

Acid Dissolution of Cupric Oxide

H. MAJIMA, Y. AWAKURA, T. YAZAKI, AND Y. CHIKAMORI

The rates of dissolution of synthetic cupric oxide in solutions containing perchloric, sulfuric, nitric or hydrochloric acid were studied using sintered disks. In each case, the dissolution rate increased with elapsed retention time until an essentially constant value was reached. This phenomenon can be attributed to an increase in the disk's effective surface area. The dissolution rate is of the first order with respect to a_{H^+} for perchloric, nitric, and hydrochloric acids, while it is of a half order for sulfuric acid. High activation energies, ranging from 12.4 to 20.5 kcal/mol, and the independence of agitation speed on cupric oxide dissolution reaction rate suggest that chemical reactions are the major determinants of dissolution rates. The addition of electrolytes having anions common with the acids resulted in an acceleration of the dissolution rate due to increases in a_{H^+} values. However, the addition of electrolytes of noncommon anions revealed a quite different effect on dissolution rate. This suggests that the adsorption and/or complexing of anions on the cupric oxide surface may have had a significant role in the determination of the dissolution rates. The type of acid used determined the identity of the adsorbed anion.

THE dissolution reaction of metal oxides in acidic solutions is widely utilized industrially. The leaching of bauxite ore and of oxidized copper ore, the upgrading of ilmenite ore, and the pickling of rolled steel are typical examples.

In the review paper written by Warren and Devuyt¹ an approximate general mechanism of the leaching of oxides was proposed based on the results observed for iron oxides, beryllium oxide, aluminum oxides, cuprous oxide and others. However, very little information is available in a form suitable for determining the mechanism of dissolution for individual metal oxide-solution systems.

In order to verify the general applicability of the mechanism proposed by Warren and Devuyt¹ for the leaching of metal oxides, it is necessary to extend the kinetic study to other systems.

The present study is concerned with the dissolution of cupric oxide in solutions containing perchloric, sulfuric, nitric or hydrochloric acid.

EXPERIMENTAL

Materials

Synthetic cupric oxide was prepared by oxidizing copper powder of high purity (99.99 pct Cu) at 850°C in an electric furnace for 20 h. The product obtained by this oxidation treatment was identified as cupric oxide by means of X-ray diffractometry, and was assayed 79.48 pct Cu.* After cooling the sample in

*Theoretical content of Cu in CuO is 79.89 pct Cu.

the furnace, the oxidation product was ground to pass through 400 mesh Tyler screen, pelletized at 16 ton/cm², and then sintered at 850°C for 50 h, followed by slow cooling in the furnace to room temperature. The disks thus prepared were mounted in epoxy resin in

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such a manner that only the mechanically polished surfaces were presented to the dissolution medium. The disks of cupric oxide were about 6 mm thick and 20 mm in diam; the exposed polished surface area was 3.14 cm². The apparent density was 5.3 g/cm³ which is about 83 pct of the theoretical density of 6.4 g/cm³.

A stirring rod made of stainless steel was fastened to each epoxy resin mount containing the cupric oxide disk.

All other chemicals used were of reagent grade. Deionized water was used in the preparation of all the solutions.

Experimental Procedure

A 500 ml glass separable flask was used for all the dissolution experiments. A sintered cupric oxide disk, facing downward, was rotated in the solution in the flask. The temperature within the reaction vessel was maintained at $\pm 0.5^\circ\text{C}$ of the desired value by a water bath. In typical experiments, the disk was rotated at 1200 rpm in a 500 ml acidic solution at a given temperature unless otherwise stated.

Analytical

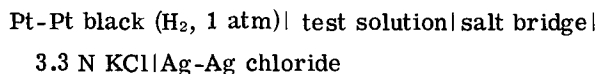
The concentration of cupric ion in solution was estimated continuously with a specific cupric ion electrode and a silver chloride reference electrode for the solution of perchloric, sulfuric and nitric acids. For hydrochloric acid solution, sample solutions were removed at appropriate times during a run and their copper contents were determined by means of an atomic absorption spectrophotometer.

Measurement of Hydrogen Ion Activity

Acidic solutions used for the dissolution of cupric oxide in this work were fairly concentrated, and therefore their behavior deviated from that predicted by Henry's Law. Thus, when the dissolution reaction is controlled by a chemical reaction at the interface

between a solid and a solution, solute activities, rather than concentrations, are the appropriate rate-law parameters, although concentrations have been customarily used as an important parameter by the most of previous researchers.

