CLXXX.—*Acid and Salt Effects in Catalysed Reactions.*
   Part IX. A General Kinetic Method for the
   Determination of the Degree of Dissociation of
   Water.

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IN Part VIII of this series of papers (this vol., p. 1146) it was shown
that the coefficients k_h and k_{OH}, which represent respectively the
catalytic activities of the hydrogen and hydroxyl ions, may be
derived from the reaction velocity and the hydrogen-ion concen-
tration which are characteristic of the isocatalytic point on the
H^+–OH^- catenary.

   On the assumption that the catalysed hydrolytic reactions in
question are such that the effect of the undissociated water molecules
may be neglected, the isocatalytic data are given by the equations

$$[H^+]_i = \sqrt{k_{OH}K_w/k_h} \ (1) \text{ and } v_i = 2\sqrt{k_h k_{OH}K_w} \quad . \quad (2)$$

If the ionisation constant, K_w, of the solvent is unknown, it is apparent that these equations afford a means of determining it. Three methods of procedure are possible, for by the combination of equations (1) and (2) we obtain

$$K_w = k_h[\text{H}^+]_i^2/k_{\text{OH}} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (3)$$

$$K_w = [\text{H}^+]_i v_i/2k_{\text{OH}} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (4)$$

and $\qquad K_w = v_i^2/4k_h k_{\text{OH}} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (5)$

These equations involve three of the four possible ternary combinations of k_h, k_{OH}, $[\text{H}^+]_i$, and v_i, and it should be noted that they all presume a knowledge of k_{OH}. The fourth combination $(k_h, [\text{H}^+]_i,$ and $v_i)$ does not provide a means of determining K_w, and this is due to the circumstance that these three quantities are uniquely connected by the relation $v_i = 2k_h[\text{H}^+]_i$.

In the application of the methods suggested by the above equations, it should be noted that the determination of the iso-catalytic data corresponding with the joint effect of the hydrogen and hydroxyl ions usually requires the stabilisation of the p_{H} value at which the velocity is measured, and this may, of course, be effected by the employment of buffer mixtures. Apart from the displacement of the isocatalytic point of the H^+–OH^- catenary by the acid and salt constituents of the buffer mixture (compare Dawson, Part VIII), there are various other points to be considered which have a direct bearing on the determination of the isocatalytic data in buffered solutions, and also on the differentiation between equations (3), (4), and (5) as a means of obtaining K_w. These are of particular importance when, as is frequently the case, the products of the hydrolytic change are acidic or basic, and thus tend to alter the p_{H} value of the medium in which the reaction is taking place.

For the sake of simplicity it may be supposed that the catalysed reaction is the hydrolysis of an ester of the acid HA, and that the p_{H} value is stabilised by a mixture of HA and the corresponding salt. If x is the ratio of acid to salt in the buffer mixture, the p_{H} value is given by $p_{\text{H}} = \log 1/K - \log x$. If, further, the smallest possible change of x which permits of the measurement of the reaction velocity is denoted by Δx, it follows that $\Delta p_{\text{H}}/\Delta x = -1/2 \cdot 3x$, or that the resulting change in the p_{H} value of the solution is inversely proportional to the acid–salt ratio of the buffer mixture. This consideration shows that buffer mixtures with a low acid–salt ratio are not generally suitable for use in the measurement of reaction velocities.

Furthermore, since the rate of change of the reaction velocity with change of p_{H} approximates to zero in the neighbourhood of the isocatalytic point, whilst $\Delta p_{\text{H}}/\Delta v$ attains its highest values in this

region, it is apparent that the minimum velocity can in general be determined with much greater accuracy than that which is associated with the determination of the hydrogen-ion concentration characteristic of the isocatalytic point. For this reason, it would appear that equation (5) is very much to be preferred to equations (3) and (4) as the basis of a method for the determination of K_w.

It is scarcely necessary to add that the absolute concentration of the buffer mixture should be as small as is consistent with the adequate stabilisation of the hydrogen-ion concentration. Less obvious is the circumstance that the mode of making up the series of buffer solutions is of considerable importance. The p_H value is determined by K and by the acid–salt ratio, but of the various possible ways in which the acid and salt may be mixed together to produce a series of buffer mixtures with the required range of p_H values, there are two sets of combinations which are unique in the sense that the mathematical treatment of the catalytic relations which are associated with their use is relatively very simple. The two sets of buffer mixtures referred to are those for which (1) the concentration (c) of the acid or (2) that (s) of the salt is kept constant.

