[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WASHINGTON SQUARE COLLEGE, NEW YORK UNIVERSITY]

Reaction Rates at Solid–Liquid Interfaces

BY CECIL V. KING

I.—Reactions in homogeneous solution occur at every conceivable velocity and range from the exceedingly slow ones to the "practically instantaneous" double decompositions. Heterogeneous solution rates, on the other hand, range from extreme slowness to an upper limit determined by the rate with which reagent can reach or product leave the solid surface under definite stirring conditions. The fact that in a number of the most rapid and clean-cut cases, the rate is nearly if not quite proportional to the diffusion coefficient of the reagent, led to the formulation of the well-known "diffusion layer" theory of Nernst.[1] The rate constants of a few such reactions are shown in Fig. 1, plotted against the diffusion coefficients of the reagents.

Two of the original postulates of Nernst are still widely accepted as essentials in the application of his theory, although they are definitely wrong, were abandoned many years ago by prominent workers in this field, and are quite unessential to the theory. They have been discussed in detail by Van Name and Hill.[2] First, the chemical or other process at the surface need not be instantaneous or even extremely rapid; if it be intrinsically much more rapid than the other processes it will have no appreciable influence on the observed rate. Second, it is unnecessary to assume that a layer of solution next the solid surface remains quite stationary with respect to the surface. It is inconceivable that chemical, adsorptive, electrical or other forces could exert such pronounced effect 10 to 100 microns from a solid surface that a sharp plane of cleavage could be established between unstirred "diffusion layer" and stirred solution. This postulate has led many workers to question the entire theory.[3,4] Van Name and Hill point out that this picture is unnecessary; that near a solid surface fluid motion *perpendicular* to the surface becomes small and does not affect materially the rate at which dissolved substances are transported to and from the surface.

Recent experiments by Fage and Townend at Cambridge University[5] make it possible to substantiate this modification of the Nernst picture. These investigators have examined the motion of colloidal particles in water flowing through a square pipe at various rates of flow in both the viscous and turbulent region. In the latter case, three-dimensional turbulence persists up to the pipe wall itself, or at least to within 6×10^{-5} cm. ($0.6\ \mu$); most of the motion at this distance, however, is parallel to the pipe wall, approaching the appearance of laminar flow. The velocity component normal to the wall drops to much lower values than the other components as the wall is approached.

In a pipe 2.2 cm. across, with an average rate of water flow, U_0, of 25 cm./sec., Fage and Townend found the average rate parallel to the pipe axis, U, to be 0.018 cm./sec. at an estimated distance of $0.6\ \mu$ from the wall (a misprint in their article would make this 0.18 cm./sec.). This becomes 0.072 cm./sec. at $2.3\ \mu$. Unfortunately they could not measure directly v, the velocity component normal to the wall, at this short distance; they say that while small, it is presumably finite. From their relation for v_1/U at greater distances we can with some uncertainty estimate that at $0.6\ \mu$, v is about $0.0003\ U$, or 5×10^{-6} cm./sec.; at $2.3\ \mu$, v is about $0.0012\ U$, or 8×10^{-5} cm./sec. These values are high rather than low, since the reported values v_1 are the maximum ones observed and probably considerably higher than the average values v. Close to the wall, as Fage and Townend point out, the flow, while not *rectilinear* because of the velocity component parallel to the wall but at right angles to the axis of flow, is essentially *laminar* because of the low values of v.

To compare the solution rates of metals with these observations, we have measured the rate of solution of zinc and magnesium disks, mounted flush with the inner walls of a similar square pipe, with acid solution flowing through at nearly the same average rate of 25 cm./sec. With 0.0495 M hydrochloric acid, 27 to 28.7×10^{-8} mole

---

[1] Nernst, *Z. physik. Chem.*, **47**, 52 (1904).

[2] Van Name and Hill, *Am. J. Sci.*, [4] **36**, 543 (1913); **42**, 307 (1916).

[3] Roller, *J. Phys. Chem.*, **35**, 1133 (1931); **36**, 1202 (1932); **39**, 221 (1935).

[4] Moelwyn-Hughes, "Kinetics of Reactions in Solution," Oxford Press, 1934, Chap. IX.

