LXVII.—*Acid and Salt Effects in Catalysed Reactions. Part VI.* The Early Stages of an Auto-catalysed Reaction. Generalised Form of the Simple Auto-catalytic Catenary.*

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THE investigation of the auto-catalytic reaction between acetone and iodine (Dawson and Powis, J., 1912, **101**, 1503) showed that when the concentration of the acetone is constant, the course of

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the reaction can be represented very accurately by the simplest possible type of auto-catalytic equation, namely, $dx/dt = kx$, where x, the observed fall in the iodine concentration after time t, affords a measure of the concentration of the hydriodic acid produced; if not too small, this may be taken to represent the hydrogen-ion concentration.

With an acetone concentration of 20 c.c. per litre ($0{\cdot}272M$), the time required at 25° to reach the stage at which the value of x can be measured by titration with $0{\cdot}01N$-thiosulphate is about 3 days. During this period, the course of the reaction cannot be followed by any direct method,* and one of the objects of this paper is to show how the nature of the changes taking place in the early stages of the reaction may be elucidated by an indirect method.

On extrapolating the straight line obtained by plotting $\log x$ against t, Dawson and Powis obtained a value of x for $t = 0$, which represented the apparent initial hydrogen-ion concentration when it was assumed that the reaction proceeded in its early stages in accordance with the equation found to represent accurately the experimental observations for the later stages. This empirically derived value of x will be referred to in this paper by "x_0." It represents the constant in the integrated form of the differential equation, which may therefore be written $k = 1/t \, . \log_e x/\text{"}x_0\text{"}$.

The experimental data showed that "x_0" is reproducible within narrow limits, but its relatively high value seemed to preclude the possibility that "x_0" could correspond with the true initial hydrogen-ion concentration of the solution. This view was supported by the fact that the addition of small quantities of alkali to the original solution made no difference in the value obtained for "x_0." On the other hand, it was found that the value of "x_0" is reduced by the addition of small quantities of hydrochloric acid and that it becomes equal to zero when the amount of added acid is sufficient to give approximately a $10^{-4}N$-solution.

More recent experiments (Dawson and Carter, J., 1926, 2282) have shown that the hydroxyl ion is a very active catalyst for the acetone–iodine reaction, and it therefore seemed very probable that the participation of hydroxyl ions in the early stages of the auto-catalytic change might be responsible for the above behaviour. It will be shown that this assumption is quite in accordance with the facts and that the initial stage of the auto-catalysed reaction is very different in character from the later stages. The analysis to be described is of particular interest in that it illustrates the possibility of obtaining detailed information relative to the mechanism

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* Conductivity measurements are not applicable and preliminary attempts to measure the hydrogen potential did not appear to be hopeful.

of a reaction at a stage which is inaccessible to direct experimental observation.

The Hydrogen-ion Concentration of the Original Solution.

In addition to acetone and iodine, the original solution contained potassium iodide, added in the molecular ratio $KI : I_2 = 2 : 1$ to dissolve the requisite amount of iodine. Since hydrogen ions are produced by ionisation of the solvent and also by hydrolysis of the iodine, it is obviously necessary to inquire under what conditions the hydrogen ions produced by the reaction and measured by x may be taken as a measure of the total hydrogen-ion concentration. It will be shown that this condition is attained when x reaches a value which may be placed at about 2×10^{-6}, and that, from the kinetic standpoint, it is not of any great importance to know the precise value of the hydrogen-ion concentration of the original solution provided that it is not greater than this limiting value.

So far as the hydrogen ions produced by the solvent are concerned, it follows at once from the equation

$$[H^+] . (x + [H^+]) = 10^{-14}$$

that $[H^+]$ may be entirely neglected when $x = 2 \times 10^{-6}$.

