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

The Rate of Dissolution of Magnesium in Acids

BY CECIL V. KING AND WILLIAM H. CATHCART

As the result of previous studies in this Laboratory, the conclusion was reached that the rate of dissolution of magnesium in acids which are neither extremely weak nor form slightly soluble magnesium salts, is controlled by the rate of convection (stirring) and by the rate of diffusion of the acid.[1-3] It has been pointed out that the theory of Nernst[4] must be modified, in that the "diffusion layer" cannot be a stagnant layer (or even a layer in which flow is laminar only), and that the thickness of this layer must vary with the diffusion coefficient of the reagent, increasing as the latter increases. Investigators in related fields have concluded that in such processes the concentration gradient near the surface is not even linear, and that there may be a wide zone in which both diffusion and convection aid in the transport of material to and from the surface.

An entirely different picture of the dissolution process has been proposed by Kilpatrick and Rushton.[5] These authors have tried to show that the rates are dependent on the acid strength, in the same manner as in homogeneous acid–base catalysis; *i. e.*, that

$$k_A = GK_A^x$$

where k_A is the dissolution rate constant, K_A the acid dissociation constant, G and x are numerical constants, the latter a proper fraction. This assumes that the rate is controlled by the chemical reaction velocity and is entirely independent of diffusion rates.

This viewpoint has been criticized before,[1-3] but it is true, as Kilpatrick and Rushton pointed out, that it has been impossible to make a satisfactory comparison of the dissolution rate constants and the meager list of diffusion coefficients to be found in the literature. For this reason it was decided to determine the diffusion coefficients of a number of weak and strong acids, in the presence of their magnesium salts (when possible), and make the comparison with dissolution rate constants determined, so far as practical, under the same conditions of reagent and salt concentration.

It was found impossible to use the dissolution rate data of Kilpatrick and Rushton in this comparison, for several reasons. First, the great variation in diffusion coefficient with salt concentration in the case of strong acids makes it necessary to know the coefficient and rate constant in the presence of sufficient salt so that the salt formed in the reaction has little or no further effect. Second, Kilpatrick and Rushton do not report the actual rate constants obtained with certain acids (tartaric, citric, bisulfate, sulfuric) but hypothetical constants calculated for the undissociated acids in these solutions. Third, consistently lower dissolution rates were found in all acids than by these authors, although every effort was made to use comparable conditions.

Consequently, dissolution rate measurements were made in the same acids whose diffusion coefficients were measured, in the presence of the same salts. With the exception of benzoic, all the acids were ones used by Kilpatrick and Rushton.

Experimental

Diffusion Rates.—Measurements were made in porous glass disk cells of the type described by McBain and Dawson;[6] in a few cases the rotating cells described by Mouquin and Cathcart[7] were used. In general, the stationary and rotating cells gave nearly the same values in the critical concentration range. Diffusion coefficients (D) were calculated as described in another paper.[8] All measurements were made at 25 ± 0.02°. Most of the measurements have an estimated accuracy of about ±1%.

In all experiments the acid concentration was near 0.05 N initially except in the case of benzoic acid. The exact concentration before and after a twenty-four- to sixty-hour run was determined in terms of a standard alkali solution, and sometimes the acid diffusing through the cell disk was determined as well. The added salt had the same concentration on both sides of the disk initially; no attempt was made to follow its movement. Conditions within the "diffusion layer" of the dissolution rate experiments can only be approximated within the cell disk at best; but, as will be seen below, certain salt concentrations allow the best comparison available.

The results of the diffusion rate measurements are summarized in Table I and shown graphically in Fig. 1. The values of D are given in cm.^{2}/min. since the dissolution rate constants were calculated in cm./min. The effect of

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[1] King and Braverman, THIS JOURNAL, 54, 1744 (1932).

[2] King, *ibid.*, 57, 828 (1935).

[3] King and Schack, *ibid.*, 57, 1212 (1935).

