Summary

The solubility of silver bromate has been determined in water–non-electrolyte mixtures at 25°, and the corresponding primary medium effects defined and evaluated. The simple Born equation was shown to be inadequate, since the observed medium effects are characteristic of the non-electrolyte as well as of the dielectric constant.

NEW HAVEN, CONNECTICUT RECEIVED DECEMBER 6, 1932
PUBLISHED MAY 6, 1933

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

The Rate of Solution of Marble in Dilute Acids

BY CECIL V. KING AND CHENG LING LIU

Introduction

It would be of considerable interest to find a solid which reacts with dilute acids or bases in solution at a rate much slower than the rate of diffusion of the latter to the solid surface. Such a reaction would present an opportunity to study the properties of undissociated acid and basic molecules in a fashion impossible heretofore. The work of Kilpatrick and Rushton[1] and of Brönsted and Kane[2] has been criticized previously.[3] Various metals dissolve in rather concentrated acids at rates supposedly independent of diffusion rates[4] but these cases are not amenable to the type of study suggested here. The idea that undissociated acids can react directly with metals is not new; experiments interpreted as proving this to be possible have appeared from time to time since the formulation of the ionization theory.[5]

In view of the present state of this problem it seems appropriate to compare the results of experiments with the metals with similar ones with a non-metal, whose solution involves no oxidation–reduction process, where we can assume the surface equilibrium to be reached "instantaneously," and whose solution rate is with a high degree of probability controlled by the various diffusion rates involved. Marble was chosen because of the ease of preparation of test samples, in spite of its obvious defects and the probable superiority of the salt of a weaker acid, as an oxide.

Boguski[6] first showed that the rate of solution of marble parallelo-

---

(1) Kilpatrick and Rushton, *J. Phys. Chem.*, **34**, 2180 (1930).

(2) Brönsted and Kane, THIS JOURNAL, **53**, 3624 (1931).

(3) King and Braverman, *ibid.*, **54**, 1744 (1932); Hammett and Lorch, *ibid.*, **54**, 2128 (1932).

(4) Centnerszwer and Zablocki, *Z. physik. Chem.*, **122**, 455 (1926); Jablczynski, Hermanowicz and Wajchselfisz, *Z. anorg. allgem. Chem.*, **180**, 184 (1929).

(5) See reference to Kahlenberg and his co-workers by King and Braverman; also a series of articles "On the Mechanism of Reduction," by H. J. Prins, to which the author has kindly called our attention; *Rec. trav. chim.*, **42**, 473, 482, 942 (1923); **44**, 876, 1050, 1093 (1925).

(6) Boguski, *Ber.*, **9**, 1442, 1599, 1646 (1876); Boguski and Kajander, *ibid.*, **10**, 34 (1877).

pipeds (with no stirring) is proportional to the molar concentration of acid and the same for several strong acids. Spring,[7] however, found the rate not to be unimolecular over the entire curve as acid is used up; and also showed that different faces of Iceland spar crystals dissolve at different rates. Tammann and Krings[8] later showed that the rate of etching of calcium carbonate crystals is intimately connected with the density of packing of calcium ions.

In his well-known exposition of the diffusion rate theory for such reactions, Brunner[9] showed that marble dissolves somewhat faster in strong acids than magnesium or magnesia, while in benzoic acid the rate was too slow and erratic, and the velocity "constants" fell off rapidly as the reaction progressed; this he attributed to incomplete neutralization of the benzoic acid at the marble surface and an accumulation of carbonic acid.

Ericson-Aurén and Palmaer,[10] while criticizing the diffusion theory as applied to the rate of solution of metals, agreed that it should apply in the cases of marble and magnesia, although it was not easy to explain such anomalies as that magnesite and dolomite dissolve more slowly in hydrochloric acid than marble does. Palmaer[11] again calls attention to these difficulties, and remarks that the application of the diffusion theory becomes very complicated if both ions and neutral molecules are involved (as in the case of a weak acid). Palmaer and his co-workers found, among other things, (1) that there is no induction period, as was supposed by Spring; (2) Iceland spar is not as suitable as marble for such experiments because of many minute fissures formed in the surface in preparing the specimen; (3) the effect of inert salts is abnormal.

A few previous experiments with marble in this Laboratory[3] showed that while marble undoubtedly dissolves somewhat faster than magnesium, zinc or cadmium, the discrepancy is not great enough to cause us to discard the diffusion rate theory altogether.

