# The Rate of Dissolution of Iron in Acids

By Morris B. Abramson and Cecil V. King

Previous work in this Laboratory has indicated that a modified Nernst diffusion layer theory accounts, in large part at least, for the dissolution rates of magnesium and marble in acids, of zinc and cadmium in acids with certain depolarizers present, of copper in ferric salt solutions (but not in acids with depolarizers), of benzoic acid in dilute alkali and for the rate of heat transfer from solid to solution.[1] Other work on magnesium in aqueous solutions[2] can for the most part be interpreted on this basis, though in ethyl alcohol solutions the rate for magnesium seems to be partly diffusion, partly chemically, controlled.[3]

Van Name and his co-workers[4] have shown very clearly the conditions under which dissolution rates are controlled by diffusion rates or by chemical rates, and have studied cases believed to be of each type. They point out that if the chemical rate is very rapid compared to the physical transport rate, the reagent concentration falls to zero at the surface and a diffusion gradient equal to the full reagent concentration will be set up; if the chemical rate is very slow, no concentration gradient between the surface and the bulk of the solution will exist; and finally if chemical and physical transport rates are comparable in magnitude, a definite reagent concentration will exist at the solid surface, less than that in the bulk of the solution. The intermediate case where both the physical and chemical factors are operative has been treated theoretically by Roller.[5]

The general criteria of a diffusion-controlled rate are: (1) Various solids dissolve in the same reagent at the same rate. (2) In different reagents the rate is an exponential function of the diffusion coefficient.[1b] (3) The rate increases with stirring speed, the exact function depending on the type of stirring. (4) The rate follows the same function of the viscosity as the diffusion coefficient. (5) The temperature coefficient is in general less than 1.5 per 10°. If the chemical

reaction is slow and controls the observed rate, then (1) the rate should be independent of stirring speed, viscosity and diffusion coefficient; and (2) the temperature coefficient should be, in general, greater than 2.0 per 10°.

Iron was chosen for the present investigation because it is less active than zinc, and its chemical reaction rate should be lower; also it was known that the metal dissolves faster in nitric acid than other dilute acids, indicating that nitrate acts as a depolarizer; and nitro compounds are reduced by iron and acid without hydrogen evolution. The disadvantages are that salts of weak acids hydrolyze and form insoluble films, and the dual valence leads to some complication, fortunately found not to be serious.

The dissolution rate of iron has not been measured previously with the present objectives in mind. The rate in more concentrated acid, with no depolarizer but with other metals as coupling agents, has been measured by Centnerszwer and Straumanis.[6]

Friend and Dennett[7] found that the rate of dissolution from a rotating iron disk, in dilute acid with no depolarizer, was linear with rotational speed up to 4000 r. p. m., and that the temperature coefficient was about 2 per 10°. Huber and Reid[8] also measured the effect of rotational speed with an iron disk, in 0.1 N sulfuric acid with no depolarizer, up to 11,360 r. p. m., and the rate of reduction of nitrobenzene in acid with the iron disk rotating up to 10,560 r. p. m.

**Experimental.**—Cylinders of the purest iron available commercially[9] of dimensions given in the figures, were rotated in 250 cc. of solution for all experiments at the lower speeds; at speeds above 6000 r. p. m. in 2000 cc. of solution. In most of the experiments the cylinders were removed, dried and weighed after five minutes in the solution at 25 ± 0.5°, and were repolished with fine emery paper before using again. The reproducibility was in general ±2 to 4% except in those cases where visible films formed on the metal.

1.—The rates were measured in four concentrations of hydrochloric acid at 2000 r. p. m., 25°, with increasing

(1) (a) King and Cathcart, THIS JOURNAL, **59**, 63 (1937); (b) King and Howard, *Ind. Eng. Chem.*, **29**, 75 (1937). Earlier references are given in these papers.

(2) Kilpatrick and Rushton, *J. Phys. Chem.*, **34**, 2180 (1930); **38**, 269 (1934).

(3) Sclar and Kilpatrick, THIS JOURNAL, **59**, 584 (1937).

