k_m)\sqrt{K} = 4{\cdot}48 \times 10^{-6}$, whence $K = 0{\cdot}94 \times 10^{-4}$. From the latter the values of $v/\sqrt{c(1-\alpha)}$ in the third line have been derived, and the plot of these against $\sqrt{c(1-\alpha)}$ gives $k_m = 3{\cdot}7 \times 10^{-6}$ and $(k_h + k_a)\sqrt{K} = 4{\cdot}68$, or $K = (4{\cdot}68/465)^2 = 1{\cdot}01 \times 10^{-4}$. The numbers in the fourth line are those calculated by use of equation (4).

The value of $K = 0{\cdot}86 \times 10^{-4}$ obtained by Lichty (*Annalen*, 1910, **319**, 380) from conductivity data is less than those for β-bromopropionic acid ($K = 0{\cdot}98 \times 10^{-4}$; Walden, *Z. physikal. Chem.*, 1892, **10**, 650) and for β-iodopropionic acid ($K = 0{\cdot}90 \times 10^{-4}$; Ostwald, *ibid.*, 1889, **3**, 193), whereas the strength of corresponding halogen-substituted acids normally increases from the iodo- to the chloro-acid. The higher value derived from the catalytic data has been confirmed by new conductivity measurements, which for $v = 16$ to $v = 256$ gave $K = 1{\cdot}04 \times 10^{-4}$.

Glycollic Acid.

c	0·01	0·02	0·05	0·1	0·2	0·4	0·5
$v\,.\,10^6$	0·585	0·882	1·495	2·31	3·61	5·86	6·79
$v/\sqrt{c(1-\alpha)}\,.\,10^6$	6·20	6·50	6·86	7·44	8·18	9·35	9·68
$v/\sqrt{c(1-\alpha)}\,.\,10^6$ (calc.)	6·24	6·47	6·94	7·47	8·21	9·27	9·70

The first-stage plot gives $k_m = 6{\cdot}0 \times 10^{-6}$ and $(k_h + k_a - k_m)\sqrt{K} = 5{\cdot}40 \times 10^{-6}$, whence $K = 1{\cdot}38 \times 10^{-4}$. From this, the values of $v/\sqrt{c(1-\alpha)}$ in the third line are derived, and the graph of these against $\sqrt{c(1-\alpha)}$ gives $k_m = 5{\cdot}7 \times 10^{-6}$ and $(k_h + k_a)\sqrt{K} = 5{\cdot}70 \times 10^{-6}$, whence $K = (5{\cdot}70/465)^2 = 1{\cdot}50 \times 10^{-4}$. The numbers in the fourth line are those derived from $v/\sqrt{c(1-\alpha)} \,.\, 10^6 = 5{\cdot}70 + 5{\cdot}70\sqrt{c(1-\alpha)}$.

Chloroacetic Acid.

c	0·005	0·01	0·02	0·05	0·1	0·2	0·5
$v \,.\, 10^6$	1·055	1·655	2·56	4·62	7·31	11·80	23·0
$v/\sqrt{c(1-\alpha)} \,.\, 10^6$	19·5	20·0	20·7	22·5	24·5	27·5	33·4
$v/\sqrt{c(1-\alpha)} \,.\, 10^6$ (calc.)	19·3	19·9	20·85	22·65	24·7	27·6	33·4

In the case of chloroacetic acid the substitution of $\sqrt{Kc}$ for $[H^+]$ is a very rough approximation, as seen when $v/\sqrt{c}$ is plotted against $\sqrt{c}$, for the points corresponding with the lower acid concentrations fall very considerably below the straight line which reproduces fairly well the data for the three most concentrated solutions. This line gives $k_m = 23{\cdot}5 \times 10^{-6}$ and $(k_h + k_a - k_m)\sqrt{K} = 16{\cdot}0 \times 10^{-6}$, whence $K = 1{\cdot}31 \times 10^{-3}$. From this preliminary value of K, the second stage of the process gives $k_m = 22{\cdot}3 \times 10^{-6}$ and $(k_h + k_a)\sqrt{K} = 17{\cdot}9 \times 10^{-6}$, whence $K = 1{\cdot}48 \times 10^{-3}$. The values of $v/\sqrt{c(1-\alpha)}$ in the third line are derived from the latter and the plot of these numbers against $\sqrt{c(1-\alpha)}$ yields $k_m = 22{\cdot}2 \times 10^{-6}$ and $(k_h + k_a)\sqrt{K} = 18{\cdot}1 \times 10^{-6}$, whence $K = 1{\cdot}51 \times 10^{-3}$. The figures in the fourth line are those given by $v/\sqrt{c(1-\alpha)} \,.\, 10^6 = 18{\cdot}10 + 22{\cdot}2\sqrt{c(1-\alpha)}$. Repetition of the second-stage process thus makes but little difference to the values obtained for k_m and K, although chloroacetic acid is not an acid which can be regarded as weak.

