CCCLXVIII.—*The Activity Theory of Reaction Velocity. The Interaction of* N-*Chloroacetanilide and Hydrochloric Acid.*

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The effect of electrolytes on the speed of reactions catalysed by acids is interpreted at the present time along two lines. On one theory, the catalyst is the hydrogen ion, its catalytic activity being proportional either to its thermodynamic activity (Harned, *J. Amer. Chem. Soc.*, 1918, **40**, 1461), which is affected by the presence of salts, or to its concentration (Brönsted and Pedersen, *Z. physikal. Chem.*, 1924, **108**, 185) as calculated from the concentration ionisation constant, which changes with the ionic strength (Arrhenius, *Z. physikal. Chem.*, 1899, **31**, 197; Brönsted, J., 1921, **119**, 574). The other theory, which has recently been extended by Dawson (Dawson and Carter, J., 1926, 2282 *et seq.*), attributes catalytic activities to the undissociated molecule and to the acid anion, as well as to the hydrogen ion. On the latter theory, the catalytic activities of the various ions are assumed to be proportional to their concentrations. It may be noted, however, that Dawson, in calculating his hydrogen-ion concentrations in acetic acid–acetate mixtures, uses a constant value for the ionisation constant of acetic acid in which he substitutes for the acid and anion concentrations (Dawson and Dean, *ibid.*, p. 2876); no allowance is made for the increase of the concentration ionisation constant (some 200%: Brönsted, *loc. cit.*; compare K_w, Harned, *J. Amer. Chem. Soc.*, 1925, **47**, 930) as the salt concentration is increased from 0 to $1{\cdot}0N$.

A factor very generally neglected in the study of acid catalysis is the effect the electrolyte may have on the active mass of the non-electrolyte, as demonstrated by the experiments of Jones and Lapworth (J., 1911, **99**, 1427), who found that the equilibrium constant of the reaction $\mathrm{EtOH} + \mathrm{CH_3{\cdot}CO_2H} \rightleftharpoons \mathrm{CH_3{\cdot}CO_2Et} + \mathrm{H_2O}$ changes by more than 100% as the amount of the catalyst, hydrogen chloride, is altered. Since the catalyst does not appear in the equilibrium constant, the velocity coefficients k and k' in the equations, $v = kC_{\text{catalyst}}C_{\text{alcohol}}C_{\text{acid}}$ and $v' = k'C_{\text{catalyst}}C_{\text{ester}}C_{\text{water}}$, must vary as the catalyst concentration changes. The general procedure has been to regard k as strictly constant, and to deduce the effective concentration of the catalyst on this assumption. It is obvious that this procedure may lead to erroneous theories. If deductions are to be made as to the effective concentrations of the catalyst, k, and therefore k/k', must be strictly constant. The equilibrium constant of a system must therefore be expressed in such a way as to be independent of the changes in medium caused by the addition of neutral salts, and the velocity equation must be modified so as to be in harmony with this equilibrium constant. An equilibrium constant of this nature was proposed by van 't Hoff (Lectures, 1898), concentrations being replaced by the ratio of concentration to the limiting solubility in the particular medium. Replacement of concentrations by this ratio in the velocity equation $v = kC$ gives $v = k_0C/S$; Dimroth (*Annalen*, 1910, **377**, 127) used this equation in studying the effects of solvents on the velocity of intramolecular transformation, and found that, whilst the classical velocity coefficient had values which differed as much as 100-fold from each other, the values of k_0 only exhibited a 3-fold variation. It would thus appear that part of the effect of the medium on reaction speed is connected with solubility. It follows that, if the solubility of a non-electrolyte, such as ethyl acetate, is decreased by the presence of electrolytes, its reactivity may be increased. This is also indicated from a consideration of the kinetic equilibrium of a solid with its saturated solution. If the solubility is decreased, a greater proportion of the solute molecules must possess sufficient translational energy to deposit themselves on the surface of the solid, and the reactivity, which depends on the proportion of molecules having an energy greater than some critical value (Arrhenius, *Z. physikal. Chem.*, 1889, **4**, 226; Hinshelwood, *Phil. Mag.*, 1925, **2**, 360), may be expected to increase (Scatchard, *J. Amer. Chem. Soc.*, 1923, **45**, 1581).