(4) Van Name and Edgar, Bosworth, Hill, *Am. J. Sci.*, **29**, 237 (1910); **32**, 207 (1911); **42**, 307 (1916).

(5) Roller, *J. Phys. Chem.*, **39**, 221 (1935).

(6) Centnerszwer and Straumanis, *Z. physik. Chem.*, **A128**, 369 (1927).

(7) Friend and Dennett, *J. Chem. Soc.*, **121**, 41 (1922).

(8) Huber and Reid, *Ind. Eng. Chem.*, **18**, 535 (1926).

(9) Svea metal furnished by the Swedish Iron and Steel Co., New York City, to whom we acknowledge our thanks. The analysis furnished indicated 99.92–99.96% Fe.

amounts of potassium nitrate added until maximum rates were reached. In one series the cylinder was polished after each run; in another series it was allowed to become fully etched. It showed a fine, uniform crystalline structure with no inhomogeneities. These maximum rates were considerably higher than with the polished cylinder. In both cases yellow films appeared at low nitrate concentrations, and the rates were quite erratic with the etched metal. No films were visible at higher nitrate concentrations and the rates became reproducible. Under similar conditions the dissolution rate of zinc is linear with nitrate concentration, and less nitrate is necessary to reach the maximum rate.

Typical rates are plotted in Figs. 1 and 2 up to the nitrate concentration at which they become constant.
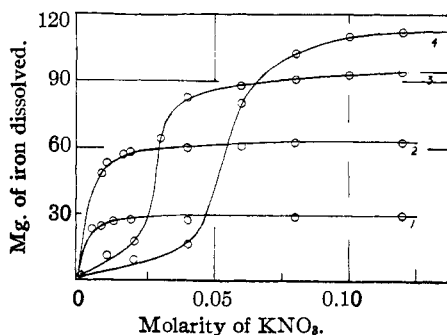


Fig. 1.—Mg. of iron dissolved in five minutes in 250 cc. of hydrochloric acid and potassium nitrate at 2000 r. p. m., at 25°: iron polished; cylinders about 1.8 cm. in diameter, 2.6 cm. in length; 1, 0.01 $N$ HCl; 2, 0.025 $N$ HCl; 3, 0.04 $N$ HCl; 4, 0.05 $N$ HCl.
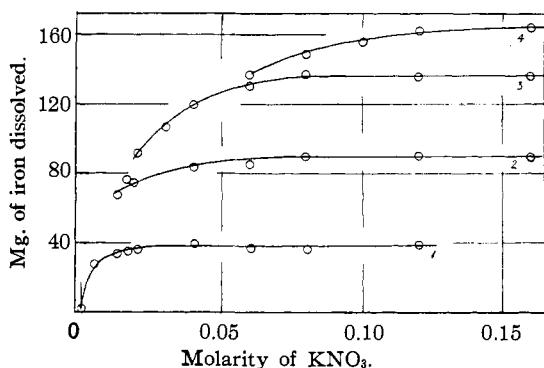


Fig. 2.—Mg. of iron dissolved in five minutes in 250 cc. of hydrochloric acid and potassium nitrate at 2000 r. p. m. at 25°: iron etched; cylinders 1.8 cm. in diameter, 2.6 cm. in length; 1, 0.01 $N$ HCl; 2, 0.025 $N$ HCl; 3, 0.04 $N$ HCl; 4, 0.05 $N$ HCl.

**2.**—Similar experiments were carried out with the polished cylinders in perchloric, nitric, sulfuric, acetic and tartaric acids with added potassium nitrate. Rates with the sulfuric and perchloric acids are shown in Figs. 3 and 4. No satisfactory maxima are reached with the higher acid concentrations, the rate increasing steadily with
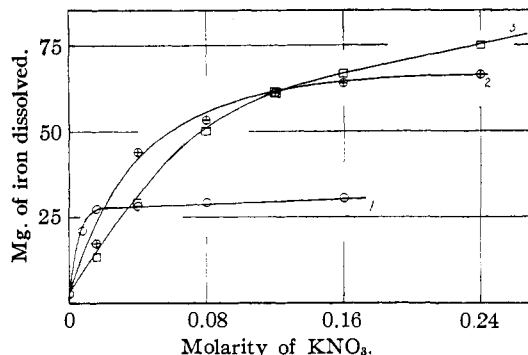