The approximate values of activities of hydrogen ions in solutions containing hydrochloric acid or perchloric acid were determined at 25°C by measuring the electromotive force of the following:



The Pt-Pt black electrode used was prepared according to the procedure discussed in a textbook.² An Ag-AgCl electrode supplied commercially was used as the reference electrode. Agar media containing 3.3 N KCl and 5.4 N NaCl were used as salt bridges for the solutions of hydrochloric acid and perchloric acid, respectively. Potassium perchlorate is known to dissolve with difficulty. To avoid the formation of insoluble potassium perchlorate, sodium chloride was used as the salt bridge for perchloric acid solutions.

The electromotive forces of these cells are expressed by Eq. [1]:

$$\text{emf}_{\text{H}^+} = -0.206 + \frac{RT}{F} \ln a_{\text{H}^+} + V_{jp} \quad [1]$$

where V_{jp} is a liquid junction potential occurring in the boundary region between the test solution and the salt bridge. The values of the liquid junction potential were evaluated with a first order approximation by applying Henderson's equation.³ The approximate values of hydrogen ion activities were then calculated from Eq. [1].

The values of hydrogen ion activity for sulfuric acid solutions were taken from Yazaki's work,⁴ as determined by using a conventional pH meter utilizing a glass electrode.

RESULTS AND DISCUSSION

Dissolution Rate Curves

A typical example of a dissolution curve obtained when a synthetic cupric oxide disk was dissolved in 0.4 M HClO₄ solution at 40°C for 9 h is shown in Fig. 1. The rate curve essentially consists of three portions; an initial linear portion, a final linear portion, and the transient curved region between these two linear portions. Similar rate-curve shapes were observed during the dissolution of cupric oxide in aqueous solution containing sulfuric, nitric, or hydrochloric acid.

In order to understand the physical meaning of the shape of these rate curves, the following experiments were made: A cupric oxide specimen was first subjected to leaching in a 0.8 M HClO₄ solution at 40°C for 9 h. During this time the final linear stage was attained. The specimen was then transferred without any further treatment into a new dissolution medium containing 0.4 M HClO₄ at 40°C. The experimental results of the second dissolution are also depicted

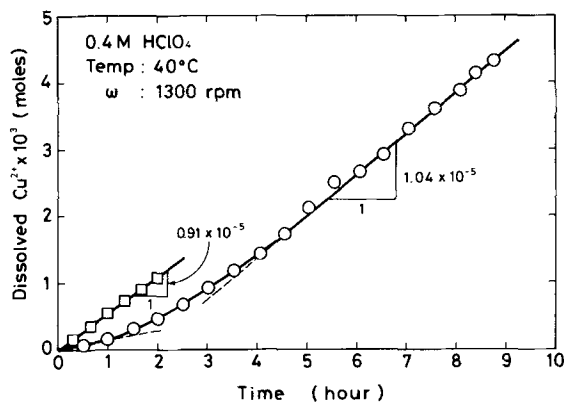


Fig. 1—Typical example of synthetic cupric oxide dissolution curve and enhanced initial rate observed by the repeated dissolution in a refreshed solution. O; Dissolution rate curve with a fresh specimen. □; Repeated dissolution rate curve.

in Fig. 1. Comparing these results, the beginning of the redissolution in 0.4 M HClO₄ after the dissolution in 0.8 M HClO₄ resembles the final portions of normal dissolution in 0.4 M HClO₄, suggesting that the effective surface areas of cupric oxide disks at the final stage of dissolution are roughly the same regardless of the HClO₄ concentration used at the constant temperature and that the surface condition of cupric oxide disk determines the relative reaction rate.

Next, the dissolution experiments were carried out in solutions containing perchloric acid whose concentration was changed from 0.2 to 0.8 M. Two kinds of apparent rates, R_i and R_f were determined from the slopes of the linear portions of the initial and final stages of each dissolution rate curve. Figure 2 plots the apparent rate of dissolution, R_i or R_f vs HClO₄ concentration at 40°C, in which n is moles of cupric ion dissolved. This data suggests that R_i and R_f are of the first order with respect to HClO₄ concentration. The ratio of apparent reaction rates, R_i/R_f , was found to be approximately 1/5 in a 0.4 M HClO₄ solution. A similar proportionality was observed when the reaction rates were obtained in solutions of different concentration levels of acids, or of different acids.