[5] Fage and Townend, *Proc. Roy. Soc.* (London), **A135**, 656 (1932).

of acid is used up per second per square centimeter of metal surface. This corresponds to all the acid in 0.0054 to 0.0058 cc. of solution. If this acid were brought to the metal surface by convection currents alone, the average speed of elements of the solution, normal to the surface, would have to be at least 0.0108 to 0.0116 cm./sec. and this would have to be true at a distance comparable to one molecular diameter from the surface. But this is half the value found by Fage and Townend for the rate parallel to the wall, along the pipe axis, at 2000 molecular diameters from the wall; and far greater than the rate normal to the wall even at the distance 0.6 μ.

We can only conclude that transport of acid normal to the wall by convection is quite negligible compared to the observed solution rate and therefore that acid reaches the wall by diffusion through some thin film of solution.

Unfortunately Fage and Townend's study of motion near the wall was not sufficiently complete to make possible a calculation of the distance at which convection actually becomes comparable to diffusion. With a concentration gradient of 0.0495 mole per liter, 27×10^{-8} mole of hydrochloric acid can diffuse per second per square centimeter through a layer about 98 μ thick, if we may consider the diffusion coefficient through the magnesium and zinc chloride formed to be essentially the same as that through 0.1 N potassium chloride, namely, 4.61 cm.^{2}/day.[6] This is the "diffusion layer" thickness calculated according to the Nernst method. It is reasonable to assume that the acid begins to diminish in concentration at about this distance. The figure cannot be accurate, however, because at this distance U is great enough to replace acid by streaming along the tube wall. For this reason we prefer to rotate metal cylinders in the acid solution rather than use fixed test pieces with acid flowing past or with external stirring.

The revised picture of the Nernst "film," then, is of a layer next the solid surface, still in "turbulent" flow, but in which the velocity component of turbulence normal to the interface is a negligible factor in transporting reagent, compared to diffusion.

II.—This revised picture of the "diffusion layer" leads to several important conclusions. Since the velocity components of turbulent flow rise regularly with distance from the interface, there is no sharply defined adhering layer. The thickness of the layer in which diffusion is important varies not only with stirring speed, but also with the diffusion coefficient of the reagent; for if the diffusion coefficient be high, the point at which diffusion becomes comparable to convection will be at a greater distance than if the diffusion coefficient be low. The nature of this dependence could be predicted if the v *versus* distance curve were known for the type of stirring used in the rate measurements. The values plotted in Fig. 1 indicate that δ, the thickness of the layer, does change with the diffusion coefficients; so few diffusion coefficients are known, especially in salt solutions, that more measurements are needed.

"Film coefficients" from heat transfer measurements indicate a much thicker film than do metal solution rates under the same conditions of stirring. This is to be expected since thermal conductivity coefficients are much higher than diffusion coefficients of solutes in the same medium; thus the distance at which convection and heat conduction become comparable is greater.

The modified picture of the "diffusion layer" probably explains why the thickness of the layer changes little with viscosity (or temperature[2,7,8,9]). As is well known, eddying is less in more viscous solutions at the same average rate of flow, and the critical speed is directly proportional to the viscosity (or strictly, to the kinematic viscosity). Thus it appears probable that v, the velocity component normal to the wall, at each distance, is inversely proportional to the viscosity. Since the diffusion coefficient is also inversely proportional to the viscosity, δ will retain the same value, independent of the viscosity, provided the density does not change significantly.

This and other questions could perhaps be answered by more detailed observations similar to those of Fage and Townend.

III.—The rate measurements of Table I and Fig. 1 were made at or interpolated to a peripheral speed of the rotating cylinder of $3000 \times 2\pi$ cm./min. The rate constants were calculated from the equation

$$\frac{dx}{dt} = k\frac{A}{V}(a - x)$$

---

(6) McBain and Dawson, THIS JOURNAL, **56**, 52 (1934).

(7) Van Name, *Am. J. Sci.*, **43**, 449 (1917).

(8) Jablczynski and Jablonski, *Z. physik. Chem.*, **75**, 503 (1910).

(9) King and Braverman, THIS JOURNAL, **54**, 1744 (1932).

TABLE I

SOLUTION RATES AT 25°, PERIPHERAL SPEED 3000 × 2π CM./MIN.