Fig. 3.—Mg. of iron dissolved in 250 cc. of solution in five minutes at 25° and 2000 r. p. m.: cylinders 1.8 cm. diameter, 2.6 cm. long; polished between runs; 1, 0.01 $N$ H$_2$SO$_4$; 2, 0.025 $N$ H$_2$SO$_4$; 3, 0.05 $N$ H$_2$SO$_4$.
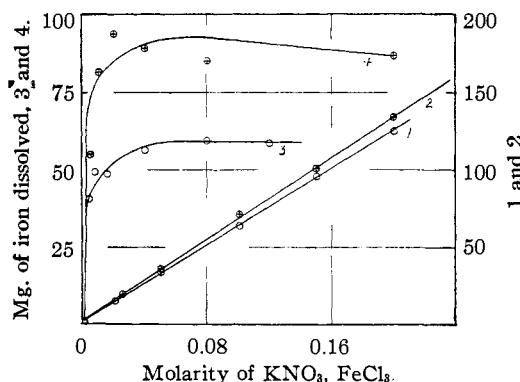


Fig. 4.—Mg. of iron dissolved in 250 cc. of solution in five minutes at 25°, at 2000 r. p. m.: cylinders 1.8 cm. diameter, 2.6 cm. long; polished between runs; 1, FeCl$_3$ + 0.01 $N$ HCl; 2, FeCl$_3$ + 0.05 $N$ HCl; 3, 0.025 $N$ HClO$_4$ + KNO$_3$; 4, 0.05 $N$ HClO$_4$ + KNO$_3$.

sulfuric, and decreasing with perchloric, acid after reaching a maximum which is lower than that in hydrochloric acid. The rates in 0.01 $N$ acids, however, are about the same as in hydrochloric acid, and those at 0.025 $N$ are only slightly lower. Added potassium nitrate did not have a very large effect on the rate in nitric acid; this is shown in Fig. 5, where the maximum rates, or the highest rates obtained, in these three acids and also in hydrochloric acid, are plotted. Only the rates in hydrochloric acid are linear with acid concentration, and none of them extrapolate to zero. The extrapolated rate may be due to a solvent reaction, which cannot be obtained experimentally at zero acid concentration because of insoluble reaction products.

The rates in acetic and tartaric acids were about one-tenth as great as in the strong acids. Visible films were formed and the rates were not very reproducible. These rates are not tabulated or shown in the figures.

**3.**—Experiments carried out in various solutions showed that the rate follows the unimolecular law over at least half the reaction in all the solutions mentioned, except those of very low nitrate concentration. The cylinders were rotated for two- or three-minute periods in the same
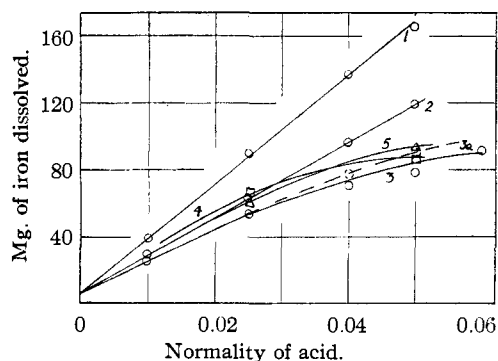
Fig. 5.—Effect of acid concentration on maximum rates of iron dissolving in 250 cc. of solution at 25° and 2000 r. p. m.: 1, HCl + KNO₃, etched iron; 2, HCl + KNO₃, polished iron; 3, HNO₃, polished iron; 3a, HNO₃ + KNO₃; 4, H₂SO₄ + KNO₃; 5, HClO₄ + KNO₃.

solution until most of the acid was used up. In calculating rate constants from the equation $k = \dfrac{2.3V}{At} \log \dfrac{a}{a-x}$ (where the symbols have the usual significance) it was assumed that two equivalents of hydrogen are used per atom of iron. The deviation from the equation in the later stages shows that this is not strictly true. Tests after the runs showed that one-tenth to one-fifth of the dissolved iron was in the ferric state, probably due to oxygen absorption or oxidation of ferrous ion by nitrate and hydrogen ion. The nitrate reduction also probably requires more than two hydrogen ion equivalents per iron atom. On the other hand, any ferric ion formed will begin to dissolve iron without using up hydrogen ion.

