CCXLV.—*The Effect of the Cohesion of the Medium on Reaction Velocity. The Velocity of Interaction of* N-*Chloroacetanilide and Hydrobromic Acid in Aqueous Solutions.*

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THE velocity of interaction of *N*-chloroacetanilide and hydrochloric acid (Soper and Pryde, J., 1927, **131**, 2767) in aqueous solution is satisfactorily expressed by the simple " activity " or van 't Hoff velocity equation (van 't Hoff, " Vorlesungen über Chemie," 1898, I, 218; Harned, *J. Amer. Chem. Soc.*, 1918, **40**, 1461), *viz.*, $v = ka_Aa_B$, if the activities are those of the reagents in the presence of each other. This equation, which is seldom obeyed (Buchböck, *Z. physikal. Chem.*, 1900, **34**, 229; Freundlich and Richards, *ibid.*, 1912, **79**, 681; von Halban, *ibid.*, 1913, **84**, 129), is the simplest of those which, when applied to a balanced reaction, lead to the exact thermodynamic equilibrium law. The general reaction velocity equation is of the type

$$v = ka_Aa_BF_1(\text{activities}) \quad . \quad . \quad . \quad . \quad F_n(\text{solvent}),$$

where the F's are functions which are common to both forward and reverse reactions. It was therefore thought possible that the constancy of the activity velocity coefficient in the interaction of *N*-chloroacetanilide and hydrochloric acid might be due to the constancy of some property of the series of solutions.

Now, one of the properties of hydrochloric acid solutions, namely, the cohesion, is seen to be practically constant, for the surface tension, which is an indication of the magnitude of the cohesion, changes only from 71·97 to 71·69 as the acid concentration increases from 0·1 to 1·0M. The effect of the cohesion of the solvent on the velocity coefficients of reactions in a series of solutions was therefore studied.

If the cohesion of the medium has any general effect on reaction speed, it may be expected that the effect will be connected primarily with the van 't Hoff or activity velocity coefficient. Examination of the results obtained for this coefficient and for the concentration velocity coefficient of a reaction in a range of solvents showed, however, that the effect of the solvent on these coefficients is in general the same (see the two coefficients for the formation of a quaternary ammonium salt in Cols. 9 and 10 of Table I, and those for an intramolecular change in Cols. 5 and 6 of Table II). Concentration velocity coefficients have therefore also been surveyed from the standpoint of possible correlation with the cohesion of the medium.

The cohesion of the medium was evaluated as $E_\sigma/v^{\frac{1}{3}}$ (Harkins, Davies, and Clarke, *J. Amer. Chem. Soc.*, 1917, **39**, 555), where E_σ is the total surface energy (in dynes/cm.) and v is the molar volume (in c.c.); and as L/v (Stefan, *Wied. Ann.*, 1886, **29**, 655), where L is the latent heat of evaporation (in joules) per mol. It was then observed that the following rules appear generally to hold:

1. *If the reaction is one in which the products are substances of higher cohesion than the reagents, then it is accelerated by solvents of high cohesion.*

In Table I the results of a number of investigations on the formation of quaternary ammonium salts have been collected. Here a substance of high polarity and high cohesion is being formed from substances of relatively low cohesion. The numbered columns give the velocity coefficients of various reactions, as follows:

(1) Triethylamine and ethyl iodide (Menschutkin, *Z. physikal. Chem.*, 1889, **5**, 589).

(2) Diethyl sulphide and ethyl iodide (Carrara, *Gazzetta*, 1894, **24**, i, 180).

(3) Triethylamine and ethyl bromide (Hemptinne and Bekaert, *Z. physikal. Chem.*, 1899, **28**, 225).

TABLE I.

