128. *The Kinetics of the Dissolution of Zinc in Aqueous Iodine Solutions. Part I.*

By L. L. Bircumshaw and A. C. Riddiford.

A preliminary study of the rate of dissolution of zinc in aqueous iodine solutions has been made. The observed rate is of first order with respect to the iodine concentration and is directly proportional to the apparent surface area of the zinc specimen over the range investigated. With the exception of specimens polished with rouge, the method of preparation of the surface is without effect on the rate. The rate is independent of the initial concentration of acid over the range N/100 to N/800. Over the temperature range 25—45°, the experimental energy of activation is 3790 cals. per mole. The energy of activation for kinematic viscous flow over the same range is 3570 cals. per mole.

Comparatively little work has been reported on the kinetics of reactions between metals and solutions of halogens. Schükarew (*Z. physikal. Chem.*, 1891, **8**, 76) investigated the rate of reaction between certain metals and iodine, but failure to provide for constant and effective stirring renders his results of uncertain value. Brunner (*ibid.*, 1905, **51**, 95) performed a few experiments on the dissolution of zinc in aqueous iodine solutions and concluded that iodine is reduced by zinc at the same rate as it is reduced electrolytically at a platinum electrode.

The major part of the work in this field has been done by Van Name and his co-workers (Van Name and Edgar, *Amer. J. Sci.*, 1910, **29**, 237; Van Name and Bosworth, *ibid.*, 1911, **32**, 207; Van Name and Hill, *ibid.*, 1913, **36**, 543; Van Name, *ibid.*, 1917, **43**, 449). Their results may be summarised as follows: (1) Under the same conditions, mercury, cadmium, zinc, copper, silver, iron, nickel, and cobalt dissolve in aqueous iodine solutions containing a large excess of potassium iodide at practically the same rate. A slight decrease in the rate of dissolution of copper and silver was attributed to the presence of traces of solid iodide at the interface. (2) The rate constants for tin and magnesium were found to be higher. For tin, the increase was ascribed to the two-stage oxidation of tin to the stannic state; for magnesium, it was thought to be due to increased stirring of the solution by the hydrogen evolved. (3) An increase in the concentration of potassium iodide produces a marked acceleration of the rate. (4) The rate is approximately proportional to the 0·8 power of the rate of stirring. (5) The observed rate decreases with increase in the viscosity of the solution and is consistently lower than the corresponding value calculated from the Arrhenius diffusion equation (*Z. physikal. Chem.*, 1892, **10**, 51). (6) The mean temperature coefficient of the reaction is 1·26 per 10° over the range 0—65°. Moelwyn-Hughes ("Kinetics of Reactions in Solution," 2nd edn., 1947, p. 357) has calculated the energy of activation to be 4040 cals. per mole.

These observations are consistent with the view that the rate is determined by the rate of transport of iodine to the metal surface. Van Name and Edgar ascribed the increase of rate with increasing potassium iodide concentration to an increase in the diffusion coefficient of the tri-iodide ion. Edgar and Diggs (*J. Amer. Chem. Soc.*, 1916, **38**, 253) confirmed this view by measuring the diffusion coefficient at 25°. They were unable, however, to correlate the change in diffusion coefficient with the change in viscosity of the solution. Similar results have been obtained by Miller (*Proc. Roy. Soc.*, 1924, *A*, **106**, 724).

Bircumshaw and Everdell (*J.*, 1942, 598) made a further study of the reaction between copper and aqueous iodine solutions, and found that for a large range of iodine concentrations the rate of reaction is unaffected by the presence or thickness of cuprous iodide films, and postulated that the reaction proceeds by the passage of both iodine and solvent through the iodide film. The rate of reaction is not dependent on the method of preparation, or degree of smoothness of the metal surface, and is unaffected by the rate of stirring provided that this is fairly high. The rate increases with increasing concentration of potassium iodide, as found by Van Name and Edgar. Bircumshaw and Everdell (*J.*, 1947, 1119) also investigated the rate of reaction between copper and solutions of iodine in organic solvents. Here the rate of reaction appears to be partly controlled by the thickness of the iodide film. The resistance to mass transfer of an iodide film has also been reported by Evans and Bannister (*Proc. Roy. Soc.*, 1929, *A*, **125**, 370). Trotman-Dickenson and James (*J.*, 1947, 736) have studied the reaction between tin and solutions of bromine and iodine in organic solvents, their results being in accord with the simple Nernst theory.

