

CCCII.—*Acid and Salt Effects in Catalysed Reactions.*  
*Part I.*

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IN previous papers it was shown that the catalytic properties of acids cannot be interpreted in terms of the simple hydrogen-ion theory, but that an explanation of the observed effects was possible when it was assumed that catalytic activity is exhibited by the non-ionised acid as well as by the hydrogen ion.

Observations on the rate of reaction of acetone with iodine in the presence of acetic, monochloroacetic,  $\alpha\beta$ -dibromopropionic, dichloroacetic, or hydrochloric acid (Dawson and Powis, J., 1913, **103**, 2135) showed that the activity of these acids varied with the concentration in a manner which could be interpreted quite satisfactorily in terms of this theory of dual action. The results for the different acids were, moreover, shown to be consistent with one another in that the several values derived for the activity coefficient of the hydrogen ion were identical within the limits of probable error. In support of the dual theory, further evidence of a different kind was afforded by a systematic investigation of the changes produced in the catalytic activity of monochloroacetic acid by the addition of varying quantities of the corresponding sodium salt (Dawson and Reiman, J., 1915, **107**, 1426). In the aggregate, the facts established in the experiments quoted may be said to constitute a very strong case for the view that the catalytic properties of acids are not confined to the activity of the hydrogen ion.

The study of the catalytic effects of acids in presence of the corresponding salts has been continued, and some of the results obtained are here briefly described. In view of the circumstance that the primary object of the experiments was to provide further

material for analysis in terms of the dual theory and to remove possible objections to the method of interpreting the previous results, it will readily be understood that much of our experimental material is not pre-eminently adapted for the discussion of views which have been evolved since the majority of the experiments were completed.

The observations to be described refer to the catalytic action of mixtures of weak acids and their corresponding salts on the reaction between acetone and iodine at 25°. For the correlation of the reaction velocities it is essential to know as accurately as possible the hydrogen-ion concentration of the solutions employed, and here it may be recalled that the interpretation of our previous results was made in terms of hydrogen-ion concentrations derived from ionisation constants in the case of weak acids, from conductivity data in the case of strong acids, and from the application of the mass law and the principle of isohydrity in the case of acid-salt mixtures.

The method used for acid-salt mixtures is admittedly open to criticism, and for this reason we directed our attention to mixtures of acetic acid and sodium acetate, for which electrometric hydrogen-ion concentrations are afforded by Walpole's careful measurements of hydrogen potential (J., 1914, **105**, 2501). The mixtures actually used by Walpole form two series: (1)  $(0.2 - x)N\text{-CH}_3\text{CO}_2\text{H} + xN\text{-CH}_3\text{CO}_2\text{Na}$ ; (2)  $(0.2 - x)N\text{-(CH}_3\text{CO}_2\text{H} + \text{NaCl}) + xN\text{-CH}_3\text{CO}_2\text{Na}$ . In the former, the total acetate concentration is constant, whilst the latter series is distinguished by constancy of both total acetate and total salt concentration. The combination of two such series of mixtures in catalytic experiments appeared to offer the possibility of eliminating the disturbing effects of the varying interionic forces which are necessarily associated with variations in salt concentration. Actually, however, the mutual relations exhibited by the velocity data for mixtures belonging to these two series are by no means of a simple kind, and such mixtures are not nearly so satisfactory for the elucidation of the relevant factors as are those series of mixtures in which the concentration of the acid is kept constant.

Walpole's measurements are, nevertheless, of considerable significance in connexion with our experiments on acetic acid mixtures. They have shown that the electrometric hydrogen-ion concentrations of solutions belonging to the above series lead to values for the ionisation constant,  $K_a = [\text{H}^+][\text{A}^-]/[\text{HA}]$ , which are not only independent of the salt/acid ratio over a very wide range, but are also in good agreement with the value of  $K_a$  given by the conductivity of solutions of the pure acid. In other words, it

seems probable that there is very little difference between the thermodynamic concentrations of the ionised acid in the presence of the salt and the concentrations indicated by conductivity data for solutions of the free acid. This relative freedom from the disturbing influence of ionic environment for mixtures of acetic acid and sodium acetate is, however, not peculiar to the ionised acid, for, by measurements of the partial pressure of acetic acid in aqueous solutions of various salts, McBain and Coleman (J., 1914, **105**, 1517) have shown that the changes of pressure produced by the addition of sodium acetate are very small compared with those produced, for instance, by sodium chloride.

The above facts are adduced with the object of emphasising the circumstance that the conditions attaching to the use of acetic acid-sodium acetate mixtures in the investigation of the problem of catalysis seemed to be particularly favourable, in that the volume concentrations of the hydrogen ion and of the undissociated acid are probably very little different from the thermodynamic concentrations. For the corresponding series of mixtures, in which the acetic acid is replaced by monochloroacetic acid, there is no evidence which bears on this question.