	$E_\sigma/v^{\frac{1}{3}}$.	L/v.	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
Hexane	9·45	243·3	0·000180	—	—	—	—	—	—	—	0·00032	0·000087
Ethyl ether	10·98	250·0	0·000757	—	—	—	—	—	—	—	0·0074	0·000160
p-Xylene	12·12	292·5	0·00287	—	0·000103	—	—	—	—	—	—	—
Toluene	12·38	315·9	—	—	—	—	0·00186	—	—	—	—	—
Ethyl benzoate	12·38	285·4	—	—	—	—	—	—	0·0024	—	1·99	0·0132
Benzene	15·29	275·0	0·00584	—	0·000228	0·000985	0·00223	0·73	0·0025	—	0·35	0·00151
Phenetole	12·75	—	0·0212	—	—	—	—	—	—	—	—	—
Ethyl acetate	13·44	384·0	0·0223	—	—	—	—	—	0·0067	—	1·21	0·0065
Tetrachloroethane	—	—	—	—	—	—	—	—	—	29·78	—	—
Chlorobenzene	14·68	360·8	0·0231	—	0·000843	—	—	—	—	—	—	—
Anisole	14·84	340·0	0·0403	—	—	—	—	—	0·021	—	—	—
Bromobenzene	15·03	360·8	0·0270	—	—	—	—	—	—	—	—	—
Chloroform	15·50	363·1	—	—	—	0·00186	—	—	—	—	2·6	0·0162
Acetone	14·46	408·3	0·0608	—	0·0024	0·269	0·0338	—	0·069	—	10·0	0·043
Nitrotoluene	15·11	—	—	—	—	—	0·0376	—	—	—	8·5	0·065
Acetophenone	15·52	330·4	0·1294	—	—	—	0·0526	—	—	—	11·3	0·077
Nitrobenzene	17·17	400·3	—	—	—	0·0135	0·0848	32·3	0·0218	37·56	12·9	0·092
Acetonitrile	18·04	564·6	—	—	—	—	—	—	—	—	47·0	0·257
Nitromethane	20·83	647·3	—	—	—	—	—	—	—	—	131·0	0·81
Alcohols.												
*iso*Amyl alcohol ...	9·75	415·5	—	—	—	—	—	—	—	—	0·57	0·0074
*iso*Butyl alcohol ...	10·07	463·4	0·0258	—	—	—	—	—	—	—	—	—
n-Butyl alcohol	10·79	480·5	—	—	—	0·0550	—	—	—	—	—	—
n-Propyl alcohol ...	11·45	555·0	—	4·7	0·00162	—	—	—	—	—	0·82	0·0072
Allyl alcohol	12·38	586·0	0·0433	—	—	—	—	—	—	—	—	—
Ethyl alcohol	12·14	673·6	0·0366	7·6	0·00197	0·0626	0·0202	17·0	—	—	1·39	0·0094
Methyl alcohol	14·01	869·0	0·0516	15·3	0·0025	0·0748	—	—	—	—	5·0	0·0181
Benzyl alcohol	14·04	493·2	0·133	—	0·00829	0·0440	—	—	—	—	76·0	0·0258

(4) Aniline and bromoacetophenone (Cox, J., 1921, **119**, 142).

(5) Pyridine and allyl bromide (Hawkins, J., 1922, **121**, 1170).

(6) Benzyl bromide with pyridine and with triethylamine (Muchin, Ginsburg, and Moissejeva, *Ukraine Chem. J.*, 1926, **2**, 136).

(7) Trimethylamine and benzyl bromide (McCombie, Scarborough, and Smith, J., 1927, 802).

(8) Aniline and methyl iodide (Essex and Gelormini, *J. Amer. Chem. Soc.*, 1926, **48**, 882).

(9) and (10) The concentration and activity velocity coefficients of the interaction of trimethylamine and *p*-nitrobenzyl chloride (von Halban, *Z. physikal. Chem.*, 1913, **84**, 128).

A reaction of a different type is the chlorination of anilides by chlorine, which results in the production of the polar substance, hydrogen chloride. This reaction is slower in acetic acid (Orton and King, J., 1911, **99**, 1185, 1369) than in water (Soper, *J. Physical Chem.*, 1927, **31**, 1192) where the cohesion is greater.

