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Supplementary Material Available: Listings of hydrogen atom parameters for **2**, anisotropic thermal parameters (*U* values) for **2** and **4**, and positional parameters of the phenyl ring carbon atoms for **2** and **4** (8 pages); a listing of calculated and observed structure factor amplitudes for **2** (38 pages). A listing of calculated and observed structure factors for **4** was deposited earlier.[9] Ordering information is given on any current masthead page.

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(18) Rauchfuss, T. B.; Weatherill, T. B.; Wilson, S. R.; Zebrowski, J. P. *J. Am. Chem. Soc.* **1983**, *105*, 6508.

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Mechanism of Dissolution of Magnetite by Oxalic Acid–Ferrous Ion Solutions

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The kinetics of the reductive dissolution of magnetite by ferrous ions in solutions of high oxalate concentration has been studied at 30 °C and various pH values. The rate-determining step is proposed to be the outer-sphere electron transfer from $Fe^{II}(C_2O_4)_2^{2-}$, located in the Stern plane, to a surface oxalate–iron(III) complex. Analysis of the work term and electron-transfer Gibbs energy shows that $Fe^{II}(C_2O_4)_2^{2-}$ is a reasonable choice for the reductant species. Dissolution also requires protonation of the surface sites, in a process described by a Freundlich-type isotherm.

Introduction

Oxalic acid is a reagent of choice in many iron oxide solvent formulations.[1] Only a few mechanistic studies are available for these dissolution processes: Sellers and Williams[2] have carried out a study of the dissolution of nickel chromium ferrites by oxalic acid solutions in the temperature range 105–160 °C, and concluded that the mechanism involves the reduction of surface Fe^{III} ions by oxalate, which yields CO_2. Thus, the mechanism is similar to the one proposed earlier for the dissolution of magnetite by thioglycolic acid.[3,4] Further examples of dissolution by reducing complexing anions involve thiocyanate and iodide.[5]

In the case of the dissolution of magnetite by oxalic acid, our own preliminary results[6,7] demonstrated that the process is autocatalytic, the mechanism involving an interfacial electron transfer between ferrous–oxalate complexes and surface ferric ions; the main reaction does not involve the oxidation of oxalate and thus differs significantly from the system studied by Sellers. Indeed, the induction period is related to the reduction of Fe^{III} by oxalate, but the ensuing fast reaction corresponds to the stoichiometry

$$Fe_3O_4 + 8HC_2O_4^- \rightarrow 2Fe(C_2O_4)_3^{3-} + Fe(C_2O_4)_2^{2-} + 4H_2O \tag{1}$$

Of course, in the presence of light, $Fe(C_2O_4)_3^{3-}$ in bulk evolves to $Fe^{II} + CO_2$; analogous species on the surface are photosensitive in a similar way.[5,8]

The electron-transfer process involved in this system was proposed to be an outer-sphere transfer from ferrous complexes to a ferric surface complex[6,7] and is thus mechanistically related to the reductive dissolution of nickel ferrite by vanadous picolinate.[9]

In the present paper we report a detailed kinetic study of this system showing that electron transfer controls the overall rate; this result is at variance with usual assumptions in the field of electrochemistry, where electron transfer is assumed to be fast and controlled by solution redox potential.[10,11] As we were mainly interested in characterizing the outer-sphere reaction, the measurements were carried out in large excess of oxalic acid. As discussed below, both the surface and the reductant were fully complexed, thus preventing the possibility of bridged intermediates that might operate in certain homogeneous electron-transfer reactions mediated by oxalate.[12] Such bridged systems can in fact be also conducive to metal oxide dissolution; this subject shall be analyzed in forthcoming papers on the dissolution of magnetite by nitrilotriacetic (NTA) and ethylenediaminetetraacetic acids (EDTA).[13,14]

Experimental Section

Reagents were of analytical purity or better and were used without further purification. Magnetite was prepared by oxidation of a slurry of ferrous hydroxide with potassium nitrate in the presence of hydrazine.[15] The slurry was obtained by adding ammonia to a $FeCl_2{\cdot}4H_2O$ solution at boiling temperature. The prepared material was found to be a nearly stoichiometric magnetite composed of cuboctahedral particles, modal edge ca. 0.1 μm, as characterized by X-ray powder diffractograms, scanning electron microscopy, and Mössbauer spectroscopy. Its specific surface was measured on a Micromeritics surface analyzer by nitrogen adsorption and BET procedures, a value of 9.7 $m^2\ g^{-1}$ being obtained.

Kinetic experiments were carried out in a cylindrical beaker, surrounded by a water jacket. Suspensions containing 40 mg of magnetite

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(1) (a) Blesa, M. A.; Maroto, A. J. G. In *Decontamination of Nuclear Facilities, Keynote Addresses*; American Nuclear Society: Niagara Falls, NY, 1982; p 1. (b) *Decontamination of Nuclear Reactors and Equipment*; Ayres, J. A., Ed.; Ronald Press: New York, 1970. (c) *Decontamination and Decommissioning of Nuclear Facilities*; Osterhout, M., Ed.; Plenum: New York, 1980.

(2) Sellers, R. M.; Williams, W. J. *Faraday Discuss. Chem. Soc.* **1984**, *77*, 265.

(3) Baumgartner, E. C.; Blesa, M. A.; Maroto, A. J. G. *J. Chem. Soc., Dalton Trans.* **1982**, 1649.

(4) Blesa, M. A.; Maroto, A. J. G., Morando, P. J. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 2345.

(5) Blesa, M. A.; Bruyere, V. I. E.; Maroto, A. J. G.; Regazzoni, A. E. *An. Asoc. Quim. Argent.* **1985**, *73*, 39.