In recent years attention has been directed towards replacement of Nernst's diffusion theory by a more adequate theoretical treatment. The complex geometry of most experimental systems precludes the complete calculation of mass transfer by convection in terms of the fluid flow in the system. By analogy with the closely related study of heat transfer, however, a semi-quantitative treatment using dimensional analysis has been developed (for details and references see Agar, *Faraday Soc. Discussion*, 1947, **1**, 26). In view of the ease with which the reaction may be followed, and the absence of complicating factors such as the formation of an insoluble film on the metal surface, gas evolution, etc., the dissolution of certain metals in aqueous iodine solutions is very suitable for the study of mass transfer in solid–liquid systems. It seemed desirable, therefore, to make a more detailed study of the kinetics of the dissolution of zinc in aqueous iodine solutions with the object of confirming that the rate is determined solely by the rate of transport of iodine to the surface.

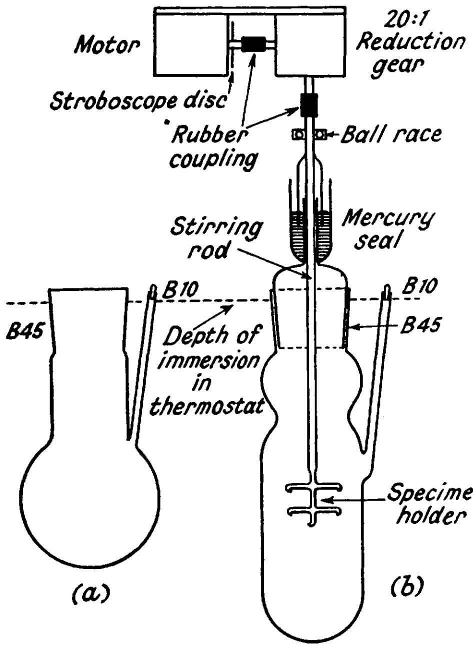
This paper reports the investigation of the following factors: (1) The surface area of the zinc specimen; (2) the method of preparing the metal surface; (3) the temperature; (4) the initial concentration of iodine; (5) the initial concentration of acid.

EXPERIMENTAL.

Materials.—"AnalaR" iodine, potassium iodide, and sodium thiosulphate were used without further purification. The absolute alcohol and benzene used in the preparation of the metal specimens were dried and redistilled before use. The zinc foil, reported to contain Fe 0·005%, Cu 0·002%, and traces of cadmium and lead, was kindly supplied by London Zinc Mills, Ltd.

Apparatus.—The apparatus was an improved form of the type used by Bircumshaw and Everdell (*loc. cit.*, 1947), and is shown in Fig. 1(*b*). The reaction vessel, mercury seal, and stirring rod are drawn to approximately one-fifth scale. The glass specimen holder was constructed so that the edges of the specimen only touched the glass at five points. The holder was slightly off-set so that the axis of the stirrer was in line with the vertical axis of the specimen. The stirrer was driven through a 20 : 1 helical reduction gear by means of a 0·02 H.P. motor. To ensure constant rates of stirring, the motor was controlled by means of a constant-voltage transformer and "Variac" transformer, a stroboscope being used. Tests showed that with this arrangement the rate of stirring could be maintained constant by manual control to within 1%. The glass sleeve of the seal was lubricated lightly with glycerol. This sleeve, together with the ball-race, ensured the absence of "whip" at the lower end of the stirring rod. The motor, stirrer, and mercury seal were mounted in fixed positions on a carrier so that the whole assembly could be raised vertically until the stirrer was out of the reaction vessel. This arrangement ensured that the geometry of the system was the same for all experiments. Fig. 1(*a*) shows a second reaction vessel used in certain experiments described in Part III of this work. It is shown here in order to facilitate comparison with the standard reaction vessel. The thermostat maintained the temperature constant to within ± 0·01°. The burette, pipettes, and thermometers used were calibrated.