These two series of buffer mixtures give isocatalytic points, the p_H values of which are, in general, less and greater, respectively, than the corresponding p_H value for the H⁺–OH⁻ catenary. The isocatalytic data $[H^+]_i$ and v_i for this catenary are given by equations (1) and (2). For the constant-acid series of buffer mixtures it has already been shown (Dawson, *loc. cit.*, p. 1149) that the corresponding data $[H^+]_i'$ and v_i' are given by

$$[H^+]_i' = \sqrt{(k_a Kc + k_{OH} K_w)/k_h} \quad . \quad . \quad . \quad . \quad (6)$$

and
$$v_i' = 2\sqrt{k_h(k_a Kc + k_{OH} K_w)} + k_m c \quad . \quad . \quad . \quad (7)$$

By proceeding in a similar manner, it is possible to derive expressions for the isocatalytic data $[H^+]_i''$ and v_i'' for a series of buffer solutions of the type $cHA + sMA$ in which the salt concentration (s) is kept constant. Certain restrictions are in this case necessary, and it will be assumed that the acid is relatively weak, that the hydrogen-ion concentration is given by $[H^+] = Kc/s$, and that k_m can be neglected in comparison with k_h.

The general equation

$$v = k_h[H^+] + k_{OH}[OH^-] + k_a[A^-] + k_m[HA]$$

may then be written :

$$v = k_h[H^+] + k_{OH} K_w/[H^+] + k_a s + k_m c$$

whence
$$v = (k_h + k_m s/K)[H^+] + k_{OH} K_w/[H^+] + k_a s.$$

Differentiation of this equation shows that the reaction velocity passes through a minimum when

$$[\text{H}^+] = [\text{H}^+]_i'' = \sqrt{k_{\text{OH}}K_w/(k_h + k_ms/K)} \quad . \quad . \quad . \quad (8)$$

By substitution of this in the previous equation, we obtain :

$$v_i'' = 2\sqrt{(k_h + k_ms/K)k_{\text{OH}}K_w} + k_as \quad . \quad . \quad . \quad (9)$$

Equations (8) and (9) express relations which are thus applicable to the isocatalytic points indicated by experiments with buffer solutions of constant salt concentration (s).

In order to illustrate the numerical differences which are involved in the use of such buffer solutions, we may compare the isocatalytic data for the acetone–iodine reaction without buffer, and the corresponding data with acetate buffers of constant-acid and of constant-salt concentration. Table I shows the values of p_H at which the reaction velocity is a minimum, the minimum ionic reaction velocity (u_i), and the minimum total velocity (v_i).

TABLE I.

Isocatalytic data with and without buffer mixtures.

Buffer mixture.	$(p_\text{H})_i$.	u_i.	v_i.
None	4·68	1·94	1·94
Acetate buffer, $c = 0\cdot01$	4·33	4·38	5·88
Acetate buffer, $s = 0\cdot01$	4·90	1·16	5·66

It is apparent that the isocatalytic data for the two series of buffer solutions differ very widely from the data which are really characteristic of the H^+–OH^- catenary. The wide deviation in this case is due to the relatively large magnitude of the ratios k_a/k_h and k_m/k_h for the acetone–iodine reaction, and it may be anticipated that the differences in question will not be so pronounced when other hydrolytic reactions are considered.

The minimum velocity, v_i, characteristic of the H^+–OH^- catenary may be derived from the minimum velocity v_i' obtained with buffers of constant acid concentration by combining equations (2) and (7), and from the minimum velocity v_i'' observed with buffers of constant salt concentration by the combination of (3) and (9).

From (2) and (7) we obtain

$$v_i = (v_i' - k_mc)/\sqrt{(1 + k_aKc/k_{\text{OH}}K_w)} \quad . \quad . \quad . \quad (10)$$

and from (3) and (9)

$$v_i = (v_i'' - k_as)/\sqrt{(1 + k_ms/Kk_h)} \quad . \quad . \quad . \quad (11)$$

If the disturbances due to the buffer mixtures are inconsiderable, as in the case when c and s are small, it may be shown that equation (10) reduces to the form

$$v_i = v_i' - k_mc - k_as' \quad . \quad . \quad . \quad . \quad . \quad (10\text{A})$$

where s' is the salt concentration at which minimum velocity is observed with buffers of constant acid concentration c.

Similarly, equation (11) assumes the form

$$v_i = v_i'' - k_a s - k_m c' \qquad . \quad . \quad . \quad . \quad (11\text{A})$$

where c' represents the acid concentration at which minimum velocity is found with buffers of constant salt concentration s.

Having thus shown how the minimum reaction velocity v_i may be derived from observations made with buffered solutions, we may proceed to the derivation of K_w on the basis of equation (5).