In regard to the hydrogen ions produced by hydrolysis of the iodine, consideration must be given to the equilibria

$$I_2 + I^- \rightleftarrows I_3^-$$

and

$$I_2 + H_2O \rightleftarrows H^+ + I^- + HIO.$$

The constant characteristic of the first equilibrium $K_1 = [I_2] . [I^-]/[I_3^-]$ is equal to $1{\cdot}38 \times 10^{-3}$ (Jakowkin, *Z. physikal. Chem.*, 1896, **20**, 19). For the second, the value of $K_2 = [H^+] . [I^-] . [HIO]/[I_2]$, according to measurements of the electrical conductivity of a saturated solution of iodine in pure water, is equal to $0{\cdot}6 \times 10^{-12}$ (Bray, *J. Amer. Chem. Soc.*, 1910, **32**, 932). The value of this constant is not nearly so trustworthy as K_1, but its accuracy is probably quite sufficient for the present purpose.

In the auto-catalytic experiments, the concentrations of the iodine and potassium iodide were for the most part 0·004 and 0·008 mol. per litre, respectively. Introducing these values into the equation for K_1, it may be shown that the ratio $[I_2]/[I^-]$ is approximately equal to 0·18. This ratio remains constant in the initial stage of the auto-catalytic change, and by reference to the equation for K_2, since $[H^+] = [HIO]$, it follows that the initial hydrogen-ion concentration due to iodine hydrolysis is given by $[H^+]_0 = \sqrt{K_2 . [I_2]/[I^-]} = 3{\cdot}3 \times 10^{-7}$. When x mols. of hydriodic acid have been produced by the acetone reaction, the concentration

$[H^+]$ of the hydrogen ions resulting from iodine hydrolysis is given by

$$[H^+] . (x + [H^+]) = (3{\cdot}3 \times 10^{-7})^2,$$

from which, if $x = 2 \times 10^{-6}$, the value obtained for $[H^+]$ is $0{\cdot}5 \times 10^{-7}$. In other words, the hydrogen ions formed by iodine hydrolysis represent only 2·5% of the total when $x = 2 \times 10^{-6}$ and may therefore without serious error be left out of account.

The foregoing analysis is necessarily antecedent to the dynamic considerations which follow. The practical outcome of it is that the total hydrogen-ion concentration throughout the initial period is determined by the concentration (x) of the auto-catalytically produced hydrogen ion. The interval for which this is not true is negligibly small.

Dynamics of the Auto-catalysed Reaction.

In accordance with the assumption that the course of the autocatalytic change is determined by the joint action of the hydrogen and hydroxyl ions, we have

$$v = v_h + v_{OH} = k_h[H^+] + k_{OH}[OH^-] \quad . \quad . \quad . \quad (1)$$

In conformity with the preceding analysis and the equation $[H^+] . [OH^-] = K_w$, equation (1) may be written

$$v = dx/dt = k_h x + k_{OH} . K_w/x \quad . \quad . \quad . \quad . \quad (2)$$

The speed of the reaction at any particular moment cannot of course be directly measured, but by integration of (2) an equation is obtained which expresses the time required for the reaction to proceed to any point represented by x. This takes the form

$$t = 1/2k_h . \log_e (k_h x^2 + k_{OH} . K_w) + \text{const.} \quad . \quad . \quad (3)$$

or, if $x = x_0$ (the true initial hydrogen-ion concentration) when $t = 0$,

$$t = 1/2k_h . \log_e (k_h x^2 + k_{OH} . K_w)/(k_h x_0^2 + k_{OH} . K_w) \quad . \quad (4)$$

By differentiation of (2) we obtain

$$dv/dx = k_h - k_{OH} . K_w/x^2 \quad . \quad . \quad . \quad . \quad . \quad (5)$$

from which it is apparent that the velocity passes through a minimum when

$$x = x_i = \sqrt{k_{OH} . K_w/k_h} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

This minimum velocity is given by

$$v_i = 2\sqrt{k_{OH} . K_w . k_h} = 2k_h . x_i \quad . \quad . \quad . \quad . \quad (7)$$

Substituting in (4) the value of $k_{OH} . K_w$ given by (6), we obtain

$$t = 1/2k_h . \log_e (x^2 + x_i^2)/(x_0^2 + x_i^2) \quad . \quad \quad . \quad (8)$$

The time required for the auto-catalytic change to proceed to any stage measured by a fall in iodine concentration equal to x may thus be calculated from (4) or (8).

