138. *The Kinetics of the Reaction between Tin and Solutions of Bromine and Iodine in Organic Solvents.*

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The reaction between tin and halogen (iodine and bromine) solutions has been studied, and the following points established: (1) The reaction is of the first order with respect to the halogen. (2) The velocity constant is proportional to the fluidity of the solvent and to the absolute temperature. (3) The variation of the velocity constant with the rate of stirring is given by the expression $k = Bs + k_0$, where B is a constant, s is the number of revolutions made by the stirrer per minute, and k_0 is the velocity constant when there is no stirring. These results may be explained on the basis of the diffusion theory (Moelwyn-Hughes, " Kinetics of Reaction in Solution ", Chapter IX, Oxford Univ. Press, 1933).

The data relating to the rate of dissolution of solids in solutions of acids and of halogens are meagre. In general, it is found that the kinetics are not governed by chemical considerations at all, but by a diffusion process, though several cases which are exceptions to the diffusion theory have been studied. Usually the chemical reaction taking place at the solid surface is relatively fast. The most comprehensive investigation designed to test the diffusion theory was carried out by Van Name and his co-workers (references in *Amer. J. Sci.*, 1917, **43**, 449); he is the principal worker in this field. Out of a dozen different metals used, it was found that two—magnesium and tin—dissolved faster than would be expected on the basis of the diffusion theory, and this clearly demanded a special explanation. The explanation offered in the case of magnesium is the stirring by hydrogen evolution, and in the case of tin, the fact that this metal can be converted into stannic halide in two stages, so that less halogen need diffuse right to the surface of the tin. Van Name used solutions of iodine in mixtures of iodides and water. Many organic solvents offer the advantage that the iodine is present in the form of simple unsolvated molecules; moreover, the viscosity can be varied over a wide range by the choice of suitable solvent, and hydrogen evolution and salt effects are avoided.

Numerous workers (Wildermann, *Z. physikal. Chem.*, 1909, **66**, 445; Brunner, *ibid.*, 1904, **47**, 56; Friend, *J.*, 1922, 41; Van Name, *loc. cit.*) have made determinations of the effect of the rate of stirring upon the kinetics of reactions governed by a diffusion process. Unless the reacting substance is attached to the blades of the stirrer or is itself the stirrer there is no reason why the stirring effect should be proportional to the rate of revolution of the stirrer. It has been found that when the reacting substance is rotated with the stirrer, a direct proportionality is observed, but when it is suspended in a stirred liquid, the velocity constant varies with the rate of revolution of the stirrer according to some fractional power slightly less than unity. Probably the latter workers just obtained constants for their own apparatus without general significance. When direct proportionality is not observed it would seem likely that attack is not uniform over the whole surface of the reacting body.

Experimental.

The Order of the Reaction.—By studying the rate of loss of weight of a tin cylinder in solutions of iodine in carbon tetrachloride at room temperature or boiling under a reflux condenser or in a chloroform solution of bromine, it was shown that the reaction was of the first order with respect to the halogen. In this case the tin cylinders, which were smoothed with a fine emery paper, were small, of about 0·32 cm. average diameter and 1·5 cm. in length. The readings were obtained by immersing a weighed tin cylinder in the halogen solution for a measured time, after which it is removed, washed in carbon tetrachloride, dried, and re-weighed. The halogen solutions were made up to a suitable initial concentration, a known weight of iodine or known volume of bromine being dissolved in 100 c.c. of solvent.

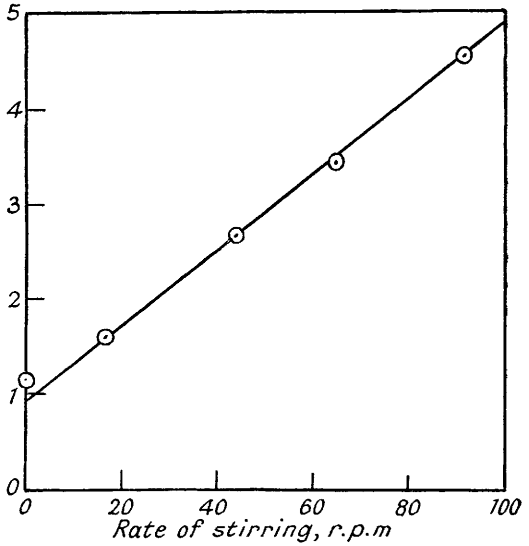
The Effect of the Surface Area of the Cylinder upon the Velocity Constant.—It would be expected, on the basis of most possible theories and certainly on the diffusion theory, that the velocity constant of the first-order reaction would be proportional to the surface area of the tin cylinder. Because of the importance of this for the purpose of correlating results obtained with different cylinders, the proportionality had to be verified. This was done by determining the velocity constant for two cylinders, one having twice the surface area of the other: the smaller was 1·87 cm. long, and the larger 4·13 cm. long, both being of 0·78 cm. diameter. The procedure was as before; the bromine solution, containing 1·9 c.c. of bromine in 50 c.c. of chloroform, was kept in a stoppered glass bottle in a thermostat maintained at 20° during the experiment. It was found that the velocity constant was proportional to the surface area of the cylinder to within 1%, the ratio of the two constants being 1 : 2·01.

