CCCLXXXIII.—*Acid and Salt Effects in Catalysed Reactions. Part II. The Minimum Reaction Velocities for Acid–Salt Mixtures.*

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IT was shown by Dawson and Carter (this vol., p. 2282) that the catalytic effects produced by acids, or by mixtures of acids with the corresponding salts, can be satisfactorily interpreted on the view that catalytic activity is exhibited not only by the hydrogen and hydroxyl ions, but also by the undissociated acid molecule and the acid ion. For the reaction between acetone and iodine in dilute aqueous solution, the various velocity coefficients in the general equation

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

were evaluated from experiments with acetic acid and with monochloroacetic acid.

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* Fowles gives no proof why $CuSO_4,Cu(OH)_2,H_2O$ is to be regarded as a "metastable solid phase" and $CuSO_4,2Cu(OH)_2$ as the stable phase; if the former were metastable to the latter, then it would have a greater solubility. Fowles states that both are "insoluble," but gives no data regarding the actual solubilities.

The observations made with acid–salt mixtures of the type $C\,.\,\mathrm{HA} + x\,.\,\mathrm{MA}$, in which the concentration (C) of the acid is constant, whilst that of the corresponding salt (x) is varied, show that with increasing salt concentration the reaction velocity falls, passes through a minimum, and then increases in a linear manner.

The object of this paper is to discuss the form of the velocity curve for mixtures of this type, and the relations which characterise the mixture for which the reaction velocity has a minimum value, and, further, to show that these are in close agreement with actual experiments. The observations have reference to acetic acid–sodium acetate mixtures, for which the concentration of the hydroxyl ion is so small that its effect can be entirely ignored.

In these circumstances, equation (1) may be written

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

and, on the assumption that the acid HA conforms to the requirements of the mass law, $[\mathrm{A}]^-$ may be replaced by $K(C - [\mathrm{H}]^+)/[\mathrm{H}]^+$, and $[\mathrm{HA}]$ by $C - [\mathrm{H}]^+$. Equation ($1a$) then becomes

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

the fourth term in which is of a negligibly small magnitude. Differentiating (2) we have

$$dv/d[\mathrm{H}]^+ = k_h - k_m - k_aKC/[\mathrm{H}]^{+2} \quad . \quad . \quad . \quad (3)$$

and, since $dv/d[\mathrm{H}]^+ = 0$ when the reaction velocity is a minimum, we obtain

$$[\mathrm{H}]_i^+ = \sqrt{k_aKC/(k_h - k_m)} \quad . \quad . \quad . \quad . \quad (4)$$

where $[\mathrm{H}]_i^+$ denotes the hydrogen-ion concentration of that acid–salt mixture for which the reaction velocity is a minimum. This mixture will be shown to be of considerable significance in the correlation of the experimental observations and will be designated for convenience as the *M.V.* mixture. According to the above equation, the hydrogen-ion concentration of the *M.V.* mixture depends on the catalytic coefficients of the hydrogen and acid ions, on the dissociation constant of the acid, and on its concentration.

If the value of $[\mathrm{H}]_i^+$ given by equation (4) is substituted in equation (2), we obtain the following expression for the minimum reaction velocity v_i, the last term in (2) being neglected :

$$\begin{aligned} v_i &= (k_h - k_m)\sqrt{k_aKC/(k_h - k_m)} + k_aKC\sqrt{(k_h - k_m)/k_aKC} + k_mC \\ &= 2\sqrt{(k_h - k_m)k_aKC} + k_mC \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5) \end{aligned}$$

In this equation, the first term corresponds with the sum of the velocities due to the hydrogen and acid ions, and it is evident that the *M.V.* mixture is characterised by the relation :

$$(v_h)_i = (v_a)_i = \sqrt{(k_h - k_m)k_aKC} \quad . \quad . \quad . \quad (6)$$

where $(v_h)_i$ and $(v_a)_i$ denote the partial velocities due to the hydrogen and acid ions at the inversion point which corresponds with the minimal velocity.

