XXXIV.—*Acid and Salt Effects in Catalysed Reactions. Part IV. Derivation of a General Equation for the Catalytic Activity of Acids. The General Catalytic Catenary.*

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The results of experiments described in previous papers (Dawson and Carter, J., 1926, 2282; Dawson and Dean, *ibid.*, p. 2872; Dawson and Hoskins, *ibid.*, p. 3166) show that the catalysing power of acid–salt mixtures of the type $c\text{HA} + x\text{MA}$ (c constant and x variable) is such that, in general, the reaction velocity falls as x increases, reaches a minimum, and then increases continuously according to the linear formula $v = a + bx$. The curves which are obtained by plotting the reaction velocity against the p_{H} value of the catalysing solution are symmetrical with respect to the point at which the velocity is a minimum.

In accordance with the equations for the hydrogen-ion concentration $[\text{H}^+]_i$ and the velocity v_i which characterise the minimum velocity (*M.V.*) mixture, namely,

$$[\text{H}^+]_i = \sqrt{k_a K c/(k_h - k_m)}$$

and

$$v_i = 2\sqrt{(k_h - k_m)k_a K c} + k_m c$$

it has also been shown that for a given acid $[\text{H}^+]_i$ is directly proportional to the square root of the acid concentration, and that the specific minimum velocity v_i/c is a linear function of the square root of the dilution of the acid.

It follows that the reaction velocities for all possible mixtures of an acid with its corresponding salts can be represented on the v–p_{H} diagram by a sheaf of curves which are catenary in type. The dimensions of the individual catenaries and the positions of their apices (the *M.V.* points) are determined by the nature of the acid and its concentration. The influence of the nature of the acid finds expression in the catalytic coefficients, k_h, k_a, and k_m for the hydrogen ion, the acid anion, and the undissociated acid molecule, respectively, and in the ionisation constant, K, of the acid. The catenary curves on the v–p_{H} diagram, it may be noted, should really be considered as the projections on this plane of catenary surfaces, the complete representation of which would necessitate the use of a tridimensional co-ordinate system with reaction velocity, acid concentration, and p_{H} as the respective co-ordinates.

Although the observations already described are such as to suggest that the relations involved are of general character, it may now be pointed out that similar catalytic phenomena have been met with as a result of the preliminary examination of many other acids. Amongst these may be mentioned oxalic acid (both in the first and second stages of dissociation), tartaric acid (first and second stages), phosphoric acid (first and second stages), and sulphuric acid (second stage). In the case of the strongest acids (such as the halogen acids, nitric acid, etc.), there is, however, no initial fall, but, on the other hand, the velocity increases continuously with the concentration of the added salt. It will be shown in due course that this behaviour of the strongest acids is not inconsistent with the views which have been developed on the basis of observations made with weaker acids.

In the circumstances, it seems desirable at this stage to indicate that the theory outlined in the previous papers of this series leads to a general formula for the catalytic effects produced by acids which, in view of its simplicity, would seem to be of considerable importance. This general formula follows directly from the equation

$$v = v_h + v_a + v_m = k_h[\mathrm{H}^+] + k_a[\mathrm{A}^-] + k_m[\mathrm{HA}] \quad . \quad . \quad (1)$$

the only assumption involved being that the dissociation of the acid conforms to the requirements of the mass law. Substituting for $[\mathrm{A}^-]$ the value given by $[\mathrm{A}^-] = K(c - [\mathrm{H}^+])/[\mathrm{H}^+]$ and for $[\mathrm{HA}]$ the value $c - [\mathrm{H}^+]$, and rearranging the terms, we get

$$v = (k_h - k_m)[\mathrm{H}^+] + k_aKc/[\mathrm{H}^+] + k_mc - k_aK \quad . \quad . \quad (2)$$