	System	$k(=D(\text{min.})/\delta)$	D(sq. cm./day)
1	Ferric nitrate on Cu[10]	0.54	0.64
2	Benzoic acid in water[11]	.71	1.08
3	Benzoic acid + H_2O_2 on Mg	.82	1.08
4	Benzoic acid + H_2O_2 on Zn	.75	1.08
5	Acetic acid + H_2O_2 on Mg	.99	1.35
6	Acetic acid + H_2O_2 on Zn	.89	1.35
7	Acetic acid + KNO_3 on Zn[9]	.88	1.35
8	NaOH on benzoic acid[11]	1.75	2.80
9	KOH on benzoic acid[11]	2.00	3.30
10	HCl + KNO_3 on Zn[9]	2.78	4.62(?)
11	HCl + KNO_3 (in 2 M NaCl) on Zn[9]	2.34	4.66(?)

where A is area in sq. cm., V is volume in cc. and the other symbols have their usual significance. Thus $k = D/\delta$ in the Nernst sense, where D is the diffusion coefficient in sq. cm./min. The diffusion coefficients were determined in this Laboratory in cells similar to those described by McBain and Dawson,[6] except that of ferric nitrate, which was estimated from the value given in the "International Critical Tables" for 18°. The values for hydrochloric acid are rather uncertain because of the large effect of salt on the diffusion coefficient.

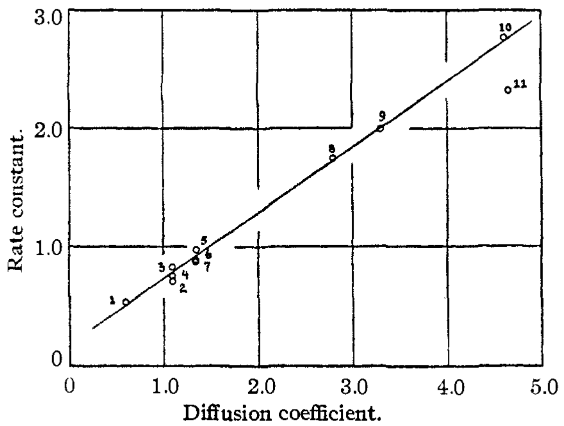

Fig. 1.—The data of Table I.

To compare solution rates with the observations of Fage and Townend, a Bakelite tube 102 cm. long and 2.2 cm. square (inside) was used. Two holes 1.9 cm. in diameter were drilled in opposite faces, 10 cm. from the downstream end, and tightly fitting zinc and magnesium disks were inserted flush with the inside wall. The ends of the pipe were cemented into holes cut in the walls of suitable small reservoirs. The downstream reservoir was fitted with a large overflow tube extending to a point about 2 cm. above the top of the square pipe. This reservoir and the pipe were filled with water; the upper reservoir was filled to a predetermined level with the acid solution. Flow was started by removing a plug from the upper end of the square tube; the level in the upper reservoir was maintained by hand regulation of the flow from a large acid supply reservoir.

These experiments are summarized in Table II. They were carried out at a higher temperature than the observations of Fage and Townend, but the difference would not be great enough to alter the conclusions.

TABLE II

SOLUTION RATE OF MAGNESIUM AND ZINC AT 25°
AREA OF DISKS, 2.84 SQ. CM.

Metal	Acid	KNO_3	Average rate of flow, cm./sec.	Mg. diss. in 5 min.
Zinc	0.0495 M HCl	0.05 M	24.1	8.0 7.5
Zinc	.0488 M HCl	.05 M	25.1	8.0 7.5
Zinc	.0492 M HAc	.05 M	24.6	3.1 3.3
Magnesium	.0497 M HCl	..	25.1	2.8 2.8

It has been reported by Kilpatrick and Rushton[12] that zinc dissolves much faster than magnesium, in the same concentrations of hydrochloric and acetic acids (containing potassium nitrate as a depolarizer for the zinc). We shall show in a later paper just how depolarizers affect the rate of solution of zinc; with sufficient oxidizing agent present a maximum is reached for each acid. This maximum is in each case the same as the rate for magnesium, within what is probably the experimental error. This is shown in Tables I and II and by numerous other experiments carried out in this Laboratory under various conditions.