The primary surface equilibrium, we assume, is reached with extreme rapidity; but for the original diffusion rate theory to be strictly valid, the attacking acid should be very strong compared to carbonic acid. In a very weak acid the rate should depend largely on the rate of diffusion of carbonic acid from the marble surface, and the rate of escape of carbon dioxide from the solution. An additional complication is introduced in this case, due to the fact that freshly formed carbonic acid is much stronger than the equilibrium mixture of carbonic acid and carbon dioxide, and that this equilibrium is not attained instantaneously. The rate of the reaction, $H_2CO_3 \rightleftarrows H_2O + CO_2$, is influenced tremendously by the

---

[7] Spring, *Z. physik. Chem.*, **1**, 209 (1887); **3**, 13 (1888).

[8] Tammann and Krings, *Z. anorg. Chem.*, **146**, 420 (1925).

[9] Brunner, *Z. physik. Chem.*, **47**, 79 (1904).

[10] Ericson-Aurén and Palmaer, *ibid.*, **56**, 689 (1906).

[11] Palmaer, "The Corrosion of Metals," Ingeniorsvetenskapsakadamien Handlingar, Stockholm, 1929, No. 93, p. 40.

*P*H of the solution; in the cases considered here the equilibrium is always over 99% to the right, but one to several seconds may be necessary for its attainment.

The rates and equilibrium points of this reaction at various values of the *P*H have been measured by a number of investigators, notably Faurholt and Saal.[12] The true ionization constant of carbonic acid

$$[H^+][HCO_3^-]/[H_2CO_3] = 5 \times 10^{-4}$$

is far greater than the pseudo constant

$$[H^+][HCO_3^-]/[H_2CO_3] + [CO_2] = 3 \times 10^{-7}$$

Marble would dissolve very much more slowly in acids weaker than formic ($K = 2.1 \times 10^{-4}$) if it were not for this diminution in the strength of the carbonic acid following its production. This factor probably modifies the solution rate with even the strongest acids, as will be shown later.

Other factors which we assume to be of minor importance are the presence of both carbonate and bicarbonate ion; disruption of the surface layer by carbon dioxide bubbles (which were probably not formed in these experiments); and the possible adsorption of hydrogen ions or acid molecules on the marble surface.[13]

According to the Nernst–Brunner theory the rate of solution for a strong acid (say HCl) would be

$$\frac{dx}{dt} = \frac{AD_{HCl}}{\delta_1}(C_0 - C_1) \qquad (1)$$

where A is area exposed, D is diffusion coefficient of HCl, δ_1 is thickness of the "diffusion layer," C_0 is bulk concentration of HCl, C_1 is concentration of acid (or H^+) next to the immediate surface of the marble. But it is also true that

$$\frac{dx}{dt} = \frac{AD_{H_2CO_3}}{\delta_2}C_s \qquad (2)$$

where δ_2 is the distance from the surface at which $C_{H_2CO_3}$ becomes negligible, and C_s is the steady surface concentration of carbonic acid. From (1) and (2) and the ionization equilibrium of carbonic acid we can solve for C_1, in terms of δ_2/δ_1, $D_{HCl}/D_{H_2CO_3}$, and $K_{H_2CO_3}$, but it is quite impossible to use the resulting equation quantitatively, in view of our lack of numerical values for these quantities. As the carbonic acid diffuses from the surfaces undoubtedly $K_{H_2CO_3}$ becomes smaller and $D_{H_2CO_3}$ changes in value; it is very probable that $\delta_2 \neq \delta_1$. Any reasonable values for the above ratios indicate that C_1 is not negligibly small even for strong acids except probably for low concentrations and low stirring speeds where we can assume that the carbonic acid is dehydrated long before it reaches the distance δ_1 from the surface and δ_2/δ_1 is very small.

---

[12] Faurholt, *J. chim. phys.*, **21**, 400 (1924); Saal, *Rec. trav. chim.*, **47**, 264 (1928).

[13] For a discussion of such adsorption on metal surfaces, see Prins, Ref. 5.

Experimental

Marble cylinders about 3.2 cm. long and 1.9 cm. in diameter were mounted either on a Bakelite shaft with the ends covered by rubber washers and Bakelite nuts, or on glass rods, held with picein cement with the ends completely covered with the same cement. The cylinders were frequently smoothed with fine emery paper, as they become rough in the acid. When a cylinder diminished in diameter enough to lower the peripheral speed as much as 5%, it was discarded and a new one substituted. The cylinders were rotated in nearly all the experiments at 4000 ± 200 r. p. m., in 2 liters of solution maintained at the desired temperature ±0.5°, in nearly all cases 25°. The rate was not followed over a large change in acid concentration in individual experiments except in a few cases to substantiate the older findings that the rates are not unimolecular over the whole course. Only the initial rates were measured for each acid concentration, over an accurately measured period of four minutes, which was chosen because the amount dissolved was sufficient to be measured accurately and still the diminution in concentration of the acid in the solution was only a few per cent. The cylinders were weighed before and after each run to 0.5 milligram, which was the limit to which a cylinder could be reweighed after washing with water and drying.