TABLE II.

	$E_\sigma/v^{\frac{1}{3}}$.	L/v.	1.	2.	3.	4.	5.	6.
Hexane	9·45	243·2	0·0877	0·0307	—	—	—	—
Xylene	12·12	292·5	0·0510	0·0196	—	—	—	—
Benzene	15·29	275·0	0·0401	0·0148	—	—	—	—
Ethyl acetate	13·44	384·0	—	—	—	—	0·0267	0·320
Chloroform	15·50	363·1	—	—	0·023	—	0·0211	0·186
Acetone	14·46	408·3	—	—	0·029	—	0·00527	0·298
Tetrachloroethane	15·61	373·5	—	—	0·023	0·2943	—	—
Nitrobenzene	17·17	400·3	—	—	0·018	0·2706	0·046	0·299
Acetonitrile	18·04	564·6	—	—	—	—	0·0047	0·195
Alcohols.								
Amyl alcohol	9·75	415·5	—	—	0·00045	—	—	—
Propyl alcohol	11·45	555·0	—	—	0·00018	—	—	—
Ethyl alcohol	12·12	673·6	—	—	—	—	0·00103	0·101
Methyl alcohol	14·01	869·0	—	—	—	—	0·00053	0·116
Benzyl alcohol	14·04	493·2	—	—	0·00010	—	0·0011	0·099

2. *If the reaction is one in which the products are substances of lower cohesion than the reagents, then it is retarded by solvents of high cohesion.*

Results which illustrate this rule are given in Table II, the velocity coefficients corresponding to reactions as follows :

(1) Acetic anhydride with *iso*propyl alcohol, a reaction in which alcohol molecules of high cohesion form an ester of low cohesion.

(2) Acetic anhydride with *iso*butyl alcohol (Menschutkin, *Z. physikal. Chem.*, 1887, **1**, 611).

(3) Decomposition of triethylsulphonium iodide (von Halban, *ibid.*, 1909, **67**, 129).

(4) Decomposition of triethylsulphonium bromide (Essex and Gelormini, *loc. cit.*).

(5) and (6) The concentration and the activity velocity coefficients of the decomposition of the methyl triazolecarboxylate studied by

Dimroth (*Annalen*, 1910, **377**, 127): here an acidic hydroxylic compound forms a ketonic compound of lower cohesion.

3. *When the products and reagents are substances of like cohesion, the solvent has relatively little influence on the reaction velocity.*

In the reaction investigated by Patterson and Montgomerie (J., 1912, **101**, 2100) where anis*syn*aldoxime is converted in the presence of ethyl tartrate into the *anti*aldoxime, the cohesions of the products and of the reagents must be approximately the same. The effect on the velocity coefficients of solvents common to this investigation and to von Halban's investigation on the formation of a quaternary ammonium salt (*loc. cit.*) are compared in Table III, where k_H is the velocity coefficient of von Halban and k_P that of Patterson and Montgomerie. It is seen that the solvent has relatively little effect on the transformation of the aldoxime. Similar behaviour is observed by Smith in the racemisation of *l*-pinene (*J. Amer. Chem. Soc.*, 1927, **49**, 43).

TABLE III.

Solvent.	k_H.	k_H/k_H(benzene).	k_P.	k_P(benzene)$/k_P$.
Benzene	0·00151	1	3·13	1
Propyl alcohol	0·0072	4·75	1·69	1·85
Ethyl alcohol	0·0094	6·23	1·87	1·68
Methyl alcohol	0·0181	12·0	2·07	1·51
Benzyl alcohol	0·0258	17·1	3·14	1·0
Acetone	0·043	28·5	0·92	3·4
Nitrobenzene	0·092	61·0	2·94	1·07

The rules advanced would appear to be connected with the influence the solvent may exert on the critical complex of the two reagents. High cohesion means unsaturation of the molecular force fields and the decomposition of a complex into substances of a higher molecular unsaturation may well be assisted by solvents which themselves possess unsaturated molecular fields. Conversely, the decomposition of the complex into substances of lower unsaturation may be retarded by such solvents, and the complex may tend to re-form the reactants.