For a fixed acid concentration, the variations in velocity are due to changes corresponding with the first two terms, and if the ionic reaction velocity is denoted by u, we may write

$$u = v_h + v_a = (k_h - k_m)[\mathrm{H}^+] + k_aKc/[\mathrm{H}^+] \quad . \quad . \quad (3)$$

If the hydrogen-ion concentration $[\mathrm{H}^+]$ is expressed in terms of the hydrogen-ion concentration $[\mathrm{H}^+]_i$ of the corresponding *M.V.* mixture, such that $[\mathrm{H}^+] = n[\mathrm{H}^+]_i$, then equation (3) may be written

$$u = (k_h - k_m)n[\mathrm{H}^+]_i + k_aKc/n[\mathrm{H}^+]_i,$$

and since $[\mathrm{H}^+]_i = \sqrt{k_aKc/(k_h - k_m)}$,

we have $u = \sqrt{(k_h - k_m)k_aKc}(n + 1/n) \quad . \quad . \quad . \quad . \quad (4)$

Since, further, the minimum ionic velocity u_i is given by

$$u_i = 2\sqrt{(k_h - k_m)k_aKc} \quad . \quad . \quad . \quad . \quad (5)$$

we obtain by combination of (4) and (5)

$$r = u/u_i = \tfrac{1}{2}(n + 1/n) \quad . \quad . \quad . \quad . \quad . \quad (6)$$

In equation (6), n represents the hydrogen-ion concentration of any solution in terms of that of the corresponding *M.V.* mixture, and may be termed the reduced hydrogen-ion concentration. Similarly, r expresses the velocity due to the hydrogen and acid anions for any solution in terms of the ionic reaction velocity of the corresponding *M.V.* mixture and may be called the reduced ionic reaction velocity.

If $\log_{10} n = (p_{\mathrm{H}})_i - p_{\mathrm{H}}$ be denoted by Δp_{H}, then Δp_{H} may be referred to as the reduced p_{H} value of the solution in question, and equation (6) may be written in the form

$$r = \tfrac{1}{2}(10^{\Delta p_{\mathrm{H}}} + 10^{-\Delta p_{\mathrm{H}}}) \quad . \quad . \quad . \quad . \quad . \quad (7)$$

This is the equation of a catenary, and it expresses quite generally the connexion between the reduced ionic velocity and the reduced p_H value for any catalysing solution. Its applicability would appear to be independent of the nature and concentration of the catalysing acid, of the temperature, of the nature of the solvent, and also of the nature of the catalysed reaction. It is therefore to be regarded as a general formula applicable to all catalysed reactions in so far as the velocity of these depends on the positive hydrogen ions and the corresponding negative anions.

It follows that the ionic reaction velocities for any acid-catalysed reaction should be representable by a single catenary curve. Equation (7) and the corresponding curve obtained by plotting the reduced ionic reaction velocity against the reduced p_H value may be termed the reduced or general catalytic catenary.

It may be noted that, in the derivation of this relation, the procedure followed is analogous to that by which the specific gas equations of the ordinary type are transformed into general reduced equations of condition.

The mathematical form of the general equation may be further simplified, for if the natural logarithm of the reduced hydrogen-ion concentration is denoted by h, *i.e.*, if $\log_e n = h$, then this equation may be written

$$r = \cosh h \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7a)$$

according to which, the reduced ionic velocity is equal to the hyperbolic cosine of the logarithm of the reduced hydrogen-ion concentration. There are obvious reasons, however, for regarding equation (7) as the more convenient form of the general relation.

Significance of the Reduced Catalytic Catenary.

The experimental data on which the foregoing views are based have reference to the catalytic behaviour of acid–salt mixtures represented by $c\text{HA} + x\text{MA}$, in which c is constant and x is variable. In accordance with the view that the salt is completely ionised, this series of mixtures may be represented by $c\text{HA} + x\text{A}^-$, for the positive ion M^+ has no measurable catalytic activity.