(6) Baumgartner, E. C.; Blesa, M. A.; Marinovich, H.; Maroto, A. J. G. *Inorg. Chem.* **1983**, *22*, 2224.

(7) Blesa, M. A.; Maroto, A. J. G. In *Reactivity of Solids*; Barret, P., Dufour, L. C., Eds.; Materials Science Monographs; Elsevier: Amsterdam, 1985; Vol. 28A, p 529.

(8) Waite, T. D.; Morel, F. M. M. *J. Colloid Interface Sci.* **1984**, *102*, 121.

(9) Segal, M. G.; Sellers, R. M. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 1149.

(10) Gorichev, I. G.; Kipriayanov, N. A. *Russ. J. Phys. Chem.* (*Engl. Transl.*) **1981**, *55*, 1558.

(11) Mouhandess, M. T.; Sharara, Z. Z.; Chassagneux, F.; Durand, B.; Vittori, O. In *Reactivity of Solids*; Barret, P., Dufour, L. C., Eds.; Materials Science Monographs; Elsevier: Amsterdam, 1985; Vol. 28A, p 549.

(12) Pennington, D. E. In *Coordination Chemistry*; Martell, A. E., Ed.; ACS Monograph 174; American Chemical Society: Washington, DC, 1978.

(13) Hidalgo, M. d. V.; Katz, N. E.; Blesa, M. A.; Maroto, A. J. G. *J. Chem. Soc., Faraday Trans. 1*, in press.

(14) Borghi, E. B.; Regazzoni, A. E.; Blesa, M. A., unpublished results.

(15) Regazzoni, A. E.; Urrutia, G. A.; Blesa, M. A.; Maroto, A. J. G. *J. Inorg. Nucl. Chem.* **1981**, *43*, 1489.

0020-1669/87/1326-3713$01.50/0

in 150 cm^3 of an oxalic acid solution of the desired pH and concentration and an adequate amount of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ were equilibrated for a certain time. Initially, this period was 24 h, but duplicate runs indicated that 3 h was enough to precondition the solid surface. Therefore, in subsequent experiments, this was used as the conditioning time. To avoid dissolution during this period, a pH of ~7.6 was maintained in the suspension. Dissolution was initiated by lowering the pH to the desired value by addition of hydrochloric acid. Fe^{II} oxidation during the conditioning period and during dissolution was avoided by bubbling purified nitrogen through the solution. To determine the amount of magnetite dissolved, samples of the magnetically stirred suspension were syringed into a large volume of water containing thioglycolic acid and ammonia in excess, thus freezing the dissolution reaction. This suspension was filtered through a Nuclepore membrane (pore size 0.45 μm), and its iron content was determined by measuring the absorbance of the red thioglycolate complex at 530 nm in a Shimadzu UV-210A spectrophotometer ($\epsilon = 3.96 \times 10^2$ m^2 mol^{-1}). In selected experiments, Fe^{III} and Fe^{II} were determined separately at the end of the reaction by colorimetric assay with *o*-phenanthroline without and with hydroxylamine hydrochloride. Dissolution rates were obtained from the slopes of the initial portions of the fraction of dissolved iron (f) (at constant solid mass and solution volume) vs time plots. This procedure is adequate for experiments carried out in the presence of enough Fe^{II} to make sure that no induction period is observed.[6] From the obtained $(\mathrm{d}f/\mathrm{d}t)_0$ values, R_0 (defined as dissolved magnetite moles per second and unit area at time zero) was calculated through the expression $R_0 = M_0^{-1}S_s^{-1}(\mathrm{d}f/\mathrm{d}t)_0$. M_0 is the molar mass and S_s the specific surface area. On the other hand, R_0 is related to the penetration rate constant $k = -\mathrm{d}r/\mathrm{d}t$ (r being the radius of the particle) through the relationship $R_0 = \rho M_0^{-1}k$, where ρ is the magnetite density, 5.2 g cm^{-3}. In the case of originally Fe^{II}-free solutions, sigmoid plots were obtained and the whole f/t profile was analyzed, assuming contracting-volume kinetics,[16] the penetration rate in this case being dependent on the instantaneous Fe^{II} concentration (see Results and Discussion: Dissolution in Oxalic Acid with No Added Ferrous Ion Media).

Results and Discussion

Adsorption of Oxalic Acid onto Magnetite. Adsorption of oxalic acid onto magnetite could not be measured directly because dissolution renders the measurements difficult. As ferric and ferrous ions are dissolved, complexation of oxalic acid decreases the acid available for adsorption, and furthermore ferrous oxalate complexes promote rapid dissolution through the fast reductive pathway (see below). Strong chemisorption is shown by electrophoretic mobility measurements;[6] magnetite particles in oxalic acid solutions show a negative charge in the whole measured pH range (pH 3–11). Thus, the positive charge of magnetite particles, immersed in aqueous solutions of indifferent electrolytes, below pH 6.5 is reversed upon oxalic acid adsorption. The ζ potentials, calculated by Wiersema's procedure[17] from the electrokinetic data, can be used to obtain the particle charge density up to the ζ plane, σ_p, through the Gouy–Chapman equation:

$$\sigma_p = -\sigma_d = \epsilon k T \kappa (2\pi e)^{-1} \sinh(-e\zeta/2kT) \qquad (2)$$

where σ_d is the charge of the diffuse layer and κ is the inverse of the thickness of the ionic atmosphere. ϵ, k, T, and e have their usual meanings.