The Effect of the Fluidity of the Solvent upon the Velocity Constant.—For this series of experiments the cylinders were small, 1·44 cm. long and 0·31 cm. in diameter, the weights being the same within 0·003 g.; they were all cut from the same tin rod, and all smoothed with the same grade of emery paper. Their surface areas may therefore be considered identical. The solvents employed were chloroform, carbon tetrachloride, and ethylene dibromide, none of which reacts appreciably with the bromine in the few hours for which the solutions are used, at the temperature of the experiment. The experiment was conducted in stoppered glass bottles in a thermostat at 20°, and the procedure was as before. The results obtained are recorded in Table I. In all cases the velocity constant is multiplied by 100. The values quoted for the fluidities are due to Thorpe and Rodger; time is expressed in minutes throughout. The values for k are obtained by using the formula $k = (1/t) \ln W_1/W_2$, where t is the time between successive weighings, and W_1 and W_2 are the weights of the tin cylinder before and after immersion. The result of this experiment shows that the velocity constant is directly proportional to the fluidity of the solvent.

Table I.

	Chloroform.		Carbon tetrachloride.		Ethylene dibromide.	
	Time.	k.	Time.	k.	Time.	k.
	80	0·124	80	0·073	80	0·043
	180	0·124	180	0·073	180	0·041
	280	0·143	320	0·076	320	0·039
	450	0·108	450	0·074	450	0·041
Mean value of k		0·124		0·074		0·041
Fluidity of solvent, $1/\eta$		177		104		58·3
$k\eta \times 10^4$		0·702		0·711		0·703

The Effect of the Temperature upon the Velocity Constant.—From the foregoing, it follows that if the temperature effect is to be investigated, allowance must be made for the variation of the fluidity with temperature. In this experiment, the tin cylinders employed were of the larger diameter and had surface areas varying between 5·5 and 6 sq. cm. Accordingly, all the velocity constants are here reduced to unit surface area. The solutions used were all of chloroform containing 20 c.c. of bromine per l. The results obtained are given in Table II: again, k is multiplied by 100, but $k\eta$ by 10^5. The product $k\eta$ divided by the absolute temperature is found to be constant, so k is directly proportional to the absolute temperature.



The Effect of the Rate of Stirring on the Velocity Constant.—To investigate the effect of altering the rate of stirring upon the velocity constant the tin cylinder was itself rotated: this is the best way to ensure that the stirring effect at the surface of the cylinder is proportional to the rate of revolution of the latter. The tin cylinder used had a short glass rod fitted into a hole bored through the radial axis; the rod was attached by a screw connector to the driving shaft of the stirrer. The rate of stirring was measured by counting the number of revolutions in 0·5 minute at convenient intervals. The bromine solution used contained 1 c.c. of bromine in 50 c.c. of chloroform and was kept at 20° in a thermostat. The results obtained are given in Table III, and are summarised in the figure, from which it will be seen that the variation of the velocity constant with the rate of stirring is given by the equation $k = Bs + k_0$.

Discussion.—The results obtained in the above experiments may be summarised in the equation $dw/dt = ZATw/\eta$, where w is the concentration of the halogen solution, dw/dt is the rate of reduction of its concentration, A the surface area of the cylinder, T the absolute temperature, η the viscosity of the solution, and Z is a constant. This may be compared with the equation obtained on the basis of the diffusion theory; it is a combination of Fick's law and the Stokes–Einstein diffusion law:

$$\frac{ds}{dt} = A\frac{dc}{dz}\frac{\boldsymbol{R}T}{\boldsymbol{N}}\frac{1}{6\pi\eta r}$$

TABLE II.

Temperature:	20°.		25°.		35°.		40°.	
	Time.	k.	Time.	k.	Time.	k.	Time.	k.
	10	0·0920	10	0·0965	10	0·1267	10	0·1588
	20	0·1081	20	0·1318	20	0·1773	20	0·1266
	30	0·1069	30	0·1312	30	0·1196	30	0·1312
	40	0·1382	40	0·1150	40	0·1082	40	0·1472
	50	0·0965	50	0·0903	50	0·1312	50	0·1289
			60	0·0903	60	0·1289	60	0·1610
			70	0·1358	70	0·1289	70	0·1266
			80	0·1266				
Mean value of k		0·1082		0·1150		0·1312		0·1404
Viscosity of $CHCl_3$		0·00564		0·00537		0·00485		0·00460
$k\eta \times 10^3$		0·7855		0·7907		0·0836		0·8111
Temp., °K.		293		298		308		313
$10^5 k\eta/T$		0·207		0·208		0·206		0·206

TABLE III.

Rate of stirring, r.p.m.:	0.		17.		44.		65.		92.	
	Time.	k.	Time.	k.	Time.	k.	Time.	k.	Time.	k.
	10	1·12	10	1·49	2·25	2·30	10	3·56	5	5·12
	20	1·07	20	1·57	17·75	2·58	20	3·51	10	4·39
	30	1·05	30	1·61	27·75	2·95	30	3·18	15	4·16
	40	1·37	41	1·57	39	2·78	40	3·57	22	5·22
	50	0·95	51	1·77	49	2·76			30	3·82
Mean value of k		1·12		1·60		2·67		3·46		4·58

where ds is the quantity of solute which crosses a boundary of area A in time dt, r is the radius of the halogen molecule and accounts for the difference in rates of reaction in the cases of bromine and iodine, and dc/dz is the concentration gradient. It will be seen that the two equations are very similar; the principal difference is that w, the concentration of the halogen solution, is replaced by dc/dz. This implies that the Nernst layer is of constant thickness and is independent of the temperature and the viscosity of the solution. Calculation of the thickness of the Nernst layer, from the experimental value for the velocity constant and the Fick–Stokes–Einstein equation, gives a value corresponding to about 10,000 molecular diameters of stannic iodide. A comparison of the rates of reaction of iodine and bromine shows that the ratio of the velocity constants under similar conditions is 3 : 4.

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