The symmetry of the reduced catalytic catenary obviously suggests the possibility of a complementary series corresponding with the formula $c\text{HA} + x'\text{H}^+$, but it does not follow that the latter can be actually realised, for although it is very probable that the strongest acids are very largely ionised, there is evidence to support the view that the ionisation is not complete. Since the non-ionised acid would appear to be a very active catalyst, it is clear that there may be a considerable difference in practice between the two stoicheiometrically complementary series of solutions.

If, however, it is assumed that the ionisation of a strong acid, *e.g.*, hydrochloric acid, is practically complete in dilute solution, and that the catalytic activity of the chlorine ion is negligible in comparison with that of the hydrogen ion, it should be possible to realise to a limited extent the series of solutions which is represented by $c\mathrm{HA} + x'\mathrm{H}^+$.

The dividing line between the stoicheiometrically complementary series of catalysing solutions corresponds with $x = x' = 0$. This corresponds with a solution of the free acid HA and it may be shown that this is represented by a point on the reduced catalytic catenary, the position of which is determined solely by the relative magnitudes of the catalytic coefficients k_h, k_a, and k_m.

It will be assumed that the acid concerned is weak and that the hydrogen-ion concentration $[\mathrm{H}^+]_0$ of the pure acid solution is given with sufficient exactness by the mass-law expression $[\mathrm{H}^+]_0 = \sqrt{Kc}$. We may then write

$$u_0 = (k_h - k_m)\sqrt{Kc} + k_a\sqrt{Kc},$$

and since

$$u_i = 2\sqrt{(k_h - k_m)k_aKc},$$

we obtain by division

$$r_0 = u_0/u_i = \tfrac{1}{2}(\sqrt{(k_h - k_m)/k_a} + \sqrt{k_a/(k_h - k_m)}) \quad . \quad . \quad (8)$$

where r_0 denotes the reduced ionic velocity for the pure acid solution.

From equations (6) and (8) it is apparent that the reduced ionic concentration of solutions of the pure acid is given by $n_0 = \sqrt{(k_h - k_m)/k_a}$, whence

$$(\Delta p_{\mathrm{H}})_0 = \log_{10}\sqrt{(k_h - k_m)/k_a} \quad . \quad . \quad . \quad . \quad (9)$$

It is thus evident that the position of the point H_0 on the catenary is determined by the magnitude of the catalytic coefficients for the acid in question.

Since the relative magnitudes of the catalytic coefficients vary widely according to the strength of the acid and according to the nature of the catalysed reaction, it is obvious that the experimental realisation of the catenary curve may be achieved much more readily with some reactions than it is with others. For such reactions as ester hydrolysis and sucrose inversion, it would seem that the coefficients k_a and k_m are very small in comparison with k_h.

According to the evidence which is available for the acetone–iodine reaction, k_m can be neglected in comparison with k_h in the case of weaker acids, whilst the ratio k_h/k_a increases with increasing strength of the acid as measured by the dissociation constant K.

Catalytic Effects due to the Hydrogen and Hydroxyl Ions.

In accordance with the very general character of the reduced catalytic catenary, it is not surprising that the catalytic effects produced by the simultaneous action of the hydrogen and hydroxyl ions should conform to the requirements of equation (7). This, indeed, may be regarded as a particular case of catalytic action in which the hydrogen ion and the acid ion (hydroxyl) are derived from or are controlled by the solvent.

The equation for the velocity of reaction may be written

$$v = k_h[\mathrm{H}^+] + k_{\mathrm{OH}}[\mathrm{OH}^-] + k_m[\mathrm{H_2O}],$$

and since $[\mathrm{H}^+].[\mathrm{OH}^-] = K_w$ and $[\mathrm{H_2O}]$ is constant, it follows that the ionic velocity u is given by

$$u = k_h[\mathrm{H}^+] + k_{\mathrm{OH}} \, . \, K_w/[\mathrm{H}^+].$$

The reaction velocity is a minimum when the hydrogen-ion concentration has the value $[\mathrm{H}^+]_i = \sqrt{k_{\mathrm{OH}} \, . \, K_w/k_h}$. Substituting this in the equation for u we obtain

