CCCXLVII.—*The Velocity of the Acid Hydrolysis of Cotton Cellulose by Hydrochloric Acid, Alone, and in Presence of Alkali Chloride.*

By Edward Hunter.

It has been shown by Åkerlöf (*Z. physikal. Chem.*, 1921, **98**, 260) that the velocity of hydrolysis of ethyl acetate by hydrochloric acid in presence of large concentrations of neutral salt is a function of the activity of the hydrogen ion, irrespective of the kation of the added chloride.

The work here described was undertaken to determine whether the principles of activity could be extended to a heterogeneous reaction catalysed by hydrogen ions. The reaction chosen is the hydrolysis or " modification " of cotton cellulose in hydrochloric acid both alone and in presence of potassium, sodium, and lithium chlorides. With dilute acid the ultimate reaction product is hydrocellulose, a solid adhering to the unchanged cotton. According to Wohl and Blumrich (*Z. angew. Chem.*, 1921, **34**, 17), this substance is a reversion product of dissolved reducing sugars (primary products of reaction) and some undissolved substance in the solid cotton. They observe that hydrocellulose is much more difficult to hydrolyse than cellulose, but it should be borne in mind that hydrolysis can be effected by prolonged heating with very concentrated acid.

EXPERIMENTAL.

Methods of Hydrolysis and Analysis.—The hydrolyses were carried out by adding 70 c.c. of the acid solution to a weighed quantity of cotton (about 2·7 g.), stirring to remove air bubbles, and immersing the reaction vessel in the thermostat. For potassium chloride and some lower concentrations of sodium chloride the vessel was a tightly-corked flask, but it was found advisable to carry out the other reactions in sealed glass tubes.

After hydrolysis the cotton was washed by water with suction, and its copper number determined by Brady's method (see also Clibbens and Geake, *Shirley Institute Memoirs*, 1924, **2**, 387). Two corrections were applied in the calculation. (1) The moisture content of the original cotton was determined by heating 1 g. samples, loosely packed in weighing bottles, at 105° to constant weight. (2) The copper number of unmodified cotton (mean of several determinations) was subtracted from the value found after hydrolysis.

When a sample of cotton was steeped in acid, the concentration of acid slowly decreased by a slight amount until an equilibrium was reached after about $2\frac{1}{2}$ days :

Time (hrs.)	0	4·75	27	64·3
Acid concentration, *N*	0·100	0·0992	0·0983	0·0980

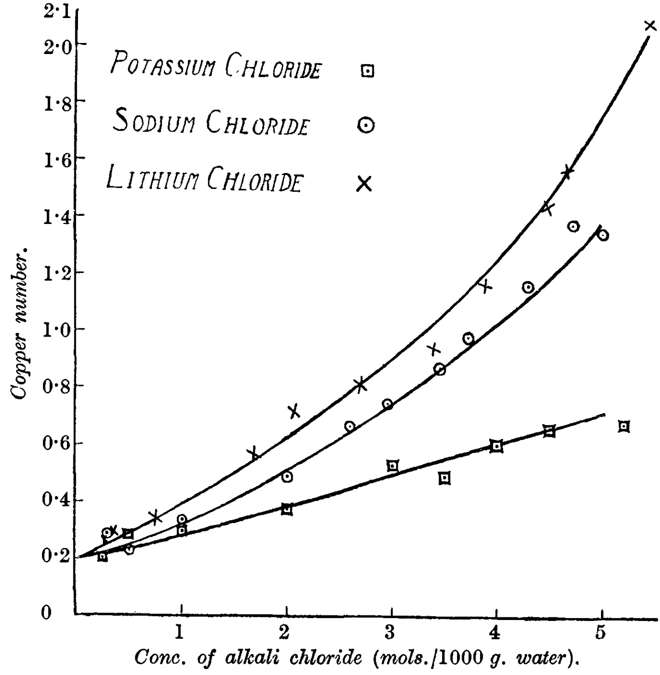
The fall in concentration in 60 hrs. of several concentrations of acid was measured :

Original concentration	0·869	0·435	0·244	0·0871
Final concentration	0·866	0·433	0·242	0·0855
Fall, %	0·35	0·46	0·8	1·8

This change in concentration is ascribed to imbibition of acid by the cotton, and it has been ignored in the velocity measurements.