Dissociation Constant of Water at 25°.

The experimental data employed in the calculation of K_w have reference to the rate of hydrolysis of ethyl acetate.

It will be assumed that k_h is given by the rate of hydrolysis in the presence of dilute hydrochloric acid. According to the data compiled by Schreiner (Z. anorg. Chem., 1921, **116**, 102), the ratio v/c is very nearly constant for values of c between 0·025 and 0·25 mol. per litre. The value adopted here is $k_h = 6·45 \times 10^{-3}$ (time in minutes).

Measurements by Arrhenius of the rate of saponification of ethyl acetate (Z. physikal. Chem., 1887, **1**, 110) give $k_{OH} = 6·58$ at 24·7°, which corresponds with $k_{OH} = 6·70$ at 25°. The data obtained by Warder (Ber., 1881, **14**, 1361) and Reicher (Annalen, 1885, **228**, 257) lead to $k_{OH} = 6·30$ at 25°. For the purpose of this paper, the mean value, $k_{OH} = 6·50$, is taken.

Karlsson (Z. anorg. Chem., 1925, **145**, 1) has recently determined the rate of hydrolysis of the ester in acetate buffers of constant salt concentration (0·02 mol. of sodium acetate per litre), and gives for $k = 1/t . \log_{10} c_0/c$ a minimum value of $0·24 \times 10^{-7}$. This, when multiplied by 2·30, gives $0·55 \times 10^{-7}$, which is taken as a measure of v_i''.

The other quantities required are k_a and k_m, and these have been furnished by systematic experiments on the hydrolysis of ethyl acetate under the catalytic influence of mixtures of the series $0·1N\text{-CH}_3\text{·CO}_2\text{H} + xN\text{-CH}_3\text{·CO}_2\text{Na}$. These experiments, which will be described in a later paper, give $k_a = 2·00 \times 10^{-7}$ and $k_m = 14·0 \times 10^{-7}$.

By substitution in equation (11) we obtain :

$$v_i = (0·55 \times 10^{-7} - 2 \times 0·02 \times 10^{-7})/$$
$$\sqrt{1 + (14 \times 10^{-7} \times 0·02)/1·85 \times 10^{-5} \times 6·45 \times 10^{-3}}$$
$$= (0·51/\sqrt{1·235})10^{-7} = 0·46 \times 10^{-7}$$

Inserting this value of v_i in equation (5) we have :

$$K_w = (0\cdot46 \times 10^{-7})^2/4 \times 6\cdot45 \times 10^{-3} \times 6\cdot5$$
$$= 1\cdot25 \times 10^{-14}.$$

The value of K_w obtained by this kinetic method depends primarily on the degree of accuracy of the measurement of v_i'' in the experiments with the buffer solutions, but there seems to be no reason why such measurements should not be made with very considerable accuracy.

It may be noted that $K_w = 1\cdot25 \times 10^{-14}$ is not far removed from the mean of those recorded in the Landolt–Börnstein–Roth tables. With the exception of Kanolt's value of $0\cdot82 \times 10^{-14}$ (*J. Amer. Chem. Soc.*, 1907, **29**, 1414), the indexed figures fall between $1\cdot04 \times 10^{-14}$ and $1\cdot42 \times 10^{-14}$. The latter values are derived on the assumptions of the classical theory, and any close comparison would necessitate a re-examination of the data from the standpoint of the modern view that the strong electrolytes are for practical purposes completely ionised.

A point of considerable interest is involved in the use of the above value of K_w for the calculation of the minimum velocity v_i from equation (2).

This gives

$$v_i = 2\sqrt{6\cdot45 \times 10^{-3} \times 6\cdot5 \times 1\cdot25 \times 10^{-14}} = 0\cdot46 \times 10^{-7}$$

which is identical with the velocity derived from equation (11). The close agreement of the observed minimum velocity when corrected for the catalytic effects of the buffer mixture with the velocity calculated from equation (2) is very significant. It would at least appear to afford substantial evidence in favour of the general accuracy of the kinetic method which has been described.

The Dissociation Constant of Water at Higher Temperatures.

In a series of experiments carried out in quartz tubes, Karlsson (*Z. anorg. Chem.*, 1921, **119**, 69) has determined the minimum rate of hydrolysis of ethyl acetate in acetate buffers of constant salt concentration ($0\cdot02$ mol. per litre) at $85\cdot5°$. The minimum velocity so obtained will be utilised here for the derivation of K_w at $85\cdot5°$.

