presented so that values over the range 250 to 3000°K. may be easily obtained by interpolation.

The $\Delta F°/T$ for $Cl_2 = 2Cl$ has been tabulated to 3000°K.

The change in heat content for the reaction $\frac{1}{2}H_2 + \frac{1}{2}Cl_2 = HCl$ has been accurately determined from the electromotive force of the hydrogen–chlorine cell and spectroscopic data. The value found was $\Delta H_{298.1} = -22,028$ calories per mole.

The entropies of hydrogen chloride and of chlorine have been calculated.

$$HCl^{35}, S_{298.1} = 44.619 \text{ E. U.}$$
$$HCl^{37}, S_{298.1} = 44.783 \text{ E. U.}$$
$$HCl_{(mixture)}, S_{298.1} = 44.658 \text{ E. U.}$$
$$Cl_2{}^{35-35}, S_{298.1} = 53.235 \text{ E. U.}$$
$$Cl_2{}^{35-37}, S_{298.1} = 53.389 \text{ E. U.}$$
$$Cl_2{}^{37-37}, S_{298.1} = 53.543 \text{ E. U.}$$
$$Cl_2 \text{ (equilibrium mixture)}, S_{298.1} = 53.310 \text{ E. U.}$$

The entropy effect of nuclear spin (unknown for Cl^{37}) has purposely been omitted from the above values so that they may be used in combination with those obtained from low temperature heat capacity measurements. The entropy of mixing in the isotopic solutions and the entropy due to the presence of two isotopes in the same molecule have been eliminated for the same reason.

It is suggested that thermodynamic properties of substances which consist of two or more isotopic molecules be based on an average set of energy levels, computed by weighting the several values in proportion to the abundance of the respective molecules. The effect of the reduction in the number of levels by molecular symmetry on the above method has been discussed.

BERKELEY, CALIFORNIA

THE RATE OF SOLUTION OF ZINC IN ACIDS

BY CECIL V. KING AND M. M. BRAVERMAN

The classical theory for the rate of solution of solids in aqueous solutions, developed by Noyes and Whitney,[1] Nernst[2] and Brunner,[3] postulates that the rate of chemical reaction in such cases is very high compared to the rate at which the active component of the solution can reach the solid surface by diffusion; hence the observed rate of dissolution will be that of diffusion to the surface through the products as they diffuse away.

[1] Noyes and Whitney, Z. physik. Chem., 23, 689 (1897).

[2] Nernst, ibid., 47, 52 (1904).

[3] Brunner, ibid., 47, 56 (1904).

. This theory can by no means be as generally applicable to heterogeneous reactions as was supposed by the originators. We may assume with Van Name and Hill[4] that at least three types of heterogeneous reaction will be encountered: (1) the chemical reaction is very much faster than the diffusion rate, and the observed rate will be controlled by the latter; (2) the chemical reaction is very slow compared to the diffusion rate and the observed rate will be controlled by the former; (3) the diffusion rate constant and the reaction velocity constant are comparable in magnitude and the observed rate will be a function of both. In addition to these three types, many complications may appear, as "local elements" in the case of impure metals, solubility of the solid in pure water to an extent comparable to the concentration of the active component in the solution, formation of films at the surface by the reaction, etc.

In the case of metallic oxides, hydroxides and carbonates dissolving in acids, we should expect the chemical reaction to be so fast that the observed rate of solution would be controlled by the diffusion process. In the case of metals dissolving in acids, however, it is possible that the chemical reaction may be slower than the diffusion process. Experiments in such systems could be used advantageously in investigating the nature of acids by determining whether, as heretofore supposed, only the hydrogen ion reacts directly with the metal or whether other acid molecules or ions also enter directly in the reaction.

Brönsted, Lowry, Dawson and their co-workers have shown that in a number of homogeneous reactions not only the H_3O^+ and OH^- ions are active as catalysts, but also other acid and basic molecules. The chief criteria of such a catalysis are: (1) lack of proportionality of the rate to the hydrogen-ion concentration as one goes from strong to weak acids; (2) proportionality of the rate to the concentration of other acid molecules in solutions in which the hydrogen-ion concentration is buffered; (3) for an homologous series of acids, log k_A (rate constant) shows a linear relation to log K_A (acid dissociation constant).
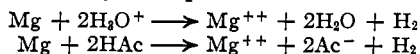
The idea that undissociated acids may react with metals is not new; Kahlenberg and his co-workers carried out many experiments designed to show that this as well as other types of reaction can take place in the absence of ions. For example, Patten[5] found that $N/10$ hydrochloric acid in dry chloroform dissolves zinc faster than $N/10$ hydrochloric acid in water (until the reaction products choke the surface), in spite of the fact that the former solution has an exceedingly low electrical conductivity. However no attempt was made to show that other acids than the H_3O^+ ion react directly with metals in aqueous solution until Kilpatrick and Rushton,[6]

[4] Van Name and Hill, *Am. J. Sci.*, **42**, 307 (1916).