Most of the experiments we describe in this paper have reference to acid-salt mixtures in which the concentration of the acid is kept constant, whilst that of the salt is varied. For such mixtures no hydrogen potentials are available, and we have therefore undertaken these measurements with a view to the determination of the hydrogen-ion concentration of the solutions employed.

*Purification of Materials.*—*Acetone* was obtained by decomposition of the sodium iodide compound and fractionation of the product; b. p. 56.2—56.3°.

*Acetic acid.* The impurities in acetic acid which react with iodine were removed by the permanganate method (Lowry and Bousfield, J., 1911, **99**, 1432). The product, after fractionation, was again treated with permanganate and the process repeated three or four times; m. p. 16.25°.

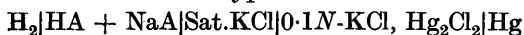
*Monochloroacetic acid.* The fraction of the commercial acid distilling at 185—186° (uncorr.) was crystallised from benzene; m. p. 60.8—60.9°.

*Sodium acetate.* The salt was recrystallised four times from conductivity water.

*Sodium monochloroacetate.* Solution prepared by neutralisation of the acid.

#### *Electrometric Measurements.*

The *E.M.F.* of cells of the type



was measured in the usual manner. The hydrogen used was passed through alkaline permanganate, saturated mercuric chloride, alkaline pyrogallol, and the solution under investigation before it entered the hydrogen vessel. The results obtained are in Tables I and II, which give the hydrogen-ion concentrations, expressed in terms of  $p_H$ , derived from the equation  $p_H = (E - 0.338)/0.0001985T$ .

TABLE I.

0.1N·CH <sub>3</sub> ·CO <sub>2</sub> H + xN·CH <sub>3</sub> CO <sub>2</sub> Na.				0.2N·CH <sub>3</sub> ·CO <sub>2</sub> H + xN·CH <sub>3</sub> ·CO <sub>2</sub> Na.		
x.	E.	T.	p <sub>H</sub> .	E.	T.	p <sub>H</sub> .
0	0.502	288°	2.87	0.492	288°	2.69
0.0048	0.534	287	3.44	0.518	288	3.15
0.0096	0.546	288	3.64	0.530	284	3.41
0.0192	0.562	286	3.94	0.544	285	3.64
0.0480	0.588	293	4.30	0.566	286	4.02
0.0961	0.604	291	4.61	0.583	287	4.30
0.1922	0.619	291	4.87	0.599	288	4.56
0.480	0.642	289	5.30	0.623	288	4.98
0.961	0.660	289	5.61	0.642	289	5.30

TABLE II.

0.05N·CH <sub>2</sub> Cl·CO <sub>2</sub> H + xN·CH <sub>2</sub> Cl·CO <sub>2</sub> Na.				0.1N·CH <sub>2</sub> Cl·CO <sub>2</sub> H + xN·CH <sub>2</sub> Cl·CO <sub>2</sub> Na.		
x.	E.	T.	p <sub>H</sub> .	E.	T.	p <sub>H</sub> .
0	0.453	286°	2.03	0.446	288°	1.89
0.01	0.466	287	2.25	0.455	291	2.03
0.02	0.475	289	2.39	0.460	287	2.14
0.04	0.484	287	2.56	0.469	288	2.29
0.10	0.505	284	2.96	0.488	289	2.62
0.20	0.517	285	3.16	0.502	287	2.88
0.50	0.530	286	3.38	0.515	286	3.12

The electrometric values of  $p_H$  recorded in the foregoing tables have been compared with the values calculated from the mass-law expression for the dissociation of the acid, *viz.*,

$$K_a = [\text{H}]^+(\alpha C' + [\text{H}]^+)/(\text{C} - [\text{H}]^+),$$

in which  $K_a$  for acetic acid =  $1.85 \times 10^{-5}$ , for chloroacetic acid in 0.05N-solutions =  $0.16 \times 10^{-2}$ , and in 0.1N-solutions =  $0.17 \times 10^{-2}$ ;  $C$  and  $C'$  are the concentrations of the acid and salt, respectively, and  $\alpha$  is the coefficient \* for the salt given by the conductivity ratio at the ionic concentration  $\alpha C'$ . In actual practice, an approximate estimation of  $[\text{H}]^+$  was made and the value of  $p_H$  calculated from the corresponding logarithmic formula

$$p_H = \log 1/K_a + \log (\alpha C' + [\text{H}]^+)/(\text{C} - [\text{H}]^+).$$

In the case of the acetic acid-sodium acetate mixtures, the calculated

\* The values of this coefficient correspond closely with the thermodynamic degrees of dissociation recorded by Lewis and Randall for a uni-univalent electrolyte.

values of  $p_H$  agree very closely with those derived from the hydrogen-potential measurements. The difference between them is less than 0.03 when the salt concentration is not greater than 0.2*N*. For the two most concentrated solutions, the divergence is greater, but this is of no consequence in so far as the velocity measurements are concerned, for in these concentrated salt solutions (0.5 and 1.0*N*) the hydrogen-ion concentration is so small that its catalytic effect is negligible. Generally speaking, the results justify the belief that for acetic acid mixtures, hydrogen-ion concentrations of the desired degree of accuracy may be obtained either from hydrogen-potential measurements or by the use of the mass-law expression.