Individual experiments could usually be duplicated on the same day with the same marble cylinder to one or two milligrams. However, curves for different cylinders or for the same cylinder after some use showed maximum differences as high as ±6 or 6.5%. Comparisons were therefore made only with constant checking to be sure the character of the marble had not changed in an unknown way.

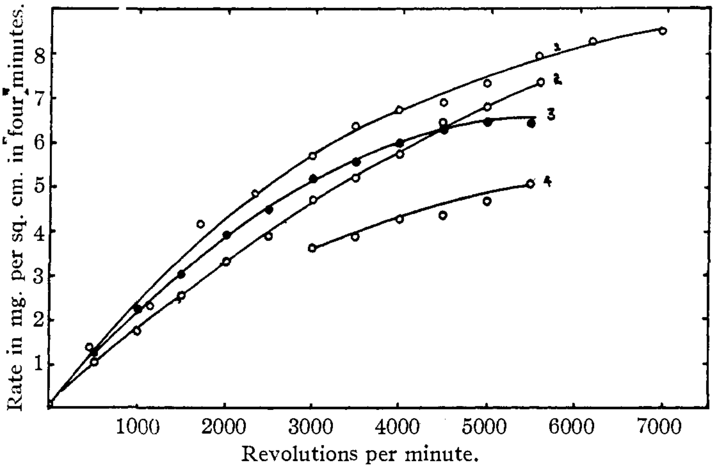

Fig. 1.—Effect of speed of rotation on rate of solution of marble cylinders, two liters of acid solution, 25°: 1, 0.0304 *M* acetic acid; 2, 0.0077 *M* hydrochloric acid; 3, 0.023 *M* acetic acid; 4, 0.0152 *M* acetic acid.

1. **Effect of Speed of Rotation.**—Figure 1 shows how the rate varies with the speed of rotation in acetic and hydrochloric acids. The relation is not linear as with magnesium and zinc, and it appears that the rate would reach a maximum at somewhat higher speeds. This curve, however, evidently does not consist of the three portions described by Centnerszwer

and Heller[14] and the supposed maximum is not to be interpreted in the same way, namely, that at high speeds the acid reaches the surface faster than it can react and the diffusion layer consequently disappears. Rather it would seem that while δ_1 probably varies as in the normal case, δ_2 increases as carbonic acid is produced faster, and the correction term C_1 in equation (1) becomes larger as the speed of rotation increases. The fact that the rate increases at all with the speed of rotation substantiates the supposition that it is controlled by diffusion processes.

2. **The Temperature Coefficient.**—Figures 2 and 3 show data for hydrochloric and acetic acids at 15, 25 and 35°. The coefficients for hydrochloric acid are: $k_{25}/k_{15} = 1.47$, $k_{35}/k_{25} = 1.32$; for acetic acid, $k_{25}/k_{15} = 1.94$, $k_{35}/k_{25} = 1.43$. One of these coefficients is higher than is true for most heterogeneous reactions, but in the main they confirm the importance of diffusion.

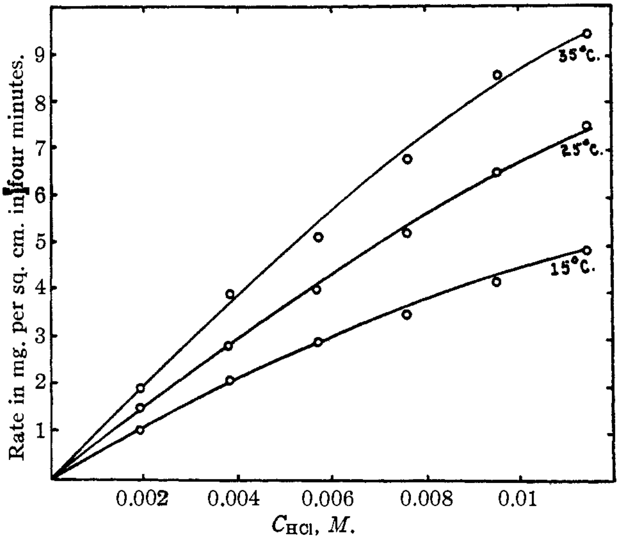

Fig. 2.—The temperature coefficient with HCl, 2 liters of solution, 4000 r. p. m.