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

[5] Kilpatrick and Rushton, *J. Phys. Chem.*, 34, 2180 (1930); 38, 269 (1934); Kilpatrick, *J. Chem. Ed.*, 8, 1567 (1931).

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

[7] Mouquin and Cathcart, *ibid.*, 57, 1791 (1935).

[8] King and Cathcart, *ibid.*, 58, 1639 (1936).

added salt is seen to divide the acids roughly into two groups: (a) the diffusion coefficients of strong acids are greatly increased by the magnesium salts and (b) the diffusion coefficients of weak to moderately strong acids are either little affected, slightly decreased or slightly increased by salt addition. Three points are worthy of note: magnesium chloride does not increase the diffusion coefficient of hydrochloric acid nearly as much as sodium chloride does;[8] sodium bisulfate and sulfuric acid have practically the same coefficients in the presence of magnesium sulfate; and some of the organic acids used have such slightly soluble (acid?) magnesium salts that sodium chloride was used as the added salt.

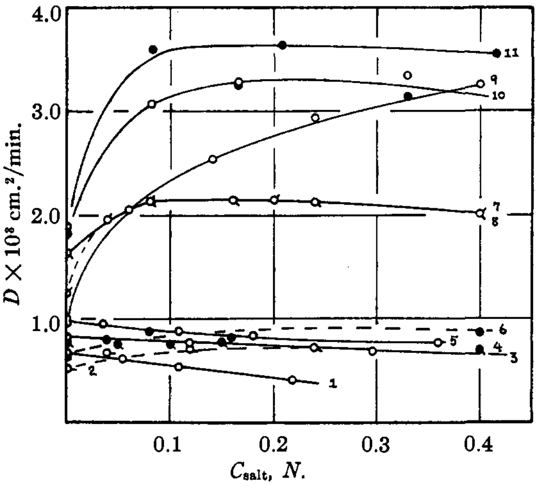

Fig. 1.—Diffusion coefficients *vs.* salt concentration. Acids: 1, benzoic; 2, citric (○⸜); 3, chloroacetic (○); 4, acetic (●⸜); 5, formic; 6, tartaric; 7, bisulfate; 8, sulfuric; 9, benzene-sulfonic; 10, hydrochloric; 11, perchloric.

Dissolution Rates.—Magnesium cylinders approximately 2.6 cm. long and 1.8–2.0 cm. in diameter were rotated in 250 cc. of the acid solution contained in a 400-cc. beaker. The temperature of the solution was kept at 25 ± 0.5°, during the five- to fifteen-minute runs. The magnesium cylinders were carefully sanded to a smooth, clean surface before each series, and weighed before and after each run to the nearest 0.5 mg.

TABLE I

DIFFUSION COEFFICIENTS OF ACIDS WITH ADDED SALTS

25 ± 0.02°

Benzoic acid (0.01 N) Sodium benzoate			Citric acid (0.05 N) Sodium chloride	
C_{salt}, N	$D \times 10^3$ cm.²/min.		C_{salt}, N	$D \times 10^3$ cm.²/min.
0	0.665	0.665	0	0.513
	.679		0.04	.685
0.0438	.620		.12	.707
.0548	.612		.24	.729
.1097	.533	.541	.40	.704
.2190	.408	.418	.60	.697

Monochloroacetic acid (0.05 N). Magnesium chloroacetate			Acetic acid (0.05 N) Magnesium acetate		
0	0.838	0.829	0	0.768	0.769
0.119	.774			.770	.783
.297	.695		0.050	.754	.782
.593	.680		.10	.762	
1.188	.682		.15	.792	
			.40	.710	
			.10 } NaCl	.826	.820
			.20	.813	.826

Formic acid (0.05 N) Magnesium formate			Tartaric acid (0.05 N) Sodium chloride		
0	0.969	0.974	0	0.657	0.648
0.036	.962		0.04	.795	
.108	.884		.08	.870	
.180	.845		.16	.826	
.360	.774		.40	.872	
.720	.677				