The highest rate constants thus obtained are given in Table I.

**4.**—Hydrogen peroxide and potassium nitrite were tried as depolarizers with hydrochloric acid. The rates obtained are shown in Fig. 6. The initial rates are nearly linear with peroxide concentration, but the maxima are not as high as with nitrate and tend to fall off with increasing peroxide at the higher acid concentrations. With nitrite the maxima are still lower and the rates fall off rapidly with higher nitrite concentration. In both cases heavy yellow or brown films account for these re-

sults. Neither substance can be considered a satisfactory depolarizer.

A few experiments showed that p-nitrophenol was even less satisfactory. Iron dissolves to some extent in persulfates; addition of hydrochloric acid had little effect on the rate.

**5.**—The rates were measured in ferric chloride solutions, with 0.01 and 0.05 M hydrochloric acid present. These rates are plotted in Fig. 4. They are linear with ferric chloride concentration at least to 0.2 M, are not greatly influenced by added acid, and follow the unimolecular law at all concentrations.

**6.**—In an attempt to explain irregularities in the preceding curves, the effect of various salts on the rate in nitric acid was determined. These rates are shown in Fig. 7. Small amounts of chloride and bromide increase the rate somewhat, while larger amounts have a remarkable depressing effect. Sulfate ion has only a retarding effect. The rates were unimolecular at low salt concentration, but in the presence of 0.08 N salt showed an autocatalytic trend where repeated runs were made in the same solution even though the iron cylinder was repolished between runs. Addition of 0.04 M potassium nitrate to 0.05 M nitric acid, 0.08 M potassium chloride nearly doubled the rate, which
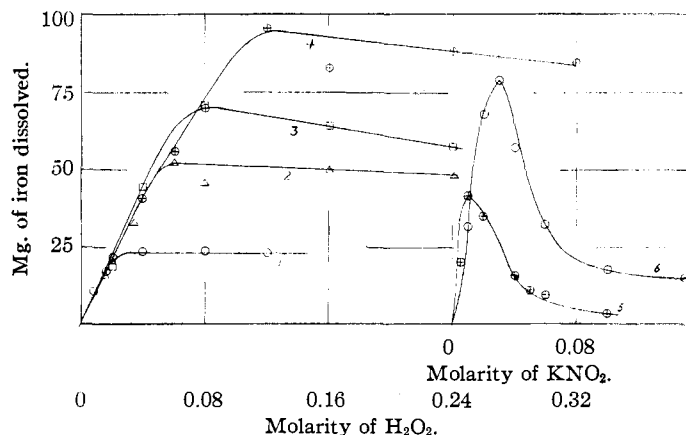


Fig. 6.—Mg. of iron dissolved in five minutes in 250 cc. of HCl with either KNO₂ or H₂O₂ at 2000 r. p. m. and 25°: 1, 0.01 N HCl + H₂O₂; 2, 0.025 N HCl + H₂O₂; 3, 0.04 N HCl + H₂O₂; 4, 0.05 N HCl + H₂O₂; 5, 0.025 N HCl + KNO₂; 6, 0.05 N HCl + KNO₂.

still was autocatalytic; addition of 0.08 M potassium nitrate increased the rate from 15 to 106 mg. dissolved in five minutes and caused the rate to become unimolecular again.