[5] Patten, *J. Phys. Chem.*, **7**, 153 (1903).

[6] Kilpatrick and Rushton, *ibid.*, **34**, 2180 (1930).

in a detailed study of the rate of solution of magnesium in monobasic acids,[7] applied the criteria of the above theory and showed that they were reasonably well fulfilled. The authors thus imply that the chemical reaction is much slower than the diffusion process and that they have measured the rate of the former. The mechanism is thus represented, for example in acetic acid, by the equations

$$Mg + 2H_3O^+ \longrightarrow Mg^{++} + 2H_2O + H_2$$
$$Mg + 2HAc \longrightarrow Mg^{++} + 2Ac^- + H_2$$

Brönsted and Kane have applied the same theory to the rate of solution of sodium from sodium amalgam by acids.[8] This reaction is complicated by the necessity of diffusion of sodium as well as of acid to the amalgam surface, and probably by adsorption of sodium in the amalgam surface.[9] The authors have, however, carefully considered the possible influence of diffusion on the observed solution rates; and conclude that this factor is all-important with the stronger acids, but that with acids of dissociation constant less than 10^{-7} the chemical reaction rates are sufficiently lower than the diffusion rates to be entirely responsible for the observed velocities.

Five observed facts have, in general, been accepted as criteria of the validity of the diffusion rate theory: (1) a number of different solids dissolve at nearly the same rate, while chemical reaction rates are seldom so nearly the same for such widely different substances; (2) the rate of stirring the solution or rotating the specimen has a very large influence on the observed rates, which is not typical of chemical processes; (3) the rate of solution is usually nearly inversely proportional to the viscosity of the solution; (4) the rates observed with different acids follow, in general, the diffusion coefficients of the acids rather than their acid strengths, although strict proportionality to diffusion coefficients obtained under entirely different experimental conditions cannot be expected; (5) the temperature coefficient of these heterogeneous reactions is usually 1.1 to 1.5 per 10° rise, while chemical reaction rates seldom have temperature coefficients less than 2. Neither Kilpatrick and Rushton nor Brönsted and Kane present experimental work to test the application of these five points in detail, and we feel that detailed study especially of (2), (3) and (5) will be necessary before their point of view can be accepted. Our own work shows that satisfactory formal agreement with the three criteria of the extended acid–base catalysis theory is not sufficient.

Experimental

For the experimental work presented here the rate of solution of zinc in acid solutions containing potassium nitrate as a depolarizer was chosen for

[7] Kilpatrick, *J. Chem. Ed.*, **8**, 1567 (1931).

[8] Brönsted and Kane, THIS JOURNAL, **53**, 3624 (1931).

[9] See Meyer, *Z. physik. Chem.*, **70**, 315 (1910), for the peculiar interfacial tension relation of sodium amalgam and solutions.

most of the experiments.   It is to be expected that zinc will react chemically more slowly than the more active magnesium and sodium, although just how much effect an efficient depolarizer has on the inherent "activity" is problematical.

When hydrogen is allowed to form on the surface of the metal, undoubtedly the purity of the metal has considerable influence on the rate, especially for metals "whose solution tension is outweighed by the overvoltage of hydrogen."[10]   It has been shown that many oxidizing agents greatly hasten the solution of such metals, especially when they eliminate hydrogen evolution entirely, even though they have no specific action on the metals themselves.[11]   Potassium nitrate was chosen as a depolarizer, since it has no specific action, eliminates hydrogen evolution entirely, forms no insoluble coating on the surface of the metal, has little effect on the rate of solution of magnesium but increases that of zinc to nearly the same value as that of magnesium, and can be replaced by certain other depolarizers with almost identical results.   Also it appears to reduce the effect of impurities in the zinc to a minimum.
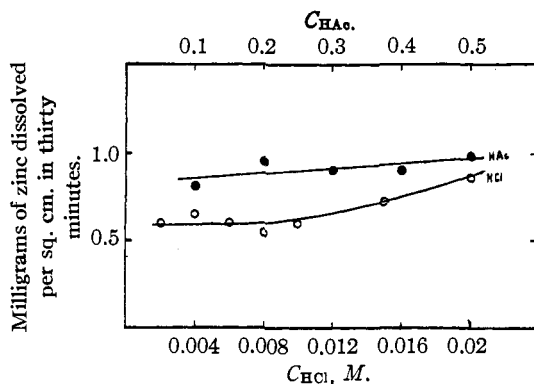

Fig. 1.—Rate of solution of zinc in hydrochloric and acetic acids at 22°, 1600 r. p. m., no oxidizing agent.

