CX.—*Acid and Salt Effects in Catalysed Reactions. Part VII. The Tridimensional Co-ordination of Catalytic Variables. Relations between the Data for Pure Acids and the Corresponding Minimum-Velocity Mixtures.*

By HARRY MEDFORTH DAWSON.

IT was shown previously (Dawson, this vol., p. 213) that the reaction velocity (*u*) attributable to the action of the hydrogen and acid ions in solutions which contain an acid–salt mixture of the type

cHA + xMA (c constant, x variable) is connected with the hydrogen-ion concentration by an equation which may be written

$$u = u_i(n + 1/n)/2 = u_i([\mathrm{H}^+]/[\mathrm{H}^+]_i + [\mathrm{H}^+]_i/[\mathrm{H}^+])/2 = u_i(10^{\Delta p_{\mathrm{H}}} + 10^{-\Delta p_{\mathrm{H}}})/2 \quad . \quad . \quad . \quad (1)$$

where n is the reduced hydrogen-ion concentration, $[\mathrm{H}^+]_i$ and u_i are respectively the hydrogen-ion concentration and the ionic reaction velocity characteristic of the minimum-velocity mixture having the same acid concentration, and $\Delta p_{\mathrm{H}} = \log_{10} n$ is the reduced p_{H} value of the solution in question.

Since $[\mathrm{H}^+]_i$ and u_i vary with the concentration of the acid, the complete representation of the catalytic relations for all possible mixtures of an acid and its salts involves the tridimensional co-ordination of ionic reaction velocity, hydrogen-ion concentration, and concentration of the acid.

If the velocity and p_{H} co-ordinates (Dawson and Dean, J., 1926, 2872) are combined with a third on which the acid is measured directly by its molar concentration, we obtain a u–p_{H}–c catalytic model which consists essentially of a catenary surface. Sections parallel to the u–p_{H} plane give simple catenary curves. The projection on the u–c plane of the points which correspond with a fixed value of n, *i.e.*, with the same reduced hydrogen-ion concentration, gives a series of parabolic curves, as may be seen by writing equation (1) in the form

$$u = \sqrt{(k_h - k_m)k_a Kc} \,.\, (n+1/n)$$

for, according to this, the ionic reaction velocity is directly proportional to the square root of the acid concentration.

The corresponding projection on the p_{H}–c plane gives curves of an exponential type, for, since $[\mathrm{H}^+] = n[\mathrm{H}^+]_i = n\sqrt{k_a Kc/(k_h - k_m)}$, it follows that

$$p_{\mathrm{H}} = \tfrac{1}{2}\log(k_h - k_m)/k_a K - \log n - \tfrac{1}{2}\log c$$
$$= \text{constant} - \tfrac{1}{2}\log c.$$

If the co-ordinates u, p_{H}, and c are replaced by $\log u$, p_{H}, and $\log c$, the loci of points corresponding with the same reduced hydrogen-ion concentration will be represented by straight lines in both the $\log u$–$\log c$ and the p_{H}–$\log c$ planes. For the relations in the $\log u$–p_{H} plane, we obtain from equation (1)

$$\log u = \log u_i/2 + \log(n + 1/n) \quad . \quad . \quad . \quad (1\text{A})$$
$$\text{or } \log u = \log u_i + \log\cosh\log_e[\mathrm{H}^+]/[\mathrm{H}^+]_i$$

which is by no means a simple curve for hydrogen-ion concentrations which are not far removed from that which characterises the minimum-velocity mixture, *i.e.*, for values of n lying between

10 and 0·1. On the other hand, it may be noted that for larger and smaller values of n, equation (1A) becomes

$$\log u = \log u_i/2 \pm \log n \quad . \quad . \quad . \quad . \quad (1\text{B})$$

which represents a pair of straight lines, which are inclined to the p_H axis at an angle of 45° and intersect at a point for which the ordinate is represented by $\log u_i/2$. These straight lines obviously correspond with conditions in which the catalytic effect is determined almost entirely by the hydrogen ion, on the one hand, or by the acid ion, on the other.

In some recent experiments on ester hydrolysis in buffer solutions, Karlsson (*Z. anorg. Chem.*, 1925, **145**, 1) has investigated the dependence of the rate on the value of p_H. By plotting empirically the logarithm of the measured velocity coefficient against p_H, he obtains two symmetrically disposed straight lines as the locus of his experimental points provided that these are not closer to the minimum than about 0·7 p_H unit. The fact that the point of intersection of these lines does not correspond with the result indicated by equation (1B) is in all probability due to the circumstance that Karlsson has omitted to take account of the catalytic effects which are produced by the constituents of the buffer solutions other than the hydrogen and hydroxyl ions.

In view of the desirability of including the entire series of p_H values, it seems probable that the most convenient space model for the representation of catalytic relations is that afforded by the use of the co-ordinates u, p_H and c. A model of this kind is illustrated in the accompanying diagram, which has been constructed from data for c values lying between 0·01 and 0·36 N and therefore falling within the range of acid concentrations for which the catalytic effect of acetic acid–sodium acetate mixtures in the acetone–iodine reaction has been actually investigated. The u and p_H axes are in the plane of the paper and the c axis runs from front to back.