The results are shown in Figure 1. According to current models for metal oxide/solution interfaces,[18,19] σ_p is the result of charge density on the surface plane (σ_0) and charge density on the inner Helmholtz plane (σ_β). In our modeling of anion chemisorption,[20,21] σ_0 is negative and determined by Γ_{ox} (the excess surface concentration of oxalic acid and oxalate species) and $(\partial\Gamma_{ox}/\partial\Gamma_{H^+})$;

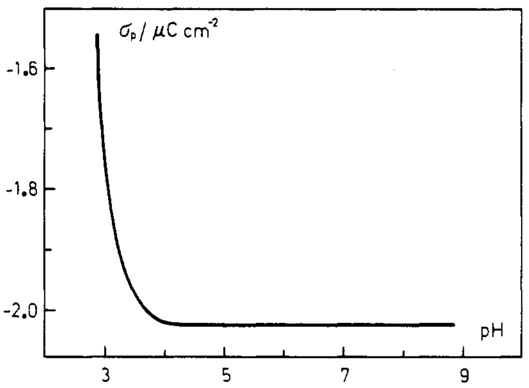
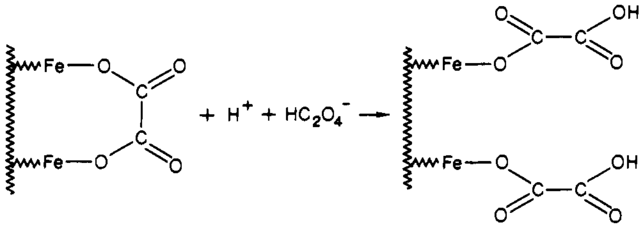


Figure 1. Magnetite particle charge density up to the ζ plane σ_p, in oxalic acid solutions as a function of pH. For the calculation procedure see text. [Oxalic acid] = 2.4×10^{-3} mol dm^{-3}; ionic strength 2.8×10^{-2} mol dm^{-3}; temperature 30 °C.

as this latter term is close to 0.5,[21,22] Γ_{ox} is much larger than (σ_0/F) (F being Faraday's number). Furthermore, counterion adsorption in the inner Helmholtz plane renders $\sigma_0 + \sigma_\beta$ much smaller in absolute value than either σ_0 or σ_β. It is therefore impossible to obtain Γ_{ox} directly from ζ potential measurements alone.

The main characteristics of oxalic acid adsorption can be inferred however from the data for adsorption onto hematite[23,24] and by comparison with EDTA adsorption.[25,26] EDTA strongly chemisorbs on magnetite in the acid pH range in a process that can be described by either one or two consecutive Langmuir isotherms.[25,26] The Langmuir constant K_s is pH dependent, with a maximum value of 2174 mol^{-1} dm^3 at pH 4.7; adsorption becomes negligible at pH >8. The same characteristics are exhibited by the adsorption isotherms of oxalic acid on hematite.[24] The reported apparent Langmuir constants at 25 °C range from 2.1 $\times$ 10^2 (pH 2.7) to 40 mol^{-1} dm^3 (pH 11), but the inspection of the adsorption isotherms shows that a saturation plateau is reached in the oxalic acid concentration range (1–6) $\times$ 10^{-3} mol dm^{-3} (suggesting a higher Langmuir constant). The data of Zhang et al.[24] also suggest that at concentrations higher than 5 $\times$ 10^{-3} mol dm^{-3} a change in the orientation of adsorbed oxalic acid may take place, e.g.



(3)

The role of possible different surface ---Fe^{III}–oxalate complexes will not be addressed in this paper, which aims essentially at describing the reaction of the fully oxalated surface.

It is interesting to analyze the value of K_s for oxalic acid from the point of view of the correlation between chemisorption and solution complexation of metal ions proposed by Stumm.[27,28] Such a correlation can be described by

$$\log K_s = \alpha \log K_b \qquad (4)$$

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(16) Brown, W. E.; Dollimer, D.; Galvey, A. K. *Reactions in the Solid State*; Bamford, C. H., Tipper, C. F. H., Eds.; Comprehensive Chemical Kinetics; Elsevier: Amsterdam, 1980; Vol. 22.

(17) Wiersema, P. H.; Loeb, A. L.; Overbeek, J. Th. G. *J. Colloid Interface Sci.* **1966**, *22*, 78.

(18) Regazzoni, A. E.; Blesa, M. A.; Maroto, A. J. G. *J. Colloid Interface Sci.* **1983**, *91*, 560.

(19) James, R. O.; Parks, G. A. In *Surface and Colloid Science*; Matijevic, E., Ed.; Plenum: New York, 1982; Vol. 12.

(20) Blesa, M. A.; Maroto, A. J. G.; Regazzoni, A. E. *J. Colloid Interface Sci.* **1984**, *99*, 32.

(21) Regazzoni, A. E.; Maroto, A. J. G.; Blesa, M. A. Presented at the 5th International Conference on Surface and Colloid Science, Potsdam, NY, 1985; to be submitted for publication.

(22) Regazzoni, A. E.; Blesa, M. A.; Maroto, A. J. G. Presented at the 2nd Argentine Meeting on Chemical Thermodynamics, San Carlos de Bariloche, Argentina, 1984.

(23) Kallay, N.; Matijevic, E. *Langmuir* **1985**, *1*, 195.

(24) Zhang, Y.; Kallay, N.; Matijevic, E. *Langmuir* **1985**, *1*, 201.

(25) Blesa, M. A.; Borghi, E. B.; Maroto, A. J. G.; Regazzoni, A. E. *J. Colloid Interface Sci.* **1984**, *98*, 295.

(26) Chang, H. C.; Matijevic, E. *Finn. Chem. Lett.* **1982**, 90.