Square plates, disks, or cylinders of the c. p. metal were attached to a bakelite shaft with bakelite nuts and rubber washers which prevented the solution from coming in contact with definite areas, in the case of the cylinders the entire end surfaces.   Undoubtedly cylinders are most satisfactory for this type of experiment, since all points on the exposed surface will have the same linear speed through the solution; but the other specimens were satisfactory for the comparative experiments in which they were used.   With the depolarizers present, there was no induction period and

[10] Centnerszwer, Z. physik. Chem., 137A, 352 (1928).

[11] Pullinger, J. Chem. Soc., 57, 815 (1890); Weeren, Ber., 24, 1785 (1891); Prins, Proc. K. Akad. Amsterdam, 23, 1449 (1921).

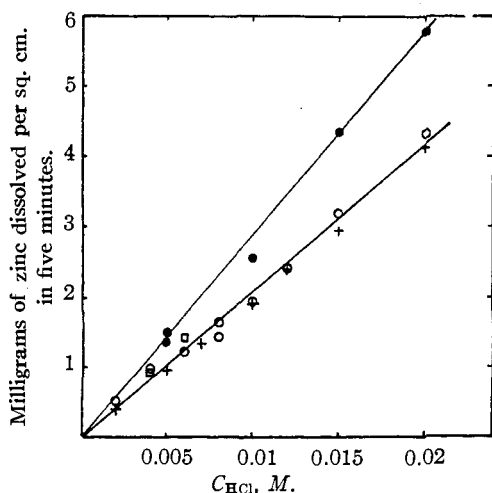the reactions were unimolecular, or nearly so. The loss in weight of the specimen during four or five minute intervals was taken as a measure of the rate constant; during this time the change in surface area was inappreciable and the decrease in acid concentration was only a few per cent. The volume of acid solution used and the temperatures are given with the tables and figures. The specimens were polished with fine emery paper before each run.

Fig. 2.—Rate of solution of zinc in hydrochloric acid at 23°: upper curve, 2800 r. p. m.; lower curve, 1600 r. p. m. O, ●, 0.05 M KNO$_3$; □, 0.1 M KNO$_3$; +, 0.04 M H$_2$O$_2$.

1. **Comparison of Different Acids.**—Figure 1 shows the results obtained with hydrochloric and acetic acids with no oxidizing agents present. The rate of solution is nearly independent of the acid concentration and probably controlled by a nearly constant rate of hydrogen elimination. In a number of dilute acid and buffer solutions, with and without added inert salts, there was no significant dependence of this initial rate on the hydrogen-ion or total acid concentration. There is probably an induction period in such solutions and they have little quantitative significance.

Figure 2 summarizes the experiments with hydrochloric acid with added potassium nitrate and hydrogen peroxide, and compares the rate at two rotational speeds. The rate is, within experimental error, proportional to the acid concentration, inde-

Fig. 3.—Rate of solution of zinc in acetic acid at 23°, 1600 r. p. m.: O, 0.05 M KNO$_3$; □, 0.10 M KNO$_3$; +, 0.04 M H$_2$O$_2$.

pendent of the particular oxidizing agent and its concentration (of course within limitations), and has little if any inert salt effect in the kinetic sense.

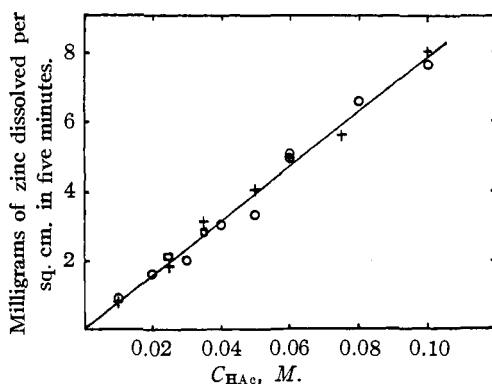In Fig. 3 are shown similar results for acetic acid. Again the rate is pro-

portional to the total acid concentration and not to the hydrogen-ion concentration; although the hydrogen ion of acetic acid accounts for some 10% of the total rate, the fact that its concentration was not con-

trolled by using buffer solutions does not obscure the conclusions to be reached.

Figure 4 gives the results for formic acid at 1600 and 2800 r. p. m.; this change in rate of rotation increases the rate 38% with hydrochloric acid and 42% with formic acid. These values were used as a basis for estimating the constant at 2800 r. p. m. for acetic acid, as this was not measured directly.

Figures 5 and 6 give measurements with glycolic, tar-

Fig. 4.—Rate of solution of zinc in formic acid at 25°, 0.05 M KNO$_3$ present;   upper curve, 2800 r. p. m.;   lower curve, 1600 r. p. m.

taric and citric acids. The latter two acids show practically the same rate, greater than the rate with hydrochloric acid at the same molar concentration.