For mixtures of chloroacetic acid and sodium chloroacetate, the agreement between the electrometric and mass-law values of  $p_H$  is not nearly so good as for the acetate mixtures. The curves obtained by plotting the two series of  $p_H$  values against the logarithm of the salt concentration ( $x$ ) are approximately linear when  $x$  is not too small. For salt concentrations less than 0.2*N*, the difference between the two curves does not exceed about 0.1 unit on the  $p_H$  scale. Since, however, differences in  $p_H$  are a measure of relative differences in hydrogen-ion concentration, the magnitude of the divergence between the two sets of values may be more appropriately shown by a comparison of the degrees of ionisation. In Table III, the percentage degrees of ionisation of the acid corresponding with the hydrogen-potential measurements are recorded under  $\alpha_1$ , whilst those derived from the mass-law are given under  $\alpha_2$ .

TABLE III.

*Ionisation of Chloroacetic Acid in Admixture with Sodium Chloroacetate ( $xN$ ).*

	$x$ .....	0.01	0.02	0.03	0.05	0.1	0.2	0.5
0.05 <i>N</i> -Acid	$\alpha_1$ .....	11.25	8.15	6.60	4.60	2.45	1.32	0.59
	$\alpha_2$ .....	10.35	7.10	5.35	3.60	1.95	1.03	0.46
0.10 <i>N</i> -Acid	$\alpha_1$ .....	9.35	7.25	5.75	4.15	2.50	1.41	0.69
	$\alpha_2$ .....	8.85	6.65	5.25	3.65	2.02	1.09	0.50

For the purpose to which the data in question are to be applied the differences between the two sets of ionisation values are not of serious moment. The series of electrometric values serves to confirm the general accuracy of the mass-law values, but if a distinction is to be made, we prefer the latter on the ground that the hydrogen-potential measurements possibly involve a diffusion potential of unknown magnitude.

#### *Measurements of Reaction Velocity.*

The procedure followed in the determination of the initial velocity of the reaction between acetone and iodine was essentially the same

as that described by Dawson and Powis (*loc. cit.*). The concentration of the acetone was throughout 20 c.c. per litre (0.272*M*), the iodine about 0.005*M*, and the temperature 25°.

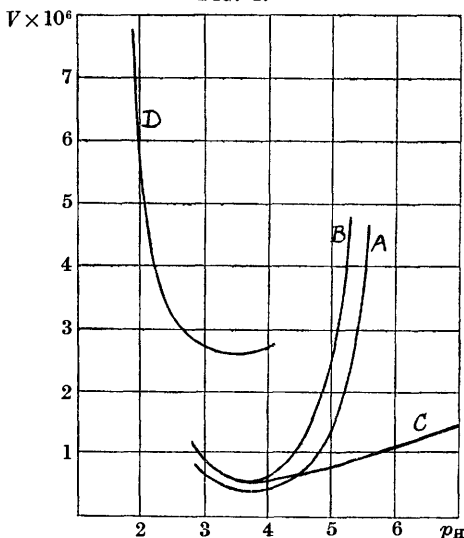
The general character of the results obtained may be described by reference to the data for catalysing mixtures represented by the general formula  $aN\text{-CH}_3\cdot\text{CO}_2\text{H} + xN\text{-CH}_3\cdot\text{CO}_2\text{Na}$ , where  $a$  is constant and  $x$  variable. As the hydrogen-ion concentration is reduced by continual increase in the proportion of sodium salt, the initial velocity falls, rapidly at first, then less and less quickly, passes through a minimum and then increases continuously, until, in presence of 1.0*N*-sodium acetate, the velocity is approximately five times as great as in the absence of salt. For salt concentrations which are well above those which correspond with the minimum velocity, the relation between the velocity and the salt concentration is almost exactly linear. In this region, the catalytic effect of the hydrogen ion is negligibly small and the observed reaction velocity must be attributed to agencies other than the hydrogen ion. If the straight line is extrapolated to  $x = 0$ , catalytic effects due to the added salt are eliminated and the residual velocity should therefore be attributable to the catalytic action of the undissociated acid. The residual velocity ( $v_r$ ) for mixtures of the series  $0.1N\text{-CH}_3\cdot\text{CO}_2\text{H} + xN\text{-CH}_3\cdot\text{CO}_2\text{Na}$  is  $0.15 \times 10^{-6}$  mol. per litre per minute; for the series  $0.2N\text{-CH}_3\cdot\text{CO}_2\text{H} + xN\text{-CH}_3\cdot\text{CO}_2\text{Na}$ , the residual velocity is  $0.30 \times 10^{-6}$  mol. per litre per minute. In other words, the residual velocity is proportional to the concentration of the acetic acid ( $a$ ) and the value of the coefficient in the equation  $v_r = k \cdot a$  is  $1.5 \times 10^{-6}$  mol. per litre per minute, which is thus identical with the value of  $k_m$  for the undissociated acid obtained from the previous experiments with acetic acid in the absence of the corresponding salt (Dawson and Powis, *loc. cit.*, p. 2143).