The present investigation has been concerned with the interaction of hydrogen bromide and *N*-chloroacetanilide (Acree and Johnson, *J. Amer. Chem. Soc.*, 1907, **39**, 410; Orton and Jones, *Brit. Assoc. Reps.*, 1910, 85): $C_6H_5\cdot NClAc + HBr = Br\cdot C_6H_4\cdot NHAc + HCl$. The relative cohesions of the products and reagents will depend, in this reaction, on the relative cohesions of *N*-chloroacetanilide and of *p*-bromoacetanilide. Since the former is very much more soluble in water, a solvent of high cohesion, it has a higher cohesion (Hildebrand) than the latter, and the reaction is one which, on the rule advanced, should be retarded by solvents of high cohesion. The activity velocity coefficient has therefore been examined in aqueous salt solutions of higher cohesion than water; in sucrose solutions, where the surface tension indicates no appreciable change in cohesion; and in aqueous methyl- and ethyl-alcoholic solutions, where the cohesion is less than in water.

The values obtained for the activity velocity coefficient, k', are given in Table IV, the speed of the reaction being defined as $-dc/dt = k'a_{NCl}a_{HBr} = k'c_{NCl}c_{HBr}f_{NCl}f_{HBr}$, c being expressed in mols. per litre, and k_2 being a concentration velocity coefficient (see p. 1880). For equimolar quantities of chloroamine and hydrobromic acid the equation becomes $-dc/dt = k'c^2_{NCl}c_2f_{NCl}f_{HBr} = k_2c^2_{NCl}$, where c_2, given in Table VI, is the constant hydrogen-ion concentration equal to the initial concentration of hydrogen bromide.

TABLE IV.

Solvent.	k_2.	f_{NCl}.	$f_{H^{\cdot}} = f_{Br'}$.	$10^3 \times k'$.	γ.
Water	32·7	1·000	0·924	3·78	71·97
0·1*M*-$NaNO_3$	23·9	1·016	0·818	3·53	72·09
0·5 ,,	18·6	1·063	0·765	3·04	72·57
1·0 ,,	17·3	1·140	0·773	2·61	73·17
1·5 ,,	17·0	1·235	0·810	2·19	73·77
2·0 ,,	16·7	1·359	0·905	1·60	74·34
0·05*M*-KNO_3	26·3	1·011	0·840	3·70	72·02
0·10 ,,	23·4	1·024	0·808	3·53	72·08
0·50 ,,	18·5	1·052	0·749	3·27	72·48
1·00 ,,	17·0	1·113	0·716	3·18	73·00
2·00 ,,	17·2	1·277	0·789	2·34	74·02
5% (Wt.) MeOH	36·4	0·811	0·995	4·57	60·98
10 ,,	41·4	0·675	1·055	5·61	54·60
15 ,,	48·0	0·518	1·094	7·94	49·89
20 ,,	57·0	0·451	1·122	10·35	46·05
25 ,,	66·9	0·308	1·173	16·4	43·00
5% (Wt.) EtOH	35·4	0·804	0·995	4·49	55·20
10 ,,	41·2	0·661	1·059	5·64	47·40
15 ,,	48·7	0·500	1·111	8·09	42·0
20 ,,	58·6	0·404	1·162	11·1	38·0
25 ,,	75·0	0·225	1·180	24·9	35·0
5% (Wt.) Sucrose	36·1	1·018	0·993	3·56	72·27
10 ,,	41·0	1·044	1·070	3·30	72·52
15 ,,	48·2	1·073	1·096	3·52	72·77
20 ,,	57·7	1·080	1·147	3·76	72·97