If each side of equation (3) is multiplied by $[H]^+$, we obtain

$$dv/d\log[H]^+ = (k_h - k_m)[H]^+ - k_aKC/[H]^+ \quad . \quad . \quad (7)$$

from which it follows that the curve obtained by plotting velocity against $\log[H]^+$ or against p_H should be symmetrical with reference to the point at which the hydrogen-ion concentration has the value $[H]^+ = \sqrt{k_aKC/(k_h - k_m)} = [H]_i^+$, *i.e.*, with reference to the point corresponding with the *M.V.* mixture.

This may be shown more clearly in the following manner. If v_1 and v_2 be the reaction velocities for mixtures of hydrogen-ion concentrations $[H]^+_1$ and $[H]^+_2$, respectively, then

$$v_1 = (k_h - k_m)[H]_1^+ + k_aKC/[H]_1^+ + k_mC$$
$$v_2 = (k_h - k_m)[H]_2^+ + k_aKC/[H]_2^+ + k_mC$$

and if $v_1 = v_2$, then

$$(k_h - k_m)[H]_1^+ + k_aKC/[H]_1^+ = (k_h - k_m)[H]_2^+ + k_aKC/[H]_2^+$$

and, on rearranging the terms, we obtain

$$[H]_1^+ \,.\, [H]_2^+ = k_aKC/(k_h - k_m) = [H]_i^{+2} \quad . \quad . \quad (8)$$

which may be written in the form

$$(p_H)_1 + (p_H)_2 = 2(p_H)_i \quad . \quad . \quad . \quad . \quad . \quad (8a)$$

According to this, the p_H value of the *M.V.* mixture is the arithmetic mean of the p_H values of any pair of solutions of the constant-acid series for which the reaction velocities are equal.

With the object of testing the relations which have been derived above, measurements have been made of the rate of interaction of iodine with acetone under the catalytic influence of mixtures belonging to the series $0{\cdot}05N\text{-}CH_3{\cdot}CO_2H + xN\text{-}CH_3{\cdot}CO_2Na$.

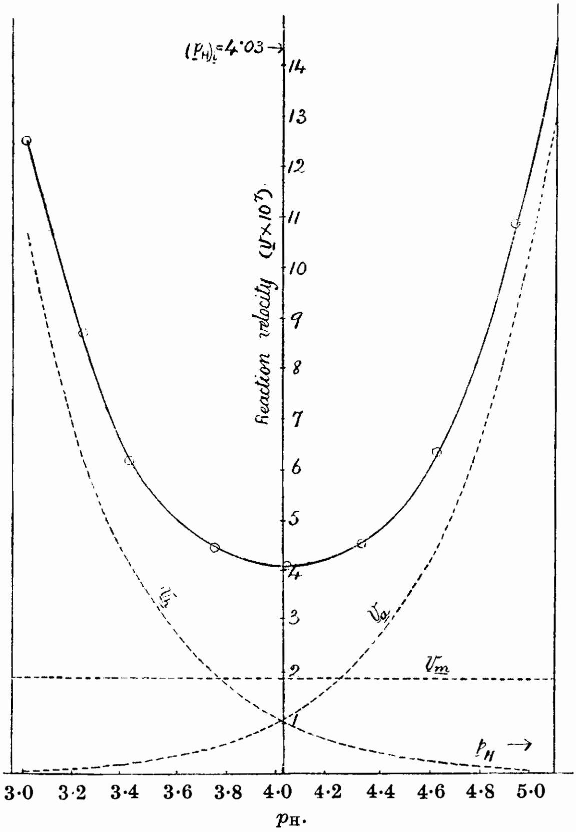
The results are represented by the continuous curve in the diagram, in which the reaction velocities obtained for the various mixtures are plotted against the p_H values, which are derived from the mass action equation :

$$p_H = \log 1/K + \log(x + [H]^+)/(C - [H]^+).$$

The dotted curves represent the calculated partial velocities due to the hydrogen ion and the acid ion respectively ; the dotted horizontal line represents the velocity due to the undissociated acid. Summation of the dotted curves corresponds with the continuous curve.