3. **Inert Salts and Sugar.**—The effect of cane sugar seems to be entirely due to the change in diffusion rates brought about by the increased viscosity of the solution. In Fig. 4 the rate is plotted against the reciprocal of the viscosity, η_0/η. Similar results have been obtained with ethyl alcohol solutions.[15] With metals the effect of inert salts is similar except for a small positive effect at low salt concentrations; this is by no means true with marble. Palmaer[11] has shown that in solutions of salts which do not affect the viscosity greatly, the rate of solution of marble is not

---

[14] Centnerszwer and Heller, *Z. physik. Chem.*, [A] **161**, 116 (1932).

[15] Jablczynski and Jablonski, *Z. physik. Chem.*, **75**, 503 (1910).

explainable by the calculated change in the diffusion coefficient of the acid; for example, in 0.3 *N* HCl + 3 *N* KCl, the rate is 23% higher than in the same HCl alone, whereas Palmaer calculates that the diffusion coefficient of the acid is increased some 148% by addition of the salt.

Figure 5 shows that 1 molar sodium chloride has a decided, though not large, positive effect on the rate in hydrochloric acid. Figure 6 shows the effect of sodium chloride in three concentrations of acetic acid; with low acetic acid concentrations there is no salt effect up to 1 molar sodium chloride, with 0.03 *M* acetic acid the effect is not large. In the first case (Fig. 5) at least three factors are present: (1) the viscosity is increased, which would diminish the rate; (2) the dissociation of the carbonic acid produced is increased, which would also diminish the rate; and (3) the diffusion coefficients of both hydrochloric and carbonic acids are increased, which would tend to increase the rate. In the second case (Fig. 6), in addition to these factors, we have the increase in the dissociation constant of the acetic acid by the salt; and it is significant that acetic acid reaches its maximum dissociation at nearly the same salt concentration which gives the maximum effect in Fig. 6, while the maximum dissociation of the

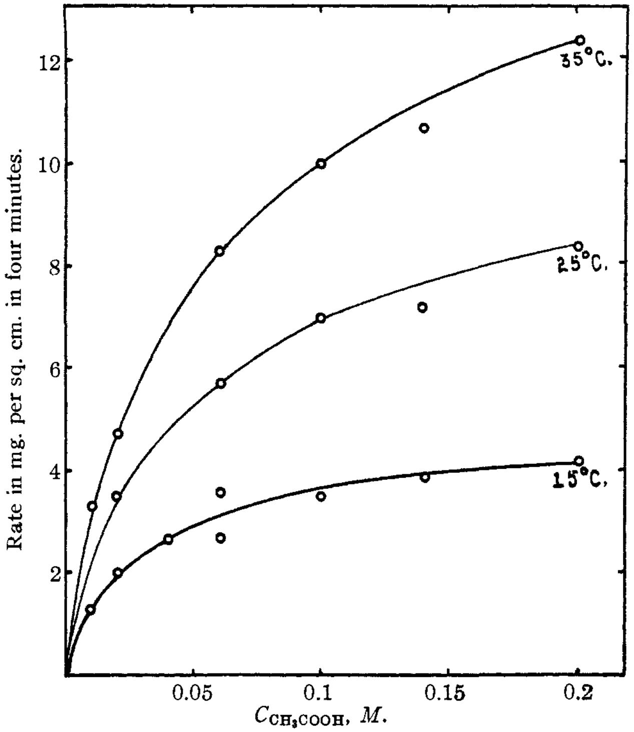

Fig. 3.—The temperature coefficient with acetic acid, 2 liters of solution, 4000 r. p. m.

ordinary equilibrium mixture of carbonic acid and carbon dioxide is at a much higher salt concentration.[16]

4. The Rate in Mixtures of Weak Acids and their Salts.—Small amounts of sodium acetate added to acetic acid reduce the rate of solution of zinc about 10%, while larger additions have no further effect unless enough is added to alter appreciably the viscosity of the solution. The equilibrium hydrogen-ion concentration at the surface of zinc must be exceedingly low and the reaction very fast, so that the zinc appears to be reacting with the undissociated acid; but marble can dissolve only very slowly in solutions of very low hydrogen-ion concentration, since displacement of carbonic acid at the surface would leave no lower hydrogen-ion concentration than is already present in the bulk of solution. Therefore, salts which repress the hydrogen ion in the solution may be expected to lower the rate continuously until a very low value is reached. This situation is shown in Fig. 7; the rate decreases tremendously with the hydrogen-ion concentration, but is not at all proportional to the latter, since the undissociated acid plays an important part in diffusing to the surface.