For the velocity of the hydrolysis (by acid of constant concentration), Birtwell, Clibbens, and Geake (*J. Textile Inst.*, 1926, **17**, T161) have submitted the formula $N_{Cu} = KT^{0\cdot6}$, where N_{Cu} is the copper number, K a velocity coefficient, and T the time of reaction in days. The results of these authors show that K is only constant within 5—10%. Furthermore, the index here given as 0·6 apparently varies with the type of cotton. For these reasons, in the present work, reaction velocities are compared by carrying out the acid steeping for exactly the same length of time in all cases, a period of 3 days at 40° being chosen as most suitable.

FIG. 1.

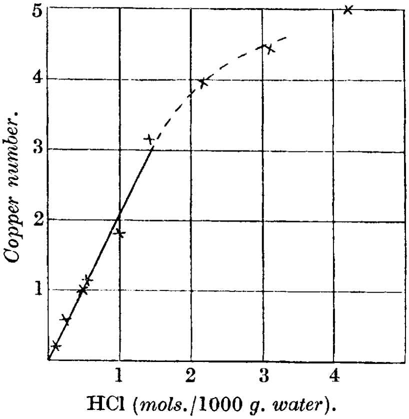


$N/10$-Acid (0·1 mol. per 1000 g. of water) was prepared by dilution of standard hydrochloric acid made by the method of Hulett and Bonner (*J. Amer. Chem. Soc.*, 1909, **31**, 390). The acid–alkali chloride mixtures were prepared by adding weighed amounts of salt to a known weight of acid. In the lithium chloride series the concentrations of acid and chloride were checked by analysis.

Results.—In Fig. 1 the copper numbers for the 3-day hydrolysis at 40° are plotted against the concentrations (x) of neutral salt in the mixture $0{\cdot}1HCl + xRCl + 1000$ g. H_2O; and Fig. 2 shows the results for pure acid of varying molality.

The last three results in the acid series do not represent the true velocity values for the corresponding molalities of acid. Two reasons can be given for this. (1) Hydrolysis with such strong acid for 3 days resulted in a complete change of form of the cotton to short thread-like particles, in place of the interwoven fibres left after more moderate modification; hence it seems likely that the hydrocellulose itself was partly decomposed by the acid. (2) In determining the copper number of such highly modified cotton samples, the amount of copper solution used in the standard method was insufficient, and it was therefore necessary to use a larger quantity, thereby deviating from the rigid conditions prescribed for the method.

FIG. 2.

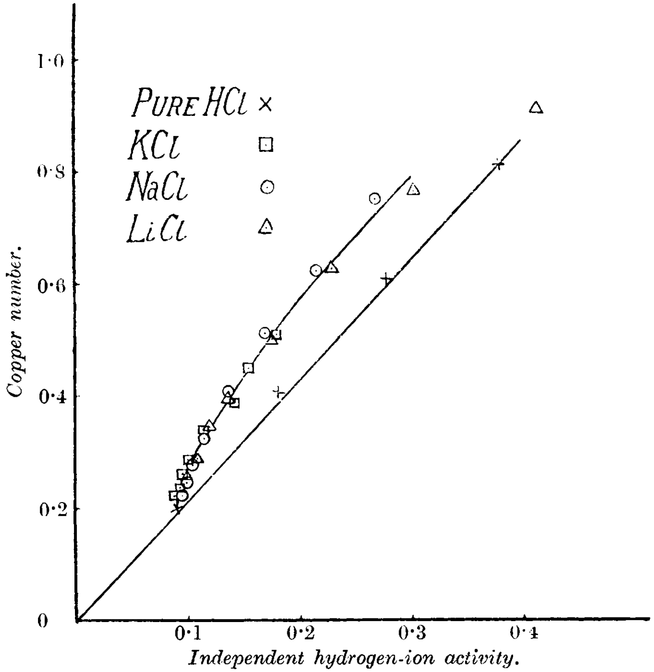


It is obvious from the diagrams that no great quantitative accuracy can be claimed for the velocity measurements. The source of the largest error is almost certainly in the process of hydrolysis, for two samples of cotton of equal weight cannot be expected to offer the same surface area to the solution. However, the results clearly show the qualitative effects upon the reaction velocity of adding alkali chloride to $N/10$-hydrochloric acid.