When the data for the experiments with mixtures of chloroacetic acid and sodium chloroacetate corresponding with the formula  $0.1N\text{-CH}_2\text{Cl}\cdot\text{CO}_2\text{H} + xN\text{-CH}_2\text{Cl}\cdot\text{CO}_2\text{Na}$  are examined in the same way, exactly similar relations are found. The residual velocity obtained by extrapolation is  $2.4 \times 10^{-6}$ , which gives for  $k_m$  the value  $24 \times 10^{-6}$ . This again is identical, within the limits of error, with the value  $k_m = 24.5 \times 10^{-6}$  derived by Dawson and Powis for the coefficient representing the catalytic activity of undissociated monochloroacetic acid from observations on the catalysing power of the free acid at a series of different concentrations. In order to illustrate diagrammatically the nature of our results in such a way as to include not only the entire range of salt concentrations, but also the results which have been obtained for mixtures in which the acid concentrations, as well as those in which the total acetate

concentration was constant, it is advantageous to plot the observed velocity against  $p_H$ . Such curves are shown in the diagram. They show that the reaction velocity is smallest in the neighbourhood of  $p_H = 3.8$  when the reaction is catalysed by the acetic acid mixtures and at about  $p_H = 3.5$  when catalysed by the chloroacetic acid mixtures.

The catalytic activity of the undissociated acid has thus been demonstrated by two independent methods. In the first of these, the evidence is based on velocity data for solutions which contain no salt and for which the hydrogen-ion concentration is derived

FIG. 1.



- A.  $0.1N\text{-CH}_3\text{-CO}_2\text{H} + xN\text{-CH}_3\text{-CO}_2\text{Na}$ . B.  $0.2N\text{-CH}_3\text{-CO}_2\text{H} + xN\text{-CH}_3\text{-CO}_2\text{Na}$ .  
 C.  $(0.2 \cdot x)N\text{-CH}_3\text{-CO}_2\text{H} + xN\text{-CH}_3\text{-CO}_2\text{Na}$ .  
 D.  $0.1N\text{-CH}_2\text{Cl-CO}_2\text{H} + xN\text{-CH}_2\text{Cl-CO}_2\text{Na}$ .

from the electrical conductance. The second method does not involve any knowledge of the degree of ionisation of the acid. It is merely assumed that the ionisation of the weak acid is reduced to a negligible value by the addition of a sufficient quantity of the corresponding salt and that the velocity, over and above that which is attributable to the added salt, represents the effect which is due to the undissociated acid. The identity of the values of  $k_m$  obtained by these independent methods affords a very remarkable confirmation of the view that catalytic activity must be ascribed to the acid in its undissociated form.

At higher salt concentrations, as already pointed out, the con-

nexion between the observed reaction velocity,  $v$ , and the concentration ( $x$ ) of the added salt may be accurately represented by the linear formula

$$v = v_r + k'x$$

in which  $v_r = k_m \cdot a$  represents the residual velocity and  $k'$  is a constant which measures the catalytic activity of the salt. The magnitude of  $k'$ , given by the slope of the linear portions of the velocity curves, depends to a large extent on the nature of the acid anion. It is very much larger for the acetate ( $k' = 4.5 \times 10^{-6}$ ) than for the chloroacetate ( $k' = 0.12 \times 10^{-6}$ ).

If we accept the view that the salts are completely ionised, it would appear that the active catalytic agents concerned are the respective anions, and that the reaction which is characterised by the coefficient  $k'$  is closely similar to the catalysed decomposition of nitroamide recently studied by Brönsted and Pedersen (*Z. physikal. Chem.*, 1924, **108**, 185). For both reactions, the catalytic activity of the acid ion increases as the dissociation constant of the corresponding acid diminishes. Such a relation would lead us to expect that the hydroxyl ion would be a very active catalyst for the acetone-iodine reaction, and there is direct evidence to support this view.

In conformity with the actual development of the theoretical interpretation we shall, however, confine our attention to experimental conditions, in which the catalytic effect of the hydroxyl ion, by reason of its very low concentration, may be left out of account. With this proviso, the results we have obtained lead to the conclusion that the observed velocity of reaction represents the sum of the effects due respectively to the catalytic action of the hydrogen ion, the undissociated acid, and the acid ion.