**7.**—The effect of rotational speed on the dissolution rate was determined in a number of solutions. These rates are plotted in Figs. 8, 9 and 10. Only in ferric chloride solution is the rate proportional to the speed up to the highest values of the latter. In all other cases the rate reaches a maximum and in hydrochloric acid decreases again at higher speeds. In the hydrochloric, perchloric and sulfuric acids, sufficient nitrate was present to give the maximum rate at 2000 r. p. m. In the more concentrated hydrochloric acid, and in nitric acid with the higher sulfate ion concentrations, the maximum rate is reached at lower stirring speeds. Apparently ions which

TABLE I

REACTION RATE CONSTANTS FOR IRON DISSOLVING IN
SEVERAL MEDIA. AVERAGE VALUES FOR THE FIRST HALF
OF THE REACTION

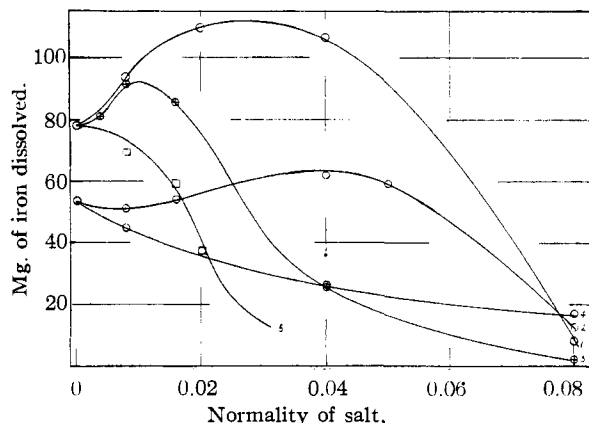| Reagent | Per. speed. cm./min. | Diff. coeff. $D \times 10^3$ cm.²/min.[1a] | 0.025 N $k$ | 0.05 N |
|---|---|---|---|---|
| Perchloric acid | 11,960 | 3.60 | 1.340 | |
| Hydrochloric acid | 11,310 | 3.30 | 1.89 | 1.47 |
| Sulfuric acid | 11,436 | 2.10 | 1.48 | 0.884 |
| Nitric acid | 11,184 | 1.57[a] | 1.06 | |
| Acetic acid | 11,686 | 0.76 | 0.170 | .116 |
| Ferric chloride | 10,932 | 0.215[12] | | .367 |

[a] Taken from "Int. Crit. Tables" for 20° (in water).

Fig. 7.—Effect of added salts on mg. of iron dissolved in 250 cc. of HNO₃ in five minutes at 2000 r. p. m., 25°: 1, 0.025 $N$ HNO₃ + KCl; 2, 0.05 $N$ HNO₃ + KCl; 3, 0.05 $N$ HNO₃ + KBr; 4, 0.025 $N$ HNO₃ + K₂SO₄; 5, 0.05 $N$ HNO₃ + K₂SO₄.

retard the rate at low speeds also lower the speed at which the maximum rate is attained.
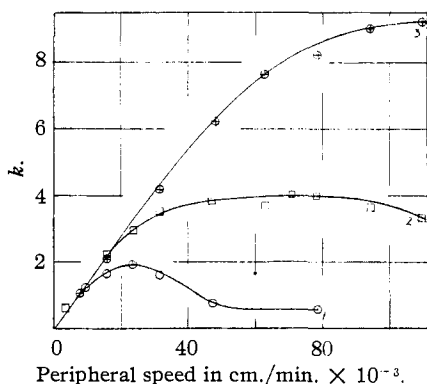


Fig. 8.—Effect of stirring on iron dissolving in HCl + KNO₃ in five minutes at 25°: 1, 0.05 $N$ HCl; 2, 0.025 $N$ HCl; 3, 0.01 $N$ HCl.

8.—Finally, temperature coefficients were determined in ferric chloride and in nitric and hydrochloric acid solutions at typical low and high stirring speeds; i. e., below and above speeds at which the maximum rates are reached in the acid solutions. Rates were run at approximately 15,

### TABLE II

ENERGIES OF ACTIVATION FOR IRON DISSOLVING IN VARIOUS SOLUTIONS. THE SOLUTIONS ARE NUMBERED TO CORRESPOND TO THE CURVES OF FIG. 11