FIG. 1.



Standard Preparation of the Zinc Specimen.—The standard specimen size was 4·0 × 3·0 cm., cut from foil 0·039 cm. thick. The dimensions of each specimen were determined by means of Vernier calipers and micrometer before use. Corrections were applied for the slight variations from the standard dimensions. The standard method of preparing the surface was to clean the specimen with cotton-wool soaked in a commercial metal-polish. The specimen was polished with clean cotton-wool until all the metal-polish had been removed. It was next washed thoroughly with distilled water, twice in absolute alcohol, and finally in pure, dry benzene. It was then dried in air and used immediately.

Method.—Unless otherwise stated, the iodine solutions contained 4 mols. of potassium iodide per atom of iodine. The standard initial iodine concentration was N/25. As found by Van Name and Edgar (*loc. cit.*), the velocity constant, in the absence of acid, falls off with time owing to the deposition of zinc hydroxide on the metal surface. To prevent this, the iodine solutions were made 0·01N. with respect to sulphuric acid immediately before use.

The standard procedure was as follows : 300 Ml. of the acidified iodine solution were transferred to the reaction vessel. The stirrer assembly and specimen were lowered into the reaction vessel, the stirrer motor was started, and the rate of stirring adjusted to the required speed by observation of the stroboscope. The standard rate of stirring was 100 r.p.m. Preliminary tests showed that two or three minutes were necessary before the rate of stirring became constant. Zero time was therefore taken as the time of withdrawal of the first sample. 5-Ml. samples were withdrawn at 5-min. intervals, and titrated with standard sodium thiosulphate. In this manner, all samples were withdrawn under exactly similar conditions. The time required for withdrawing a 5-ml. sample was approximately 5 secs., so that no appreciable loss of iodine took place. Blank runs, in which the specimen was replaced by a piece of glass cut to the same dimensions, confirmed that the loss of iodine by evaporation at 25° and 45° was negligible. With few exceptions, experiments were performed at least in duplicate. Standard runs were conducted at frequent intervals to ensure the constancy of the apparatus.

Surface Area of the Zinc Specimen.—Three sizes were studied, the standard size, 3·0 × 3·5 cm., and 3·0 × 3·0 cm. Table I shows the observed values of the velocity constant. The reaction is of first order with respect to the iodine concentration, *i.e.*, $2{\cdot}303v.\mathrm{d}(\log c)/\mathrm{d}t = -kc$, where v is the volume of solution in ml., c is the concentration of iodine in g.-atoms per litre, and k is the velocity constant. Allowance must be made for the stepwise change in the volume of solution. The velocity constant per unit area, k_1, was evaluated graphically by means of the expression : $k_1t = \frac{2{\cdot}303}{A}\Sigma v\ .\ \Delta\log c$, where t is the time in

TABLE I.

Initial concentration of iodine = N/25; 100 r.p.m.; 25°.

Dimensions of specimen, cm.	3·0 × 3·0	3·0 × 3·5	3·0 × 4·0
k_1 (obs.), cm. min.$^{-1}$	0·133, 0·133	0·133, 0·130	0·133, 0·133

minutes, A is the area in sq. cm., and $\Delta \log c$ signifies the difference in $\log c$ at the beginning and end of an interval for which the volume is v (Bradley, *Trans. Faraday Soc.*, 1938, **34**, 278).