$$u_i = 2\sqrt{k_h \, . \, k_{\mathrm{OH}} \, . \, K_w},$$

whence

$$\begin{aligned} r &= \tfrac{1}{2}([\mathrm{H}^+]/[\mathrm{H}^+]_i + [\mathrm{H}^+]_i/[\mathrm{H}^+]) \\ &= \tfrac{1}{2}(n + 1/n) \\ &= \tfrac{1}{2}(10^{\Delta p_{\mathrm{H}}} + 10^{-\Delta p_{\mathrm{H}}}), \end{aligned}$$

or the same result as that which was obtained for the reduced ionic velocity due to the joint catalytic effect of any acid HA in conjunction with the corresponding salt.

In view of the very weak acidic character of water, it is probable that the magnitude of the coefficient k_m is very small in comparison with k_h and k_{OH}, in which case the ionic velocity u is identical with the actually measured velocity v.

The main difference between the catalytic effects which are produced by the combined action of the hydrogen and hydroxyl ions, as compared with those which have been observed for the catalysing action of acid–salt mixtures in the acetone–iodine reaction, lies in the fact that k_{OH}/k_h is greater than unity, whilst for the acids used in the acetone experiments k_a/k_h is less than unity.

A reaction in which the joint action of hydrogen and hydroxyl ions has been studied is the hydrolysis of methyl acetate at 25°, for which, according to Wijs (*Z. physikal. Chem.*, 1893, **11**, 492; **12**, 514), the value of k_{OH}/k_h is about 1400, and since the hydrogen-ion concentration corresponding with minimum reaction velocity is given by $[\mathrm{H}^+]_i = \sqrt{k_{\mathrm{OH}}K_w/k_h}$, it follows that $(p_{\mathrm{H}})_i = 5{\cdot}43$ if K_w is equal to 10^{-14}. The neutral point characterised by $p_{\mathrm{H}} = 7$ lies, therefore, on the right-hand side of the catalytic catenary. In these circumstances, it is obvious that the addition of acid ion (hydroxyl) in the form of, say, sodium hydroxide to pure water will not diminish, but on the contrary, will increase the reaction velocity, and that the attainment of the *M.V.* point will necessitate the diminution of the hydroxyl-ion concentration by the addition of hydrogen ions. The so-called neutral point for water corresponds in the more general case with a solution of the free acid HA, the hydrogen-ion concentration of which has already been denoted by $[H^+]_0$. The H_0 points are characterised by equality of the concentrations of the hydrogen ion and the corresponding anion, whereas the H_i points are distinguished by the equality of the catalytic effects which are produced by the positive and negative ions. Since $(\Delta p_H)_0 = \frac{1}{2} \log (k_h - k_m)/k_a$, it is clear that the H_0 point will be situated on one branch of the catalytic catenary if the ratio $(k_h - k_m)/k_a$ is greater than unity, and on the other branch if the ratio is less than unity. When k_m can be neglected in comparison with k_h, the relative positions of the H_0 and H_i points will be determined by k_h/k_a.

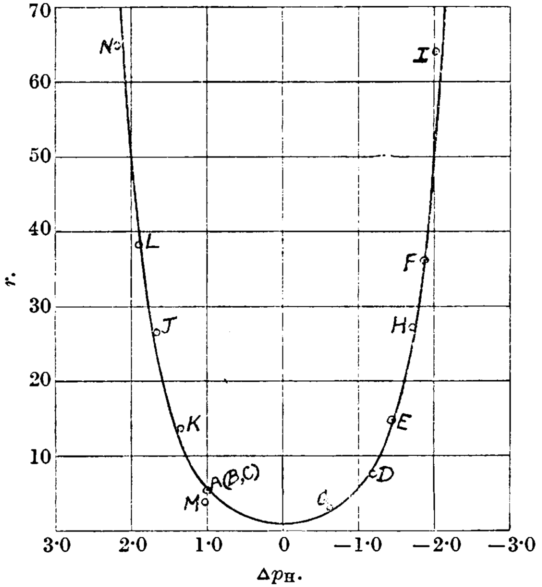
The relations described point strongly to the undesirability of differentiating between the hydroxyl ion and other acid ions. The catalytic behaviour of the hydroxyl ion is indeed so closely similar to that of other acid ions that there appears to be no valid reason for the commonly accepted view that the hydroxyl ion is distinguished from other negative ions in its catalytic properties. In due course, experiments will be described which show directly that negative ions, other than hydroxyl, have very highly developed catalytic activity.