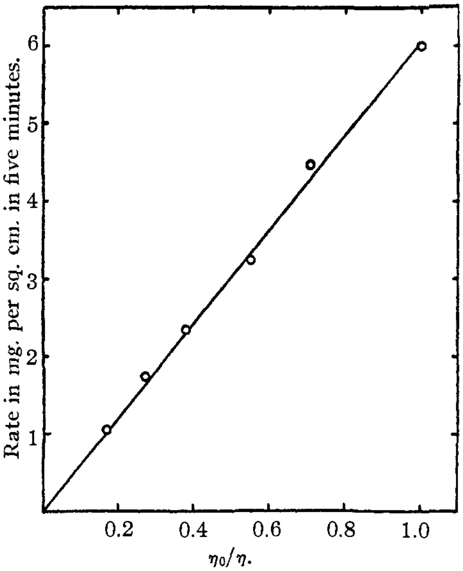

Fig. 4.—The effect of cane sugar on the rate, 1 liter of 0.0269 M acetic acid, 4000 r. p. m., 25°.

5. Comparison of the Rates in Different Acids.—Curves showing the initial rates in a number of acids are given in Fig. 8. Table I gives the ionization constants, diffusion constants, and solubilities of the calcium salts for most of these acids, as the rates seem to be dependent on all these factors.

In the most dilute solutions, the rates parallel the ionization constants, except for tartaric acid, whose calcium salt is the least soluble, and for succinic, the only other polybasic acid except citric. In more concentrated solutions this relation is modified chiefly for those acids whose salts have only a limited solubility. The solubility of the salts was never exceeded throughout the two liters of solution during these four-minute runs, but they were undoubtedly often precipitated on the marble surface.

If the diffusion constants are multiplied by the basicity of the acids,

---

(16) See Chase and Kilpatrick, THIS JOURNAL, **53**, 2589 (1931).

the rates in dilute solutions also parallel these figures, although there is no strict proportionality. The rates are undoubtedly highly dependent on the hydrogen-ion concentration, the diffusion rate, and the nature and concentration of the undissociated acid.

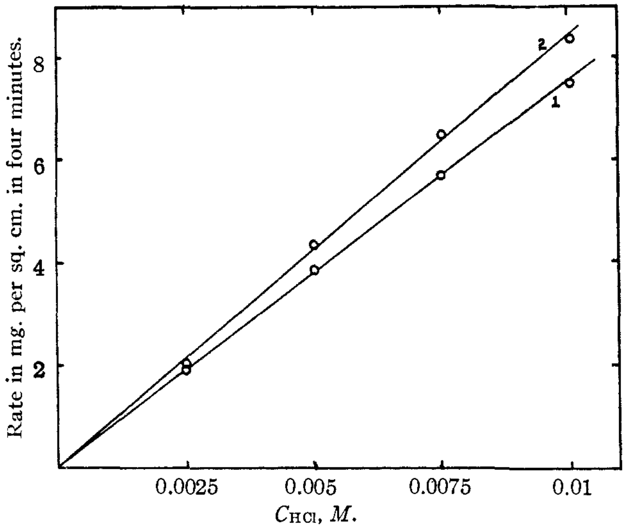

Fig. 5.—The effect of 1M NaCl on the rate in HCl, 2 liters of solution, 4000 r. p. m., 25°; 1, HCl alone; 2, HCl + 1 M NaCl.

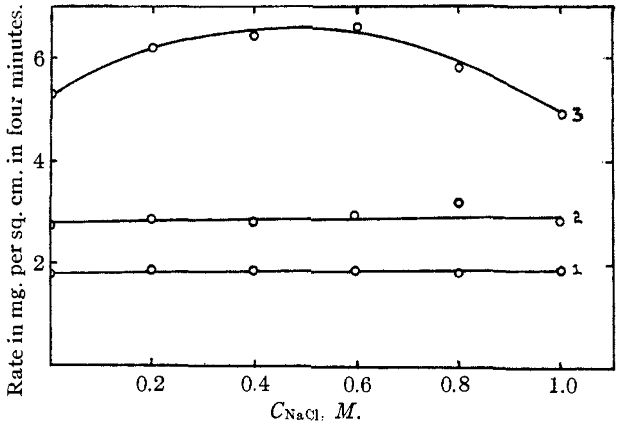

Fig. 6.—The effect of NaCl on the rate in acetic acid, 2 liters of solution, 4000 r. p. m., 25°: 1, 0.0051 M acid; 2, 0.0102 M acid; 3, 0.0306 M acid.