(27) Hohl, H.; Sigg, L.; Stumm, W. In *Particulates in Water*; Kavanaugh, M. C., Leckie, J. O., Eds.; Advances in Chemistry 189; American Chemical Society: Washington, DC, 1980; Chapter 1.

(28) Schindler, P. W. In *Adsorption of Inorganics at Solid-Liquid Interfaces*; Anderson, M. A., Rubin, A. J., Eds.; Ann Arbor Science: Ann Arbor, MI, 1981; Chapter 7.

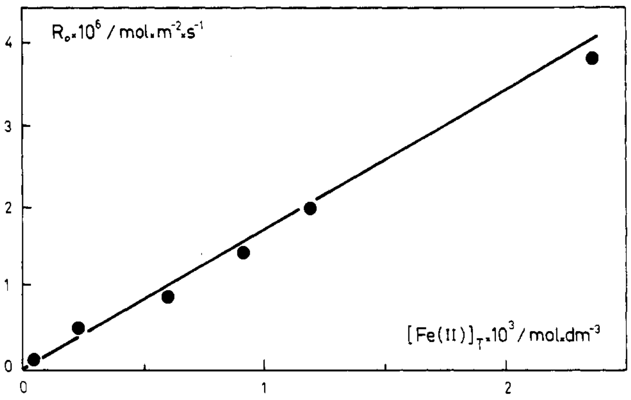

Figure 2. Initial dissolution rate of magnetite in oxalic acid solutions, R_0, as a function of added [Fe^{II}]. [Oxalic acid] = 0.1 mol dm^{-3}; pH 4.1; temperature 30 °C. Solid line was obtained by using eq 14.

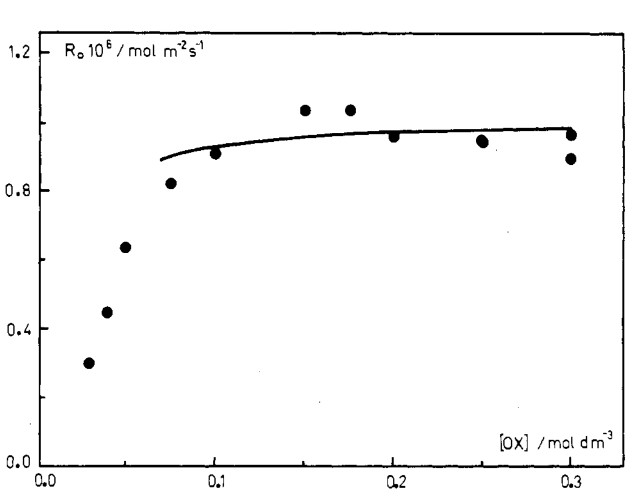

Figure 3. Initial dissolution rate of magnetite, R_0, as a function of [oxalic acid]. [$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$] = 6.05×10^{-4} mol dm^{-3}; pH 4.1; temperature 30 °C. Solid line was obtained by using eq 14 and plotted only for [oxalic acid] $\geq$ 0.08 mol dm^{-3} (see text).

where K_b is the first stability constant of $Fe(C_2O_4)^+$ in solution[29] and α is a constant. A picture reasonably consistent with the previous considerations is reached by setting $\alpha \cong 0.5$; then log $K_s \cong 3.6$, corresponding to saturation coverage at oxalic acid concentrations on the order of 0.005 mol dm^{-3}. The proposed value for α is reasonable, considering that chemisorption of oxalic acid can be described as a "semicomplexation" reaction on the surface. It can be safely concluded that the dissolution measurements have been carried out with a fully oxalated surface in experiments performed at pH 3–4 (at much higher or lower acidities, this may be no longer true).

Chemisorption has been confirmed by IR measurements of oxalic acid adsorption on ferrihydrite obtained by hydrolysis of Fe^{III} salts.[30-32]

Because of the above mentioned ambiguities in the characteristics of oxalic acid adsorption, we shall restrict ourselves to systems containing high ligand concentration (of the order of 0.1 M). The case of lower coverages or conformational changes is analyzed in separate papers dealing with the systems Fe_3O_4/nitrilotriacetic acid[13] and Fe_3O_4/EDTA.[14]

Dissolution in Oxalic Acid–Ferrous Ion Media. The initial rate of dissolution of magnetite in oxalic acid solutions is negligible in the absence of ferrous ions. Upon addition of Fe^{II}, the initial rate increases linearly with [Fe^{II}], as shown in Figure 2 for pH 4.1 and total oxalic acid concentration [ox] = 0.1 mol dm^{-3}.

Oxalic acid concentration affects the rate far beyond the range in which adsorption equilibrium is established; a saturation rate is achieved only at [ox] > 0.15 mol dm^{-3}: see Figure 3. Acidity influences the rate as shown in Figure 4.

The data presented in Figures 2–4 can be interpreted in terms of the mechanism

$$\text{---Fe} + \text{ox} \rightleftharpoons \text{---Fe–ox} \qquad (5)$$

Equation 5 represents a fast adsorption preequilibrium between surface Fe^{III} ions (represented as ---Fe) and oxalate ions. Although not explicitly indicated in eq 5, H$^+$ ions are involved in this process; "ox" denotes any species derived from oxalic acid, i.e. [ox] = [$H_2C_2O_4$] + [$HC_2O_4^-$] + [$C_2O_4^{2-}$], and eq 5 must be understood as involving charged species. In particular, as explained above, the original surface species ---Fe in eq 5 bear positive charges in the pH range studied, and the resulting species ---Fe–ox are negatively charged. At high oxalic acid concentrations, eq 5 is completely displaced to the right. As stated above, below 0.1 M, deviations are expected due to the complexities of the adsorption process; thus, the present model, assuming complete surface coverage by oxalic acid and only one type of surface complex, does not adequately fit the curve of Figure 3 below ca. 0.08 M. This region is analyzed in other papers.[13,14] Equation 6 represents proton adsorption described empirically by a

$$\text{---Fe–ox} + H^+ \rightleftharpoons \text{---Fe–ox}(H^+) \qquad (6)$$

Freundlich isotherm, eq 7, and indicates that protons are required

$$[\text{Fe–ox}(H^+)] = K_H[H^+]^n \qquad (7)$$

for dissolution in addition to protons involved in equilibrium 5; n is typically ca. 0.5. Expression 7 may or may not represent a restricted fraction of a Langmuir isotherm.