Testing the Reduced Catalytic Catenary.

The data available for submitting the general catalytic catenary to the test of experiment are limited to those furnished by observations on the velocity of the acetone–iodine reaction and to Karlsson's data (*Z. anorg. Chem.*, 1921, **119**, 69) for the rate of hydrolysis of methyl and ethyl acetates at 85·5° in aqueous solutions buffered by the addition of mixtures of acetic acid and sodium acetate. The p_H values of these buffered solutions were determined electrometrically at 85·5° and from a series of observations with each of the two esters Karlsson has derived the minimum reaction velocities and the corresponding $(p_H)_i$ values, a knowledge of which is required for the purpose of the test.

Critical inspection of Karlsson's data shows that the accuracy attained in the individual experiments is not of a high order, and for this reason it is only possible to consider those observations in which the effect of errors of experiment is as small as possible. Whatever the nature of the catalysed reaction, the nearer we approach the apex of the catalytic catenary, the more accurate must be the measurements if they are to be utilised for the purpose of testing the general equation which has been derived.

The accompanying diagram shows the general catalytic catenary with r as ordinate and Δp_H as abscissa. The points shown on the diagram and indicated by capital letters refer to experimental observations, the nature of which is summarised in the table on p. 221. Subject to the above consideration, the observations have been selected from the available material so as to cover as wide a range as possible. In the case of the acetone–iodine reaction—points A to K—the observations include data for both acetic and chloroacetic acids in the presence and absence of the corresponding salts. The table gives the values of p_H, $(p_H)_i$, v, v_i, u, and u_i, from which the required values of Δp_H and r have been computed. The numbers expressing the reaction velocities are the actual velocities in g.-mols. per litre per minute multiplied by 10^6. Karlsson's numbers have therefore been multiplied by 2·30.



The general or reduced catalytic catenary.

In reference to the table of results it should be noted that the data for the 0·05, 0·1, and 0·2N-acetic acid solutions (points A, B, and C) give values for r and Δp_H which are identical within the limits of

TABLE I.

Characterisation of the Points included in the Diagram of the General Catalytic Catenary.