Sodium bisulfate (0.05 N) (Normality = Molarity) Magnesium sulfate		Sulfuric acid (0.05 N) Magnesium sulfate		
0	1.64	0	1.24	1.26
0.08	2.13	0.04	1.95	
.16	2.14	.08	2.11	
.24	2.12	.20	2.14	
.40	2.02	.40	2.02	

Benzenesulfonic acid (0.05 N) Magnesium benzenesulfonate			Hydrochloric acid (0.05 N) Magnesium chloride		
0	0.986	1.07	0	1.88	
0.06	2.06		0.082	3.07	
.14	2.54		.165	3.28	
.24	2.94		.330	3.35	
.40	3.26		.659	2.27	2.22
.80	3.31		.823	1.90	1.89
			.165[a]	3.24	
			.330[a]	3.15	
			.823[a]	2.24	

Perchloric acid (0.05 N) Magnesium perchlorate			Pyridinium chloride (0.05 N) 0.05 N Pyridine both top and bottom of cell. Magnesium chloride			
0	1.82	1.84	0	0.967	0.891[a]	0.915[a]
0.083	3.59		0.016	.815	.848[a]	
.208	3.64		.08	.780	.767[a]	
.416	3.56		.20	.698	.788[a]	
.832	2.93		.40	.670	.762[a]	

[a] In rotating cell.

Velocity constants were calculated from the equation

$$k = \frac{2.3V}{At} \log \frac{a}{a - x}$$

where V = volume of solution in cc., A = area of surface in sq. cm., t = time of run in minutes, a = dissolving capacity of the solution in any units and x = amount dissolved in the same units as a. The values of k should thus be comparable with constants obtained by Kilpatrick and Rushton.

Since the latter authors either ran their experiments at, or calculated the constants to a surface (peripheral) speed of 2000 cm./min., all our experiments were run at this peripheral speed. For instance, a cylinder 2.54 cm. long, 1.99 cm. in diameter was rotated at 320 r. p. m. (=2000 cm./min.) for five minutes in 0.0516 *N* perchloric acid, and 24.0 mg. of magnesium was dissolved. The dissolving capacity of the solution was 157 mg. of magnesium. Then

$$k = \frac{2.3 \times 250}{15.8 \times 5} \log \frac{157}{157 - 24} = 0.524$$

As the cylinder diameter decreased, the rotational speed was increased to keep the peripheral speed at 2000 cm./min. A cylinder 2.64 cm. long and 1.86 cm. in diameter was rotated at 340 r. p. m. for five minutes in 0.0562 *N* sodium bisulfate and 22.5, 23.5 mg. of magnesium was dissolved. The dissolving capacity of the solution was 171 mg. of magnesium. Then as an average

$$k = \frac{2.3 \times 250}{15.4 \times 5} \log \frac{171}{171 - 23} = 0.468$$

No attempt was made to obtain greater accuracy than ±5%. The method of obtaining rates and calculating constants is given in detail because all our values of *k* are only one-third to one-half as large as those obtained by Kilpatrick and Rushton under presumably comparable conditions. We have found, as they also state, that *k* is independent of length or diameter of cylinder, volume of solution and concentration of acid. Hence we can only conclude that some "apparatus constant" was different in the two cases.

The results of the rate experiments are summarized in Table II and shown graphically in Fig. 2. Several points are worthy of note.

(1) There was no loss in weight in solutions of benzoic acid containing sodium benzoate, and the cylinder acquired a visible white film. With hydrogen peroxide present hydrogen evolution was partly suppressed, the rate was somewhat increased in the acid alone and was normal in acid +0.2 *N* benzoate, but fell off in the presence of more concentrated sodium benzoate.