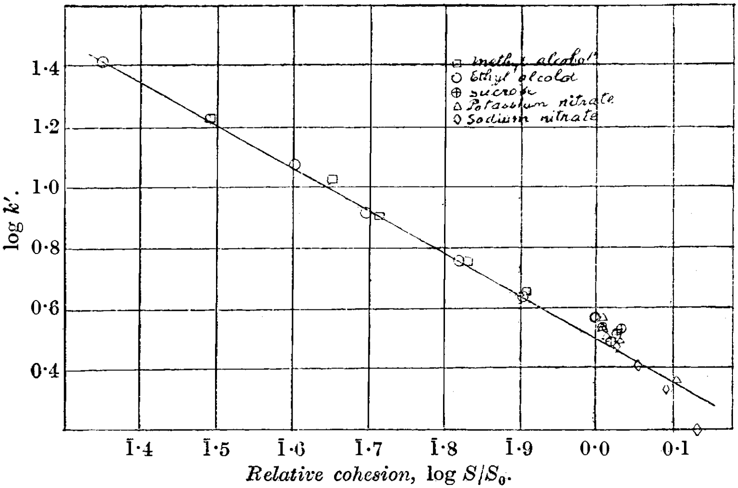
It will be seen on comparing k' with the surface tension (γ) that the behaviour anticipated from the cohesion rule is observed. In sucrose solutions, where the surface tension is approximately constant as in hydrochloric acid solutions (see p. 1874), there is only a slight variation in the activity or van 't Hoff velocity coefficient.

An independent method of deducing the cohesion of a medium, due to Mortimer (*J. Amer. Chem. Soc.*, 1922, **44**, 1416; 1923, **45**, 633), is based on Hildebrand's theory that positive deviations from Raoult's law are due to differences in the cohesion of the two components of the solution. Mortimer evaluates the cohesion from the factor p in the solubility–temperature equation

$$\log N = (1/T - 1/T_m)pL_f/2{\cdot}303R,$$

where L_f is the latent heat of fusion of the solid and T_m is its melting point. The factor p is proportional to the difference in cohesion of solute and solvent. For the same solute at constant temperature, p = constant × $\log N$ = constant × log (solubility). We have, therefore, in the solubility of any non-polar substance in the aqueous medium in which the reaction has been investigated, a measure of the differences of the cohesions of solvent and solute, so long as complex formation does not occur. The greater the solubility of the non-polar substance, *e.g.*, *N*-chloroacetanilide, the less the difference in the cohesions of solute and solvent, and the lower the cohesion of the solvent. So long as the cohesions of solute and solvent are widely separated, one may regard the differences of

FIG. 1.



cohesion of solute and solvent as a measure of the cohesion of the solvent and put cohesion as proportional to $-\log S$. The van 't Hoff velocity coefficients are plotted against the cohesion thus deduced in Fig. 1, which incorporates all the measurements. The points lie on a straight line, the equation of which is $\log k' = -1{\cdot}4 \log S +$ constant, giving a relation of the type $k' = Ce^{\lambda(\text{cohesion}) - E/RT}$ where C and λ are constants.

EXPERIMENTAL.

The Mechanism of the Reaction.—As it was possible that chloroanilides might be produced to some extent when *N*-chloroacetanilide and hydrobromic acid interact, the residual solution from equimolecular amounts of the reagents was analysed for bromide by precipitating the halides as silver salts and determining the loss in weight on their complete conversion to chloride. The bromide present was negligible and the reaction may therefore be represented as

$$\begin{tikzcd}
HBr + C_6H_5{\cdot}NClAc \arrow[r, "I"] & BrCl + C_6H_5{\cdot}NHAc \arrow[r, "II"] \arrow[dl] & Br{\cdot}C_6H_4{\cdot}NHAc + HCl \\
BrCl(+ HBr) \arrow[r] & Br_2 + HCl \arrow[r, "+C_6H_5{\cdot}NHAc"] & Br{\cdot}C_6H_4{\cdot}NHAc(+ HBr) + HCl
\end{tikzcd}$$