The van 't Hoff equilibrium constant is a partial statement of the activity constant. Defining the activity, a_A, of a substance A by the expression $F_A = C_A + RT \log a_A$, where F_A is the partial free energy and C_A is a constant, and putting $F_A + F_B = F_P + F_Q$ as the condition * of equilibrium in the system $A + B \rightleftharpoons P + Q$, it is seen that $a_A a_B / a_P a_Q$ is constant and independent of the medium. The modified velocity equation corresponding to the classical equation is thus $v = k a_A a_B$, but it is important to note that this equation is only one of a number which, when applied to a balanced reaction, satisfy the activity equilibrium constant. The general velocity equation is of the type

$$v = k_0 a_A a_B F_1 \text{ (activities)}.\ F_2 \text{ (specific effect of solvent)}.\ F_3 \ldots F_n, \qquad (1)$$

with the stipulation that the functions F_1, F_2 . . ., should be common to both the forward and the reverse reactions of the reversible change.

The object of the present work was to test the equation $v = k a_A a_B$, or, if this was inadequate, some equation of the general type (1), and for this purpose a knowledge of the activities of the reacting substances in the presence of each other is necessary. Whilst the effect of small concentrations of a non-electrolyte on the activity of an electrolyte is negligible, the electrolyte may exert a large effect on that of the non-electrolyte. The determination of the activity of a substance in the presence of those reagents which are causing its decomposition is difficult, and it does not suffice to regard the salting-out effect of all electrolytes as identical at equivalent concentrations. It has been possible to overcome this difficulty in the study of the interaction of hydrochloric acid and *N*-chloroacetanilide (Orton and Jones, *Rep. Brit. Assoc.*, 1910,

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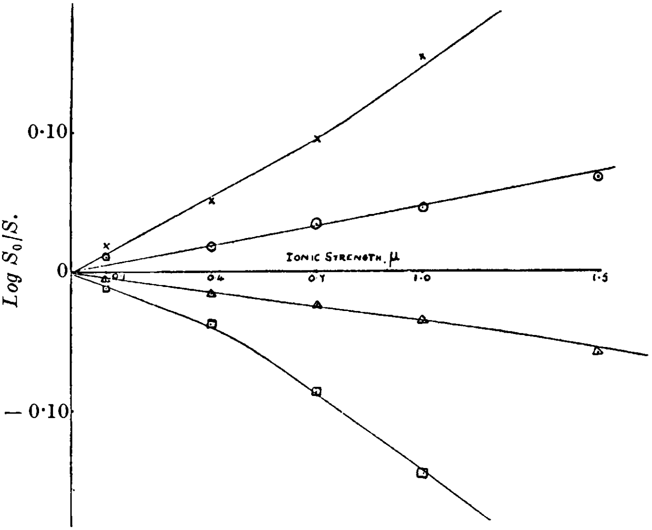
* This is permissible if a displacement of the equilibrium is not attended by a change in the ionic strength (Soper, *J. Physical Chem.*, 1927, **31**, Nov.).

85; Rivett, *Z. physikal. Chem.*, 1913, **82**, 301; Harned and Seltz, *J. Amer. Chem. Soc.*, 1922, **44**, 1475), for both hydrogen and chlorine ions must be present before the *N*-chloroacetanilide reacts, and it was therefore possible to measure separately the effects of these ions on the activity of the chloroamine. It was found that the replacement of the chloride ion by the nitrate ion raised the solubility of the chloroamine in a certain ratio, which depended on the salt concentration, but was otherwise independent of the kation present. From the solubility in nitric acid, that in hydrochloric acid could be deduced, and the activity coefficient was found in this way to change by 13% over the hydrochloric acid range examined (0·1—1·5*M*). The results are given graphically in Fig. 1, where the logarithm of the activity coefficient of the chloroamine (the ratio of the solubility in water to that in the salt solution) has been plotted against the ionic strength.