In explanation of the model, it should be pointed out that the catenary surface has a definite boundary on the left-hand side. For a given acid concentration, the catenary cross-section terminates at a point which corresponds with the salt-free solution of the acid. Such points for $c = 0{\cdot}01$ and $c = 0{\cdot}04$ are indicated on the photograph by $(u_0)_{.01}$ and $(u_0)_{.04}$, respectively. The projection of these terminal points on the u–p_H plane gives an exponential curve corresponding with the equation

$$u_0 = (k_h + k_a - k_m)10^{-p_H} \quad . \quad . \quad . \quad . \quad (2)$$

In the u–c plane, the projection is represented by a parabolic curve.

The model suggests that the catenaries become narrower as

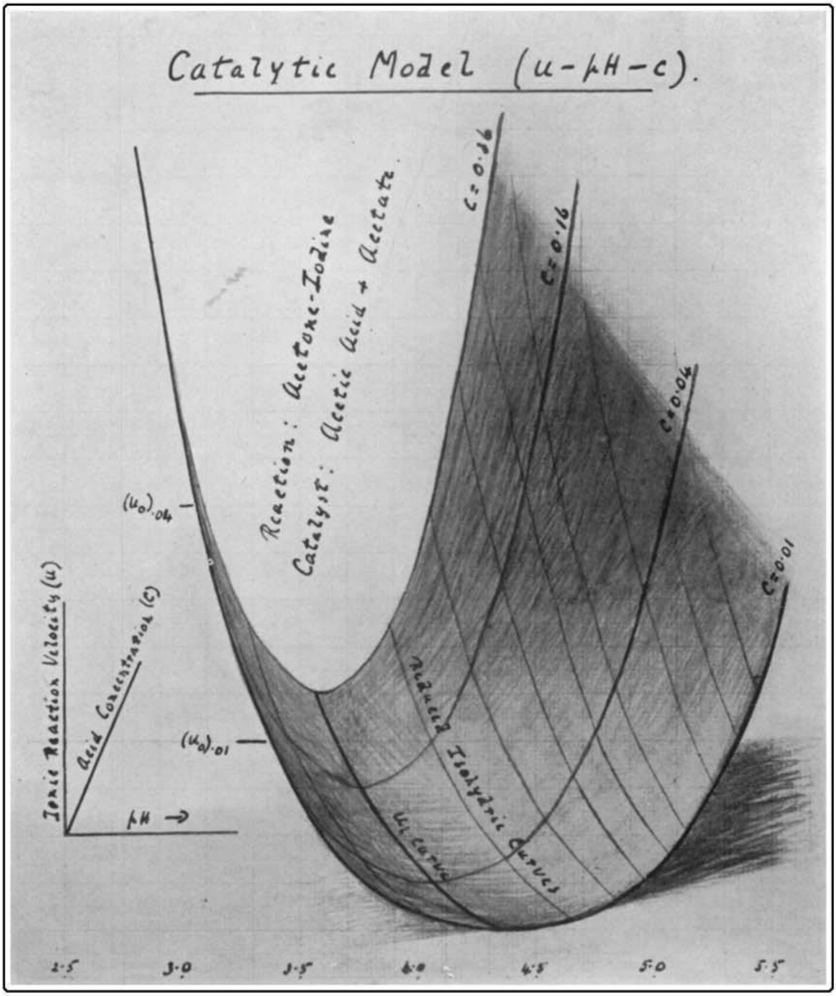

*Illustration of the connexion between catalytic activity, acid concentration, and p_H value.**

[To face page 758.]

the concentration of the acid increases. This is true in a certain sense, but it should be noted that the breadth of each catenary at the level of its terminal point on the pure acid side is the same for all catenary cross-sections in that this breadth is measured by $2 \log n_0$, where n_0 depends on the nature of the acid but is independent of its concentration. It has been shown in fact (Dawson, *loc. cit.*, p. 217) that both $n_0 = [H^+]_0/[H^+]_i$ and $r_0 = u_0/u_i$ are independent of c, and since $u_i = 2\sqrt{(k_h - k_m)k_aKc}$, it follows that $u_0 - u_i$ will increase with c and therefore that the catenaries will become extended in the vertical direction as the concentration of the acid increases. This is clearly shown in the diagram.

The lines drawn across the catenary surface from front to back represent approximately the loci of points which have the same reduced hydrogen-ion concentration (n); such points may be described as reduced isohydric points.

To convert the u–p_H–c model into a v–p_H–c model, every point would have to be raised in the vertical direction by k_mc.

Finally, it may be noted that the space model has a definite termination in the direction of the c axis and that the limiting catenary in the $c = 0$ plane is a catenary which is characteristic of the combined effects of the hydrogen and hydroxyl ions.