where either bromine or bromine chloride may be the brominating agent. Addition of a readily brominated substance such as anisole to the reaction mixture did not cause a marked increase in the velocity of disappearance of the chloroamine, the concentration of which was measured by the iodine titre of the solution after addition to potassium iodide. The speed does not therefore depend on a relatively slow reaction between bromine and acetanilide in equilibrium with *N*-chloroacetanilide and hydrobromic acid, but on the rate at which the brominating agent is produced (stage I). The reaction is analogous to that between *N*-chloroacetanilide and hydrochloric acid in water, where the speed is governed by the rate at which chlorine is produced (*J. Physical Chem.*, 1927, **31**, 1192), although in acetic acid (Orton and Jones, *loc. cit.*) the rate is governed by the second of the consecutive stages. As in the interaction of *N*-chloroacetanilide and hydrochloric acid in aqueous solution, the addition of acetanilide to the mixture of *N*-chloroacetanilide and hydrobromic acid caused a small increase (some 6%) in the observed rate of fall of titre, but this is probably due to the elimination, by the introduction of the readily *C*-brominated acetanilide, of the formation of *N*-bromoacetanilide which appears in the iodine titre and reduces its rate of fall.

In accordance with this view, increase of the acetanilide concentration beyond a certain limit, *e.g.*, 0·01*M*, had no further effect on the observed rate of fall of iodine titre, which therefore, when acetanilide is present, measures the rate of production of the brominating agent.

Since the hydrogen-ion concentration is constant during the interaction (owing to the rapidity of stage II), the velocity equation may be simplified from $v = kc_{\text{NCl}}c_{\text{H}}c_{\text{Br}}$ to $v = k_2c_{\text{NCl}}c_{\text{Br}}$, and in accordance with this equation it was found that k_2 was independent of the relative amounts of the chloroamine and bromide ion present, but varied directly as the hydrogen-ion concentration.

As the measurements of the velocity coefficients in the various media were made in the presence of 0·01M-hydrobromic acid, the rate of hydrolysis of the chloroamine to hypochlorous acid under the influence of the hydrogen ion ($k = 0·3 \times 10^{-5}$; Soper and Pryde, *loc. cit.*) is negligible in comparison with velocity coefficients which range from 20 to 75. The small acid concentrations employed cause the present investigation to be much simpler than that of the interaction of N-chloroacetanilide and hydrochloric acid: in particular, the activities of the chloroamine in the various media do not require correction in the reaction mixture for the effect caused by the presence of the other reactant, hydrobromic acid.

Measurement of the Velocity Coefficient.—N-Chloroacetanilide was found to be sufficiently stable in all the media, there being no fall of titre in 2 hrs. and only 0·3% (approx.) in 18 hrs. The reaction mixture was prepared by adding the requisite quantity of 0·1N-hydrobromic acid in the specified medium to N-chloroacetanilide and acetanilide also dissolved in the medium, both solutions having previously attained the temperature of the thermostat, *viz.*, 25·00°. In this way the heat of mixing was minimised. The temperature of the reaction mixture was maintained constant to ± 0·01° by placing in it a thin-walled coil of glass tubing through which the thermostat water was driven; without this device, owing to the heat of the reaction, the temperature rises about 0·15°, corresponding to a 5% change in the reaction velocity.

A pipette standardised to remove 10 c.c. of liquid at 25° was used to withdraw portions of the mixture, which were run into acidified potassium iodide and titrated with thiosulphate in a current of nitrogen. The mean deviation from the mean of the values obtained for the velocity coefficient in 2—4 experiments in each medium was about 1%, which corresponded with the precision to be expected from the degree of temperature control. A typical example is given in Table V, the thiosulphate being 0·01004N.

TABLE V.

$NaNO_3 = 1·0M$; $:NCl = HBr = 0·01M$.