Figure 7 summarizes measurements for boric acid and the ammonium ion (*i. e.*, solutions of ammonium chloride). The rates are very low, but fairly reproducible.

Fig. 5.—Rate of solution of zinc in glycolic acid at 23°, 2800 r. p. m.; 0.05 M KNO$_3$ present.

These rates are summarized in Table I and plotted in Fig. 8. The constants given have the dimensions of milligrams of zinc dissolved per square centimeter per five minutes per mole of acid per liter. The values have been calculated roughly for the undissociated acid present only, by assuming that hydrogen ion has the same effect per mole with all acids as with acetic acid (see Fig. 11). This is not strictly valid, but will serve our purpose here.

It is quite unlikely that we can attach any significance to the fact that on this log k_A–log K_A plot, the points, with the exception of the polybasic and very weak acids, lie near the straight line indicated. It seems more probable that the rates are determined largely by the diffusion rates, with
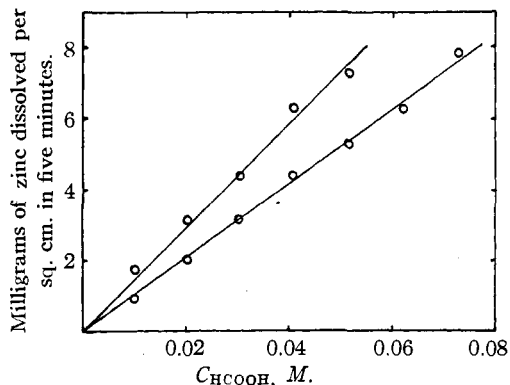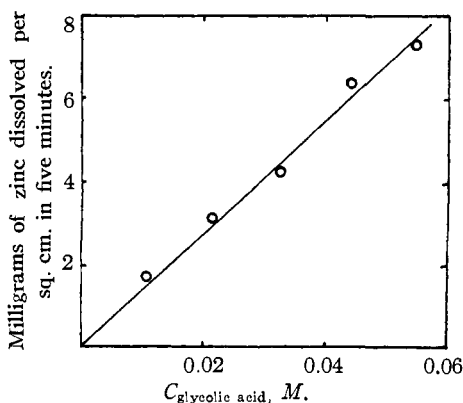
TABLE I

SUMMARY OF RATES OF SOLUTION OF ZINC IN ACIDS

3 × 3 cm. Squares of zinc rotated 2800 r. p. m. in 500 cc. of solution containing 0.05 M KNO$_3$, 23 ± 1 °C.

Acid	k_A	Log k_A	Log k_A
H$_3$O$^+$	287	2.46	1.74
Tartaric	280	2.45	$\overline{3}$.04
Citric	290	2.46	$\overline{4}$.90
Formic	116	2.06	$\overline{4}$.32
Glycolic	112	2.09	$\overline{4}$.18
Acetic	97	1.99	$\overline{5}$.26
Mono-hydrogen-citrate ion	123[a]	2.09	$\overline{6}$.51
Boric	2.0	0.30	$\overline{10}$.81
Ammonium ion	1.65	.22	$\overline{10}$.75

[a] Calculated from experiments with a cylinder at 4000 r. p. m.

the possible exception of those for boric acid and the ammonium ion. In these cases the low values may be due to the slowness of the chemical reaction or more likely to the formation of insoluble reaction products. The high rates with ta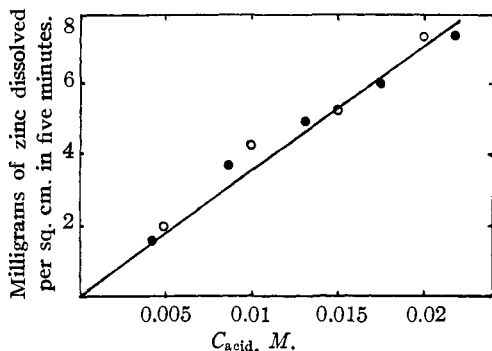rtaric and citric acids are probably due to the fact that when the acid molecules reach the metal surface by diffusion they may furnish two and three hydrogen ions, respectively.

Fig. 6.—Rate of solution of zinc in citric and tartaric acids at 23°, 2800 r. p. m.; 0.05 M KNO$_3$ present: ●, citric acid; ○, tartaric acid.

2. **Temperature Coefficients.**—In Figs. 9 and 10 are shown the temperature coefficients, for hydrochloric and acetic acids. These were measured by rotating zinc disks 4 cm. in diameter, 2 mm. thick, clamped on a shaft with bakelite nuts and rubber washers 2 cm. in diameter, at a speed of 4000 r. p. m. The coefficients are: for acetic acid, $k_{25}/k_{15} = 1.28$ and $k_{35}/k_{25} = 1.26$; for hydrochloric acid, $k_{25}/k_{15} = 1.29$ and $k_{35}/k_{25} = 1.13$. The last value seems low and may be in error for some reason; our main point is to show that the values are typical of diffusion coefficients and much too low to be considered typical of chemical reaction rates.

