127. *The Kinetics of the Dissolution of Zinc in Aqueous Iodine Solutions. Part IV.**

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The results reported in previous papers may be correlated by means of the expression $Nu = 0{\cdot}558 Re^{0{\cdot}56} Pr^{0{\cdot}27}$, in agreement with the theory developed by Levich. The fluid flow is but slightly turbulent. The reaction may be used to characterise the fluid flow in other solid–liquid systems. The validity of Buben and Frank-Kamentzkiĭ's treatment is discussed.

From the work reported in Parts I—III (*J.*, 1951, 598, 1490, and preceding paper) it is concluded that the observed rate of dissolution of zinc in aqueous solutions of iodine is determined solely by the rate of transport of iodine to the metal surface. This system, therefore, is suitable for the characterisation of the fluid flow in other solid–liquid systems. In this connection, it seems desirable to see how far the results obtained for the present system may be correlated by dimensional analysis (see Agar, *Faraday Soc. Discuss.*, 1947, **1**, 26).

The surface of the specimen may be regarded as the only boundary surface of the system. This is justified on the following grounds. First, an increase in the initial volume of solution has but a small effect on the observed value of k_1, the rate constant per unit area at unit volume, as will be seen from Table 1. Duplicate runs were performed in a second reaction vessel [Fig. 1(*a*), Part I], the initial volume of solution being 350 ml. The observed values of k_1 (0·133, 0·133) are closely similar to the values recorded in Table 1,

Table 1.

Initial vol. of soln., ml.	300	350	400
Mean k_1 (obs.) †	0·130	0·130	0·134

† Throughout this paper, k_1 is given in the units cm. min.$^{-1}$, except in Table 2.

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* Part III, preceding paper.

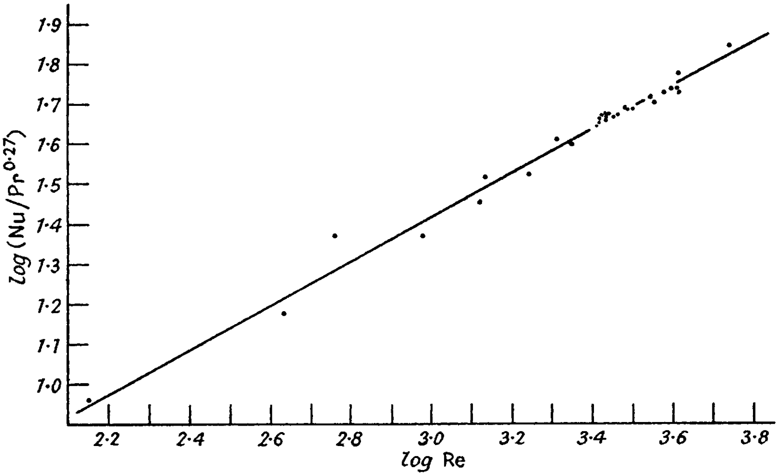
the inference being that the containing walls are too far from the specimen to affect the observed rate. Moreover, the theory developed by Levich (*Acta Physicochim., U.R.S.S.*, 1942, **17**, 257) and utilised in the preceding paper requires that the only surface of discontinuity in the system be that of the solid–liquid interface. The measure of agreement found between values of δ, the thickness of the "diffusion layer," calculated from Levich's theory and from the simple Nernst theory suggests that for the present system the assumption is justified.

In these circumstances, the problem reduces to the determination of the relation between k_1, the characteristic velocity of the system U, the characteristic length l, the coefficient of diffusion of iodine D, the kinematic viscosity of the solution ν, and the mean height of the surface irregularities h. The relation between these six quantities may be expressed as a relationship between four dimensionless groups as follows :

$$\left(\frac{k_1 l}{D}\right) = A'\left(\frac{Ul}{\nu}\right)^a\left(\frac{\nu}{D}\right)^b\left(\frac{h}{l}\right)^c$$

where the ratio k_1l/D is termed Nusselt's number *Nu*; Ul/ν, Reynold's number *Re*; ν/D, Prandtl's number *Pr*; and h/l is the relative roughness of the surface. A' is a number dependent only on the shape of the specimen and the type of fluid flow. As discussed in Part I, Nikuradse (*Forschungsheft* No. 361, Suppl. to *Forschung auf dem Gebiete des Ingenieurwesens*, 1933, 4*B*, July/August) has shown that relative roughness over the range 1/507 to 1/15 is without effect on the friction factor in the region of non-turbulent flow, but that it has considerable effect in the case of turbulent flow. This effect becomes important at an *Re* which is smaller the larger the value of the relative roughness. Since the values of h/l for the present system are small and, as will be shown shortly, the flow was but slightly turbulent, the index c on the relative roughness may be set equal to zero.