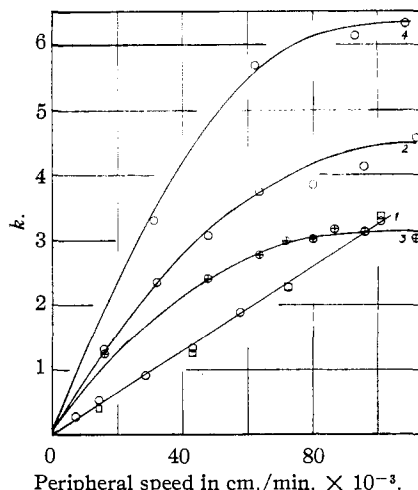| | Solution | R. p. m. | $A$, cal. | $\dfrac{k_{298}}{k_{288}}$ |
|---|---|---|---|---|
| 1 | 0.025 $N$ HCl + 0.10 $M$ KNO₄ | 2,000 | 5,194 | 1.35 |
| 2 | .025 $N$ HCl + 0.10 $M$ KNO₃ | 12,000 | 13,020 | 2.14 |
| 3 | .05 $N$ HCl + 0.18 $M$ KNO₃ | 1,500 | 4,576 | 1.29 |
| 4 | .05 $N$ HCl + 0.18 $M$ KNO₃ | 3,000 | 12,240 | 2.05 |
| 5 | .05 $N$ HCl + 0.18 $M$ KNO₃ | 8,000 | 14,480 | 2.34 |
| 6 | .025 $M$ FeCl₂ | 10,000 | 6,109 | 1.43 |
| 7 | .05 $M$ FeCl₃ | 2,000 | 5,491 | 1.38 |
| 8 | .05 $N$ HNO₃ | 12,000 | 12,120 | 2.04 |



Fig. 9.—Effect of stirring on iron dissolving in several media in five minutes at 25°: 1, 0.025 $M$ FeCl₃ ⊙, and 0.05 $M$ FeCl₃ ☐; 2, 0.025 $M$ HNO₃; 3, 0.05 $M$ HNO₃; 4, 0.025 $N$ HClO₄ + KNO₃.
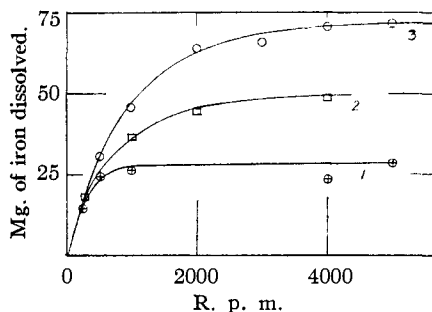


Fig. 10.—The effect of stirring on the amounts of iron dissolving in 250 cc. of solution in five minutes at 25°: 1, 0.025 $N$ HNO₃ + 0.04 $N$ K₂SO₄; 2, 0.025 $N$ HNO₃ + 0.008 $N$ K₂SO₄; 3, 0.025 $N$ H₂SO₄ + 0.16 $M$ KNO₃.

25, 35° and in some cases at 45°. The rate constants are plotted in Fig. 11 and average values of the Arrhenius "$A$" are given in Table II with the temperature coefficients from 15–25°.

These temperature coefficients evidently fall into two distinct groups. In ferric chloride at low and high stirring speeds and in the other solutions at low stirring speeds, the temperature coefficients lie between 1.29 and 1.43; in the acid solutions at higher speeds, at which the maximum dissolution rates have been reached, the temperature coefficients lie between 2.04 and 2.34. Obviously two different reaction mechanisms are involved.

### Discussion

According to the criteria given in the introduction, the effect of stirring speed and the low and high temperature coefficients indicate that these two mechanisms which control the dissolution rates are (a) diffusion and (b) chemical reaction.
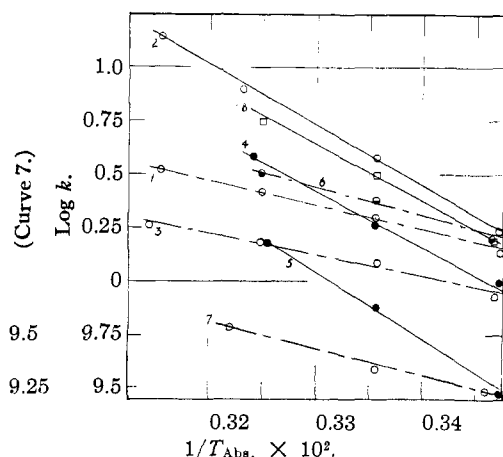
Fig. 11.—Effect of temperature on the rate constants. For legend, see Table IV.