3. **Effect of a Common Ion with Acetic Acid.**—Figure 11 shows the effect of adding comparatively small amounts of sodium acetate to acetic acid. Zinc disks rotating at 4800–5000 r. p. m. were used in these experiments. The effect is similar to that found by Kilpatrick and Rushton with magnesium. In the pure acetic acid we are measuring the rate due to the

combined diffusion of (1) dissociated acetic acid and (2) undissociated acid. In the presence of even 0.02 M sodium acetate, we are practically measuring the rate due to diffusion of undissociated acid alone, and further additions of the salt have a neg-
ligible effect. It will be noted that the portion of the rate due to the hydrogen ion (no sodium acetate present) is rather larger than would be expected if the chemical reaction rate were being measured (see Fig. 2). We have no way of deciding from these or any other of the experiments whether undissociated acetic acid or only hydrogen ion can actually react with the zinc. After some sodium acetate has been added, although dissociation is negligible so far as diffusion rates are concerned, the rate of dissociation is undoubtedly so high that all the acid could easily dissociate before reaction with no appreciable effect on the observed rate.

Fig. 7.—Rate of solution of zinc in boric acid and ammonium chloride at 23°, 1600 r. p. m., 0.05 M KNO$_3$ present: ●, boric acid: O, ammonium chloride.

Figure 12 shows the effect of adding hydrochloric acid to a fixed amount of the acetic acid. The first addition of the strong acid represses the ionization of the weak one to a value negligible so far as diffusion rates are concerned; and with larger additions the rates are additive.
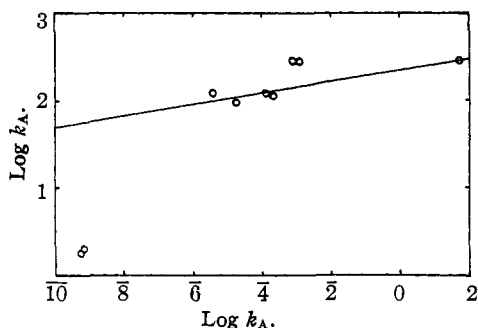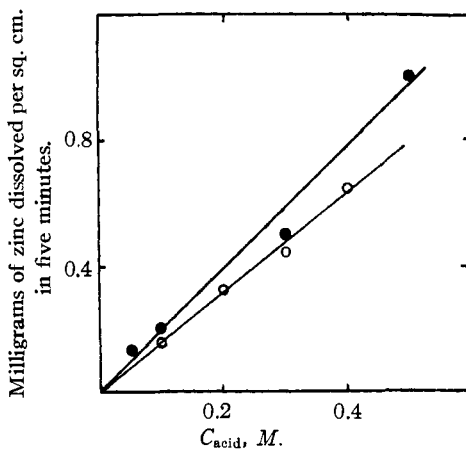
4. Effect of Rotational Speed.—The effect of increasing the speed of rotation of magnesium and zinc cylinders in hydrochloric and acetic acids is shown in Figs. 13 and 14. The rate increases apparently with some fractional power of the rotational speed (or perhaps better, the linear speed of the surface) up to about 1000 r. p. m.; above this point with the first power, or nearly so (in the case of zinc in hydrochloric acid), up to 5600 r. p. m. The rate has usually been found proportional to a fractional power of the rate of

Fig. 8.—The data of Table I.