Anticipating the suggestion that the required p_H data might have been obtained by direct hydrogen-potential measurements, it may be pointed out that such is not the case. Electrometric and other thermodynamic methods in their application to electrolytes provide data which have reference to the mean activities of the positive and negative ions and not to the individual activities of these as separate entities. Furthermore, it may be added that there is substantial evidence in our results, not only for the view that salts are completely ionised, but also that catalytic activity is directly proportional to the volume concentration of the molecular or ionic catalyst concerned, and has no apparent connexion with thermodynamic activity. In support of this statement, attention may be directed to the results obtained for the catalytic activity of the acetate ion in experiments with mixtures $0 \cdot 1N\text{-}CH_3 \cdot CO_2H + xN\text{-}CH_3 \cdot CO_2Na$ at salt concentrations so large that the catalytic effect of the hydrogen ion may be left out of account.

FIG. 1.



In Table I, cols. 1 and 2 give respectively the concentration of the sodium acetate and the observed velocity; col. 3 gives the velocity diminished by that due to the undissociated acid, *i.e.*, the velocity v_a due to the acetate ion. Col. 4 gives the ratio of this velocity to the salt concentration (x) and col. 5 the ratio to αx, where α is the conductivity ratio Λ/Λ_∞. The data refer to a concentration of acetone = 20 c.c. per litre.

TABLE I.

x.	$v_{obs.} \, . \, 10^6$.	$v_a \, . \, 10^6$.	$v_a \, . \, 10^6/x$.	$v_a \, . \, 10^6/\alpha x$.
0·1	0·60	0·45	4·50	5·77
0·2	1·04	0·89	4·45	6·10
0·3	1·51	1·36	4·53	6·57
0·4	1·95	1·80	4·50	6·82
0·5	2·45	2·30	4·60	7·30
1·0	4·6	4·45	4·45	8·40

The constancy of the numbers in col. 4 affords strong support for the view that the activity of the acid ion is simply proportional to its concentration and that the salt is fully ionised.

In accordance with evidence of this kind, the concentration of the anion in the formula employed for the calculation of p_{H} has been made equal to $x + [\mathrm{H}]^+$.

On referring to the diagram, it will be observed that the velocity–p_{H} curve is quite symmetrical with respect to the point which corresponds with the *M.V.* mixture. The degree of symmetry may be judged from the data in Table II, in which the p_{H} values for pairs of solutions which are equally active as catalysts are recorded under $(p_{\mathrm{H}})_1$ and $(p_{\mathrm{H}})_2$. These values are those read from a large-scale plot on which horizontal lines were drawn for the series of reaction velocities shown under v in cols. 1 and 4. In accordance with equation (8*a*) the arithmetic mean of these p_{H} values should be equal to a constant which represents the value of $(p_{\mathrm{H}})_i$. It will be seen that the actual mean values are very nearly constant and that the p_{H} value of the *M.V.* mixture for the series $0{\cdot}05N$-$\mathrm{CH_3{\cdot}CO_2H} + xN$-$\mathrm{CH_3{\cdot}CO_2Na}$ is equal to 4·03. The value of $[\mathrm{H}]_i^+$ derived from the equation $[\mathrm{H}]_i^+ = \sqrt{k_a K C (k_h - k_m)}$, using the values of k_h, k_a, and k_m recorded by Dawson and Carter (*loc. cit.*), is $[\mathrm{H}]_i^+ = 0{\cdot}0_4967$, whence $(p_{\mathrm{H}})_i = 4{\cdot}012$ in close agreement with the value derived from the velocity curve.

TABLE II.

p_{H} Values of catalytically equivalent mixtures.

$v \, . \, 10^8$.	$(p_{\mathrm{H}})_1$.	$(p_{\mathrm{H}})_2$.	$\frac{1}{2}[(p_{\mathrm{H}})_1 + (p_{\mathrm{H}})_2]$.	$v \, . \, 10^8$.	$(p_{\mathrm{H}})_1$.	$(p_{\mathrm{H}})_2$.	$\frac{1}{2}[(p_{\mathrm{H}})_1 + (p_{\mathrm{H}})_2]$.
50	3·63	4·43	4·03	90	3·22	4·84	4·03
60	3·46	4·59	4·025	100	3·16	4·90	4·03
70	3·36	4·70	4·03	110	3·10	4·96	4·03
80	3·28	4·78	4·03	120	3·04	5·01	4·025