It was found by Spring[7] that marble dissolved in acetic acid only one-twentieth as fast as in hydrochloric acid. This is probably true over a small concentration range in solutions 0.1 molar or stronger, as can be estimated from the curves of Figs. 2 and 3; at 25 and 35°, the rate in 0.2 *M* acetic acid is less than 20% greater than in 0.01 *M* hydrochloric acid. This, however, is due to the fact that the acetic acid curves bend over so rapidly with increasing concentration; in dilute solutions, as is

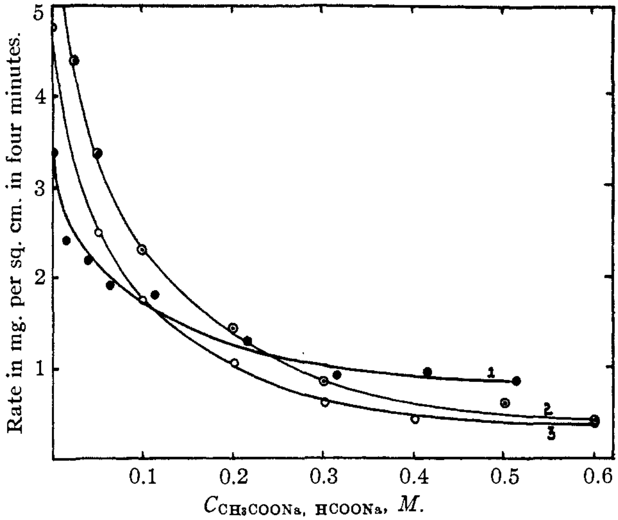

Fig. 7.—The rate in solutions of weak acids and their salts, 2 liters of solution, 4000 r. p. m., 25°: 1, 0.0074 *M* formic acid; 2, 0.04 *M* acetic acid; 3, 0.02 *M* acetic acid.

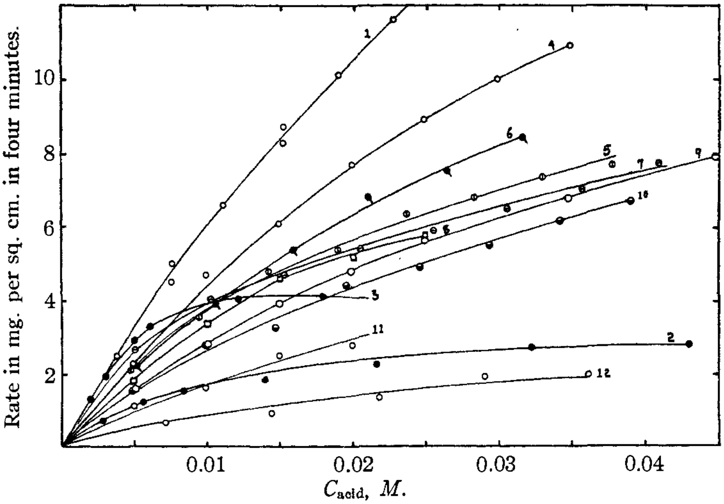

Fig. 8.—Comparison of the rates in a number of acids, two liters of solution, 400 r. p. m., 25°: 1, hydrochloric; 2, tartaric; 3, citric; 4, formic; 5, glycolic, 6, lactic; 7, succinic; 8, benzoic; 9, acetic; 10, propionic acids; 11, ferric nitrate; 12, chromic chloride.

seen in Fig. 8, the rate in acetic acid is about 40% of that in hydrochloric acid. This is approximately the same relation as that found in the case of zinc and magnesium; in fact, in dilute solutions the marble seems to behave in every way like the metals with the exception that the rates are a few per cent. higher.

TABLE I

	Acid	K_1(ion) × 10^5	Approx. D(sq. cm./day)	Approx. soly. Ca salt (25°, moles/1000 g. H_2O)
1	Hydrochloric	...	2.3	7.4
2	Tartaric	110	0.4	0.002
3	Citric	80	.4	.002
4	Formic	21	.9	1.3
5	Glycolic	15	..	...
6	Lactic	14	..	0.34
7	Succinic	6.6	.7	.08
8	Benzoic	6.6	.75	.10
9	Acetic	1.8	.7	2.2
10	Propionic	1.4	.5	2.1
Ferric ion $Fe(H_2O)_6^{+++}$		630	..	...
Chromic ion $Cr(H_2O)_6^{+++}$		1.26	..	...

