126. *The Kinetics of the Dissolution of Zinc in Aqueous Iodine Solutions. Part III.**

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Zinc, copper, amalgamated copper, brass, lead, and nickel dissolve in aqueous iodine solutions at the same rate under the same experimental conditions. The observed rate of dissolution of zinc is independent of the crystal face exposed to attack, but is a function of the rate of stirring and is higher on the leading edges of the specimen than on the trailing edges. The results are in agreement with Levich's theory. It is concluded that the observed rate is determined solely by the rate of transport of iodine to the metal surface.

On the basis of experimental results reported in Parts I and II (*J.*, 1951, 598, 1490) it was concluded that the observed rate of dissolution of zinc in aqueous iodine solutions is at least partly determined by the rate of transport of iodine to the metal surface, and that it is independent of the rate of recession of products from the surface, under the conditions studied. The experiments described in this paper were designed to find whether the rate of chemical reaction at the surface makes any contribution to the observed rate of dissolution. The following points have been investigated: (1) The rate of dissolution of certain other metals in aqueous iodine solutions; (2) the rate on different crystal faces of the zinc specimen; (3) the influence of the rate of stirring; (4) the variation in the observed rate on the leading and the trailing edges of the specimen.

Experimental

The apparatus and experimental method have been described (Part I, *loc. cit.*). The solutions were initially N/25 in iodine and N/100 with respect to sulphuric acid. The temperature was 25° ± 0·01°. Except where otherwise stated, the rate of stirring was 100 r.p.m.

Rate of Dissolution of Other Metals.—The rate of dissolution of copper in a solution of standard composition (4N/25-potassium iodide), and of copper, amalgamated copper, brass, lead, and nickel-foil specimens in solutions 4N. with respect to potassium iodide, was studied. The copper, lead, and nickel foil were of high purity. The copper and lead were supplied by I.C.I. Metals Ltd., through the courtesy of Dr. Maurice Cook. The brass sample was not analysed. The observed values of k_1, the rate constant per unit area at unit volume, are recorded in Table 1; the corresponding value for zinc foil (Table I, Part II) has been included for comparison. In the case of copper in the 4N/25-potassium iodide solution, and of lead, a fall-off in the observed rate occurred after 15 min. This effect was traced to the separation of solid cuprous and lead iodides, respectively, neither of which adhered firmly to the metal surface: initial values of k_1 are therefore recorded for these runs.

Table 1.

Metal	Concn. of KI, moles/l.	k_1 (obs.)*	Metal	Concn. of KI, moles/l.	k_1 (obs.)*
Copper	0·16	0·113,† 0·114 †	Lead	4·0	0·163 †
Copper	4·0	0·165	Nickel	4·0	0·164, 0·164
Amalgamated copper	4·0	0·165	Zinc	4·0	0·164
Brass	4·0	0·166			

* Here and throughout, k_1 is given in the units cm. min.$^{-1}$ † Initial value.

Rate on Different Crystal Faces.—To determine whether the observed rate varies on different faces, two cast-zinc cylinders were used. In one, the crystal *c* axes were orientated parallel to the axis of the cylinder, in the other, radially. The cylinders were carefully machined to the required dimensions such that the curved surface was equal in area to a standard size specimen, drilled along the axis, mounted on glass stirring rods, and the ends coated with "Tufnol" lacquer. Before use, they were etched for 10 sec. in 5N-hydrochloric acid to remove the worked surface. Care was taken to ensure that the two cylinders were rotated at the same

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* Part II, *J.*, 1951, 1490.

point in the reaction vessel. Between runs they were stored under 0·003N-sulphuric acid. The observed values of k_1 are recorded in Table 2. In Fig. 1, values of the function $(\Sigma v\,.\,\Delta \log c)/A$ (see Part I) are shown plotted against time for one run with each cylinder. The origin for one run is displaced to distinguish the experimental points; the standard slope for zinc foil is included for comparison.

TABLE 2.

Orientation of *c*-axes	k_1 (obs.)	Mean k_1	Orientation of *c*-axes	k_1 (obs.)	Mean k_1
Horizontal	0·114, 0·113	0·114	Vertical	0·112, 0·109	0·111

Rate of Stirring.—The effect of varying the rate of rotation of the specimen was investigated over the range 50—200 r.p.m. In each case, the rate of stirring was maintained constant to within ±1% by means of the stroboscope and manual control described in Part I. The observed values of k_1 are recorded in Table 3. The log–log plot of the mean values of k_1 against rate of stirring is shown in Fig. 2.