Connexion between the Catalytic Constants and the Quantities n_0 and r_0.

In the previous derivation of the relations connecting $n_0 = [H^+]_0/[H^+]_i$ and $r_0 = u_0/u_i$ with the catalytic constants, it was assumed that the acid is weak and that the hydrogen-ion concentration of the pure acid solution is given by $[H^+]_0 = \sqrt{Kc}$. It is now possible to remove this restriction and to show that the relations are applicable to any acid which ionises in accordance with the mass law. For the pure acid, the reaction velocity is given by

$$v_0 = k_h[H^+]_0 + k_a[A^-]_0 + k_m(c - [H^+]_0),$$

and since $[H^+]_0 = [A^-]_0$,

$$v_0 = (k_h + k_a - k_m)[H^+]_0 + k_mc.$$

The ionic reaction velocity is therefore

$$u_0 = (k_h - k_m + k_a) . [H^+]_0 = (k_h - k_m + k_a)n_0[H^+]_i,$$

and since $u_i = 2(k_h - k_m) . [H^+]_i$

we obtain $u_0/u_i = (k_h - k_m + k_a)n_0/2(k_h - k_m)$ . . . (3)

Since, further, $u_0/u_i = (n_0 + 1/n_0)/2$ . . . . . . (4)

it follows that

$$n_0(1 + 1/n_0^2) = n_0[1 + k_a/(k_h - k_m)]$$

whence $$n_0 = \sqrt{(k_h - k_m)/k_a} \quad . \quad . \quad . \quad . \quad . \quad . \qquad (5)$$

and by substitution in equation (3) or (4)

$$r_0 = u_0/u_i = (k_h - k_m + k_a)/2\sqrt{(k_h - k_m)k_a} =$$
$$[\sqrt{(k_h - k_m)/k_a} + \sqrt{k_a/(k_h - k_m)}]/2 \quad . \quad . \quad . \qquad (6)$$

Equations (5) and (6) are identical with those obtained previously on a restricted basis. They will now be examined with reference to the data which have been obtained for acetic acid as catalyst in the acetone–iodine reaction.

The relevant numbers which refer to 25° and to an acetone concentration of 20 c.c. per litre are collected in Table I. The measured velocities v_0 have been obtained by Mr. A. Key for another purpose. The values of u_0 are given by $u_0 = v_0 - k_m c$. The u_i and $[H^+]_i$ values are those recorded by Dawson and Hoskins (J., 1926, 3166), and the $[H^+]_0$ values are derived from $[H^+]_0 = \sqrt{K(c - [H^+]_0)}$ with $K = 1{\cdot}85 \times 10^{-5}$.

TABLE I.

c.	$u_0 . 10^6$.	$u_0 . 10^6$.	$u_i . 10^6$.	u_0/u_i.	$[H^+]_0 . 10^4$.	$[H^+]_i . 10^4$.	$\frac{[H^+]_0}{[H^+]_i}$.
0·01	0·216	0·201	0·041	4·90	4·22	0·47	9·0
0·05	0·512	0·437	0·089	4·91	9·52	0·93	10·2
0·1	0·762	0·612	0·123	4·97	13·5	1·32	10·2
0·2	1·170	0·870	0·164	5·30	19·2	1·90	10·1
0·5	2·10	1·35	0·270	5·00	30·4	3·05	10·0
[1·0	3·25	1·75	0·44	4·0	43·0	5·90	7·3]

Except in the case of the most concentrated acid solution, which shows very markedly the disturbing effects which have been attributed to complex-ion formation, it is apparent that the constancy of the ratios $[H^+]_0/[H^+]_i$ and u_0/u_i is as good as could possibly be expected. Taking $k_h = 465 \times 10^{-6}$, $k_a = 4{\cdot}5 \times 10^{-6}$, and $k_m = 1{\cdot}5 \times 10^{-6}$, the value of u_0/u_i according to equation (6) is 5·13, whilst the value of $[H^+]_0/[H^+]_i$ according to equation (5) is 10·15. The relations between the data for the pure acid solutions and the corresponding minimum-velocity mixtures are thus in satisfactory agreement with the theory over the concentration range $c = 0{\cdot}01$ to $c = 0{\cdot}5$. It is, of course, recognised that the nature of the equations in question is such that the data for an acid for which k_h is not so large compared with k_a or k_m would furnish a more interesting test of their validity, but such data are not yet available.

Summary.

The spatial co-ordination of catalytic variables is considered and the characteristic features of a model, constructed on the basis

of ionic reaction velocity, p_H, and acid concentration co-ordinates, are described.

A general proof is given of the equations which connect the catalytic coefficients k_h, k_a, and k_m with the hydrogen-ion concentrations and the ionic reaction velocities for solutions of the pure acids and of the corresponding minimum-velocity mixtures.

The experimental data for the catalytic effects produced by acetic acid in the acetone–iodine reaction are shown to be in close agreement with these equations over the acid concentration range $c = 0{\cdot}01$ to $c = 0{\cdot}5$.

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