(10) L. Weidenhammer, Ph.D. Dissertation, New York University, 1934.

(11) S. S. Broudy, Ph.D. Dissertation, New York University, 1934.

(12) Kilpatrick and Rushton, *J. Phys. Chem.*, **38**, 269 (1934).

Kilpatrick and Rushton's experiments in which the viscosity of the acid solution was changed by adding cane sugar are also in error. This is shown in Table III.

TABLE III

SOLUTION RATE OF MAGNESIUM CYLINDER 2.04 CM. IN DIAMETER, 2.50 CM. LONG, IN 500 CC. OF 0.02725 *M* ACETIC ACID AT 25°

R. p. m.	k (no sugar)	k' (0.6 *M* sugar)	k' calcd. (= $0.55k$)
1200	0.448	0.264	0.246
		.259	
1000	.378	.230	.207
	.378	.220	
600	.273	.150	.150
300	.179	.103	.099

Kilpatrick and Rushton, in interpreting their work with magnesium, have disregarded a fundamental law of kinetics, namely, that the observed rate of a reaction must be that of the slowest reaction which occurs. Since in this case transport of acid to the magnesium surface is the slowest process, rate measurements give no indication whatever of the mechanism of the chemical process.

In conclusion, the author wishes to acknowledge his obligation to Professor Henri Mouquin and to Mr. Aaron Spector, whose critical discussions have been of great assistance in preparing this paper.

Summary

Recent experimental studies of fluid motion near a solid surface have made it possible to compare semi-quantitatively the convective transport of fluid toward the surface with the solution rates of magnesium and zinc in acids, under identical conditions. The conclusion is reached that diffusion constitutes the last step in transport of acid to the metal surface.

It is shown that two of the original postulates of the Nernst "diffusion layer" theory of solution rates are untenable but unnecessary in the application of the theory. A rational modification of the Nernst theory is shown to be necessitated by hydrodynamics in the case of a limited number of systems.

NEW YORK, N. Y. RECEIVED JANUARY 28, 1935

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Detection and Colorimetric Estimation of Micro Quantities of Bromide

BY V. A. STENGER AND I. M. KOLTHOFF

The reaction of bromide and a suitable oxidizing agent with fluorescein, giving rise to the formation of eosin, has been employed[1] for the colorimetric determination of small quantities of bromide in the presence of chloride. In a study of other indicators for the purpose we have found that phenol red has distinct advantages over fluorescein. They are (1) that it serves also as indicator in the adjustment of the *p*H of the liquid, (2) that the color change is more pronounced and (3) that amounts of bromide from 1 to 18 micrograms can be determined with greater relative accuracy.

Phenol red, with a color change from yellow to red over the *p*H interval 6.4–8.0, reacts with very dilute hypobromite in weakly alkaline solution to form an indicator of the brom phenol blue type, which changes from yellow to blue-violet over the *p*H range 3.2–4.6. We have found that the oxidation of bromide and the bromination of phenol red take place readily with the use of calcium hypochlorite in a borax buffer at *p*H 8.7–8.8. In the absence of bromide very small amounts of chlor phenol red are formed, with a *p*H range 5.0–6.6. By making the color comparison at a *p*H of 5.0–5.4, all the unbrominated phenol red and any trace of chlor phenol red will be in the yellow form, whereas the brominated compound will be reddish to violet depending upon its concentration. Thus, a sharp differentiation may be made between varying amounts of bromide originally present. With a given amount of phenol red, the violet color will have its maximum intensity when four atoms of bromide are available for each molecule of indicator, indicating that tetrabromphenolsulfophthalein is formed.

Reagents

Calcium Hypochlorite.—"H. T. H." from the Mathieson Alkali Works, New York, was extracted with water and

---

[1] H. Baubigny, *Compt. rend.*, **125**, 654 (1897); F. L. Hahn, *ibid.*, **197**, 245 (1933). See also R. Lorenz, E. Bergheimer and E. Grau, *Z. anorg. allgem. Chem.*, **136**, 90 (1924); M. A. Labat, *Bull. soc. chim.*, [4] **9**, 393 (1911); A. V. Pavlinova, *Chem. Abstr.*, **25**, 2076 (1931).