The curves of Fig. 1 resemble those connecting molality of added chloride with hydrogen-ion activity in solutions of the type used. This suggests a connexion between hydrolysis velocity and the hydrogen-ion activity of the acid solutions. The curves in Fig. 3 have been obtained by plotting Harned's values for hydrogen-ion activity in solutions of this type (*J. Amer. Chem. Soc.*, 1920, **42**, 1808) against the copper numbers for corresponding molalities, as read off from Figs. 1 and 2. Harned's data refer to 25°, but only a small error is introduced by applying them to 40°.

It will be seen from the diagram that in pure acid there is a simple direct proportionality between hydrogen-ion activity and copper number (velocity of reaction) for activities of the same order as those of the acid–alkali chloride series. No such simple relation exists for the acid–salt mixtures. Plotted separately, the results for each series give a smooth curve. The three curves are practically coincident near their origin, and are only slightly divergent with increasing molality. In Fig. 3 a single curve has been drawn for the three series; this originates on the pure acid curve at the hydrogen-ion activity of *N*/10-acid, and then rises above it. Since Harned's values are limited to solutions which are not stronger than 3*M* with respect to added chloride, the ultimate trend of the activity–velocity curves has to be left undefined—they may either become parallel to the pure acid line or intersect it at very high values of the hydrogen-ion activity.

Fig. 3.



For the range examined, the notable fact is that, of two solutions having the same hydrogen-ion activity, that with neutral salt present gives a higher reaction velocity than that with acid alone. In attempting an explanation of this fact, it seems natural to assume that reaction occurs between dissolved reactants in a thin layer of solution touching the surface of the solid cotton; in these circumstances Brönsted's equation (*Z. physikal. Chem.*, 1925, **115**, 337) can be expected to hold, *viz.*, $v = ka_A a_B/f_X$, where v is the velocity, k a velocity coefficient, a_A and a_B are the activities of the reactants, and f_X is the activity coefficient of the "critical complex." If the reaction be written as $H^{\cdot},H_2O$ + Cellulose $\longrightarrow$ [(Cellulose),$H^{\cdot}$,H_2O] $\longrightarrow$ Hydrocellulose + $H^{\cdot}$, one obtains the expression $v = ka_H a_C/f_X$,

a_H and a_C being the respective activities of the hydrogen ion and the neutral cellulose, and f_X having its former significance. Since the cellulose is a neutral molecule, the expression can be modified to $v = ka_Hc/f_X$, where c is the concentration of cellulose. Apart from the independent hydrogen-ion activity, the important variant in this expression is f_X, for the critical complex is a charged molecule, the activity coefficient of which may be expected to be very responsive to changes in the activities of the other reactants. Now, for similar hydrogen-ion activity, the saline solutions have a far greater molality of electrolyte than the salt-free solutions. In Fig. 3 the highest molality of pure acid is 0·5, whilst that of the acid–chloride solutions reaches 3·1. Hence any effect upon the activity coefficient of the " critical complex " with increasing molality of electrolyte will be shown to a more pronounced degree in the latter type of solution. The relative form of the activity–velocity curve for such solutions and for salt-free solutions is explained if it is accepted that addition of large quantities of electrolyte to the solution lowers f_X, for the velocity of the reaction is inversely proportional to this activity coëfficient. The gradual divergence of the activity–velocity curves for the three different chlorides can then be ascribed to slight differences in the quantitative effects of each salt on the " critical complex."

The author's thanks are due to Professor A. J. Allmand, under whose direction the work was carried out, and to Dr. D. A. Clibbens, who supplied the cotton and gave very helpful advice.

UNIVERSITY OF LONDON,
KING'S COLLEGE.

[*Received, May* 23*rd*, 1928.]