FIG. 1.

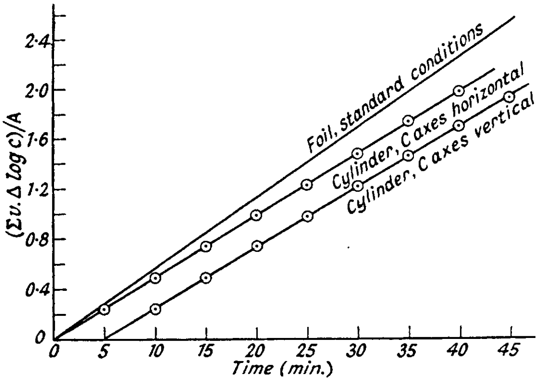

FIG. 2.

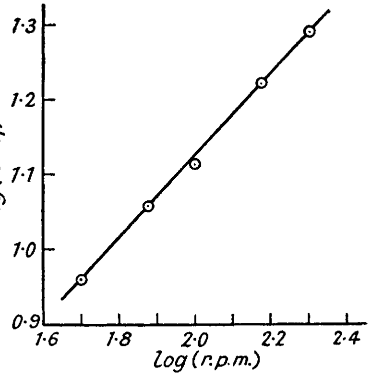

TABLE 3.

Rate of stirring, r.p.m.	50	75	100	150	200
k_1 (obs.)	0·0919, 0·0910	0·114, 0·113	0·130, 0·130	0·167, 0·166	0·198, 0·194
Mean k_1	0·0915	0·114	0·130	0·167	0·196

Rate on the Leading and the Trailing Edges.—Examination of the specimen after a run frequently revealed a difference in the extent of attack on the leading and the trailing edges. This effect was particularly noticeable in the runs in very dilute iodine solutions reported in Part I, large patches of the original polished surface being left on the trailing edges. To investigate the effect, one half of each side of a standard size specimen was coated with "Tufnol" lacquer so that by placing it in the specimen holder one way up the two leading edges were exposed, whereas by placing it in the holder the other way up the two trailing edges were exposed to attack. Preliminary tests confirmed that the coating was resistant to attack and penetration by iodine. The observed values of k_1 are recorded in Table 4. The results for one run in which the leading edges and for one in which the trailing edges of the same specimen were exposed are shown in Fig. 3.

TABLE 4.

	Specimen no. 1	Specimen no. 2
Leading edge attack : k_1	0·135	0·135
Trailing edge attack : k_1	0·125	0·127
Mean k_1	0·130	0·131

DISCUSSION

The fact that, under the same conditions, copper, amalgamated copper, brass, lead, nickel, and zinc dissolve at the same rate within the limits of experimental error confirms the work of Van Name and his co-workers (*Amer. J. Sci.*, 1910, **29**, 237; 1911, **32**, 207), and suggests that the observed rate is determined solely by the rate of transport of iodine to the metal surface. If, then, the rate of chemical reaction at the surface is too fast to influence the observed rate, the latter should be independent of the crystal face exposed to attack. No reaction for which the observed rate varies on different faces of a zinc crystal has been reported in the literature, but for other systems the difference is quite marked; *e.g.*, Spring (*Z. physikal. Chem.*, 1888, **2**, 13) found the rate of dissolution in dilute acids of Iceland spar at surfaces cut parallel to the crystal axis to be *ca.* 1·3 times larger than at surfaces cut parallel to the natural plane of cleavage. As is well known, measurements of physical properties of zinc crystals show similar variations. Thus, Bochvar and Sviderskaya (*Chem. Abs.*, 1946, **40**, 2369) report that the coefficient of linear expansion along the main axis of the hexagonal prism is 3·7 times larger than the corresponding value measured normal to this axis; McLennan, Ruedy, and Cohen (*Proc. Roy. Soc.*, 1928, *A*, **121**, 9) find the corresponding ratio of the magnetic susceptibilities to be 1·6. The observed ratio, 1·03, for the rate of dissolution of the two zinc cylinders would therefore suggest that the observed rate is the same in each case, within the experimental limits of error.