The rates in chromic and ferric salts are not as high as would be expected from the dissociation constants of the hydrated ions (Table I), probably because of the precipitation of the hydroxides or basic salts on the marble surface. Such a precipitate was visible with the ferric nitrate solution used, and even the addition of considerable strong acid to the solution did not prevent its formation. There was no such increase in the rate as roseo salts give with sodium amalgam.[2]

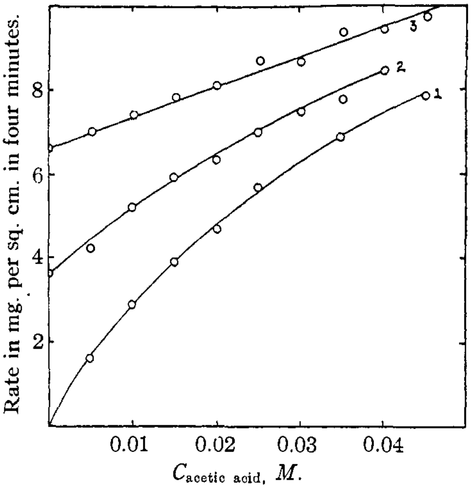

Fig. 9.—The rate in mixtures with fixed HCl, varying acetic acid concentrations, two liters of solution, 4000 r. p. m., 25°: 1, no HCl; 2, 0.00385 M HCl; 3, 0.0077 M HCl.

6. **The Rate in Mixed Acid Solutions.**—As was shown in Section 4, the rate in a weak acid is reduced tremendously by addition of a salt of that acid. The weak acid can be buffered in a solution of considerable hydrogen-ion concentration by adding a strong acid. In this type of solution zinc dissolves at a rate which can be considered additive for the strong acid and the undissociated weak acid; but this is not true for marble. As constant amounts of hydrochloric acid are added to vary-

ing concentrations of acetic or formic acids (Figs. 9 and 10), the effect of the weak acid becomes less and less, the more hydrochloric acid is present. With sufficient hydrochloric acid present, which apparently means when the ionization of the weak acid is repressed sufficiently, the rate curves become linear. This is apparently the only type of solution in which we can separate the effects of hydrogen ion and undissociated acid; and since the more strong acid present, the lower the slope of these curves, it appears that weak acid with its ionization totally repressed would not dissolve marble at all, no matter what the hydrogen-ion concentration of the solution.

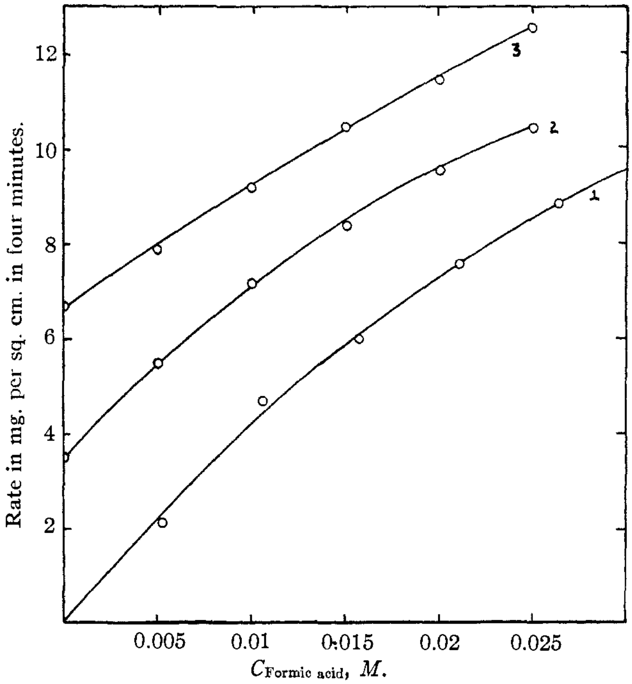

Fig. 10.—The rate in mixtures with fixed HCl, varying formic acid concentrations, two liters of solution, 4000 r. p. m., 25°: 1, no HCl; 2, 0.00385 *M* HCl; 3, 0.0077 *M* HCl.

The depressing effect of citric acid on the rate in hydrochloric acid (Fig. 11) is probably specific for citric acid. It was hoped with these experiments to eliminate the effect of the low solubility of calcium citrate, but it is doubtful if this was accomplished.

7. **Discussion.**—Our experiments have by no means fully explained the rate of solution of marble, but rather have emphasized its complexity. It seems clear, however, that the rate is controlled by the diffusion rates of the acid, the calcium salt, the carbonic acid and carbon dioxide, and the carbonic acid–carbon dioxide–water equilibrium, and the rate of its

attainment. It is useless to discuss the possible effect due to the small second dissociation of carbonic acid and other minor effects, since we cannot even qualitatively ascribe any of the rate to them.