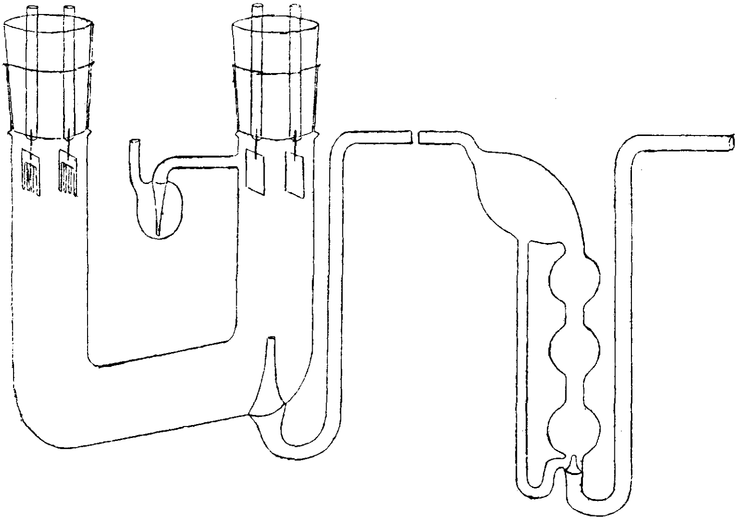
t (mins.).	Titre, c.c.	k_2.	t (mins.).	Titre, c.c.	k_2.
2·09	14·10	—	3·15	12·60	—
4·72	10·60	17·74	5·57	9·90	17·87
7·80	8·21	17·75	8·25	8·05	17·54
11·02	6·61	17·94	10·82	6·84	17·40
14·22	5·58	17·80	13·92	5·71	17·70
17·17	4·85	17·88	16·98	5·00	17·39
	Mean	17·82 ± 0·07		Mean	17·59 ± 0·17

Other values of k_2: 17·16 ± 0·07 and 17·11 ± 0·02.

The Activity of the Chloroamine.—The activity coefficient of the chloroamine was calculated on the assumption that the activity of the solid at 25·0° is equal to its concentration in its saturated aqueous solution, *i.e.*, $f = S_{\text{water}}/S_{\text{medium}}$, where S_{water} and S_{medium} are the respective solubilities (mols./litre) at 25·0° in water and in the medium concerned. The method used for measuring the solubility of the chloroamine has already been described (J., 1927, **131**, 2768). The solubility in water at 25° was found to be 0·01390 mol. per litre; its temperature coefficient is approximately 0·0004 mol. per litre per degree and the temperature was controlled to 0·1°. The values obtained for the activity coefficient are given in Table IV.

The Activity of Hydrobromic Acid in Aqueous Media.—A diagram of the cell Ag,AgCl|HBr soln.|H_2(Pt) is given in Fig. 2. Compressed electrolytic hydrogen was purified by passage over palladised copper at 300°, through alkaline permanganate, concentrated sulphuric acid, caustic potash, and finally through a solution similar to that in the cell. Satisfactory hydrogen electrodes for use in aqueous salt solution, in aqueous-alcoholic solutions, and in aqueous sucrose solutions were obtained by platinising the electrode in 1% chloroplatinic acid solution with a 2-volt accumulator for 5 mins., for 15 mins., and for 30 mins., respectively. The silver bromide electrodes consisted of a bundle of platinum foil covered first with granular silver deposited from a 5% silver cyanide solution by a current of 0·002 amp. for 24 hours, and secondly, after washing, with an anodic deposit of silver bromide by electrolysis in hydrobromic acid solution similar in composition to that to be examined

FIG. 2.



in the cell. Measurements of the *E.M.F.* of two cells each containing duplicate electrodes were taken every ½ hour until constancy was attained. The observed *E.M.F.*'s were corrected for variations from 760 mm. of the partial pressure of the hydrogen which is known from the atmospheric pressure and the vapour pressure of the solution. The results obtained are given in Table VI, where p_{H_2} is the partial pressure of the hydrogen in mm., and c_2 the concentration of hydrogen bromide in mols./litre.

TABLE VI.