On the assumption of transport control, the remaining results are readily interpreted. The dependence of k_1 on the rate of stirring is a characteristic feature of such reactions; as will be seen from Fig. 2, the dependence may be expressed $k_1 = 0{\cdot}0103\ (\text{r.p.m.})^{0{\cdot}56}$, the power being in reasonable agreement with the square-root relationship deduced by Levich (*Acta Physicochim. U.R.S.S.*, 1942, **17**, 257). From the results the variation of δ, the thickness of the Nernst diffusion layer (*Z. physikal. Chem.*, 1904, **47**, 52), with rate of stirring can be calculated. On the simple Nernst theory $\delta = D/k_1$, where D is the coefficient of diffusion of iodine. Values calculated from this expression, by using the value $D = 1{\cdot}22 \times 10^{-5}$ cm.^{2} sec.$^{-1}$ obtained from the empirical relation derived in Part II (*loc. cit.*), are recorded in Table 5. Also shown are the values calculated from Levich's expression $\delta = 1{\cdot}613 D^{\frac{1}{3}} \nu^{\frac{1}{6}} \omega^{-\frac{1}{2}}$, where ω is the angular velocity of the specimen, and ν the kinematic viscosity of the solution. [*Note.* Levich (*loc. cit.*) obtained the value 1·62 for the constant of proportionality, but this is based on too small a value of the function Γ (4/3) coupled with a slight arithmetical error.]

FIG. 3.

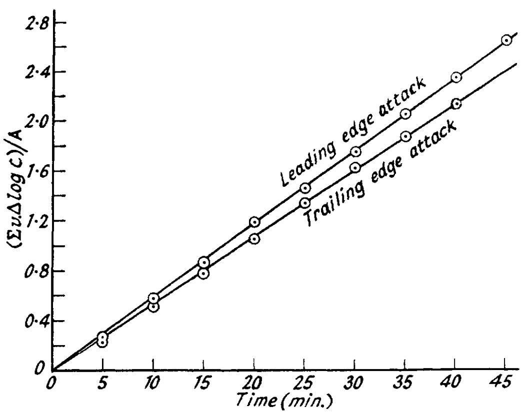

TABLE 5.

ω, rad. sec.$^{-1}$	5·23	7·85	10·5	15·7	20·9
$10^3\ \delta$ (calc. from Nernst eqn.), cm.	7·98	6·40	5·61	4·37	3·72
$10^3\ \delta$ (calc. from Levich eqn.), cm.	7·36	6·01	5·20	4·25	3·68

The agreement is satisfactory, particularly at the higher rates of stirring, as required by Levich's treatment. Although this author derived the expression for the particular case of a plane disc electrode rotating about an axis perpendicular to the plane, he observes that it should be of wider application. The independent nature of this check is of importance since, for the plane disc electrode and for the present system, it now seems possible to calculate the thickness of the conventional diffusion layer without reference to the experimentally observed rate. However, these values are to be regarded as expressing the mean thickness of the layer rather than the actual thickness at any given point on the surface, since the results reported in Table 4 show that the rate is some 7% higher on the leading edges of the specimen than on the trailing edges. This difference is almost certainly due to slight turbulence of the fluid flow, as is shown by the fact that the value of the " stirring coefficient," 0·56, is slightly higher than the value of 0·5 derived by Levich for non-turbulent flow. This point is considered further in the following paper.

Comparison of the rate of dissolution of copper in the presence of a film of cuprous iodide ($k_1 = 0{\cdot}114$) with the standard rate of dissolution of zinc ($k_1 = 0{\cdot}130$), together with the fact that for copper the rate falls off with time, suggests that the film offers resistance to the transfer of iodine to the surface. This is in agreement with the observed fall-off in the rate of dissolution of lead in the presence of a film of lead iodide, and for zinc in the absence of acid, *i.e.*, in the presence of a film of hydroxide (Fig. 4, Part I). Similar results have been reported by Van Name and Edgar (*loc. cit.*, 1910). On the other hand, Bircumshaw and Everdell (*J.*, 1942, 598) found that slowly deposited films of cuprous iodide offer no resistance to mass transfer in aqueous systems.

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