At the one extreme marble dissolves in hydrochloric acid with a rate controlled largely by the diffusion rate of the strong acid. At the other extreme it dissolves in a very weak acid with a rate controlled chiefly by the rate of dehydration of carbonic acid and diffusion of carbon dioxide from the surface. (For instance, in *p*-nitrophenol, $K = 7 \times 10^{-8}$, marble dissolves about 0.5% as fast as in hydrochloric acid of the same molar concentration.) In acids of intermediate strength these factors and others are operative.

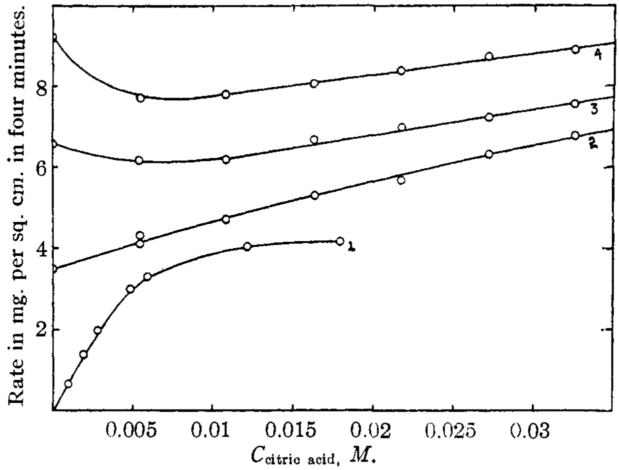

Fig. 11.—The rate in mixtures with fixed HCl, varying citric acid concentrations, two liters of solution, 4000 r. p. m., 25°: 1, no HCl; 2, 0.00385 *M* HCl; 3, 0.0077 *M* HCl; 4, 0.0116 *M* HCl.

It is interesting to note that if the rates for the acids whose salts are soluble (Fig. 9) are plotted against the hydrogen-ion concentration (say the average for the four-minute runs), straight lines are obtained, which, however, do not extrapolate to the origin. That is, for any one weak acid, the rate is proportional to the hydrogen-ion concentration, but the proportional constant is different for each acid, greater for the stronger acids than for the weaker. This again reflects the effect of the undissociated molecules and is to be expected since the hydrogen ion of the solution must primarily determine the hydrogen-ion concentration at the marble surface by influencing the strength and the speed of dehydration of the carbonic acid and the rate of diffusion of the attacking acid, while the undissociated portion of the acid can diffuse to the surface but probably not react as such.

The curve for hydrochloric acid is undoubtedly linear in solutions of as low concentrations as the hydrogen-ion concentration of the weaker acids. The curve, however, deviates from linearity at much lower concentrations than is the case with metals. This must be due to a change in the ratio δ_2/δ_1 of equation (4) with hydrochloric acid concentration, or a change in the character of the carbonic acid diffusion layer which gives a similar effect.

Summary

The rate of solution of marble cylinders rotating in dilute solutions of a number of acids and acid mixtures has been measured. Concentration–initial rate curves have been plotted, the effects of rate of rotation and temperature coefficients measured, the effect of inert salt on weak and strong acids and buffer salts on weak acids determined; mixtures of weak and strong acids and solutions of ferric and chromic salts were used.

It has been shown that the rate follows the usual criteria of the diffusion rate theory, but that the original theory must be modified because of the facts that (1) carbonic acid is in no case negligibly weak, (2) freshly liberated carbonic acid is a much stronger acid than the usual equilibrium mixture of carbonic acid and carbon dioxide and (3) the dehydration of carbonic acid is slow enough to influence the rate tremendously.

The rates are not unimolecular and it has been shown that the reason lies in the above facts. A number of similarities and differences between the behavior of metals and marble have been pointed out and discussed.

NEW YORK, N. Y.

RECEIVED DECEMBER 13, 1932
PUBLISHED MAY 6, 1933

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 298]

Purification and Ultraviolet Transmission of Ethyl Alcohol

BY LOUIS HARRIS

Ninety-five per cent. grain alcohol is the customary source for pure absolute ethyl alcohol. In a recent publication, Leighton, Crary and Schipp[1] called attention to the precautions necessary and have shown by measurements of the ultraviolet absorption how the various treatments in the purification affect the transmission. Our experience with 95% alcohol confirms, in general, the finding of these authors. It seems, however, that the effect of these treatments would depend in some measure on the source of the alcohol.

We have found that commercial absolute alcohol[2] showed a fair transmission in the ultraviolet (a two-centimeter layer transmitted 50% at 2500 Å.) which improved after one distillation. Commercial absolute

---

(1) Leighton, Crary and Schipp, THIS JOURNAL, **53**, 3017 (1931).

(2) U. S. Industrial Alcohol Sales Co., Baltimore, Maryland.