The equation for the observed velocity may therefore be written :

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

in which  $k_h$ ,  $k_m$ , and  $k_a$  represent respectively the catalytic coefficients for the hydrogen ion, the acid molecule, and the acid ion. The relative importance of the three partial velocities depends on the concentrations of the respective catalytic agents and on the relative magnitudes of the corresponding coefficients. By the continued addition of salt to a given solution of the free acid, it may be possible to realise successively conditions in which the dominant catalyst is either the hydrogen ion, the undissociated acid, or the acid anion.

In the case of acetic acid, for which the coefficients ( $\times 10^6$ ) have the values  $k_h = 442$ ,  $k_m = 1.5$ , and  $k_a = 4.5$ , this has been actually accomplished, as may be seen from an inspection of Table IV, in



which the relevant data for mixtures  $0.1N\text{-CH}_3\text{-CO}_2\text{H} + xN\text{-CH}_3\text{-CO}_2\text{Na}$  are set out in detail. Col. 1 gives the salt concentration; col. 2 the concentration of the hydrogen ion  $[\text{H}]^+$ , from which the concentrations of the undissociated acid,  $[\text{HA}] = 0.1 - [\text{H}]^+$ , and of the acid ion,  $[\text{A}]^- = x + [\text{H}]^+$ , may be derived; cols. 3, 4, and 5, the partial velocities  $v_h$ ,  $v_m$ , and  $v_a$  due to the hydrogen ion, undissociated acid, and acid ion, respectively; col. 6 gives the total velocity calculated from equation (1), and col. 7 gives the velocity actually observed.†

TABLE IV.

Catalyst:  $0.1N\text{-CH}_3\text{-CO}_2\text{H} + xN\text{-CH}_3\text{-CO}_2\text{Na}$ .

$x$ .	$[\text{H}]^+ \cdot 10^4$ .	$v_h \cdot 10^6$ .	$v_m \cdot 10^6$ .	$v_a \cdot 10^6$ .	$v_{\text{cal.}} \cdot 10^6$ .	$v_{\text{obs.}} \cdot 10^6$ .
0	13.5	0.596	0.148	0.006	0.75	0.75
0.005	3.67	0.162	0.149	0.024	0.335	0.36
0.010	2.00	0.088	0.150	0.046	0.285	0.31
0.020	1.06	0.047	0.150	0.090	0.29	0.31
0.025	0.86	0.038	0.150	0.113	0.30	0.32
0.050	0.45	0.020	0.150	0.225	0.395	0.405
0.1	0.24	0.010	0.150	0.450	0.61	0.60
0.2	0.13	0.006	0.150	0.900	1.055	1.04
0.3	0.09	0.004	0.150	1.350	1.505	1.51
0.4*	0.07	0.003	0.150	1.800	1.95	1.95
0.5*	0.06	0.002	0.150	2.250	2.40	2.45
1.0*	0.03	0.001	0.150	4.500	4.65	4.6

Examination of the table shows that there is close agreement between the calculated and observed reaction velocities over the entire range of acid-salt mixtures. At low salt concentrations, the chief catalyst is the hydrogen ion, but between 0.01 and 0.025*N* concentrations the largest effect is produced by the undissociated acid, and at still higher concentrations the dominant part is played by the acetate ion.

The results for a similar series of mixtures with acid of 0.2*N* concentration are given in Table V in abbreviated form, the partial velocities being omitted. The agreement between the calculated and observed velocities is very similar to that in the previous table.

TABLE V.

 $0.2N\text{-CH}_3\text{-CO}_2\text{H} + xN\text{-CH}_3\text{-CO}_2\text{Na}$ .

$x$ .....	0	0.004	0.010	0.020	0.050	0.10	0.20	1.0*
$[\text{H}]^+ \cdot 10^4$ ...	19.2	8.13	3.92	2.10	0.88	0.47	0.25	0.07
$v_{\text{cal.}} \cdot 10^6$ ...	1.15	0.68	0.52	0.485	0.565	0.77	1.21	4.80
$v_{\text{obs.}} \cdot 10^6$ ...	1.16	0.65	0.50	0.46	0.545	0.775	1.27	4.8

Attention may now be directed to the results of experiments

† The difference between the calculated values given by equation (1) and the more general equation (2) (considered later) increases from  $0.01 \times 10^{-6}$  for  $x = 0.2$  to  $0.05 \times 10^{-6}$  for  $x = 1.0$ . For the sake of simplicity we have considered it preferable to use the original simple form of our equation for this type of acid-salt mixture.

with catalytic mixtures corresponding with the series  $(0.2 - x)N\text{-CH}_3\cdot\text{CO}_2\text{H} + xN\text{-CH}_3\cdot\text{CO}_2\text{Na}$ , in which the total acetate concentration is constant. For the mixtures in this series, the hydrogen-ion concentration is that given by Walpole's hydrogen-potential measurements. In the case of the free acid, the value has been derived from  $K_a = 1.85 \times 10^{-5}$ .