If x is large and x_0 small relatively to x_i, these equations may be written

$$t = 1/2k_h \,.\, \log_e k_h x^2/k_{\text{OH}} \,.\, K_w \quad . \quad . \quad . \quad . \quad . \quad (4\text{A})$$

and

$$t = 1/2k_h \,.\, \log_e x^2/x_i^2 = 1/k_h \,.\, \log_e x/x_i \quad . \quad . \quad (8\text{A})$$

respectively. If x_i in equation (8A) is replaced by "x_0," it becomes identical with the empirical equation used by Dawson and Powis. It is thus possible to give a simple interpretation to the empirical quantity "x_0" which was introduced as a measure of the apparent initial acidity in conformity with the simple hydrogen-ion theory of catalysis. It is indeed evident that "x_0" is a measure of the hydrogen-ion concentration at the point of minimum velocity. We have therefore

$$\text{"}x_0\text{"} = x_i = \sqrt{k_{\text{OH}} \,.\, K_w/k_h} \quad . \quad . \quad . \quad . \quad (9)$$

and since k_h, K_w, and "x_0" are known, this relation may be used for the determination of k_{OH}. For "x_0" the mean value of four experiments recorded by Dawson and Powis is $2{\cdot}07 \times 10^{-5}$, and since $k_h = 4{\cdot}68 \times 10^{-4}$ * and $K_w = 10^{-14}$, we obtain

$$k_{\text{OH}} = 19{\cdot}9 \text{ (say 20)}.$$

According to this result, the activity of the hydroxyl ion is about 43,000 times that of the hydrogen ion.

An approximate evaluation of k_{OH} was attempted by Dawson and Carter from observations on the catalytic activity of mixtures of acetic acid and sodium acetate belonging to the series $(0{\cdot}2 - x)CH_3{\cdot}CO_2H + xCH_3CO_2Na$, from which $k_{\text{OH}} = 10$. There can be no doubt that very much greater weight must be attached to the value given by the auto-catalytic experiments.

In reference to equations (8) and (8A) it may be noted that the experimental constancy of "x_0" justifies the conclusion that the true initial hydrogen-ion concentration (x_0) of the acetone–iodine–iodide solution is so small compared with that corresponding with minimum velocity (x_i) that x_0^2 may be neglected in comparison with x_i^2.

From equation (8) the time required to reach the value $x = 2 \times 10^{-6}$ (see pp. 460, 461) is found to be $t = 9{\cdot}7$ minutes. This is very small compared with the time which elapses before the reaction reaches the measurable stage (not less than 3 days), and it follows

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* The coefficient given by Dawson and Powis is 0·1035 (time in hours, acetone concentration = $1M$); when time is expressed in minutes, and the coefficient is referred to 20 c.c. of acetone per litre, it has the value $4{\cdot}68 \times 10^{-4}$.

that the commencement of the reaction could be identified without appreciable error with the time at which the total hydrogen-ion concentration begins to be determined by the auto-catalytically produced hydrogen ion.

It is of interest to note that the total time of reaction given by (8) may be divided into two periods, the first (t_1) representing the time required for the attainment of minimum velocity, whilst the second (t_2) represents the period in which the velocity of the reaction is continually increasing. The values of t_1 and t_2 are given by

$$t_1 = 1/2k_h \,.\, \log_e (x_i^2 + x_i^2)/x_i^2 = 1/2k_h \,.\, \log_e 2 \quad . \quad . \quad (10)$$

$$t_2 = 1/2k_h \,.\, \log_e (x^2 + x_i^2)/2x_i^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10\text{A})$$

Substituting $k_h = 4{\cdot}68 \times 10^{-4}$, equation (10) shows that the maximum time required for the attainment of minimum velocity is 12 hrs. 20 minutes. If the p_H value of the original solution is greater than 6, the actual time will differ from the maximum time by less than 5 minutes, and the actual and maximum times may therefore be regarded as identical.