In the following table, the results of the measurements are summarised, and for comparison the values of K derived from conductivity measurements are added in the last column.

Acid.	$k_m \times 10^6$.	K (from catalytic data).	K (from conductivity).
Propionic	1·1	$1{\cdot}38 \times 10^{-5}$	$1{\cdot}4 \times 10^{-5}$
Acetic	1·35	$1{\cdot}85 \times 10^{-5}$	$1{\cdot}85 \times 10^{-5}$
Succinic	4·3	$6{\cdot}30 \times 10^{-5}$	$6{\cdot}55 \times 10^{-5}$
β-Chloropropionic	3·7	$1{\cdot}01 \times 10^{-4}$	$1{\cdot}04 \times 10^{-4}$
Glycollic	5·7	$1{\cdot}50 \times 10^{-4}$	$1{\cdot}52 \times 10^{-4}$
Chloroacetic	22·2	$1{\cdot}51 \times 10^{-3}$	$1{\cdot}55 \times 10^{-3}$

From the table it is evident that k_m increases in general with the strength of the acid. The slightly anomalous value for succinic acid may possibly be connected with the fact that this is dibasic and is in other ways not directly comparable with the other members of the series. In all cases the ionisation constants derived from the catalytic data are in close agreement with those given by the conductivity of the acid in dilute solution.

According to equation (2), the hydrogen-ion concentration is given by $[H^+] = (v - k_m c)/(k_h + k_a - k_m)$, and provided k_a and k_m are known, the ionisation constant may be derived by substitution of this value of $[H^+]$ in $K = [H^+]^2/(c - [H^+])$. The result is illustrated by reference to the data for glycollic acid :

c	0·01	0·02	0·05	0·1	0·2	0·4	0·5
$[H^+] . 10^3$ ...	1·15	1·67	2·64	3·79	5·38	7·80	8·58
$K . 10^4$	1·50	1·53	1·47	1·49	1·49	1·55	1·50

Consideration of the Factors which affect the Value of K.

The determination of K and k_m by the method based on equation (4) involves the assumption that the ionisation constant K and the catalytic coefficients k_h, k_a, and k_m are not affected by changes in the concentration of the acid. From experiments on the catalytic activity of acids in solutions of catalytically inert salts (Dawson and Key, this vol., pp. 1239, 1248), it would appear that k_h increases continuously with the salt concentration, whereas k_a and k_m are but slightly affected by changes in the ionic environment. These experiments show, further, that the ionisation constant K increases with the salt concentration to a maximum and then diminishes as the proportion of salt in the solution is further increased.

The ionic concentration of the salt-free solutions with which we are concerned in this paper increases with the total acid concentration, but, in general, the ionic strength ($\mu = c\alpha$) is less than 0·01. In these circumstances, there will be no appreciable alteration in the values of the several catalytic coefficients, but since the ionisation constant increases rapidly with the ionic concentration at low values of the latter, it may be anticipated that K will increase somewhat as the concentration of the acid increases. On the other hand, it is well known that the addition of non-electrolytes to the aqueous solution of a weak electrolyte reduces the ionisation of the latter, and this factor may be expected to play some part in the more concentrated acid solutions. It seems possible, in fact, that the constancy of K, which is indicated by the catalytic data, may be due in some measure to the opposite effects which are produced by the ionised acid and by the non-ionised acid respectively.

Since the thermodynamic ionisation constant K_a is given by

$$K_a = a_{H^+} . a_{A^-}/a_{HA} = (f_+f_-/f_0) \times [H^+][A^-]/[HA]$$

in which f_0 is approximately equal to unity, the connexion between K and K_a may be written $K = K_a/f_+f_- = K_a/f_\pm^2$, where $f_\pm$ is the mean activity coefficient of the ions. Furthermore, the relation between $f_{\pm}$ and the ionic strength μ may be expressed in the form $\log 1/f_{\pm} = a\sqrt{\mu} - b\mu$, in which the second term may be neglected for small values of μ and, in accordance with the Debye–Hückel theory, a may be given the value 0·5 when the ions concerned are univalent. On replacing the ordinary by the natural logarithm, we obtain $\log_e 1/f_{\pm} = 1{\cdot}15\sqrt{\mu}$, whence $K = K_a . e^{2{\cdot}30\sqrt{\mu}}$ or $\sqrt{K} = \sqrt{K_a} . e^{1{\cdot}15\sqrt{c\alpha}}$. When this is introduced into equation (4), the latter takes the form

$$v/\sqrt{c(1-\alpha)} = (k_h + k_a)\sqrt{K_a} . e^{1{\cdot}15\sqrt{c\alpha}} + k_m\sqrt{c(1-\alpha)} \quad . \quad (6)$$