Nature of catalyst or catalysed reaction.	p_H.	$(p_H)_i$.	Δp_H.	v.	v_i.	u.	u_i.	r.
A. $0{\cdot}05N\text{-}CH_3{\cdot}CO_2H$.	3·01	4·03	+1·02	0·50	0·164	0·425	0·089	4·8
B. $0{\cdot}1N\text{-}CH_3{\cdot}CO_2H$.	2·87	3·88	+1·01	0·75	0·273	0·60	0·123	4·9
C. $0{\cdot}2N\text{-}CH_3{\cdot}CO_2H$.	2·72	3·72	+1·00	1·16	0·465	0·86	0·165	5·2
D. $0{\cdot}05N\text{-}CH_3{\cdot}CO_2H$ + $0{\cdot}16N\text{-}CH_3{\cdot}CO_2Na$.	5·24	4·03	−1·21	0·724	0·164	0·649	0·089	7·3
E. $0{\cdot}1N\text{-}CH_3{\cdot}CO_2H$ + $0{\cdot}4N\text{-}CH_3{\cdot}CO_2Na$.	5·33	3·88	−1·45	1·95	0·273	1·80	0·123	14·6
F. $0{\cdot}1N\text{-}CH_3{\cdot}CO_2H$ + $1N\text{-}CH_3{\cdot}CO_2Na$.	5·73	3·88	−1·85	4·60	0·273	4·45	0·123	36·2
G. $0{\cdot}2N\text{-}CH_3{\cdot}CO_2H$ + $0{\cdot}1N\text{-}CH_3{\cdot}CO_2Na$.	4·33	3·72	−0·61	0·775	0·465	0·475	0·165	2·9
H. $0{\cdot}2N\text{-}CH_3{\cdot}CO_2H$ + $1N\text{-}CH_3{\cdot}CO_2Na$.	5·43	3·72	−1·71	4·80	0·465	4·50	0·165	27·2
I. $0{\cdot}2N\text{-}CH_3{\cdot}CO_2H$ + $2N\text{-}CH_3{\cdot}CO_2Na$.	5·73	3·72	−2·01	10·9	0·465	10·6	0·165	64
J. $0{\cdot}1N\text{-}CH_2Cl{\cdot}CO_2H$.	1·91	3·56	+1·65	7·75	2·60	5·35	0·20	26·7
K. $0{\cdot}1N\text{-}CH_2Cl{\cdot}CO_2H$ + $0{\cdot}02N\text{-}CH_2Cl{\cdot}CO_2Na$.	1·21	3·56	+1·35	5·12	2·60	2·72	0·20	13·6
L. Hydrolysis of methyl acetate.	2·83	4·70	+1·87	1220	32	1220	32	38
M. Hydrolysis of methyl acetate.	3·69	4·70	+1·01	122	32	122	32	3·8
N. Hydrolysis of ethyl acetate.*	2·85	5·05	+2·20	980	15	980	15	65

* The values assigned by Karlsson to $(p_H)_i$ and u_i for the hydrolysis of ethyl acetate are 5·10 and $6{\cdot}8 \times 10^{-6}$, respectively. The values adopted in the table are 5·05 and $6{\cdot}5 \times 10^{-6}$, which would appear to be more nearly in accordance with the graph of Karlsson's experimental data.

error. This result is entirely in accordance with equations (8) and (9), which give respectively $r = 5{\cdot}0$ and $\Delta p_H = 0{\cdot}99$, values which are independent of the concentration of the acid.

Having regard to the nature of the variations which are represented in the table and on the diagram—variations in the nature of the catalysed reaction, in the nature and type of the catalyst, and in the temperature of the respective observations—the concordance between the experimental data and the theoretical deductions is such as to justify the belief that the reduced catalytic catenary represents a very general expression for the effects produced by the joint action of the catalytically active ions which are formed by the dissociation of acids.

Finally, it may be noted that the movement of an index point along the general catenary from left to right represents, not only the changes in catalytic activity which are produced by the addition of a salt to the corresponding acid, but also a continuous series of H_0 points corresponding with pure acids for which the relative catalytic activity of the acid anion increases whilst the ionisation constant decreases.

Summary.

A general equation for the velocity of chemical change has been derived which expresses the catalytic effects produced by acids, either alone or in the presence of the corresponding salts.

This equation may be written in the form

$$r = \tfrac{1}{2}(10^{\Delta p_H} + 10^{-\Delta p_H}),$$

in which r is the velocity due to the positive and negative ions expressed in terms of the velocity for the corresponding *M.V.* mixture, and Δp_H is the difference between the p_H values of the solution in question and of the *M.V.* mixture.

The above expression, which corresponds with a catenary curve, may be termed the general or reduced catalytic catenary. It appears to be capable of very wide application and is independent of the nature of the catalysing acid, of its concentration, of the temperature, of the nature of the solvent, and of the type of the catalysed reaction.

The general catalytic catenary has been tested by reference to the data which are available for the purpose.

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