Influence of the Method of Preparation of the Surface.—In addition to the standard method of preparing the zinc surface, eight other methods were investigated, including etching it with acid for periods between 5 and 60 secs., abrasion with carborundum powder, polishing with concentrated nitric acid, electrolytic polishing (see Lacombe, Morize, and Chaudron, *Rev. mét.*, 1947, **44**, 87), and polishing with jeweller's rouge. With the exception of the last, the method of preparation of the surface was without effect on the observed rate within the limits of experimental error (mean value of k_1 = 0·131 cm. min.$^{-1}$). A marked increase in rate was observed for specimens polished with rouge (k_1 = 0·144, 0·146 cm. min.$^{-1}$). Surfaces so prepared show a coloured appearance, with marked scratches. Under the microscope, particles of rouge are seen embedded in the metal. The plot of $(\Sigma v \,.\, \Delta \log c)/A$ against t is shown in Fig. 2, together with the graph for a run with an electrolytically polished specimen.

FIG. 2.

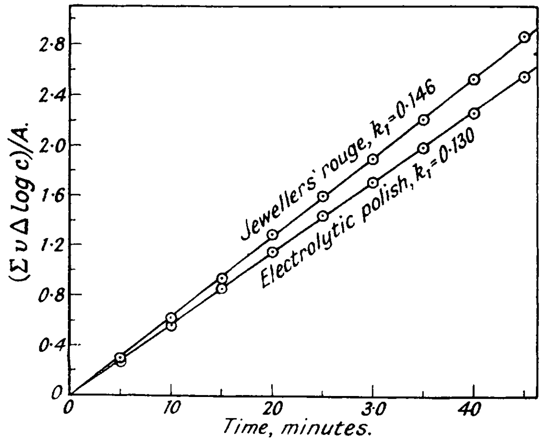
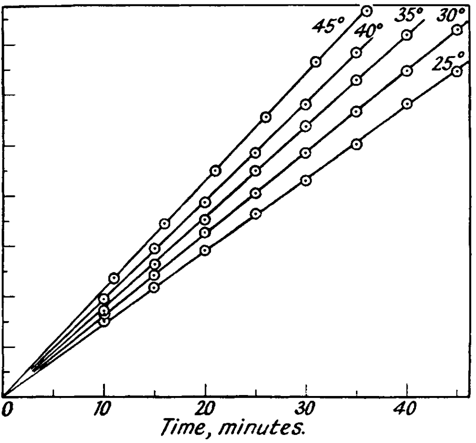


FIG. 3.



Temperature Coefficient.—The rate of reaction was studied at five temperatures over the range 25—45°. The observed values of k_1 are recorded in Table II. Fig. 3 shows the plot of $(\Sigma v \,.\, \Delta \log c)/A$ against t for one run at each temperature. In each case the initial concentration of iodine was N/25, and the rate of stirring 100 r.p.m. The kinematic viscosity, ν, and the density of the iodine solutions were determined at each temperature. The kinematic viscosity was determined with an Ostwald type viscometer corrected for deviations from Poiseuille's law. Values for the absolute kinematic viscosity of water were taken from Bingham and Jackson's results (Goldstein, "Modern Developments in Fluid Dynamics," 1943, Vol. I, p. 5), and values for the density of water from Chappuis's data (Kolthoff and Sandell, "Textbook of Quantitative Inorganic Analysis," 1946, p. 764).

TABLE II.