The constant ratio of R_i/R_f was also obtained when the dissolution experiments were done at different temperatures. Figure 3 is an Arrhenius plot of the data observed for the dissolution in a 0.8 M HClO₄

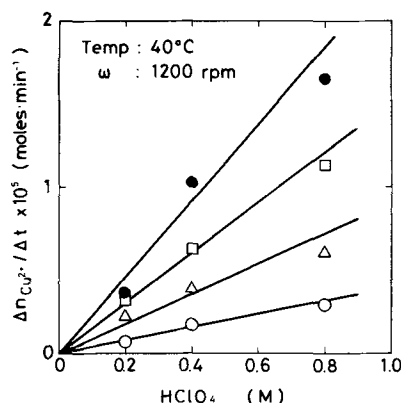


Fig. 2—First-order dependence of reaction rates on HClO₄ acid concentration at the equimolar reaction points. O; Initial slope, Δ; Slope (2.5×10^{-4} mol), □; Slope (5.0×10^{-4} mol), ●; Final slope.

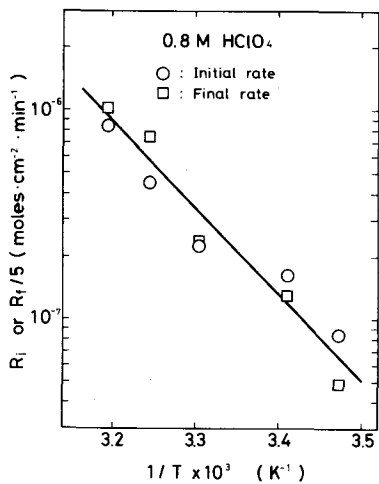


Fig. 3—Relationship between R_i or $R_f/5$ and $1/T$.

solution, in which the logarithm of R_i or $R_f/5$ is plotted against $1/T$. It was found that the plots lie on the same straight line.

Cross sections of the sintered disks before and after the dissolution at 40°C in 0.8 M HClO_4 solutions for 9 h were observed under a microscope. These observations revealed an increased roughness of the reacting surface of the cupric oxide disk at the final stage of dissolution.

Surana and Warren⁵ observed a rate curve shape similar to that of the present study. They studied the acid leaching of goethite, observing that the apparent rates increased during the leaching. To postulate a leaching mechanism which involves both uniform dissolution of the mineral surface and, under certain conditions, pitting, faceting or anisotropic dissolution, they used a rate equation of the following type:

$$\frac{d[\text{Fe}]_{\text{aq}}}{dt} = k' + 2k''t \quad [2]$$

where k' and k'' are constant.

However, it may be concluded from the findings of the present study that the final stage of the cupric oxide dissolution was controlled by the same mechanism as that for the initial stage. The only difference between two stages appears to be the effective surface area. Therefore, this rate equation was not used. Rather, the rates determined from the initial slopes of the reaction curves were used to examine the effects of variables. This is because the effective surface areas of the cupric oxide disks were almost the same at the initial stage of dissolution in each experiment.

Kinetic Limitations

The effect of temperature on the amount of copper dissolved by the four acids is shown in Fig. 4. The rates were displayed on an Arrhenius plot to determine the activation energies for the dissolution of cupric oxide in each acid. The least squares fit to the various acids data yielded activation energies ranging from 12.4 to 20.5 kcal/mol. When cupric oxide was dissolved in a 0.2 M HCl solution containing the same amount of sodium chloride, an activation energy of

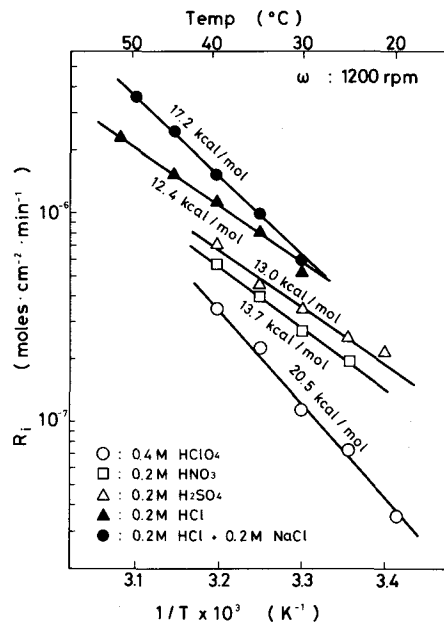


Fig. 4—Arrhenius plots for dissolution of synthetic cupric oxide in various acidic solutions.