We may now proceed to make a comparison of the time observed for the reaction to proceed to a given point in the measurable stage with that calculated from the general equation (8). Provided that the point in question lies within the measured region, its actual value is not of any great importance. It may be conveniently taken as the point corresponding with $x = 10^{-3}$ ($p_H = 3$). When a 25 c.c. sample of the solution is titrated with 0·01*N*-thiosulphate, this corresponds with a fall of 5·0 c.c. in the amount of thiosulphate required, a quantity which can be measured without sensible error. The observed times are those derived from the straight-line plots of log x against t. The relevant data are given in Table I. In all the experiments, with one exception, the original solution contained 20 c.c. of acetone, 0·004 mols. of iodine and 0·008 mols. of potassium iodide per litre. In Expt. 3, the concentrations of the iodine and iodide were respectively 0·005 and 0·01. When alkali or acid was added, this is shown in column 2.

TABLE I.

Expt. No.	Substances added to the iodine–iodide solution.	$t_{obs.}$ (hrs.).	$t_{cal.}$ (hrs.).
1	None.	133	138
2	None.	135·5	138
3	None.	141	138
4	4×10^{-5} *N*-NaOH	138	138
5	2×10^{-5} *N*-HCl	121	126
6	4×10^{-5} *N*-HCl	107	112
7	8×10^{-5} *N*-HCl	88	89

The agreement between the observed and the calculated time intervals is such as to justify the conclusion that the course of the auto-catalytic change is in accordance with the views which have been put forward.

In order to facilitate the visualisation of the early stages of the reaction, the appended diagram (upper curve) shows the variation of $\log x$ with t. In the measurable stage, the relation between these is linear, but in accordance with the equation

$$d \log x/dt = k_h + k_{\mathrm{OH}} \cdot K_w/x^2 \quad . \quad . \quad . \quad . \quad (11)$$

[an alternative form of equation (2)] the slope of the initial portion of the curve increases continuously as x diminishes. The lower curve in the diagram shows the dependence of the reaction velocity on the time. In drawing this curve, corresponding values of x and t were derived from equation (8) on the assumption that x_0 is negligibly small, and the required velocities were then calculated from equation (2). The relevant numbers are shown in Table II.

FIG. 1.

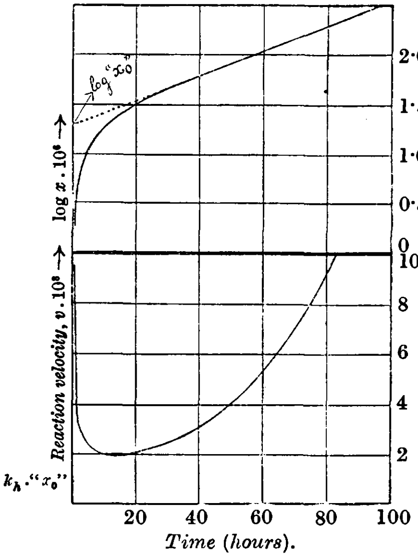

Diagram showing $\log x - t$ *and* $v - t$ *curves.*

In the region of actual measurement, the velocity–time curve is exponential and corresponds with the equation $v = k_h \,.\, x_i \,.\, e^{k_h t}$, which represents the integrated form of $dx/dt = k_h x$ when the value of x for $t = 0$ is made equal to $x_i =$ "x_0."