Temp.	k_1 (obs.), cm. min.$^{-1}$.	Mean k_1, cm. min.$^{-1}$.	d, g./ml.	ν, centistokes.
25°	0·133, 0·132, 0·133, 0·132	0·133	1·0205	0·870
30	0·150, 0·150, 0·149, 0·147, 0·148	0·149	1·0204	0·783
35	0·164, 0·168, 0·164, 0·163, 0·164, 0·165, 0·164, 0·169	0·165	1·0188	0·708
40	0·182, 0·179, 0·183	0·181	1·0180	0·648
45	0·191, 0·200, 0·208, 0·197, 0·195	0·198	1·0162	0·597

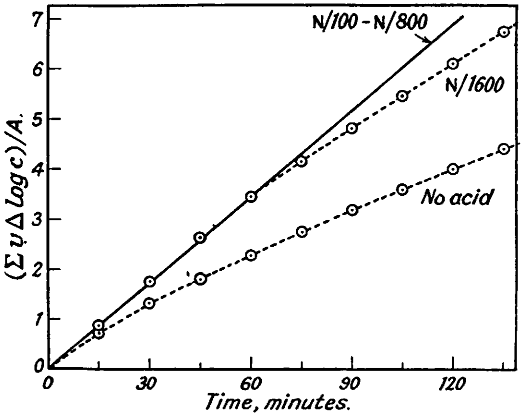
Initial Concentration of Iodine.—The effect of varying the initial concentration of iodine over the range 0·002—0·16N. was studied at 25° and 100 r.p.m. With the exception of the 0·002N-solution, which did not contain potassium iodide, the solutions always contained 4 g.-equivs. of this salt per g.-equiv. of iodine initially present. A 1% solution of sodium starch glycollate (1 : 10) (Peat, Bourne, and Thrower, *Nature*, 1947, **159**, 810) was used as indicator for the titrations. The observed values of k_1 are recorded in Table III, together with the determined values of the kinematic viscosity and density of the iodine solutions.

TABLE III.

Initial concn. of I, g.-equiv./l.	k_1 (obs.), cm. min.$^{-1}$.	Mean k_1, cm. min.$^{-1}$.	d, g./ml.	ν, centistokes.
0·002	0·129, 0·129	0·129	0·9972	0·903
0·005	0·129, 0·127	0·128	1·0009	0·897
0·01	0·129, 0·128	0·129	1·0025	0·891
0·02	0·131, 0·129	0·130	1·0087	0·883
0·04	0·131	0·131	1·0205	0·870
0·08	0·131, 0·135, 0·134	0·133	1·0404	0·846
0·16	0·136, 0·136	0·136	1·0888	0·799

Initial Concentration of Acid.—The effect of varying the initial concentration of sulphuric acid over the range 0—0·01N. was investigated. 5-Ml. samples were withdrawn every 15 mins. The results are shown in Fig. 4 (the experimental points for the runs using N/100-, N/200-, N/400-, and N/800-acid fall closely on the full line, and have been omitted for the sake of clarity). In each case, the initial concentration of iodine was N/25, the rate of stirring and temperature being standard.

FIG. 4.



DISCUSSION.

The investigations reported in this section of the work were conducted with a view to establish standard conditions and as such need little discussion. That the reaction is of first order with respect to the concentration of iodine is shown by Figs. 2 and 3. From the results reported in Table I, it is seen that the observed velocity is directly proportional to the apparent surface area of the specimen over the range investigated. It is permissible, therefore, to correct for the slight variations in size of different specimens from the standard dimensions. Such corrections, and in particular the reduction of the observed velocity constant to unit area, do not imply that the rate of reaction is uniform over the whole area of the surface. From general considerations this would seem unlikely for systems of the geometrical form used in this investigation. Under certain conditions the rate can be shown to differ at different points on the surface. Evidence in support of this view will be reported in Part III. Nevertheless, the use of the rate constant per unit area, k_1, may be justified by regarding it as the average rate per unit area. As will be seen from the results, it is reproducible.