The maximum rates for the polished cylinders in dilute hydrochloric acid at 2000 r. p. m. (Fig. 1), agree well with those found previously for zinc and magnesium. For example, from a cylinder of zinc 2.44 cm. in diameter, 1.88 cm. long, 3.75 mg. of zinc dissolves per sq. cm. in five minutes in 500 cc. of 0.0142 $M$ hydrochloric acid at 25°, 1440 r. p. m.[10] From this we calculate $k = 1.87$, in excellent agreement with the value 1.89 of Table I obtained at the same peripheral speed. Comparison with the work of King and Schack[11] at higher peripheral speeds also shows good agreement.

In ferric chloride at 2000 r. p. m. (Fig. 4), the value of $k$ is 0.357. A copper cylinder of similar diameter, in dilute ferric chloride at 2000 r. p. m., gives a somewhat higher value, $k = 0.500$.[12] In ferric chloride at a peripheral speed of 24,000 cm./ min. (about 4000 r. p. m., Fig. 9), the rate constant for iron is about 0.755; at the same peripheral speed the rate constant for copper in ferric chloride with no added acid is 0.829 (ref. 12, Table VI). The rate of dissolution of copper in ferric nitrate is lower and under similar conditions the rate constant is 0.666 (ref. 12, Table V).

The etched iron dissolves considerably faster than the polished metal and we must attribute this to the increased surface, in spite of statements frequently made to the effect that etching or pitting has little effect on these diffusion-controlled rates. Such tests usually have been made at comparatively low stirring speeds. Experiments in this Laboratory have shown that magnesium is little affected by polishing or etching,

(10) King and Braverman, This Journal, **54**, 1744 (1932).
(11) King and Schack, ibid., **57**, 1212 (1935).
(12) King and Weidenhammer, ibid., **58**, 602 (1936).

while c. p. zinc dissolves more slowly if not frequently cleaned and polished, due to accumulation of impurities on the surface.

If the rates are actually controlled by the chemical reaction at higher stirring speeds, it is difficult to see why the rate should decrease as the speed increases, in certain solutions (Fig. 8). This is in some way connected with the retarding effect of chloride ion, as shown at 2000 r. p. m. (Fig. 7). The more chloride or sulfate ion present, the lower the speed at which the maximum rate is reached (Figs. 8 and 10). Undoubtedly the rate at 2000 r. p. m., 0.08 $N$ chloride or sulfate (Fig. 7) would be "chemically controlled" (high temperature coefficient). This chloride ion effect is sufficient to obscure the effect, at the maximum, of increasing the hydrogen ion concentration (Fig. 8).

It is evident that the rate in hydrochloric acid at low nitrate concentrations (Fig. 1) is influenced both by film formation and by a slow "chemical rate." The maximum rate is not reached sharply and the excess nitrate necessary for the maximum rate increases with the acid concentration. The rate is also lower in stronger than in more dilute acid in this region, at the same nitrate concentration. This indicates that considerable excess nitrate must be present at the immediate surface of the metal if hydrogen ion is to react as rapidly as it reaches the surface, i. e., if the hydrogen ion concentration is to fall to zero at the surface.

The same thing is true of sulfuric though not of perchloric acid. It seems probable that this need for excess nitrate ion and also the retarding effect of chloride, bromide and sulfate ions is connected with the efficiency of nitrate as a depolarizer. The oxidizing potential of nitrate may be barely high enough to overcome the overvoltage of hydrogen on iron under the conditions present, and either this potential or the overvoltage may be influenced by various ions, or the latter by the rotational speed; it seems unlikely that a true chemical rate would vary in this way with salt concentration and stirring speed, with otherwise constant conditions. Also the large increase in rate on addition of excess nitrate (to 0.05 $M$ nitric acid, 0.08 $M$ potassium chloride, already noted) indicates that the effect of chloride and other ions is to diminish the depolarizing action of nitrate.