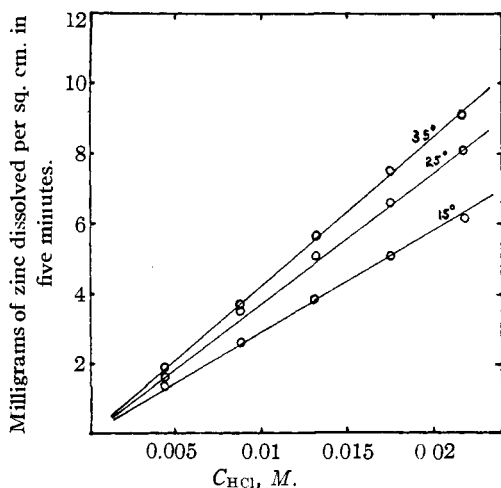stirring the solution or rotating the specimen, although in some cases the relation is linear;[12] but we have seen no results recorded at the higher speeds used here. The lack of any tendency for the curves to flatten must indicate that the observed solution rates are still controlled by the diffusion process. If we accept the Nernst picture of a "diffusion layer" surrounding the solid, the thickness of the layer can be calculated from the expression $k = D/\delta$ where k is the observed solution rate, D the diffusion coefficient, and δ the thickness of the layer. It is unlikely that the relation shown in Figs. 13 and 14 can continue until the diffusion layer becomes only a few molecules thick; but if the chemical reaction is not too fast it may be possible to attain such speeds that diffusion to the surface takes place more rapidly than the
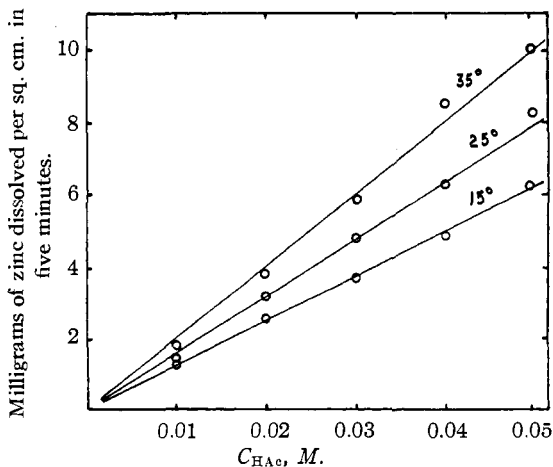

Fig. 9.—Temperature coefficient of rate of solution of zinc in hydrochloric acid, 0.05 M KNO₂ present, 4000 r. p. m.

Fig. 10.—Temperature coefficient of rate of solution of zinc in acetic acid, 0.05 M KNO₃ present, 4000 r. p. m.

chemical reaction. However, frictional heating effects and other distur-

12 Klein, Z. anorg. allgem. Chem., 137, 56 (1924).

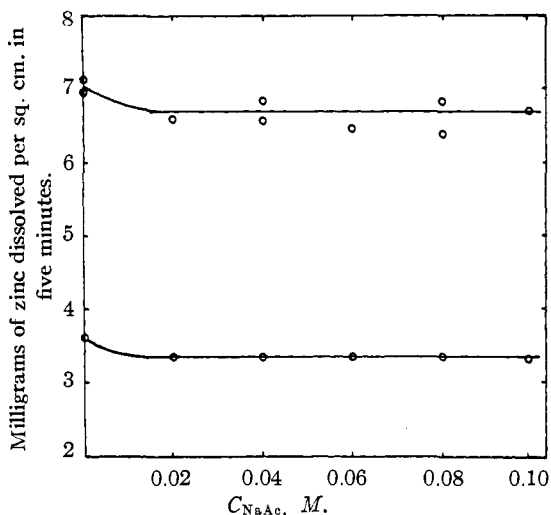bances apparently unimportant at 5600 r. p. m. with the cylinders used here, may become so at slightly higher speeds.

Fig. 11.—Effect of repressing the ionization of acetic acid (0.0122 and 0.0245 M) on its rate of dissolving zinc. 0.05 M KNO₃ present, 25–26°, 4800–5000 r. p. m., 500 cc. solution.

5. Effect of Viscosity Changes.—From the experimental relation between viscosity and diffusion rates $D\eta$ = constant, where η is the viscosity of the medium, and the relation $k = D/\delta$, it is seen that k will be inversely proportional to the viscosity, assuming δ to remain constant. Table II and Fig. 15 show the effect on the rate of solution of zinc obtained by changing the viscosity of a hydrochloric acid solution by adding cane sugar, alcohol and the salts listed. The viscosity values were taken from the

TABLE II

Rate of solution of zinc at 25° in 1000 cc. of 0.007 M HCl + 0.05 M KNO₃, 4000 r. p. m.; diameter of cylinder, 1.94 cm.

Additional solute	η_0/η	Mg. diss./sq. cm. in five min.
. . .	1	3.58
0.3 M sugar	0.71	2.68
.6 M sugar	.55	2.00
.9 M sugar	.38	1.45
1.2 M sugar	.27	0.94
1.5 M sugar	.17	.61
2.0 M NaCl	.80	2.81
2.0 M KCl	1.01	3.67
1.22 M MgSO₄	0.43	1.06
2.44 M MgSO₄	.17	0.39
24.7 vol. % C₂H₅OH	.49	1.73