(2) The same rate was found in sodium bisulfate and sulfuric acid solutions, within experimental error, and this is true in the presence of magnesium sulfate. The rate decreases as sulfate is added while in the other stronger acids the rate increases when salt is added. The cylinder ac-

TABLE II

DISSOLUTION RATE CONSTANTS OF MAGNESIUM IN ACIDS WITH ADDED SALTS AT 25 ± 0.5°

Benzoic acid (0.02 *N*)
Sodium benzoate

C_{salt}, *N*	$C_{H_2O_2}$, *M*	*k*	
0	0	0.200	0.195
0.20	0	0	
.40	0	0	
0	0.07	0.249	
.20	.07	.195	
.40	.07	.056	

Citric acid (0.055 *N*)
Sodium chloride

C_{salt}, *N*	*k*
0	0.139
0.20	.146
.40	.146
.60	.154

Monochloroacetic acid (0.0518 *N*). Magnesium chloroacetate

0	0.273	0.250
0.121	.245	
.242	.223	
.362	.234	
.483	.213	
.604	.213	

Acetic acid (0.0597 *N*)
Magnesium acetate

0	0.186	0.177	0.182
0.10	.177		
.20	.177		
.30	.182		
.40	.167		

Formic acid (0.0582 *N*)
Magnesium formate

0	0.236	0.220	0.227
0.112	0.236		
.223	.225		
.335	.197		
.446	.197	0.173	

Tartaric acid (0.0621 *N*)
Sodium chloride

0	0.172	0.172	0.177
0.20	.181		
.30	.172		
.40	.190		
.60	.181		

Sodium bisulfate (0.0562 *N*)
(Normality = Molarity)
Magnesium sulfate

0	0.457	0.480
0.20	.436	
.40	.414	

Sulfuric acid (0.0575 *N*)
Magnesium sulfate

0	0.458	0.458
0.20	.447	
.40	.416	
.60	.396	

Benzenesulfonic acid (0.050 *N*) Magnesium benzenesulfonate

0	0.518	0.499	0.502
0.10	0.604		
.20	.616		
.30	.592		

Hydrochloric acid (0.050 *N*)
Magnesium chloride

0	0.497	0.497
0.097	.596	
.194	.621	
.291	.647	
.388	.647	0.611
.486	.596	

Perchloric acid (0.0516 *N*)
Magnesium perchlorate

0	0.524	0.524
0.10	.597	
.20	.621	.621
.30	.597	
.40	.597	
.50	.572	

Pyridinium chloride (0.060 *N* + 0.040 *M* pyridine) Magnesium chloride

0	0.650	0.627	0.606
0.20	.669		
.40	.680		
.60	.659		

(0.030 *N* Pyridinium chloried +0.070 *M* Pyridine)

0	0.351	
0.20	.430	
.40	.430	0.410
.60	.390	

quired a thin brown film, slowly in the acid or bisulfate solutions, more rapidly the more concentrated the magnesium sulfate.

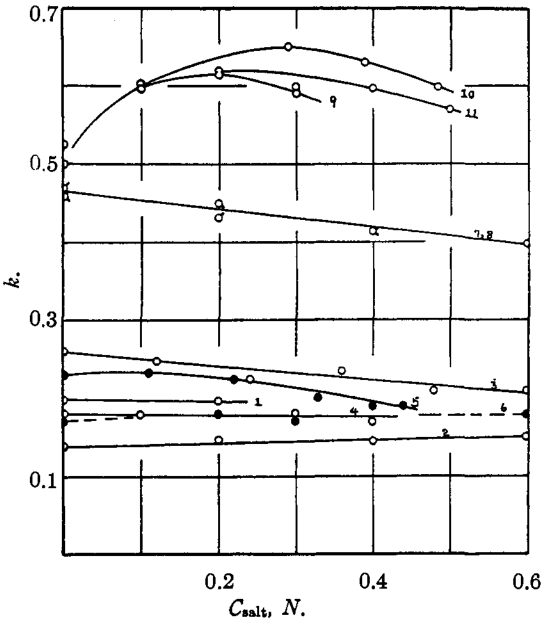

Fig. 2.—Dissolution rate constants *vs.* salt concentration. Acids: numbered as in Fig. 1.