17.2 kcal/mol was obtained. This value was a little larger than for 0.2 M HCl solution without the addition of sodium chloride. However the reason could not be determined in this study.

The high activation energy resulting from the cupric oxide dissolution would appear to preclude rate control by diffusion of either reactants to the surface or reaction products from the surface of the rotating disk. The rate would not be expected, therefore, to depend on the rate of rotation of the cupric oxide disk. Figure 5 suggests that no such dependence on rotation rate exists for cupric oxide dissolution at 30°C in the aqueous solution of the acids. Within the experimental error, rates were independent of the rotation speeds above 300 rpm. Similar results were obtained for the dissolution of cupric oxide in a hydro-

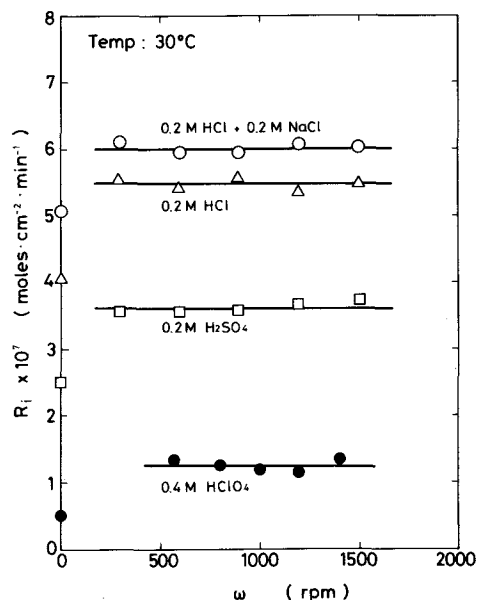


Fig. 5—Dissolution rates of synthetic cupric oxide disks at different rotation speeds at 30°C in various acidic solutions.

chloric acid solution containing sodium chloride. From the fact that the almost constant rates were obtained at all the rotation speeds except the extreme condition of 0 rpm, it is reasonable to expect that chemical reaction limitations will be of major importance.

Effect of Acid Concentration

The cupric oxide dissolution rates were measured at different concentration of the four acids. Figure 6 shows the effects of the initial acid concentration on the dissolution rate of cupric oxide at 30°C. The dissolution rate is of the first order with respect to acid concentration for hydrochloric, nitric, and perchloric acids.

The effect of sulfuric acid concentration on cupric oxide dissolution is different from the effect of acid concentration for other acids. In this case, the observed slope of the $\log R_i / \log a_{H^+}$ plot is 0.5 at concentrations of sulfuric acid above 0.05 M as shown in Fig. 7. The other acids produce slopes much greater.

At a constant hydrochloric acid concentration of 1 M, the effect of the addition of sodium chloride on the dissolution rates of cupric oxide were determined at 30°C over the concentration range of 0.5 to 2 M NaCl. The results were superimposed on Fig. 7. These observed rates lie on the same straight line of $\log R_i / \log a_{H^+}$ as the plots obtained for solutions containing hydrochloric acid alone. Based upon the accuracy of the measurements of a_{H^+} , we may assume a first order dependency between reaction rates and a_{H^+} values. This means that the addition of sodium chloride to a hydrochloric acid solution leads to an increase in a_{H^+} , and thus accelerates the dissolution of cupric oxide. A similar tendency was observed when sodium perchlorate was added to a perchloric acid solution, as shown in Fig. 7.

Recently, Shevelev *et al*⁶ studied the kinetics of the dissolution of copper(II) oxide in sulfuric acid. They concluded that the oxide dissolves by a topochemical mechanism, involving intermediate formation of a nonstoichiometric higher oxide CuO_2 of peroxide type. In the present study, there does not appear to be a need to consider such a mechanism.

Effect of Anions of Dissolution Acid

When sodium chloride was added to a perchloric acid solution the result shown in Fig. 8 was obtained. At low concentration levels of sodium chloride, the dissolution rates of cupric oxide increased sharply from the rate of dissolution in 1 M $HClO_4$ solution. When the concentration of sodium chloride reached 0.5 M in 1 M $HClO_4$ -NaCl, the dissolution rate became comparable to cupric oxide dissolution in a hydrochloric acid solution.