FIG. 1.



△ HCl, ▣ HNO_3, × KCl, ⊙ KNO_3 *solutions.*

Measurement of the Rate of Interaction of Hydrochloric Acid and N-*Chloroacetanilide.*—The transformation of *N*-chloroacetanilide to *o*- and *p*-chloroacetanilides was shown by Orton and Jones (*loc. cit.*) to involve two successive stages: first, an interaction of the hydrochloric acid and the chloroamine with the production of chlorine, and secondly, reaction between the chlorine and the acetanilide. It has since been shown by one of us (*J. Physical Chem.*, 1927, **31**, 1192) that the speed of the transformation is approximately equal to that of the first stage, but that the measurement of the rate of reaction is complicated by simultaneous *N*-chlorination of the chloroanilides which are produced. The effect of this was shown to be that the rates of the transformation as ordinarily measured indicate an apparent reactivity of the hydrochloric acid, which is too great in the more concentrated acid solutions. In order to measure the true rate at which chlorine is being formed, it is necessary to have present excess of some substance which is readily chlorinated and does not itself react with the hydrochloric acid or the chloroamine. Acetanilide, phenol, and *p*-cresol have been used for this purpose, and have given identical results.

It is possible that chlorine may be produced from a chloroamine by two mechanisms: (1) a direct interaction of hydrochloric acid and the chloroamine the rate of which it is desired to measure, and (2) a primary hydrolysis of the chloroamine to hypochlorous acid, followed by the rapid interaction of hydrochloric and hypochlorous acids, giving chlorine (k_2 at 25° $= 1{\cdot}0 \times 10^6$; Soper and Smith, J., 1926, 1582). If (2) occurs appreciably, the rate of chlorine formation will be greater than the rate of interaction of the chloroamine and hydrochloric acid. In aqueous solution, the rate of hydrolysis of *N*-chloroacetanilide is very slow, for in the presence of phenols with which hypochlorous acid reacts rapidly, no detectable disappearance of the chloroamine occurred in 7 hours. In acid solution, the rate of hydrolysis becomes measurable. It is unaffected by the amount of phenol present, is proportional to the acid strength, and is practically the same for nitric, sulphuric, and perchloric acids of the same concentration. If the rate of hydrolysis is the same in hydrochloric acid as in other acids, it is approximately 6% of the rate of chlorine formation in $0{\cdot}1M$-hydrochloric acid and decreases to 0·4% in $1{\cdot}5M$-acid. The rates of chlorine formation corrected for the rate of hydrolysis of the chloroamine give the speeds of direct interaction of the chloroamine and hydrochloric acid.

Activity of the Hydrochloric Acid.—Since the general activity reaction-velocity equation has been developed from the free-energy condition for equilibrium, $F_A + F_B = F_P + F_Q$, which applies strictly only to those equilibria in which a slight displacement does not affect the ionic strength, it is necessary to examine the reaction $(HCl \rightleftharpoons H^{\cdot} + Cl') + {:}NCl \longrightarrow Cl_2 + {:}NH$, more closely. Although the chlorine does not remain in the system, but is immediately taken up by other substances which are present, the velocity equation must satisfy the equilibrium conditions which would be attained were the chlorine to remain free in the system. For a slight displacement of the above equilibrium such that dn mols. of hydrogen chloride disappear, there is a disappearance of $2dn$ ions, with a consequent decrease in the free electrical energy of the medium (Soper, *loc. cit.*). This change in the free energy of the medium is independent of whether the un-ionised acid or the ions actually react with the chloroamine. The equilibrium condition is therefore

$$- dF_{\mathrm{H}^{\cdot}} - dF_{\mathrm{Cl}'} - dF_{:\mathrm{NCl}} + dF_{\mathrm{Cl}_2} + dF_{:\mathrm{NH}} - dF_{\mathrm{medium}} = 0. \quad (2)$$