If the limiting ionic strength is taken as 0·01, which is greater than that of any of the solutions used in the catalytic experiments, except for the more concentrated solutions of the chloroacetic acid series, the limiting value of $e^{1{\cdot}15\sqrt{c\alpha}}$ is approximately 1·12, which signifies that an increase of 12% in the value of $v/\sqrt{c(1-\alpha)}$ might conceivably be debited to the change in the ionic environment in proceeding from $\mu = 0$ to $\mu = 0{\cdot}01$. This increase of 12%, although only a small fraction (see tables) of the actually observed increase in $v/\sqrt{c(1-\alpha)}$, represents the maximum increase which can be attributed to the ionic effect, for it takes no account of the opposing influence of the second term in the equation $\log 1/f_{\pm} = a\sqrt{\mu} - b\mu$. The influence of the un-ionised acid in the more concentrated solutions is also ignored. So far as the present series of experiments is concerned, it is perhaps still more important to bear in mind that all the solutions examined contained a small quantity of potassium iodide (0·002 mol. per litre). The presence of the latter diminishes very appreciably the variation of K which may be attributed to the increasing concentration of the ions in passing from the weaker to the stronger solutions. This may be illustrated by reference to the specific case of propionic acid for which $e^{1{\cdot}15\sqrt{\mu}}$ increases from 1·058 for $c = 0{\cdot}01$ to 1·083 for $c = 0{\cdot}5$. The corresponding increase in $e^{1{\cdot}15\sqrt{\mu}}$ for glycollic acid is from 1·065 for $c = 0{\cdot}01$ to 1·12 for $c = 0{\cdot}5$. In such circumstances, it is not difficult to understand that the catalytic data are generally consistent with the assumption of a constant value for K.

In this connexion, attention may be directed to the experimental data obtained by Dawson and Powis (*loc. cit.*) for the much stronger dichloroacetic acid at concentrations between $c = 0{\cdot}01$ and $c = 0{\cdot}2$. In the application of equation (4) to these results, the values of $v/\sqrt{c(1-\alpha)}$ have been derived from $K = 5{\cdot}0 \times 10^{-2}$ (Drucker, *Z. physikal. Chem.*, 1904, **49**, 563) :

Dichloroacetic Acid.

c	0·01	0·02	0·05	0·1	0·2
$v \cdot 10^6$	4·10	7·95	18·1	32·7	59·6
ca	0·00854	0·0153	0·0309	0·0500	0·0780
$v/\sqrt{c(1-a)} \cdot 10^6$	107·3	116·0	131·0	146·2	170·6
$v/\sqrt{c(1-a)} \cdot 10^6$ (calc.)	110·6	116·7	130·6	147·7	172·8

The plot of $v/\sqrt{c(1-\alpha)}$ against $\sqrt{c(1-\alpha)}$ gives a straight line, the slope of which yields $k_m = 200 \times 10^{-6}$. The numbers in the last horizontal line are those derived from $v/\sqrt{c(1-\alpha)} \cdot 10^6 = 103{\cdot}0 + 200\sqrt{c(1-\alpha)}$. As in the case of the weaker acids, these results indicate that the catalytic data for dichloroacetic acid can be satisfactorily co-ordinated in terms of equation (4) with a constant value of K. It is to be noted, however, that the solutions of dichloroacetic acid contained a larger quantity of potassium iodide, *viz.*, 0·008 mol per litre. This would certainly tend to reduce the influence of the ionised acid on the value of K. At the same time, the ionic strengths of this series of solutions (see third line of table) are of such magnitude that the second term in the equation $\log 1/f_{\pm} = a\sqrt{\mu} - b\mu$ cannot entirely be left out of account. Without entering into a more minute discussion of the matter in this paper, we would further suggest that it is improbable that the polarising influence of ionic environment, as measured by a, is independent of the nature of the positive and negative ions, even when these carry the same charge. There is, indeed, a substantial amount of evidence to support the view that such influence is specific even at very low ionic concentrations.

In conclusion, attention may be directed to the very general applicability of the catalytic method as a means of determining the degree of ionisation of an acid. If the values of k_h, k_a, and k_m are known, the method may be applied to solutions of the acid in pure water or in solvents which contain relatively large quantities of catalytically inert salts. The conductivity method fails completely when foreign electrolytes are present in more than very small amounts, and since the mobility of the ions is so largely affected by interionic forces, it is at the best limited to solutions of low ionic strength.

Summary.

The catalytic effects produced by propionic, acetic, succinic, β-chloropropionic, glycollic, and chloroacetic acids have been studied with reference to the variation of the catalysing power with the concentration.

It is shown that the connexion between the reaction velocity and the concentration affords a means of determining the ionisation

constant of the acid as well as the catalytic activity of the undissociated acid.

The ionisation constants derived from the catalytic data are in close agreement with those afforded by the electrical conductivity of dilute solutions of the acids.

In general, the catalytic activity of the undissociated acid increases with the ionisation constant.

The relation between the catalytically determined constant K and the thermodynamic constant K_a is considered in reference to the various factors which affect the value of K under the conditions which obtain in the experimental determinations.

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