As the ratio of salt to acid in this series of mixtures increases, the values of  $[\text{H}]^+$  and  $[\text{HA}]$  diminish continuously and equation (1) would suggest that the reaction velocity should eventually rise to a maximum limiting value given by  $v = k_a[\text{A}]^- = 4.5 \times 10^{-6} \times 0.2 = 0.9 \times 10^{-6}$ . This, however, is not the case. For the last member of the series  $(0.002N\text{-CH}_3\cdot\text{CO}_2\text{H} + 0.198N\text{-CH}_3\cdot\text{CO}_2\text{Na})$  the observed value exceeds this limit by 40%. Moreover, there is a systematic divergence between the observed and calculated velocities for solutions of low acid concentrations, in that the difference between them increases continuously as the concentration of the acid is reduced.

For the solutions in question, the hydrogen-ion concentration is very small, and since the product  $[\text{H}]^+ \cdot [\text{OH}]^-$  is constant, it would seem that conditions have been reached in which the concentration of the hydroxyl ion is such that its catalytic effect must be taken into account. If the velocities for the mixtures containing 0.01, 0.005, and 0.002*N*-acid are calculated from equation (1) and subtracted from the observed velocities, the differences should represent the partial velocities due to the hydroxyl ion in the three experiments concerned. From these numbers the catalytic coefficient for the hydroxyl ion may be derived from the equation  $v_{\text{OH}} = k_{\text{OH}} \cdot [\text{OH}]^- = k_{\text{OH}} \cdot K_w / [\text{H}]^+$ , in which  $K_w$  is the ionisation constant for water  $= 1 \times 10^{-14}$ . The numbers obtained in this way for the three acid-salt mixtures in question are respectively 9.0, 11.5 and 9.2, giving as a mean  $k_{\text{OH}} = 10$ .

The concordance between the separate values is as good as could possibly be expected and is obviously quite consistent with the view that such mixtures provide conditions in which the hydroxyl ion takes a measurable part in the catalysis of the reaction. In order to include the range of conditions which are afforded by mixtures in which the acid concentration is small and the ratio of salt to acid large, it is evident that equation (1) must be extended to include a term corresponding with the hydroxyl ion. The complete equation thus becomes

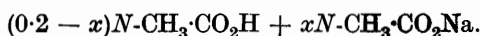
$$\begin{aligned} v &= v_h + v_m + v_a + v_{\text{OH}} \\ &= k_h[\text{H}]^+ + k_m[\text{HA}] + k_a[\text{A}]^- + k_{\text{OH}}[\text{OH}]^- \quad (2), \end{aligned}$$

in which the coefficient  $k_{\text{OH}}$  is very much greater than any of the

other three. The ratio  $k_{\text{OH}}/k_h$  is given by  $10/(442 \times 10^{-6})$  and, according to this, the catalytic activity of the hydroxyl ion is more than 20,000 times as great as that of the hydrogen ion.

Table VI affords a comparison of the velocities calculated from equation (2) with those actually observed. The arrangement is similar to that adopted in Table IV.

TABLE VI.



$x$ .	$[\text{H}]^+ \times 10^4$ .	$v_h \times 10^6$ .	$v_m \times 10^6$ .	$v_a \times 10^6$ .	$v_{\text{OH}} \times 10^6$ .	$v \times 10^6$ (calc.).	$v \times 10^6$ (obs.).
0	19.2	0.848	0.297	0.009	nil	1.15	1.16
0.015	2.51	0.110	0.278	0.069	nil	0.455	0.46
0.024	1.58	0.070	0.264	0.109	nil	0.445	0.44
0.036	1.00	0.044	0.246	0.162	nil	0.45	0.46
0.053	0.63	0.028	0.221	0.239	0.001	0.49	0.495
0.074	0.40	0.018	0.189	0.333	0.002	0.54	0.54
0.098	0.25	0.011	0.153	0.441	0.004	0.61	0.59
0.141	0.11	0.004	0.089	0.635	0.010	0.74	0.74
0.158	0.063	0.002	0.063	0.711	0.016	0.795	0.80
0.171	0.041	0.002	0.045	0.770	0.024	0.84	0.835
0.181	0.025	0.001	0.030	0.815	0.040	0.885	0.88
0.190*	0.013	nil	0.015	0.855	0.077	0.945	0.94
0.195*	0.0062	nil	0.008	0.878	0.160	1.045	1.07
0.198*	0.0025	nil	0.003	0.891	0.400	1.295	1.26

The agreement between the calculated and observed reaction velocities is clearly such as to warrant the conclusion that the catalysis of the reaction takes place in accordance with equation (2). In view of the relations  $K_a = [\text{H}]^+[\text{A}]^-/[\text{HA}]$  and  $K_w = [\text{H}]^+[\text{OH}]^-$ , this equation may be written in the form

$$v = k_h[\text{H}]^+ + k_m \cdot [\text{HA}] + k_a \cdot K_a[\text{HA}]/[\text{H}]^+ + k_{\text{OH}} \cdot K_w/[\text{H}]^+ \quad (3),$$

in which the only variable parameters are the concentrations of hydrogen ions and of undissociated acid. Since the last two terms in equation (3) both involve the concentration of the hydrogen ion to the inverse first power, it is apparent that series of acid-salt mixtures, in which the concentration of the acid is kept constant, do not afford the appropriate conditions for distinguishing experimentally between the catalytic effects which are produced by the acid ion and the hydroxyl ion, respectively. This is exactly in accordance with our experience.