The interaction of hydrochloric acid and the chloroamine is apparently of the third order, but since it has the normal temperature coefficient (Harned and Seltz, *loc. cit.*), whilst a true termolecular reaction, involving the simultaneous collision of 3 molecules, has a temperature coefficient of nearly unity (Bodenstein, *Z. physikal. Chem.*, 1922, **100**, 68), it is probable that the reaction is one involving the un-ionised hydrogen chloride and the chloroamine. The partial free energy of the un-ionised hydrogen chloride is connected with those of the hydrogen and chlorine ions by the equation

$$- dF_{\mathrm{HCl}} + dF_{\mathrm{H}^{\cdot}} + dF_{\mathrm{Cl}'} + dF_{\mathrm{medium}} = 0 \quad . \quad . \quad (3)$$

where the dF_{medium} corresponds to the increase in the electrical free energy of the medium due to the formation of $2dn$ ions.

Combining (2) and (3), we have

$$- dF_{\mathrm{HCl}} - dF_{:\mathrm{NCl}} + dF_{\mathrm{Cl}_2} + dF_{:\mathrm{NH}} = 0,$$

or
$$F_{\mathrm{HCl}} + F_{:\mathrm{NCl}} = F_{\mathrm{Cl}_2} + F_{:\mathrm{NH}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and substitution for $F_{\mathrm{HCl}} = RT \log a_{\mathrm{HCl}} + C_{\mathrm{HCl}}$ etc., gives

$$a_{\mathrm{HCl}} a_{:\mathrm{NCl}} / a_{\mathrm{Cl}_2} a_{:\mathrm{NH}} = \text{constant},$$

corresponding to the simple activity reaction-velocity equation

$$v^{*} = - dc_{:\mathrm{NCl}}/dt = k_0 a_{\mathrm{HCl}} a_{:\mathrm{NCl}} = k_0 a_{\mathrm{HCl}} f_{:\mathrm{NCl}} c_{:\mathrm{NCl}}. \quad . \quad . \quad . \quad (5)$$

Values of a_{HCl} are given by *E.M.F.* measurements on hydrochloric acid concentration cells without liquid junction, for in a slight displacement of the system in equilibrium the electrical work $dnE\mathrm{F}/N$ is balanced by the change in the partial free energy of

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* The speed is regarded as the number of g.-mols. of the reagents reacting in unit time *per unit volume*, rather than the number reacting per unit weight of solution, for the activity is connected, as was pointed out by Scatchard (*loc. cit.*), with the number of molecules possessing a certain critical energy which enables them to pass through, or react with, unit area of the boundary surface in unit time. If one imagines a number of planes of unit area immersed in the solution, then those molecules possessing sufficient energy to carry them through the surface will also pass through each of these planes. If the planes are of infinitesimal thickness and are arranged so as to form a solid cube, the activity will measure the number of molecules possessing a certain critical energy in that cube, *i.e.*, in unit volume. The number of molecules reacting should also, therefore, have reference to unit volume.

the hydrochloric acid caused by its transference from cell to cell together with the net change in the electrical energy of the two media, *i.e.*,

$$dnE\mathrm{F}/N = -dF_{\mathrm{H^{\cdot}I}} - dF_{\mathrm{Cl\,I}} - dF_{\mathrm{medium\,I}} + dF_{\mathrm{H^{\cdot}II}} + dF_{\mathrm{Cl'II}} + dF_{\mathrm{medium\,II}}$$

which, on being combined with (3), gives

$$dnE\mathrm{F}/N = -dF_{\mathrm{HCl\,I}} + dF_{\mathrm{HCl\,II}}$$

and $E\mathrm{F} = RT \log (a_{\mathrm{HCl\,II}}/a_{\mathrm{HCl\,I}}) + \text{constant}$.

Comparison of (5) with the equation $v = kc_{:\mathrm{NCl}}$ used in evaluating a velocity coefficient at any one acid concentration indicates that $k/a_{\mathrm{HCl}}f_{:\mathrm{NCl}}$ should be constant at constant temperature, unless the speed is affected by viscosity.