Up to now, the question of the existence of both ---Fe^{II} and ---Fe^{III} sites in magnetite has not been addressed. The reductive dissolution pathway requires that the relevant metal centers be ---Fe^{III}. Dissolution of ---Fe^{II} keeps pace with phase transfer of ---Fe^{III} because of the higher lability of O–Fe^{II} bonds.[33-37] In what follows, the oxidation state of involved Fe centers will be indicated for the sake of clarity.

$$\text{---Fe}^{III}\text{–ox}(H^+) + Fe(C_2O_4)_2^{2-} \rightleftharpoons \text{---Fe}^{III}\text{–ox}(H^+)\cdots Fe(C_2O_4)_2^{2-} \qquad (8)$$

Equation 8 corresponds to the adsorption equilibrium for $Fe(C_2O_4)_2^{2-}$, assumed to be represented by

$$K^{int} = [\text{---Fe}^{III}\text{–ox}(H^+)\cdots Fe(C_2O_4)_2^{2-}] \times [\exp(-2e\psi_\beta/kT)]/\{[\text{---Fe}^{III}\text{–ox}(H^+)][Fe(C_2O_4)_2^{2-}]\} \qquad (9)$$

This expression is used to describe counterion adsorption in the "triple-double layer" description of the metal oxide/solution interface.[18,19] [In fact, ψ_β is not known. As ψ_β and ψ_d ($=\zeta$) are usually found to be roughly proportional (see ref 19 and 34), calculations with eq 9 can be performed by using ψ_d; this procedure includes in K^{int} a constant additional term.] For a negative ion and a negative surface, the surface concentration of adsorbed ions must be very low. The use of this formalism is equivalent to the approach normally employed to describe the formation of precursor complexes in charge-transfer processes.[38] In our case, when both reactants are similarly charged, the work term used to describe the Gibbs energy involved in the close approach of the ions is

$$W = -RT \ln K^{int} = 2e\psi_\beta \qquad (10)$$

In the present system electron transfer itself is postulated to be the rate-determining step:

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(29) Smith, R. M.; Martell, A. E. *Critical Stability Constants*; Plenum: New York, 1974.

(30) Parfitt, R. L.; Russell, G. D.; Farmer, V. C. *J. Chem. Soc., Faraday Trans. 1* **1976**, *72*, 1082.

(31) Parfitt, R. L.; Russell, G. D.; Fraser, A. R.; Farmer, V. C. *Nature (London)* **1974**, *248*, 220.

(32) Parfitt, R. L.; Farmer, V. C.; Russell, G. D. *J. Soil Sci.* **1977**, *28*, 29.

(33) The possibility of enhancing dissolution rates by taking advantage of the lability of lower oxidation states was recognized as early as 1964: Zabin, B. A.; Taube, H. *Inorg. Chem.* **1964**, *3*, 963.

(34) Blesa, M. A.; Maroto, A. J. G. *J. Chim. Phys.* **1986**, *83*, 757.

(35) Bruyere, V. I. E.; Blesa, M. A. *J. Electroanal. Chem.* **1985**, *182*, 141.

(36) Valverde, N.; Wagner, C. *Ber. Bunsen-Ges. Phys. Chem.* **1976**, *80*, 330.

(37) Valverde, N. *Ber. Bunsen-Ges. Phys. Chem.* **1976**, *80*, 333.

(38) Sutin, N. In *Progress in Inorganic Chemistry*; Lippard, S. J., Ed.; Wiley: New York, 1983; Vol. 30.

$$\text{---Fe}^{\text{III}}\text{–ox(H}^+)\cdots\text{Fe}^{\text{II}}(\text{C}_2\text{O}_4)_2{}^{2-} \xrightarrow{k_{\text{ET}}} \text{---Fe}^{\text{II}}\text{–ox(H}^+)\cdots\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_2{}^{-} \quad (11)$$

Many studies have been reported in the literature concerning electron-transfer reactions of oxalato complexes in solution;[12] usually the conditions explored correspond to the operation of inner-sphere mechanisms in which oxalate acts as a bridging ligand. In the present case however, we have restricted our analysis to the case where there is a large excess of ligand as compared to metal ions. Although this is not a guarantee that outer-sphere mechanisms operate, evidence from related systems also suggests that this is the case: in the dissolution of magnetite by ferrous–EDTA mixtures, different reactivity patterns are apparent in systems where [Fe(II)]/[EDTA] is larger or smaller than 1,[14] and these observations have been shown to imply ---Fe^{III}–EDTA–Fe^{II} bridged intermediates in the former case and pairs ---Fe^{III}–EDTA···Fe^{II}–EDTA in the latter. Also, as shown below, the data on the present system can be interpreted on the assumption that the usual relationships for outer-sphere electron transfer hold valid.