Amongst the pairs of catalytically equivalent solutions, the one which includes the pure acid (no salt) is of particular interest. If $[\mathrm{H}]_0^+$ and $[\mathrm{H}]_s^+$ denote the hydrogen-ion concentrations of the pure acid and of the catalytically equivalent acid–salt mixture, then according to equation (8), $[\mathrm{H}]_0^+[\mathrm{H}]_s^+ = k_aKC/(k_h - k_m)$, and from the mass law $[\mathrm{H}]_0^+ = \sqrt{K(C - [\mathrm{H}]_0^+)}$, or, approximately, $[\mathrm{H}]_0^+ = \sqrt{KC}$. Combination of these equations leads to the relation

$$[\mathrm{H}]_s^+ = k_a\sqrt{KC}/(k_h - k_m) \quad . \quad . \quad . \quad . \quad (9)$$

The value of $[\mathrm{H}]_s^+$ given by this equation for the acid–salt mixture which has the same catalytic activity as $0{\cdot}05N$-acetic acid is $0{\cdot}0_598$, whilst the value derived from the curve in the diagram is $0{\cdot}0_594$.

Since k_m is very small compared with k_h in the case of weak acids, $k_h - k_m$ may be replaced by k_h. The equations for the hydrogen-ion concentration and the reaction velocity characteristic of the *M.V.* mixture then become :

$$[\mathrm{H}]_i^+ = \sqrt{k_aKC/k_h} \text{ and } v_i = 2\sqrt{k_hk_aKC} + k_mC.$$

In postponing the discussion of relations in which the minimum reaction velocity v_i is involved, it may be pointed out that the degree of accuracy now attainable in the measurement of the reaction velocities is very much greater than that which characterised some of the earlier measurements. Further work, in which attention is being directed to the precise determination of the catalytic coefficients and the minimum reaction velocity, is in progress.

EXPERIMENTAL.

The acetone was purified by treatment with sodium iodide, and the acetic acid by the chromic acid method described by Orton and Bradfield (J., 1924, **125**, 960). The velocity measurements at 25° were made with solutions containing 50 c.c. of acetone per litre and the original concentration of the iodine was approximately $0{\cdot}003M$.

Blank experiments without acetone showed that the loss of iodine was within the limits of experimental error.

In deriving the initial velocity from the actual speed of the auto-catalysed reaction, the usual procedure was followed. Whilst in the presence of little or no salt the auto-catalytic effect is very appreciable, it may be noted that in presence of larger quantities of salt the buffer action of the latter tends to reduce very greatly the auto-catalytic effect.

The initial velocities (mols. per litre per minute) actually obtained in the experiments are recorded in Table III, which shows also the salt concentration (x), the hydrogen-ion concentration $[H]^+$, and the corresponding value of p_H.

TABLE III.

x	0·001	0·002	0·005	0·01	0·02	0·04	0·06	0·08	0·16
$[H]^+ . 10^4$......	9·53	5·79	3·85	1·78	0·916	0·463	0·232	0·116	0·058
p_H	3·02	3·24	3·41	3·75	4·04	4·33	4·63	4·94	5·24
$v . 10^6$	1·250	0·870	0·620	0·450	0·412	0·456	0·635	1·040	1·810

Summary.

The significance of the reaction velocity minimum for acid–salt mixtures of the type $C . \mathrm{HA} + x . \mathrm{MA}$ is discussed.

Equations are derived connecting the hydrogen-ion concentration and the reaction velocity characteristic of the minimum velocity (*M.V.*) mixture with the catalytic coefficients for the hydrogen ion, the acid ion, and the undissociated acid.

It is shown that, for a given acid concentration, catalytically equivalent solutions are those for which the product of the hydrogen-ion concentrations is constant and equal to the square of the hydrogen-ion concentration of the *M.V.* mixture; in other words, that the velocity–p_H curve is symmetrical with respect to the *M.V.* point.

Evidence is adduced in support of the view that salts in aqueous solution are completely ionised, and that the catalytic activity of a catalyst is proportional to its concentration and has no apparent connexion with the thermodynamic activity.

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