Effect of Viscosity.—Since activities, and therefore activity equilibrium constants, are independent of viscosity, it is possible to show theoretically by consideration of the equilibrium, $A \rightleftharpoons P + Q$, that if the velocity of a unimolecular reaction is unaffected by viscosity, then that of a bimolecular reaction should also be unaffected; for application of the reaction-velocity equation to such an equilibrium gives $K = k_1/k_2$, and if K and k_1 are independent of viscosity, then k_2 must also be independent of it. This argument applies to any reaction-velocity equation of type (1).

In Table I the relative viscosities of the acid media (Green, J., 1908, **93**, 2023) have been included. The molalities (g.-mols. of acid per 1000 g. of water) are given in the first column, k' is the rate of chlorine formation, k'' the rate of hydrolysis of the chloroamine, $k = k' - k''$ is the rate of interaction of the chloroamine and hydrochloric acid, and a_{HCl} the activity measured electrometrically by Scatchard (*J. Amer. Chem. Soc.*, 1925, **47**, 641).

TABLE I.

C_{HCl}.	$10^3 . k'$.	$10^4 . k''$.	$10^3 . k$.	$a_{\mathrm{H^{\cdot}}}a_{\mathrm{Cl'}}$.	$f_{:\mathrm{NCl}}$.	$\dfrac{k}{a_{\mathrm{HCl}}f_{:\mathrm{NCl}}}$.	η.
0·1	0·52	0·32	0·49	0·00642	0·989	0·0767	1·000
0·2	1·88	0·58	1·82	0·02397	0·980	0·0775	1·005
0·3	4·06	0·96	3·95	0·05239	0·972	0·0775	1·011
0·4	7·11	1·25	6·98	0·09242	0·964	0·0783	1·017
0·5	10·8	1·50	10·6	0·1448	0·957	0·0772	1·023
0·6	16·0	1·92	15·8	0·2134	0·951	0·0778	1·029
0·7	21·9	2·24	21·7	0·2966	0·947	0·0779	1·035
0·8	29·1	2·54	28·9	0·3985	0·939	0·0773	1·042
0·9	38·2	2·88	37·9	0·5204	0·932	0·0779	1·043
1·0	48·2	3·24	47·9	0·6675	0·925	0·0776	1·054
1·5	124	4·80	124	1·843	0·877	0·0767	1·083

The values of $k/a_{\mathrm{HCl}}f_{:\mathrm{NCl}}$ are constant to within 1%, which is of the order of the experimental error, whilst the viscosity changes by 8%. The observed rates of reaction may therefore be regarded as supporting the simple activity velocity equation for a reaction between neutral molecules in aqueous media. They do not necessarily indicate that the reactivity of an ion is proportional to its thermodynamic activity.

On Brönsted's theory (*Z. physikal. Chem.*, 1922, **102**, 169),

$$\begin{aligned} v &= kc_{:\mathrm{NCl}}\, c_{\mathrm{HCl}} f_{:\mathrm{NCl}} f_{\mathrm{HCl}} / f_{(:\mathrm{NCl},\mathrm{HCl})} \\ &= kc_{:\mathrm{NCl}}\, a_{\mathrm{HCl}} f_{:\mathrm{NCl}} / f_{(:\mathrm{NCl},\mathrm{HCl})}, \end{aligned}$$

and comparison with the simple activity equation shows that, in order to account for the observed facts, the activity coefficient of the critical complex (:NCl, HCl) must be constant to within 0·5% over the acid range examined (0·1—1·5M). This is unlikely in view of the solubility changes which apparently almost invariably occur on addition of electrolytes to a solution.

EXPERIMENTAL.