A few experiments showed that addition of sucrose has the normal effect in those solutions giving definitely diffusion-controlled rates (i. e., rate inversely proportional to viscosity). Sucrose

added to sulfuric acid (plus potassium nitrate) at a stirring speed high enough to give the maximum rate, diminishes the rate to the same extent, which does not indicate a chemically-controlled rate.

For these reasons we hesitate to call the rate at higher stirring speeds a true chemical rate until it has been investigated further. It is probable that a very high stirring speed, or a sufficiently high concentration of certain salts, would reduce the rate to the value it has with no depolarizer present, where the temperature coefficient is also high[7]; in this case the mechanism might also be identical.

The increase in the rate in nitric acid on addition of small amounts of chloride and bromide (Fig. 7) may be ascribed to an increase in the diffusion coefficient of the acid. While the diffusion coefficient of nitric acid has not been determined in the presence of salts, it is lower than that of hydrochloric acid in water ("International Critical Tables").

The maximum rates in the various acids at 2000 r. p. m. are roughly proportional to the diffusion coefficients, except for perchloric acid, as shown in Table I. Because of the irregularities found, including film formation with the weaker acids, a quantitative comparison would be impossible.

## Summary

The rate of dissolution of very pure iron has been measured in solutions of several acids, with potassium nitrate, hydrogen peroxide, potassium nitrite and p-nitrophenol as depolarizers. Of these only the nitrate was found to be reasonably satisfactory as a depolarizer.

The rate was studied as a function of the depolarizer concentration, the acid concentration, the concentration of various added salts, the stirring speed and the temperature. The rate was also measured in ferric chloride solutions of various concentrations, at various stirring speeds and temperatures, with and without added acid.

The rate is shown to be diffusion-controlled under all conditions in ferric chloride; at low stirring speeds in hydrochloric acid with sufficient nitrate present, and approximately so in nitric acid with certain chloride concentrations. Under other conditions (higher stirring speeds, higher salt concentrations, low nitrate concentrations) it is in whole or part controlled by a slower reaction perhaps of chemical nature at the metal surface.

Under conditions where the rate is diffusion-controlled, the temperature coefficient is about 1.35 per 10°; where it is "chemically" controlled, the temperature coefficient is 2.0–2.4 per 10°. The activation energies vary accordingly.

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# Studies of Purified Palladium Sols Prepared by Electric Sparking

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The series of investigations of different purified and concentrated Bredig sols of the noble metals,[2] carried out at this Institute over a period of years, has been continued with the study of palladium sols. As in the previous studies our concern was to observe the relations between origin of charge and stability on the one hand and inorganic chemical properties of palladium on the other by physical-chemical methods of analysis. Thus it was possible to make comparisons in the same

way with the other sols of noble metals already investigated.

The methods of preparing, purifying and concentrating were disintegration by the electric spark and an improved process of electrodecantation.[2]

One of the first results was that it is impossible to prepare a palladium sol by electrodispersion in *conductivity water* (spec. cond. 7 × 10⁻⁷ mho). Regardless of the dispersion time, in every case precipitates are formed instantly. This behavior contrasts with that of platinum and silver.[2b,c] The explanation is that pallado oxide is less acid than platino oxide[3]; a hydroxo acid of palladium is not known, while a hydroxo acid of platinum

(1) The experiments were carried out at the Institut für medizinische Kolloidchemie der Universität Wien in 1936 and 1937.

(2) (a) Gold sols: Pauli, *Naturwissenschaften*, **20**, 551 and 573 (1932). with many references to literature; Pauli and Russer, *Kolloid. Z.*, **58**, 22 (1932); Eirich and Pauli, *ibid.*, **67**, 186 (1934); Pauli, Russer and Brunner, *ibid.*, **72**, 26 (1935); (b) platinum sols: Pauli and Schild, *ibid.*, **72**, 165 (1935); Pauli and Baczewski, *Monatsh.*, **69**, 204 (1936); (c) silver sols: Löffler and Pauli, *Kolloid. Z.*, **60**, 146 (1932); Hoff and Pauli, to be published, with list of literature.

(3) P. Pascal and P. Baud, "Traité de Chimie Minérale," Tome XI, Masson et Cie, Paris, 1932, p. 793.