With the exception of specimens polished with rouge, the method of preparing the surface appears to be without effect on the observed rate. The fact that scratched or deeply etched specimens react at the same rate as highly polished specimens would seem to indicate that the rate is dependent on the apparent area, and not on the true surface area. This would follow from the simple Nernst diffusion theory provided the height of the surface irregularities is small compared with the mean thickness of the diffusion layer (see Brunner and Tolloczko, *Z. physikal. Chem.*, 1900, **35**, 283). In terms of the fluid flow in the system, the picture is rather more complex. The relative roughness of the surface is defined as the ratio of the mean height of the surface irregularities to the characteristic length of the system. For fluid flow through a pipe, where the characteristic length is taken to be the internal diameter of the pipe, Nikuradse (*Forschungsheft* No. 361, Suppl. to *Forschung auf dem Gebiete des Ingenieurwesens*, 1933, 4*B*, July/August) has shown that wall roughness over the range 1/507 to 1/15 is without effect on the friction factor in the region of laminar flow, but that it has considerable effect in the case of turbulent flow. In a later part of this work it will be shown that there are grounds for believing the flow to be non-turbulent under the experimental conditions used in this investigation. One would therefore expect the method of preparing the surface to be without effect on the observed rate, provided that the rate is determined solely by the rate of a transport process. The penetration of rouge into a zinc surface when used as a polishing agent has also been reported by Vernon, Akeroyd, and Stroud (*J. Inst. Metals*, 1939, **65**, 301) in their study of the rate of oxidation of zinc. For this reaction, the rouge appeared to have little effect on the observed rate. No explanation has been found for the marked increase in rate for the reaction with iodine.

The mean temperature coefficient over the range 25—45° is 1·22 per 10°, *i.e.*, of the same order as that of the diffusion coefficients of several solutes in liquids over the same range. Applying the method of least squares to the 25 values of k_1 recorded in Table II, we find the velocity constant per unit area to be given by the expression $k_1 = 78{\cdot}1 \exp. (-3790/\boldsymbol{R}T)$. E_A, the experimental energy of activation, is in good agreement with the value 4040 cals./mole calculated from Van Name's data for cadmium by Moelwyn-Hughes (*loc. cit.*). Edgar and Diggs (*loc. cit.*) studied the diffusion of iodine in potassium iodide solutions at 25°. Miller's investigations were similarly confined to one temperature (19·91°). From their results, the activation energy of the diffusion process, E_D, is about 5000 cals./mole, the small temperature range making any closer evaluation impossible.

The influence of viscosity on the rate of reaction has been studied in more detail, and will be reported in Part II. It will be shown that the observed rate is a function of the kinematic viscosity (*i.e.*, the ratio of the coefficient of dynamic viscosity to the density) rather than of the dynamic viscosity. It was for this reason that no effort was made to measure the densities with any great accuracy. The values of the kinematic viscosity are thought to be correct to within 0·5%, and are given by the expression $\nu = 2{\cdot}10 \times 10^{-5} \exp. (3570/\boldsymbol{R}T)$. The similarity in magnitude between the activation energy for kinematic viscous flow, E_ν, and E_A is of interest. It is usual to find values of the activation energy for dynamic viscous flow, E_η, slightly smaller than E_D (see Taylor, *J. Chem. Physics*, 1938, **6**, 331). Similarly, E_ν will usually be smaller than E_D. Thus, Orr and Butler (*J.*, 1935, 1273), studying the diffusion of deuterium hydroxide in water, found E_D to be 5300 cals./mole over the range 0—45°. Over the same range, both E_η and E_ν have the same value, *viz.* 4200 cals./mole.

From Table III it is seen that the observed rate constant varies but slightly with the initial concentration of iodine. Variation is most marked at the higher concentrations, and is almost certainly due to the lowering of the viscosity of the solution by the increased concentration of potassium iodide. The variation is not large enough to show whether k_1 is inversely proportional to the viscosity. With the exception of the two largest values, all the values of k_1 are constant within the limits of experimental error. It is of interest to note that the velocity in the absence of potassium iodide is of the same value.

Variation of the initial concentration of acid over the range N/100—N/800 is without effect on the observed rate. The fall in the rate with time in the absence of acid is marked, and moreover is not reproducible. Examination of specimens after runs without acid shows that the surface is covered irregularly with white patches of hydroxide.

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