In reference to the very wide variation of the conditions under which the velocity of the reaction has been measured by the use of acetic acid-salt mixtures, it may be pointed out that the final products are not independent of the hydrogen-ion concentration of the solution. In those experiments in Tables IV, V, and VI which are distinguished by a star in the salt column ( $x^*$ ), it was observed that iodoform was formed. Although we do not propose to discuss here the mechanism of the reaction between acetone and iodine

apart from the catalytic effects which are associated with it, it may be stated that low values of hydrogen-ion concentration undoubtedly provide conditions which facilitate the progress of those reactions which succeed the slow reaction the velocity of which has been measured, and lead ultimately to the separation of iodoform. The disturbing effect of these after-reactions is, we believe, almost entirely eliminated by our experimental procedure, in which the initial velocity of the slow primary reaction is measured. For this reason, we do not propose to discuss here certain observations which have reference to the formation of iodoform as the final product of the reaction.

It should, however, be stated that the formation of hydriodic acid as a product associated with the primary reaction constitutes a factor which of necessity tends to complicate the determination of the initial velocity when the proportion of acid to salt becomes very small. This ratio is 1 : 100 in the last recorded experiment in Table VI, and although it may be possible to make measurements with solutions which contain a still smaller proportion of acid, it will be readily understood that such measurements would necessitate special precautions in the experimental conditions to ensure that the value of the ratio  $[H]^+ / [OH]^-$  is not unduly disturbed in the very earliest stage of the reaction by the hydriodic acid which is formed.

In Table VII are recorded the data for mixtures of monochloroacetic acid and sodium monochloroacetate. Some of these measurements were made by Dawson and Reiman, and for the observations at high salt-concentrations we are indebted to Mr. C. R. Hoskins. Since chloroacetic is a much stronger acid than acetic, there are no effects which are attributable to the hydroxyl ion. The velocities of reaction have been calculated from the equation

$$v = 442 \times 10^{-6}[H]^+ + 24 \times 10^{-6}[HA] + 0.12 \times 10^{-6}[A]^-$$

TABLE VII.

$x$ .	0.05N-CH <sub>2</sub> Cl-CO <sub>2</sub> H + $x$ N-CH <sub>2</sub> Cl-CO <sub>2</sub> Na.			0.1N-CH <sub>2</sub> Cl-CO <sub>2</sub> H + $x$ N-CH <sub>2</sub> Cl-CO <sub>2</sub> Na.		
	$[H]^+ \times 10^2$ .	$v \times 10^6$ (calc.).	$v \times 10^6$ (obs.).	$[H]^+ \times 10^2$ .	$v \times 10^6$ (calc.).	$v \times 10^6$ (obs.).
0	0.82	4.63	4.90	1.22	7.50	7.75
0.01	0.518	3.37	3.38	0.884	6.10	6.18
0.02	0.356	2.69	2.70	0.667	5.19	5.12
0.03	0.268	2.32	2.29	0.523	4.59	4.52
0.05	0.180	1.96	1.84	0.363	3.92	3.77
0.10	0.098	1.62	1.50	0.202	3.26	3.04
0.20	0.0515	1.44	1.34	0.109	2.88	2.64
0.50	0.021	1.35	1.35	0.045	2.65	2.65
0.896				0.023	2.60	2.53
1.57				0.015	2.63	2.64
2.13				0.010	2.70	2.69
3.20				0.008	2.82	2.80

in which, in accordance with the assumption of complete ionisation of the salt,  $[A]^- = x + [H]^+$  where  $x$  is the stoichiometric salt concentration. The values of  $[H]^+$  are based on the mass-law formula with  $K_a = 0.16 \times 10^{-2}$  for the 0.05*N*-acid series, and  $K_a = 0.17 \times 10^{-2}$  for the 0.1*N*-acid series.

In regard to the variations in the effects of the three catalyts the chloroacetic acid mixtures are not quite so interesting as the acetic acid mixtures, but there can be little doubt that the relations involved are of the same kind.

By the detailed study of the catalytic properties of mixtures of a weak acid with its corresponding salt, it has thus been possible to show that catalytic effects must be attributed to the hydrogen ion, the acid molecule, and the acid ion. In the absence of salt, the relations will, of course, be the same, and the relative importance of the catalytic effects due to the ions and molecules respectively will depend on the concentration of the acid. By the addition of salt, the relative magnitudes of the effects can be altered within wider limits for the purpose of actual measurement and conditions may actually be realised in which either of them has the dominant rôle. When the acid is weak and the ratio of salt to acid becomes sufficiently great, a fourth catalytic effect, namely, that due to the hydroxyl ion, comes into play.