(3) The rate in pyridinium chloride is higher than would be expected from the diffusion coefficient of Table I, but it decreases tremendously in the presence of excess pyridine. This was not known when the diffusion coefficients were measured, and it must be concluded that the measurements were not made under comparable conditions. This system is therefore omitted in further comparison.

(4) In every case except that of sulfuric acid and the bisulfate, the dissolution rates and diffusion coefficients change in the same direction on addition of salt. The magnitude of the change in dissolution rates is less than in diffusion coefficients, as would be expected from the diffusion theory; for even if pure acid is present initially, the magnesium salt is formed next the surface immediately.

Comparison of Diffusion and Dissolution Rates.—Values of D and k considered to be most nearly comparable were selected and are tabulated in Table III. The method of selection of most of the values is obvious; if the diffusion coefficient and the rate constant reach a maximum or a plateau near the same salt concentration, these values were chosen. In the case of sulfuric acid and the bisulfate, it seemed better to take the rate constant for the pure acid, but the maximum diffusion coefficient in the presence of salt.

Table III

Comparison of Diffusion Coefficients and Dissolution Rate Constants

Acid	$D \times 10^3$, cm.^{2}/min.	k, cm./min.
Benzoic	0.65	0.20
Citric	.70	.15
Monochloroacetic	.70	.23
Acetic	.76	.18
Formic	.85	.22
Tartaric	.85	.18
Sodium bisulfate	2.10	.46
Sulfuric	2.10	.46
Benzenesulfonic	3.00	.61
Hydrochloric	3.30	.64
Perchloric	3.60	.62

Discussion

While the dissolution rates do not fall in exactly the same order as the diffusion coefficients, the general trend is striking. Part of the lack of uniformity among the weaker acids undoubtedly is due to the fact that acids having salts of low solubility give low dissolution rates because of film formation. We cannot, however, account for the discrepancies among chloroacetic, formic and acetic acids, nor among benzenesulfonic, hydrochloric and perchloric acids.

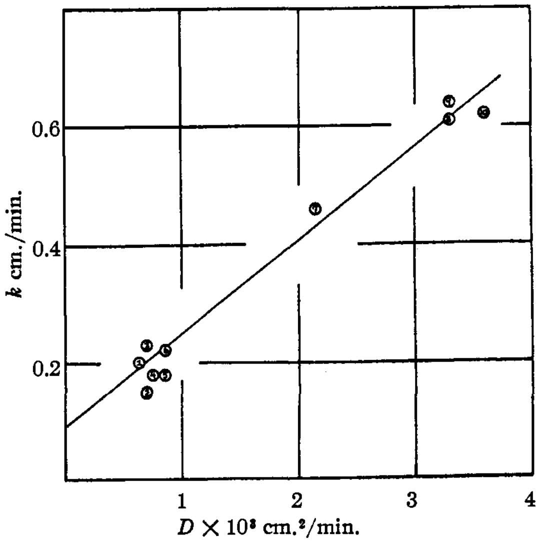

Fig. 3.—Dissolution rate constants *vs.* diffusion coefficients. Acids: 1, benzoic; 2, citric; 3, chloroacetic; 4, acetic; 5, tartaric; 6, formic; 7, sulfuric and bisulfate; 8, benzenesulfonic; 9, hydrochloric; 10, perchloric.

As shown in Fig. 3, the relation between k and D is reasonably well represented by a straight line which, however, does not pass through the origin. This type of relation was found before for dissolution rates in experiments with metal and other cylinders rotating at a higher speed in appropriate reagents.[2] Explanations of this extrapolation to a finite rate constant at zero diffusion coefficient are unsatisfactory, and as shown elsewhere[9] it is more probable that the true relation is of an exponential type

$$k = \alpha D^x$$

being nearly linear over the range of values plotted in Fig. 3. This exponential relation is consistent with a diffusion layer whose thickness increases with increasing diffusion coefficient, as is necessary from a consideration of turbulence in the solution near the metal surface.[2] Such a relation is also predicted from the expressions of Colburn[10] and Chilton and Colburn[11] derived to correlate heat and mass transfer in gas–liquid and gas–solid systems. The exponent x is given as $^2/_3$ by these authors.