The process represented by eq 11 is an exoergonic one; $\Delta G°$ is sensitive to the complexation state of dissolved and surface Fe^{III} and Fe^{II} species:

$$\Delta G° = -RT \ln (K_2{}^{\text{III}}/K_2{}^{\text{II}}) + \bar{\alpha}\, RT \ln (K_1{}^{\text{III}}/K_1{}^{\text{II}}) \quad (12)$$

[In the derivation of this expression, there is an implicit assumption that the Fermi energy of electrons in the solid surface is determined by the surface complexation equilibria (5) and (6).]

In eq 12, bulk complexation stability constants K's are identified by a Roman numeral superscript (II or III), indicating the iron ion oxidation state, and an Arabic numeral subscript (1 or 2), indicating the number of bound oxalate ions per iron ion; $\bar{\alpha}$ is the average value of α (eq 4) for Fe^{II} and Fe^{III}. In the derivation of 12, surface species are assumed to be 1:1 (Fe:ox ratio) and their stability constants are estimated by using eq 4; protonation influence is disregarded. The further negative contribution to $\Delta G°$ from the decrease of the negative charge of the adsorbed ion is also neglected.

Introducing literature K values,[29] we obtain

$$\Delta G° = -36.28 \text{ kJ mol}^{-1} \quad (13)$$

Dissolution is finally achieved by fast desorption of $\text{Fe}(\text{C}_2\text{O}_4)_2{}^-$ and fast phase transfer of Fe^{II}–ox(H^+).

For [ox] ≫ $[\text{Fe}^{\text{II}}]_{\text{T}}$ (total added ferrous concentration), the initial rate of dissolution for the above mechanism is

$$\begin{aligned} R_0 &= k_{\text{ET}}K^{\text{int}}[\exp(2e\zeta/kT)][\text{---Fe}^{\text{III}}\text{–ox(H}^+)][\text{Fe}(\text{C}_2\text{O}_4)_2{}^{2-}] \\ &= k_{\text{ET}}K^{\text{int}}[\exp(2e\zeta/kT)]K_{\text{H}}[\text{H}^+]^n[\text{Fe}^{\text{II}}]_{\text{T}}K_2{}^{\text{II}}[\text{ox}]/(Q^2 + K_1{}^{\text{II}}[\text{ox}]Q + K_2{}^{\text{II}}[\text{ox}]^2) \end{aligned} \quad (14)$$

where

$$Q = K_{\text{a},1}{}^{-1}K_{\text{a},2}{}^{-1}[\text{H}^+]^2 + K_{\text{a},2}{}^{-1}[\text{H}^+] + 1 \quad (15)$$

$$K_{\text{a},1} = [\text{H}^+][\text{C}_2\text{O}_4\text{H}^-]/[\text{C}_2\text{O}_4\text{H}_2]$$

$$K_{\text{a},2} = [\text{H}^+][\text{C}_2\text{O}_4{}^{2-}]/[\text{C}_2\text{O}_4\text{H}^-]$$

Equation 14 has been derived by using eq 9 and 7 and mass balance equations for species containing oxalate and Fe^{II}. In the case of oxalate mass balance, due to the above mentioned condition of $[\text{ox}]_{\text{T}} \gg [\text{Fe}^{\text{II}}]$, the concentration of species ---Fe–ox(H^+), $\text{Fe}(\text{C}_2\text{O}_4)_2{}^{2-}$, and $\text{Fe}(\text{C}_2\text{O}_4)$ could be safely neglected. Equation 14 represents well the whole set of data included in Figures 2–4, with $n = 0.41$ and $k^{\text{exptl}} = k_{\text{ET}}K^{\text{int}}K_{\text{H}} \exp(2e\zeta/kT) = 0.09 \text{ mol}^{-0.41} \text{ dm}^{4.23} \text{ s}^{-1} \text{ m}^{-2}$; note that n and k^{exptl} are the only adjustable parameters required to fit the experimental data. Full lines in Figures 2–4 correspond to the fit obtained by using these parameters.

This mechanism traces the influence of the concentration of oxalic acid (Figure 3) back to the complexation equilibria

$$\text{Fe}^{2+} + \text{C}_2\text{O}_4{}^{2-} \rightleftharpoons \text{FeC}_2\text{O}_4 \quad (K_1{}^{\text{II}}) \quad (16)$$

$$\text{FeC}_2\text{O}_4 + \text{C}_2\text{O}_4{}^{2-} \rightleftharpoons \text{Fe}(\text{C}_2\text{O}_4)_2{}^{2-} \quad (K_2{}^{\text{II}}/K_1{}^{\text{II}}) \quad (17)$$

The data in Figure 3 are the basis for postulating $\text{Fe}(\text{C}_2\text{O}_4)_2{}^{2-}$ as the electroactive species. The electroactive species should be the one that maximizes $k_{\text{ET}}K^{\text{int}} \exp(2e\zeta/kT)$; according to the Marcus–Hush theory, the problem can be focused as the minimization of $W + \Delta G^{\ddagger}$, where both magnitudes are given by

$$W = 96.5z\psi_\beta \quad (18)$$

$$\Delta G^{\ddagger} = (1 + \Delta G°/\lambda)^2\lambda/4 \quad (19)$$

In eq 18, ψ_β expressed in volts yields the work term in kilojoules per mole; in eq 19, the Gibbs activation energy for electron transfer is related to the reorganization energy λ and the change in standard Gibbs energy of the process, $\Delta G°$, calculated by equations similar to eq 12, as applied to $\text{Fe}(\text{C}_2\text{O}_4)$, $\text{Fe}(\text{C}_2\text{O}_4)_2{}^{2-}$, and $\text{Fe}(\text{C}_2\text{O}_4)_3{}^{4-}$ as potential electroactive species.