Landolt-Börnstein "Tabellen," in the case of cane sugar by interpolation. The effect of 0.007 M hydrochloric acid and 0.05 M potassium nitrate on the viscosity was neglected.
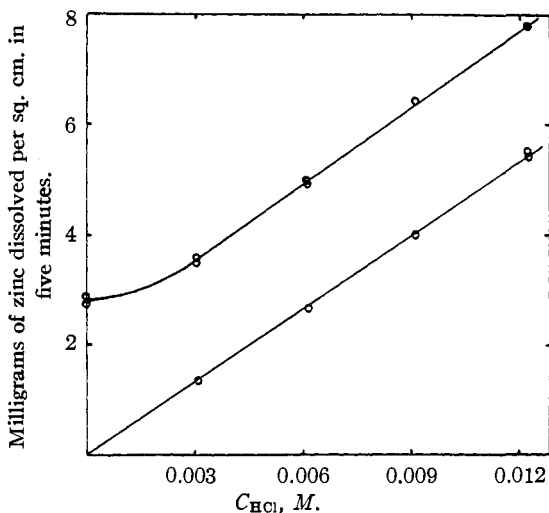

Fig. 12.—Rate of solution of zinc in mixed HCl and acetic acid: lower curve, HCl alone; upper curve, 0.0122 M acetic acid + HCl; 0.05 M KNO$_3$ present, 25–26°, 3800–4000 r. p. m., 500 cc. of solution.

That the inverse proportionality holds rather well is shown in Fig. 15. The results with magnesium sulfate may be in error because the solutions
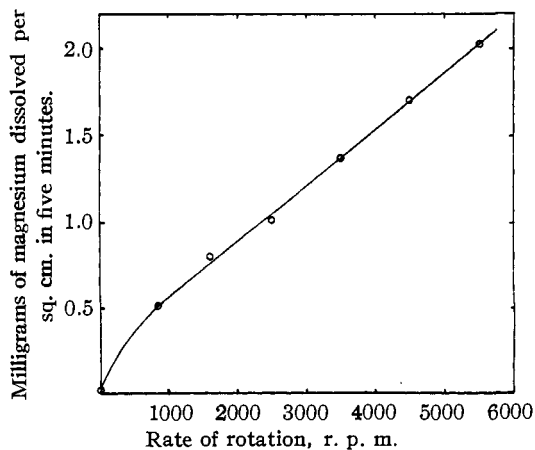

Fig. 13.—Effect of rotational velocity on rate of solution of a magnesium cylinder 2.16 cm. in diameter, 2.50 cm. long, in 0.0071 M HCl at 25°, 1 liter of solution.

were not made up very carefully; or possibly HSO_4^- ion may be formed in solutions of these high sulfate ion concentrations (?). The effect of salts is seen to be not a kinetic one, but merely due to the change in the viscosity of the solution.

Van Name and Hill[13] have measured the effect of alcohol up to 3 M and sugar up to 1 M on the rate of solution of cadmium in iodine-potassium iodide solutions. The results, when plotted as in Fig. 15, give a similar relation.[14]

Brönsted and Kane[8] mention the experiments of Zecchini[15] on the rate of solution of zinc in hydrochloric acid in a number of different solvents, and find it difficult to explain the rates as those of the chemical reaction. Zecchini's results are rather irregular but, considering the possible errors of the experiments, the rates, when plotted against $1/\eta$ for the pure solvents, do not fall unreasonably far from a straight line passing through the origin. Factors such as the solubility of zinc chloride and the over-voltage of hydrogen in the particular solvent must be important but, whatever the mechanism of the actual chemical reaction, the observed rates must be controlled largely by the diffusion process.
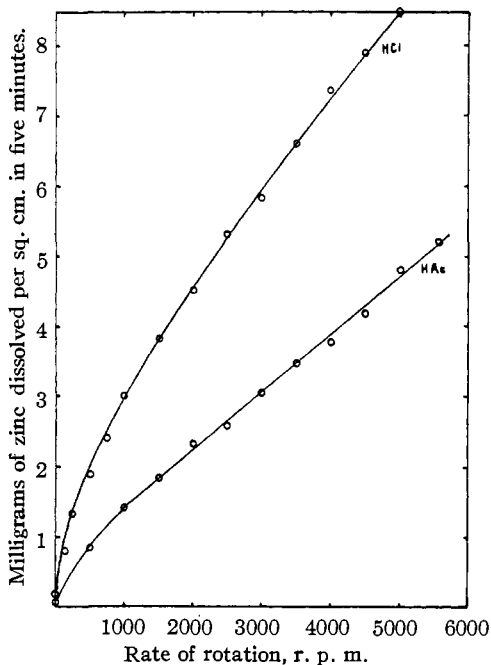

Fig. 14.—Effect of rotational velocity on rate of solution of a zinc cylinder 2.44 cm. in diameter, 1.88 cm. long, in 0.0142 M HCl and 0.0192 M acetic acid at 25°, 0.05 M KNO_3 present, 500 cc. of solution.

6. **Comparison of Different Solids.**—Magnesium, zinc and cadmium dissolve at far different rates in acid solutions containing no oxidizing agents, and the rate varies greatly with the purity of the metal. However, with potassium nitrate present, the rates are not widely different, and not far different from the rate of solution of marble. Table III gives quantitative results for these four substances.