Measurement of the Solubility of N-*Chloroacetanilide in Acid and Salt Solutions.*—Excess of *N*-chloroacetanilide was added to the salt solution and shaken for 15 minutes at 25·0°; 10 c.c. of the clear solution were then removed by a pipette attached to a glass tube, on the lower end of which was mounted a perforated platinum plate covered with filter-paper. The chloroamine present was estimated by running it into acidified potassium iodide solution and titrating the liberated iodine with *N*/100-thiosulphate. The mean of four titrations was taken after saturation was attained (approx. 15 mins.). The measured solubilities of *N*-chloroacetanilide (in g.-mols. per litre) in potassium chloride, potassium nitrate, and nitric acid solutions are given in Table II, together with the calculated solubility in hydrochloric acid.

TABLE II.

Ionic strength.	0·0.	0·1.	0·4.	0·7.	1·0.	1·5.
Solubility in KCl ...		0·01323	0·01232	0·01105	0·00963	0·00880
,, KNO_3 .	(0·01383)	0·01350	0·01325	0·01275	0·01243	0·01178
,, HNO_3 .		0·01418	0·01511	0·01680	0·01935	0·02295
,, HCl ...		0·01398	0·01434	0·01461	0·01495	0·01577

Speed of Chlorine Formation from N-*Chloroacetanilide and Hydrochloric Acid.*—The effect of increasing the concentration of acetanilide, phenol, or *p*-cresol on the rate of fall of the iodine titre of a mixture of *N*-chloroacetanilide and hydrochloric acid is shown in Table III :

TABLE III.

HCl = 0·2M :NCl = 0·01M ; temp. = 25·0°.

Concentration of phenol, *p*-cresol, or acetanilide, M	0·01.	0·02.	0·03.
100k' (acetanilide)	0·183	0·188	0·188
100k' (phenol)	0·186	0·188	0·188
100k' (*p*-cresol)	—	0·188	0·188

The limiting value for k which corresponds to the rate of chlorine formation from 0·01 M-chloroamine and 0·2M-hydrochloric acid is thus 0·00188. The limiting values for other acid concentrations are given in Table I. Care was taken when mixing the aqueous solution of chloroamine with the calculated weight of hydrochloric acid solution to adjust the initial temperatures so as to compensate for the heat of mixing. The speed of the reaction in the presence of 1·5M-hydrochloric acid is too great to allow of pipetting out portions of the mixture, and portions were therefore poured into weighed flasks containing potassium iodide and sodium acetate at 10-sec. intervals, the flasks were reweighed, and the contents titrated.

Speed of Hydrolysis of N-*Chloroacetanilide.*—Determinations of the rate of hydrolysis of the chloroamine were carried out in aqueous sulphuric, nitric, and perchloric acids, *p*-cresol being present in solution to remove the hypochlorous acid as formed. In the absence of acid, there is no detectable disappearance of the chloroamine in 7 hours. The rate of disappearance of chloroamine in the presence of acid follows a unimolecular velocity equation and the results obtained are summarised in Table IV.

TABLE IV.

:NCl = 0·01M ; *p*-cresol = 0·1M ; temp. = 25·0°.

Concentration of acid.	H_2SO_4.					HNO_3.	$HClO_4$.
	0·1	0·2	0·4	0·8	1·0	1·0	1·0
$k'' \times 10^4$	0·321	0·584	1·25	2·54	3·24	3·24	3·70

Summary.

1. Since concentration equilibrium constants are affected by the presence of electrolytes, the classical velocity coefficients are not true constants, and the use of an equation, $v = kf_{\text{catalyst}}C_AC_B$, for determining the effective concentration of the catalyst is not justifiable. Attention has therefore been redirected to the general form of a reaction-velocity equation.

2. The simplest type of the generalised equation applying to reactions involving neutral molecules, *viz.*, $v = ka_Aa_B$, is found to be in agreement with observations on the rate of interaction of hydrochloric acid and N-chloroacetanilide. The activities of the reagents used in the velocity equation are those which obtain in the presence of each other. Actually, the activity of the chloroamine was found to be progressively decreased by 13% as the hydrochloric acid concentration was increased from 0·1 to 1·5M.

3. The measurement of reaction speed in mols. transformed in unit time *per unit volume*, rather than per unit weight of solution, is justified on theoretical grounds.

4. A proof is advanced that reaction velocity is independent of viscosity.

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