Of the molecular and ionic entities which are commonly supposed to be present in aqueous solutions of mixtures of acids and their salts, *viz.*,  $H^+$ ,  $M^+$ ,  $A^-$ ,  $OH^-$ ,  $HA$ , and  $H_2O$ , four have been found to act as catalyts in the acetone-iodine reaction. There is no evidence that the metallic cation has any measurable activity, but our experiments have not been specifically designed to detect any very small effect of this kind. We also see no reason for attributing activity to the water molecule. The fact that the activity of the undissociated acid falls rapidly as the tendency to ionise diminishes—for acetic acid it is only about  $\frac{1}{16}$  as large as for monochloroacetic acid—would suggest that the activity of the water molecule is very small.

It is extremely probable that the relative magnitudes of the various catalytic coefficients will vary widely with the nature of the catalysed reaction. In this connexion it may be noted that in the reaction between monochloroacetone and iodine, which appears to be closely similar to the reaction we have studied, the catalytic coefficients for the hydrogen ion and the undissociated acetic acid are much smaller in comparison with the coefficient for the acetate ion than is the case for the acetone reaction. On the other hand, the measurements of Arrhenius (*Z. physikal. Chem.*, 1890, 5, 1) on the inversion of sucrose would seem to show that the

catalytic activities of the undissociated acid and of the acetate ion are exceedingly small in comparison with that of the hydrogen ion.

The possibility of realising conditions in which, by adjustment of the acid-salt ratio, the chief catalytic effect is due to the hydrogen ion, the undissociated molecule, or the acid ion, depends on the dissociation constant of the acid and on the absolute concentration.

By the addition of sodium chloride or other catalytically inert salt to the catalysing mixture of acetic acid and sodium acetate, changes in the velocity of reaction are produced which depend on the composition of the mixture, *i.e.*, on the relative magnitudes of the effects which are attributable to the positive ion, the negative ion and the undissociated molecule respectively.

In conclusion, it may be noted that measurements of the velocity of the acetone reaction with strong acids as catalysts (compare Dawson and Crann, J., 1916, 109, 1262) have been previously interpreted in a manner analogous to that adopted for the weak acids, the conductivity ratio  $\lambda/\lambda_{\infty}$  being used as a measure of the hydrogen-ion concentration. The experimental data suggested that the undissociated molecules of these strong acids are more active catalysts than the hydrogen ion ( $k_m > k_n$ ). Accepting the view that such acids are completely ionised, the previous interpretation of the velocity data can no longer be maintained. It seems possible that the phenomena observed in the action of the strong acids may be due, not to effects which are directly comparable with those described here for the weaker acids, but to changes in the activity of the hydrogen ion which are attributable to changes in environment such as are responsible for the difference between thermodynamic and volume concentrations. So far as the catalytic experiments described in this paper are concerned, the question of distinguishing between the activity and the stoichiometric concentration of the catalytically active agents does not appear to be of primary importance, although it is by no means suggested that such distinction can be always ignored.

In accordance with previous practice, the values of the velocity coefficients recorded in this paper refer to a concentration of 20 c.c. of acetone per litre. To express them in terms of 1 g.-mol. of acetone per litre, the numbers in question must be multiplied by  $1/0.272 = 3.67$ .

#### *General Conclusions.*

The phenomena observed in the catalysis of a reaction in aqueous solutions of weak acids and mixtures of these with the corresponding salts lead to the conclusion that catalytic effects are attributable to the hydrogen ion, the undissociated acid, the acid ion, and the hydroxyl ion.

The general equation, in terms of which the observed reaction velocities can be expressed, is of the form :

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

in which  $k_h$ ,  $k_m$ ,  $k_a$  and  $k_{OH}$  are the respective velocity coefficients.

By suitable adjustment of the proportions in which acetic acid is mixed with sodium acetate, any one of the four catalysts may be made to play the dominant rôle as catalytic agent. Both for acetic and monochloroacetic acids, the values obtained for the catalytic coefficient of the undissociated acid by two entirely independent methods are identical within the limits of experimental error.

The relative values of the coefficients  $k_h$ ,  $k_a$ , and  $k_m$  vary widely with the strength of the acid as measured by its dissociation constant.

In view of the composite nature of the catalytic phenomena, the effects produced by the addition of a foreign, catalytically inert, salt will depend on the nature of the dominant catalyst and such effects will not in general be directly comparable with one another.

The electrometric values of the hydrogen-ion concentration of solutions containing mixtures of chloroacetic acid and its sodium salt are in satisfactory agreement with those derived from the mass law. The agreement is, however, not so close as that shown by mixtures of acetic acid and sodium acetate.

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