From these findings, it is evident that the adsorption of anions on the surface of cupric oxide and/or the complexing of the copper with anions play an important role in cupric oxide dissolution. Three observations support this conclusion. Firstly, the dissolution rates of cupric oxide in different acid solutions were quite different, even when those values were compared at constant a_{H^+} value, as shown in Fig. 7.

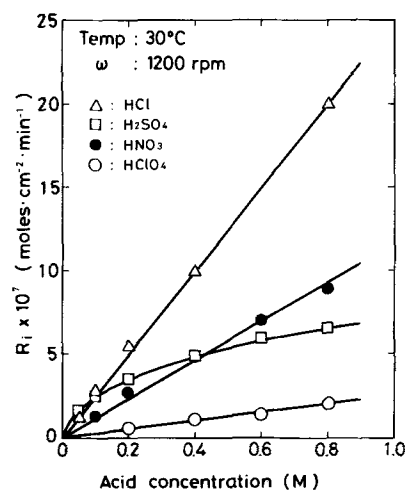


Fig. 6—Rates of dissolution of synthetic cupric oxide disks vs acid concentrations in the aqueous solutions of various acids at 30°C.

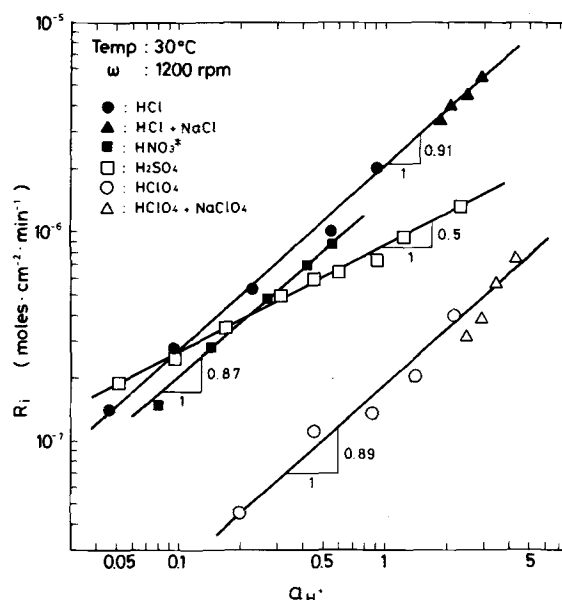


Fig. 7—Effect of a_{H^+} on the dissolution rates of synthetic cupric oxide disks in various acids at 30°C. Rates were plotted against mean activities of HNO_3 taken from the data compiled by Dobos.⁹

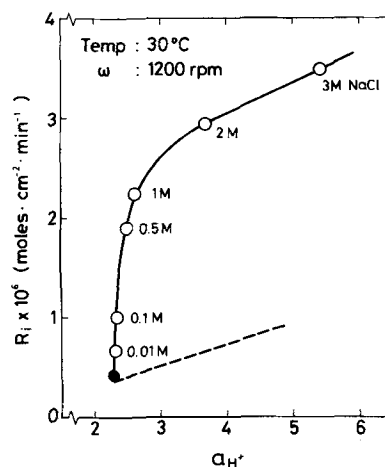


Fig. 8—Effect of sodium chloride addition on the dissolution rate of synthetic cupric oxide disk in 1 M $HClO_4$ solution at 30°C. ●; 1 M $HClO_4$, Dotted line; Effect of $NaClO_4$ addition.

For example, the dissolution rate of cupric oxide in hydrochloric acid was about 10 times faster than in perchloric acid. This result suggests that the dissolution of cupric oxide was certainly affected by anions.

Secondly, the sequence of dissolution rate of cupric oxide in the four acids coincided with the order of polarizabilities of anions, as shown in Table I.⁷ The affinity of an anion for the cupric oxide surface is related directly to that ion's polarizability. The strong adsorption of anions on copper site may result in a lowering of the chemical bond strength between copper and oxygen, thus enhancing cupric oxide dissolution.

Although it is well known that perchlorate ions or nitrate ions form weak complexes with copper, the order of the complexing power of chloride ions and sulfate ions to copper⁸ is related directly to the dissolution rate of cupric oxide observed in this study.