A further relation which characterises the velocity–time curve may be noted. When $k_{\mathrm{OH}} \,.\, K_w$ is replaced by $k_h x_i^2$, equation (11) assumes the form

$$d \log x/dt = k_h(x^2 + x_i^2)/x^2 \quad . \quad . \quad . \quad . \quad (12)$$

and from (5) we obtain

$$dv/d \log x = k_h(x^2 - x_i^2)/x \quad . \quad . \quad . \quad . \quad (13)$$

Combining these equations, there results

$$dv/dt = k_h^2(x^4 - x_i^4)/x^3 \quad . \quad . \quad . \quad . \quad (14)$$

which, for relatively large values of x, takes the form

$$dv/dt = k_h^2 x \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

which may, of course, be obtained directly from $v = k_h \,.$ "x_0" $. \, e^{k_h t}$.

TABLE II.

$x . 10_6$.	p_H.	t (mins.).	$v . 10^8$.	$x . 10^6$.	p_H.	t (mins.).	$v . 10^8$.
2	5·70	9·7	10·1	50	4·30	2055	2·74
4	5·40	39·1	5·19	100	4·00	3410	4·88
6	5·22	86·6	3·62	200	3·70	4860	9·46
8	5·10	149	2·88	500	3·30	6820	23·5
10	5·00	225	2·47	1000	3·00	8290	46·8
20·7	4·68	740	1·94				

The asymmetry of the velocity–time curve, as shown by the diagram, is at once apparent from equation (14).

Generalised Form of the Auto-catalytic Catenary.

In previous papers (Dawson and Dean, J., 1926, 2872; Dawson and Hoskins, J., 1926, 3166), it was shown that the catalytic effects resulting from the joint action of the positive and negative ions produced by the ionisation of an acid of constant concentration can be represented by a catenary curve when the reaction velocity is plotted against p_H. The curve connecting the velocity of the auto-catalytic change discussed in this paper with $\log x$ (or p_H) is of exactly the same type [compare equation (5)]. In reference to the auto-catalytic catenary, it is to be noted, however, that this represents the *actual* course of the chemical change. The movement of an index point along the catenary corresponds *de facto* with the continuously successive stages of the auto-catalysed reaction.

Following the procedure described in the derivation of the general catalytic catenary (Dawson, this vol., p. 215), and expressing the auto-catalytic reaction velocity in terms of the minimum velocity ($r = v/v_i$), and the hydrogen-ion concentration in terms of its value at the point of minimum velocity ($n = x/x_i$), it may be shown that the reduced velocity r at any stage of the reaction is given by

$$r = \tfrac{1}{2}(n + 1/n) = \tfrac{1}{2}(e^h + e^{-h}) = \cosh h \quad . \quad . \quad (16)$$

where h is the natural logarithm of the reduced hydrogen-ion concentration, n.

Since this equation contains no specific constants, it represents a generalised form of auto-catalytic catenary which should be applicable to all auto-catalysed reactions of the type under discussion. It should therefore be independent of the nature of the particular substances taking part in the change, of the temperature, and of the solvent.

Summary.

It has been shown that the phenomena associated with the auto-catalytic reaction of acetone with iodine in aqueous solution can be interpreted in terms of the joint catalytic activity of the hydrogen and hydroxyl ions.

Equations have been derived which show that the reaction velocity falls to a minimum and then increases.

The time calculated for the reaction to proceed to any given point is in close agreement with experiment.

The constant which in terms of the simple hydrogen-ion theory appears to measure the initial hydrogen-ion concentration is found to represent the actual hydrogen-ion concentration at the point of minimum velocity.

The value of this constant affords a means of determining the catalytic coefficient of the hydroxyl ion.

It is further shown that the auto-catalytic catenary obtained by plotting v against p_H can be put into a general form by expressing the velocity and hydrogen-ion concentration in terms of those values which characterise the point of minimum velocity. The actual course of the auto-catalytic change is then given by $r = \cosh h$, where r is the reduced velocity and h is the natural logarithm of the reduced hydrogen-ion concentration.

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