Medium.	*E.M.F.*	$c_2 \times 10^2$.	p_{H_2}.	*E.M.F.* (corr.).
Water	0·3139	1·00	741	0·3143
0·1*M*-$NaNO_3$	0·3201	0·997	732	0·3207
0·5 ,,	0·3243	0·985	734	0·3248
1·0 ,,	0·3245	0·970	734	0·3250
1·5 ,,	0·3230	0·955	736	0·3234
2·0 ,,	0·3181	0·941	736	0·3185
0·05*M*-KNO_3	0·3189	0·998	736	0·3193
0·1 ,,	0·3210	0·996	736	0·3214
0·50 ,,	0·3262	0·975	741	0·3266
1·00 ,,	0·3291	0·960	737	0·3295
2·00 ,,	0·3263	0·923	737	0·3267
5% (wt.) MeOH	0·3101	0·990	737	0·3105
10 ,,	0·3080	0·982	737	0·3084
15 ,,	0·3064	0·976	733	0·3069
20 ,,	0·3054	0·970	735	0·3059
25 ,,	0·3036	0·962	733	0·3041
5% (wt.) EtOH	0·3101	0·990	741	0·3105
10 ,,	0·3080	0·982	748	0·3082
15 ,,	0·3058	0·976	744	0·3061
20 ,,	0·3039	0·970	750	0·3041
25 ,,	0·3032	0·963	735	0·3037
5% (wt.) Sucrose	0·3096	1·010	735	0·3101
10 ,,	0·3043	1·039	734	0·3048
15 ,,	0·3020	1·060	734	0·3025
20 ,,	0·2986	1·081	730	0·2992

The value for the *E.M.F.* of the cell when the medium is 0·01*N*-aqueous hydrobromic acid, *viz.*, 0·3143 volt, is in fair agreement with the value 0·3141 volt found by Lewis and Storch (*J. Amer. Chem. Soc.*, 1917, **39**, 2544); the activity of hydrobromic acid in other solvents relative to the foregoing is given by the relation

$$E_{0\cdot01} - E_2 = \frac{RT}{F} \cdot \log\frac{a_{2\mathrm{HBr}}}{a_{1\mathrm{HBr}}} = \frac{RT}{F} \cdot \log\frac{f_{2\mathrm{H}^{\cdot}} f_{2\mathrm{Br}'} c_2^{\,2}}{f_{1\mathrm{H}^{\cdot}} f_{1\mathrm{Br}'} c_1^{\,2}}$$

where $f_{1\mathrm{H}^{\cdot}} = f_{1\mathrm{Br}'}$ has been taken as 0·924 (Livingstone, *ibid.*, 1926, **48**, 45). The activity coefficient of hydrobromic acid in the various media is thus given by

$$\log f_{2\mathrm{H}^{\cdot}} f_{2\mathrm{Br}'} = F/RT \, . \, (E_{0\cdot01} - E_2) + 2 \log 0{\cdot}924 + 2 \log 0{\cdot}01/c_2$$

and the values obtained in this way for $f_{2\mathrm{H}^{\cdot}} = f_{2\mathrm{Br}'}$ are given in Table IV.

Summary.

1. The study of the reaction velocity coefficient in relation to the cohesion of the medium shows that if the reaction is one where the products are of greater cohesion than the reagents, it is accelerated by solvents of high cohesion, whilst if the products are of lower cohesion than the reagents, the reaction is retarded by such solvents. When products and reagents are substances of like cohesion, the solvent has relatively little effect.

2. When the cohesion of the medium is constant, the van 't Hoff or activity velocity coefficient is constant. This is in conformity with other evidence that the cohesion of the solvent more directly affects this coefficient than the concentration velocity coefficient.

3. The reaction $C_6H_5\cdot NClAc + HBr \rightarrow Br\cdot C_6H_4\cdot NHAc + HCl$, where the products are of less cohesion than the reagents, has been studied in various aqueous media. In sucrose solutions, where the surface tension is nearly the same as in water, the activity velocity coefficient is practically constant. In salt solutions, where the cohesion increases, the activity velocity coefficient decreases, whilst in aqueous solutions of alcohols, where the cohesion decreases, the activity velocity coefficient increases, in accordance with theory.

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