From a log–log plot of k *vs.* D, the best value of x for these data is found to be approximately 0.70. In Fig. 4, values of k are plotted *vs.* $D^{0.70}$; the linear relation is at least as good as that of Fig. 3. The straight line is represented by the equation

$$k = 0.36D^{0.70}$$

A similar exponential relation holds for the data of ref. 2 and also of ref. 9. In the latter case, values for heat transfer are represented by the same equation as values for dissolution rates.

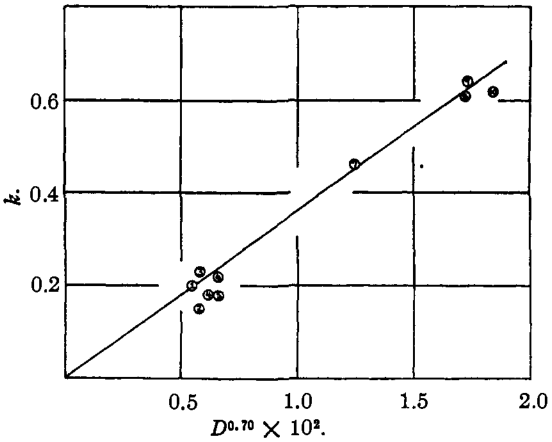

Fig. 4.—Dissolution rate constants *vs.* diffusion coefficients to the 0.70 power. Acids: numbered as in Fig. 3.

Summary

The diffusion coefficients of twelve acids have been measured in the porous glass disk type of diffusion cell, alone and in the presence of their magnesium salts when possible, otherwise with other salts present.

The dissolution rate of magnesium from cylinders rotating with a peripheral speed of 2000 cm./min. has been measured in the same acids in the presence of the same salts.

A comparison of diffusion coefficients and dissolution rate constants shows that they can be correlated fairly satisfactorily. The correlation is in agreement with a modification of the Nernst theory for such dissolution rates, and also with the Chilton–Colburn relations for heat and mass transfer at a phase boundary.

New York, N. Y. Received September 9, 1936

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[9] King and Howard, *Ind. Eng. Chem.*, **29**, 75 (1937).

[10] Colburn, *Trans. Am. Inst. Chem. Engrs.*, **29**, 174 (1933).

[11] Chilton and Colburn, *Ind. Eng. Chem.*, **26**, 1183 (1934).

[Contribution No. 581 from the Kodak Research Laboratories]

Studies in the Cyanine Dye Series. VII. New Dyes Containing Three Heterocyclic Nuclei

By L. G. S. Brooker and L. A. Smith

Cyanine dyes have been described in which a quinoline nucleus is linked through either the 2- or 4-position to a second heterocyclic nucleus. In the present paper, dyes of a new type are described in which a quinoline nucleus is linked through both of these positions to two other nuclei. These dyes differ from the previously known trinuclear dyes of the neocyanine type[1] since in the latter two nuclei are linked together by a three-carbon chain, the third nucleus forming part of a group attached to one of the carbon atoms of this chain.[2-5]

If 2,4-dimethylquinoline ethiodide (I) is treated with an excess of 2-iodoquinoline ethiodide in the presence of triethylamine, both methyl groups take part in the reaction, and a

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(1) Dundon, Schoen and Briggs, *J. Opt. Soc. Am.*, **12**, 397 (1926).

(2) Hamer, *J. Chem. Soc.*, 1472 (1928).

(3) Brooker, Hamer and Mees, *J. Opt. Soc. Am.*, **23**, 216 (1933).

(4) König, *Z. wiss. Phot.*, **34**, 15 (1935).

(5) Hamer, *J. Soc. Chem. Ind.*, **54**, 640 (1935).