The results of parametric calculations are shown in Figure 5, where ψ_β and λ are taken as arbitrary parameters and the fields of prevalence of each reductant ion are indicated. As data for the stability constant of $\text{Fe}(\text{C}_2\text{O}_4)_3{}^{4-}$ are unavailable, two cases were examined, assuming (arbitrarily) $K_3{}^{\text{II}}/K_2{}^{\text{II}} = 1$ or 10. Figure 5 shows that the $\text{Fe}(\text{C}_2\text{O}_4)_2{}^{2-}$ field spans ψ_β and λ within reasonably wide brackets.

It is thus seen that the choice of $\text{Fe}(\text{C}_2\text{O}_4)_2{}^{2-}$ is also reasonable on a theoretical basis. Note however that nonspecific Fe^{II} adsorption (physisorption) is assumed. This is reasonable in high excess of oxalic acid, as used in the present study, but may not be true for other systems or experimental conditions. For instance, in the dissolution of magnetite by NTA/Fe^{II}, evidence points to a chemisorptive process of FeNTA^-, even at high H_3NTA concentrations.[13] In these cases, an electron-transfer rate-determining step may be compatible with a fractional reaction order on Fe^{II} ($n \sim 0.5$); such an order is therefore ambiguous as evidence for fast electrical equilibration between redox couples and the oxide surface, followed by a slower, rate-determining ion transfer across the interface.

Such a mechanism has been proposed by Gorichev[10] on the basis of the influence of added Fe^{II} and Fe^{III} on the exchange current density in metal oxide electrodes. In our case, added Fe^{III} does not affect the rate (except in a photochemical process; see below); this, together with the first-order dependence on Fe^{II}, is an argument against such electrical equilibration. In the early experiments of Valverde and Wagner,[36,37] the rate of dissolution of magnetite in the presence of $\text{V}^{\text{III}} + \text{V}^{\text{IV}}$ was shown to be dependent upon the total concentration of the redox couple and not only on the ratio $[\text{V}^{\text{III}}]/[\text{V}^{\text{IV}}]$. These observations also point to a slow electron-transfer process across the interface under adequate conditions. This does not preclude that, under other conditions, electron transfer may become equilibrated as compared to slower chemical bond rupture processes. This is discussed in more detail in ref 34.

For the postulated mechanism to be correct, the rate of Fe^{II} transfer across the interface must be fast. In principle, for this process, eq 20 should hold for the involved current density. Here

$$i = i_0 \exp[az'e(\psi_0 - \psi_\beta)/kT] \quad (20)$$

a is the electrochemical phase transfer coefficient, $\psi_0 - \psi_\beta$ the (negative) potential drop from the surface to the inner Helmholtz plane, and z' the charge of the transferred ion. Sellers[39] has shown by electron microscopy techniques that Fe^{II} generated in the surface by electron transfer from solution is more reactive than normal lattice Fe^{II}, and thus i_0 can be expected to be high. As z' is likely to be zero (corresponding to the transfer of ferrous oxalate) or negative, the potential drop does not hinder dissolution (it may rather assist Fe^{II} phase transfer).

Dissolution in Oxalic Acid with No Added Ferrous Ion Media. Oxalic acid dissolved magnetite even in the absence of added Fe^{II}; it also dissolves ferric oxides at high temperatures[2] or in the presence of light.[6,40] Two different processes are involved. In

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(39) Allen, G. C.; Sellers, R. M.; Tucker, P. M. *Philos. Mag. B* **1983**, *48*, L5.

(40) Litter, M. J.; Liberman, S. J.; Blesa, M. A., unpublished results.

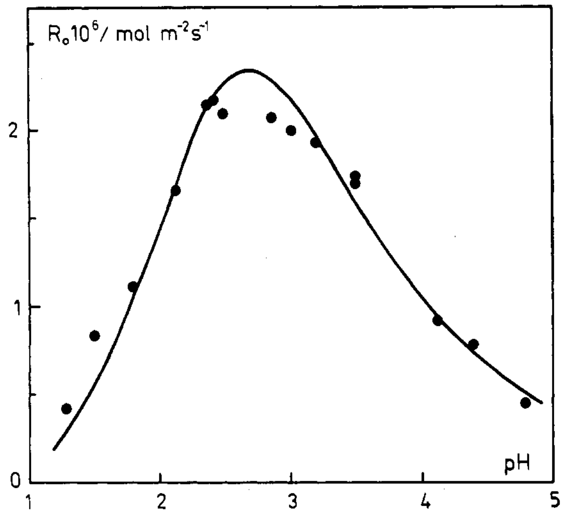

Figure 4. Influence of pH on the initial dissolution rate of magnetite, R_0. [Oxalic acid] = 0.1 mol dm^{-3}; [$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$] = 6.05×10^{-4} mol dm^{-3}; temperature 30 °C. Solid line was obtained by using eq 14.