It is to be noted that the values of k_h and k_{OH} cannot be obtained by direct observations at this temperature. Within the range at which direct measurement is possible, both coefficients have been determined at a series of temperatures, and it has been shown that in both cases the influence of temperature on the velocity coefficient can be accurately represented by the Arrhenius formula

$$\log_e k'/k = A(1/T - 1/T').$$

This equation has consequently been utilised to obtain the required values of k_h and k_{OH} at $85\cdot5°$.

The value of k_h for $25°$, in combination with the velocity coefficients for dilute hydrochloric acid at $20°$ (Poma, *Medd. Vetenskaps. Nobelinst.*, 1912, **2**, No. 11) and at $35°$ (Karlsson, *loc. cit.*), gives $A = 8440$, and from this the value $k_h = 0\cdot770$ at $85\cdot5°$ is obtained.

The measurements of Warder and of Reicher (*loc. cit.*) over the range $0—40°$ give $A = 5578$, from which $k_{OH} = 148\cdot7$ at $85\cdot5°$. Karlsson's value for $k = 1/t \cdot \log_{10} c_0/c$ is 68×10^{-7}, and this, when multiplied by $2\cdot30$, gives $v_i'' = 156 \times 10^{-7}$.

The coefficients k_a and k_m required for the buffer correction in accordance with equation (11) are not available, but as a first approximation it may be assumed that the relative effect of the buffer on the minimum velocity is the same at $85\cdot5°$ as at $25°$. According to this, $v_i = 46/55 \, v_i'' = 0\cdot835 \, v_i'' = 130 \times 10^{-7}$. Inserting this value of v_i in equation (5), we obtain $K_w = 37 \times 10^{-14}$.

The chief objection to the above assumption is involved in the decrease in the value of the dissociation constant K of acetic acid with rise of temperature. By interpolation from the recorded values at $25°$, $100°$, and $156°$, we obtain $K = 1\cdot25 \times 10^{-5}$ at $85\cdot5°$, and when this correction is introduced, the relation between v_i and v_i'' becomes $v_i = 0\cdot80 \, v_i''$ and the value of $K_w = 34 \times 10^{-14}$.

There are two recorded series of measurements of K_w at high temperatures with which the above value may be compared. Lorenz and Böhi (*Z. physikal. Chem.*, 1909, **66**, 733) have derived values between $0°$ and $100°$ from measurements of the *E.M.F.* of the cell $0\cdot1N\text{-HCl}|0\cdot1N\text{-KCl}|0\cdot1N\text{-KOH}$, whilst Noyes, Kato, and Sosman (*ibid.*, 1910, **73**, 1) base their values for $100°$, $156°$, $218°$, and $306°$ on conductivity data obtained in connexion with the determination of the degree of hydrolysis of ammonium acetate.

Since the heat of ionisation of water varies very considerably with the temperature, the plot of $\log K_w$ against $1/T$ does not give a straight line, but the curvature of the plot is so small that there is no difficulty in estimating the value of K_w at $85\cdot5°$. For the *E.M.F.* data, the graph gives $K_w = 44 \times 10^{-14}$, whilst the hydrolytic measurements lead to $K_w = 28 \times 10^{-14}$.

The value $K_w = 34 \times 10^{-14}$ afforded by the kinetic method described in this paper thus lies between the two values which have been previously put forward. This again may be regarded as evidence in support of the belief that the determination of the minimum reaction velocity of hydrolytic reactions under the stabilised p_H conditions which are afforded by the use of buffer solutions, provides a method for the determination of the degree of dissociation of water which should yield results of considerable accuracy. With the

description and illustration of the method, the main object of this paper has been attained, and until further observations are made, it is obviously not possible to discuss in detail the merits of the kinetic method in relation to those of previous methods.

Summary.

A general kinetic method for the determination of the dissociation constant of water is described.

In accordance with the equation $K_w = v_i^2/4k_h k_{OH}$, the method involves the determination of k_h and k_{OH} and of the minimum velocity v_i, which is characteristic of the H^+–OH^- catenary.

The value of v_i is derived from measurements of the minimum reaction velocity in buffer solutions of constant acid or constant salt concentration.

For temperatures at which the coefficients k_h and k_{OH} cannot be directly measured, the required values are obtained by the use of the Arrhenius formula.

From Karlsson's measurements of the minimum speed at which ethyl acetate is hydrolysed in acetate buffers, the values derived for K_w are $1\cdot25 \times 10^{-14}$ at $25°$ and 34×10^{-14} at $85\cdot5°$.

The acid and salt effects associated with the use of buffer solutions for the stabilisation of p_H in reaction velocity measurements are discussed.

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