Thirdly, as shown in Fig. 8 an sharp increase in dissolution rates was observed for cupric oxide dissolved in a 1 M HClO₄ solution with the addition of up to 0.5 M of sodium chloride. This may be attributed to the adsorption of chloride ions on the surface of the cupric oxide and/or the strong complexing of copper with chloride ions, which lowers the chemical bond strength between the copper and oxygen atoms. The change of the dissolution rate with the addition of more than 0.5 M sodium chloride may be explained as follows: The adsorption and/or complexing are completed around the sodium chloride concentration of 0.5 M. Then the increase in the dissolution rate by the addition of sodium chloride is due to the increase in a_{H^+} value. The addition of sodium chloride to a 1 M HCl solution or the addition of sodium perchlorate to a 1 M HClO₄ solution resulted in the increase in a_{H^+} values as shown in Fig. 7.

In regard to this, Warren and Devuyt¹ pointed out that the adsorption of anions constituting the leaching acid has a significant role in determining the overall rate of oxide leaching. When anion adsorption is relatively weak, the rate of leaching, R , can be expressed by Eqs. [3] and [4], respectively.

$$R = K \frac{K_1 a^2}{1 + K_1 a} \quad [3]$$

$$R = K' \frac{K_1 a}{1 + K_1 a} \quad [4]$$

Where $a = [H_3O^+]$, K_1 = equilibrium constant of surface protonation reaction, and K and K' = constants.

However, the rate curves observed for the dissolution of cupric oxide in this work did not show a clear resemblance to either Eqs. [3] or [4]. This suggests that the role of anions of the acid for the cupric oxide dissolution is somewhat different from the model proposed by Warren and Devuyt. As mentioned before, the same dissolution rate could not be observed for the different acids even though the hydrogen ion activity was the same. Also, an abrupt increase in the dissolution rate was observed at low concentrations of sodium chloride when sodium chloride was added to a perchloric acid solution.

From these findings, it can be concluded that the adsorption of anions on the surface of the cupric oxide disks was fast and strong, and thus the surface was substantially saturated with adsorbed anions. A

Table I. Polarizabilities of Some Ions

Ion	Polarizability, cm ² /mol
Cl ⁻	8.9
SO ₄ ²⁻	3.9
NO ₃ ⁻	3.6
ClO ₄ ⁻	3.3

dissolution attack by hydrogen ions would then occur on this surface saturated by anions.

Rate Equation

From the experimental results obtained, we may consider that the following rate equation can be generally applied to the dissolution of cupric oxide:

$$R = kS[\text{Acid}]^n \\ = k'S^*a_{H^+}^n \quad [5]$$

where k and k' are rate constants; S and S^* are the surface area and the effective surface area saturated with anions of acids, respectively; $[\text{Acid}]$ is the concentration of acid; a_{H^+} is the activity of hydrogen ions and n is a constant having a value of 1 for perchloric, nitric, and hydrochloric acids and of 0.5 for sulfuric acid. It may be reasonable to consider that the dissolution mechanism of cupric oxide in a sulfuric acid solution is more complicated than in an acid solution containing perchloric, nitric, or hydrochloric acid. At present, the effect of the reaction rate on a_{H^+} for sulfuric acid is difficult to interpret. This difficulty may relate to the fact that in sulfuric acid, HSO₄⁻ is the dominant species, but only SO₄²⁻ is adsorbed. However, unfortunately, no definite conclusion can be drawn due to the absence of quantitative data.

CONCLUSIONS

The rates of dissolution of cupric oxide in four different acids were studied using sintered disks. In each case, dissolution increased with elapsed retention time until an essentially constant value was reached. This phenomenon can be attributed to an increase in the effective surface area of the cupric oxide disk. The dissolution rate is of the first order with respect to a_{H^+} for perchloric, nitric, or hydrochloric acid, while it is of a half order for sulfuric acid.

Generally, the addition of an electrolyte having anions in common with the acid results in an acceleration of the dissolution rate. This phenomenon is attributed to the increases in a_{H^+} value for 1 M HCl and 1 M HClO₄ solutions. The addition of sodium chloride in a 1 M HClO₄ solution causes an abrupt increase in the dissolution rate at sodium chloride concentrations up to 0.5 M. The addition of sodium chloride at more than 0.5 M causes an increase in the dissolution rate comparable to that in a hydrochloric acid solution. These phenomena suggest that anions play an important role in the dissolution of cupric oxide. The rate controlling process must be a chemical attack by hydrogen ions on the surface of the

cupric oxide, saturated with adsorbed anions. The type of acid used determines the identity of the adsorbed anion.

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