FIG. 1.



The characteristic velocity of the system is taken to be the linear velocity of the edge of the specimen and l to be one half the width of the specimen, $L/2$, whence $Re = (\pi L^2 n)/2\nu$, where n is the number of revolutions of the specimen per sec. Then since, as shown in Parts II and III, k_1 is proportional to $n^{0{\cdot}56}$ and to $\nu^{-0{\cdot}76}$, whilst $D = 0{\cdot}0529(1/\nu)^{0{\cdot}63}$, the Reynold's power $a = 0{\cdot}56$ and the Prandtl power $b = 0{\cdot}27$. Finally, the value of the number A' may be calculated from the experimental results. Values so calculated are shown in the last column of Table 2, in which are tabulated values of k_1, ν, U, D, *Nu*, *Re*, and *Pr*. Under the heading "System" references to the experimental sections are given, thus II. 1 denotes Part II, Table 1, etc. As will be seen, the calculated value of A' is constant and has a mean value of 0·558. The maximum deviation from the mean value is 8·2%, the average deviation being 3·4%. This is considered satisfactory in view of the fact that *Re* has been varied over a 38-fold range, whilst the variation in *Pr* is 238-fold. Hence, for the present system, $Nu = 0{\cdot}558 \,.\, Re^{0{\cdot}56} \,.\, Pr^{0{\cdot}27}$. In Fig. 1 log $(Nu/Pr^{0{\cdot}27})$ is shown plotted against log *Re*, the solid line representing the above expression. In view of the somewhat uncertain diffusion data, the correlation is satisfactory.

TABLE 2.

System	10^3k_1, cm. sec.$^{-1}$	$10^2\nu$, cm.^{2} sec.$^{-1}$	U, cm. sec.$^{-1}$	10^5D, cm.^{2} sec.$^{-1}$	*Nu*	*Re*	*Pr*	*A′*
II. 1	2·18	0·870	15·7	1·22	269	2710	716	0·577
,,	2·22	0·819	,,	1·27	263	2880	648	0·560
,,	2·32	0·751	,,	1·33	261	3140	564	0·549
,,	2·48	0·659	,,	1·45	257	3580	455	0·533
,,	2·65	0·628	,,	1·49	266	3750	421	0·548
,,	2·73	0·600	,,	1·53	267	3930	391	0·547
,,	2·73	0·581	,,	1·57	262	4050	371	0·534
,,	2·72	0·577	,,	1·57	259	4080	367	0·528
II. 2	1·78	1·065	,,	1·07	249	2210	993	0·549
,,	1·43	1·350	,,	0·923	232	1750	1 460	0·525
,,	1·15	1·782	,,	0·774	222	1320	2 300	0·520
,,	0·878	2·479	,,	0·629	210	950	3 940	0·512
,,	0·483	5·490	,,	0·381	190	429	14 400	0·513
,,	0·237	16·58	,,	0·190	187	142	87 300	0·580
II. 3	2·17	0·889	,,	1·20	271	2650	742	0·584
,,	2·18	0·833	,,	1·25	262	2830	666	0·559
,,	2·32	0·786	,,	1·30	268	3000	605	0·568
,,	2·18	0·876	,,	1·21	271	2690	724	0·580
,,	2·32	0·769	,,	1·32	264	3060	584	0·558
,,	2·55	0·677	,,	1·42	269	3480	476	0·560
,,	2·12	0·904	,,	1·19	268	2610	762	0·576
,,	2·07	0·905	,,	1·19	261	2600	763	0·563
,,	2·02	0·917	,,	1·18	257	2570	780	0·555
,,	2·12	0·877	,,	1·21	263	2690	725	0·564
III. 3	1·53	0·870	7·85	1·22	188	1350	716	0·593
,,	1·90	0·870	11·8	1·22	234	2030	716	0·589
,,	2·17	0·870	15·7	1·22	267	2710	716	0·572
,,	2·78	0·870	23·6	1·22	343	4060	716	0·588
,,	3·27	0·870	31·4	1·22	403	5420	716	0·587