[13] Van Name and Hill, *Am. J. Sci.*, [4] **36**, 543 (1913).

[14] The viscosities of sugar solutions given by Van Name and Hill are apparently somewhat in error.

[15] Zecchini, *Gazz. chim. ital.*, **27**, 466 (1897).

TABLE III

QUANTITATIVE RESULTS

Rates of solution at 25°, 1000 cc. of solution, 4000 r. p. m., 0.05 M KNO$_3$ used with Mg, Zn, Cd

	Diameter of cylinder, cm.	Milliequivalents of solid per cc.	Milliequivalents diss. per sq. cm. in 4 min.	
			0.007MHCl	0.03MHAc
Mg	1.91	145	0.094	0.124
Zn	1.95	220	.086	.128
Zn^a	1.95	220	.080	.109
Cd	1.97	154	.076	.094
CaCO$_3$	1.87	540	.116	.134

^{a} "Spectroscopically pure" zinc furnished by the New Jersey Zinc Co., to whom we wish to express our thanks.

It does not seem plausible that rates so nearly the same can be rates of chemical reaction for substances so widely different in chemical activity and in concentration. More probably the differences are due to differences in the solubility and d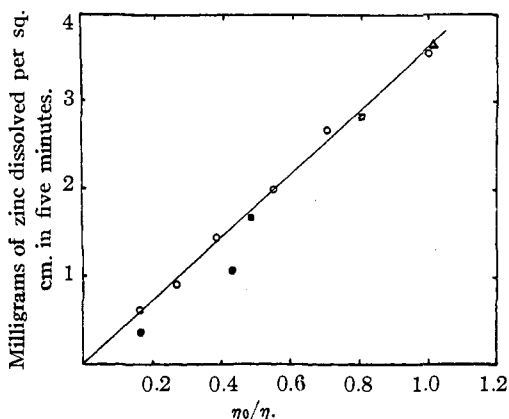iffusion rates of the reaction products and their effects on the diffusion rates of the acids. The higher values for marble in both acids might be explained by the disruptive effect of carbon dioxide bubbles on the "diffusion layer;"[16] but it is doubtful whether such bubbles were formed during four minutes of rotation in these solutions. Furthermore, the corresponding values for magnesium in similar solutions containing no potassium nitrate were: in 0.007 M HCl, 0.086 milliequivalent, somewhat lower than with nitrate present; in 0.03 M HAc, 0.134 milliequivalent, somewhat higher

Fig. 15.—Dependence of the rate of solution of zinc in hydrochloric acid on the viscosity of the solution, 25°, 0.05 M KNO$_3$ present, 4000 r. p. m.: O, sugar solutions; ●, 1.22 and 2.44 M MgSO$_4$; □, 2 M NaCl; ■, 24.7 volume % ethyl alcohol; △, 2 M KCl.

than with nitrate present. In this case the solutions became cloudy with very small hydrogen bubbles; their formation does not have a pronounced or consistent effect.

Van Name and Hill have proposed another explanation for small differences in the rate of solution of various metals in acid ferric chloride and ferric alum solutions.[17] If the rates of the chemical reactions are not very

[16] See Van Name and Hill, *Am. J. Sci.*, [4] **36**, 543 (1913).

[17] Van Name and Hill, *ibid.*, [4] **42**, 307 (1916).

much higher than the diffusion rates, they may have a noticeable effect on the solution velocities. The rates for marble, magnesium, zinc and cadmium are in the order one should expect if this explanation applies; but, if this were true, the differences would probably be more pronounced at this rotational speed.

A rough calculation from the experiments of Brönsted and Kane indicates that under the conditions described in Table III, 0.03 M $H_2PO_4^-$ ion would dissolve approximately 0.1 milliequivalent of sodium from an amalgam containing 0.14 milliequivalent per cc. (above which value the rate of solution is independent of the sodium concentration),[18] which suggests that this rate may likewise be controlled by the diffusion rate of the acid.

Summary

The rate of solution of zinc has been measured in a number of different acids. The simplification of the results obtained in the presence of certain oxidizing agents has been shown, the effect of acid concentration, rate of rotation and the temperature coefficient have been studied; and a comparison of the rate with those for other metals and marble has been made.

The results have been discussed from the viewpoints of the old "diffusion rate" theory and the Brönsted–Kilpatrick theory. While the former theory is not altogether satisfactory without modification, certain results are definitely contradictory to the latter.

It is impossible to decide at present whether other acids than the H_3O^+ ion react directly with magnesium, zinc, cadmium and marble, since previous experiments have measured rates controlled largely or entirely by diffusion rates.

NEW YORK, N. Y.

---

[18] Fraenkel and Heinz, *Z. anorg. allgem. Chem.*, **133**, 153 (1924).