According to Levich (*loc. cit.*) the equations for the rotating disc system are of the form :

$$\text{Non-turbulent flow}: \; Nu = A' \,.\, Re^{0{\cdot}5} \,.\, Pr^{0{\cdot}33}$$
$$\text{Turbulent flow}: \; Nu = B \,.\, Re^{a} \,.\, Pr^{0{\cdot}33}$$

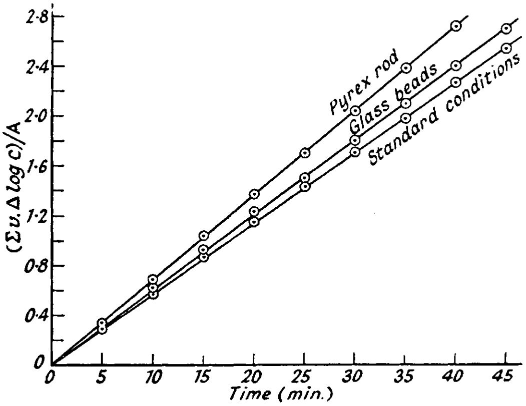
i.e., the dependence of *Nu* on *Pr* is the same for both types of flow. The change in flow-type is accompanied by a change in the "apparatus number," and in the dependence of *Nu* on *Re*. As the degree of turbulence increases, *a* increases from 0·5 to a limiting value of unity. That in fact there is a lower critical Reynold's number for stirred systems, analogous to the system of pipe-flow, has been shown by Hixson and Luedeke (*Ind. Eng. Chem.*, 1937, **29**, 927) and by Hixson and Baum (*ibid.*, 1941, **33**, 478; 1942, **34**, 194). The present results are in reasonable agreement with Levich's theory, the power of *Re* indicating that the flow was but slightly turbulent.

This was confirmed experimentally by rotating a specimen in 300 ml. of water and inserting permanganate solution from a fine capillary tube. At all rates of stirring used in the present investigation, filaments originating along the height of the specimen flowed in circular paths about the axis of rotation. Moreover, the degree of turbulence in the system could readily be increased. Pyrex rod, 1 cm. in diameter, was drawn into 4-cm. lengths with pointed ends. A number of these, of total volume 50 ml., were packed into the bottom of the reaction vessel. In the lower layer, the lengths were packed vertically; the few remaining lengths were placed on top to form a second layer. Fig. 2 shows values of the function $(\Sigma v \,.\, \Delta \log c)/A$ (see Part I) plotted against time for one run; also shown is the plot for a run using glass beads, 0·4 cm. in diameter, of total volume 50 ml. The effect is large, and surprisingly reproducible. Thus, for runs using the Pyrex rod were found values of $k_1 = 0{\cdot}157, 0{\cdot}155, 0{\cdot}157, 0{\cdot}158$.

From the simple Nernst theory, k_1 should be directly proportional to D (*i.e.*, *Nu* should be constant), provided the rate of stirring is constant. Examination of the relevant values recorded in Table 2 shows that *Nu* is in fact approximately constant except for the cases where very viscous solutions were used. It is a feature of the study of transport-controlled reactions that it is necessary to vary the experimental conditions over very wide ranges in order to be able to check the validity of any conclusion.

Lastly, mention should be made of Buben and Frank-Kamenetzkiĭ's extension (*J. Phys. Chem. U.S.S.R.*, 1946, **20**, 225) of the dimensional treatment to systems in which the flow is strongly turbulent. These authors postulate that for the limiting case of pure turbulence k_1 must be independent of both D and ν, *i.e.*, k_1 is entirely determined by the rate of flow. To express this condition they write $k_1 = MU$, where M is termed Margulis's number. As the limiting case of complete turbulence of flow is approached, M must tend to a constant value. Since this limiting case is not attainable in practice, M will always depend in some way on *Re* and *Pr*, this dependence being smaller the greater the degree of turbulence. They show that, under conditions of strong turbulence of flow, M is of the same order of magnitude (*ca.* 5×10^{-5}) for the dissolution of several solids in aqueous solutions at room temperature. However, for the more viscous solutions used in the present investigation, M is of the same order of magnitude under flow conditions far removed from strong turbulence. One must conclude that there is some doubt as to the validity of their extension as it stands at present.

FIG. 2.



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