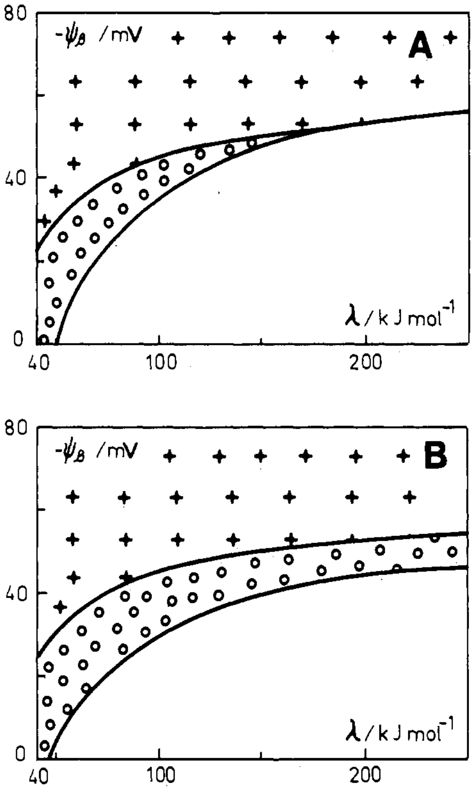

Figure 5. Parametric calculations of $W + \Delta G^*$: +++, domain where minimum $W + \Delta G^*$ values were obtained for FeC_2O_4; OOO, domain for $Fe(C_2O_4)_2^{2-}$; blank area, domain indicating prevalence of $Fe(C_2O_4)_3^{4-}$. In part A, $K_3^{II}/K_2^{II} = 1$; in part B, $K_3^{II}/K_2^{II} = 10$ was assumed (see text).

the dark, magnetite dissolves through an autocatalytic process characterized by a rather long induction period, followed by fast dissolution.[6] During the induction period, ferrous ion leaching takes place; as these ions build up in solution, reductive dissolution accelerated in time takes place, giving rise to a typical sigmoidal dissolution profile.

Assuming a three-dimensional contracting-geometry rate law, a straightforward analysis of the rate expression yields

$$d[Fe^{II}]/dt = k_{Fe}[Fe^{II}]S + v_0 = k'_{Fe}[Fe^{II}]\{[Fe^{II}]_{tot} - [Fe^{II}]\}^{2/3} + v_0 \quad (21)$$

where k'_{Fe} is related to the penetration rate constant k by the expression

$$k = k'_{Fe}M_0^{1/3}V_{sol}^{1/3}w_0^{-1/3}\rho^{-1}S_s^{-1}[Fe^{II}] + k_0 \quad (22)$$

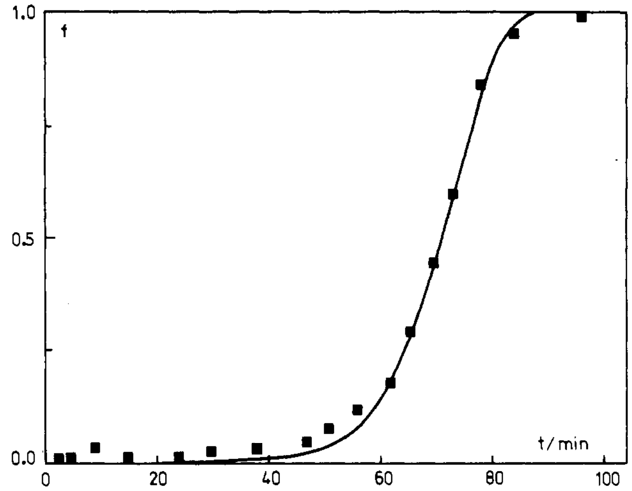

Figure 6. Dissolved iron fraction, f, vs time for a system in which no Fe^{II} has been added: ■, experimental points; —, curve calculated by using integrated eq 21. [Oxalic acid] = 0.1 mol dm^{-3}; pH 4.1; temperature 30 °C.

[S is the instantaneous available surface area, $[Fe^{II}]_{tot}$ is the Fe^{II} concentration reached upon total dissolution of magnetite, v_0 is an empirical rate representing any dissolution process independent of [Fe^{II}] (e.g. slow reduction by oxalate), and V_{sol} and w_0 are the solution volume and the mass of magnetite to be dissolved.] This expression reaches a maximum value when the fraction f = dissolved magnetite/total magnetite = 0.6. This agrees well with experimental results. The f/time profile can also be calculated and compared with experimental results: this is done in Figure 6.

Under visible light, photochemical charge transfer in surface (Fe^{III}–oxalate) complexes provides an additional pathway to start dissolution. In homogeneous solution, photolysis of $Fe(C_2O_4)_3^{3-}$ takes place with high quantum yields in a wide range of wavelengths, the products being Fe^{II} and CO_2.[41] Illumination of iron(III) oxides or magnetite suspensions in the presence of oxalic acid enhances dissolution. A detailed study of these processes is under way.[40]

The photochemical (and probably even the thermal) charge transfer is of significance also in dissolution processes due to other polycarboxylates such as EDTA or nitrilotriacetic acid. Recently, it has been shown that irradiation in the metal-to-ligand charge-transfer band of surface Fe^{III}–citrate complexes brings about dissolution of lepidocrocite.[8] In all these systems, direct light absorption by the semiconductor (generating conduction electron/hole pairs) may eventually also give rise to reductive dissolution.[8,40,42,43] Radiolytic generation of Fe^{II} has also been shown to be conducive to iron oxide dissolution.[44,45] Photochemical electron transfer is also involved in the dissolution of MnO_x oxides.[46-48]

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Registry No. Fe_3O_4, 1317-61-9; Fe^{2+}, 15438-31-0; $H_2C_2O_4$, 144-62-7.

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(41) Calvert, J. G.; Pitts, J. N., Jr. *Photochemistry*; Wiley: New York, 1966; p 783.
(42) Cunningham, K. M.; Goldberg, M. C.; Weiner, E. R. *Photochem. Photobiol.* **1985**, *41*, 409.
(43) Gratzel, M.; Kiwi, J.; Morrison, C. L.; Davidson, R. S.; Tseung, C. C. *J. Chem. Soc., Faraday Trans. 1* **1985**, *81*, 1883.
(44) Buxton, G. V.; Rhodes, T.; Sellers, R. M. *Nature (London)* **1982**, *295*, 583.
(45) Buxton, G. V.; Rhodes, T.; Sellers, R. M. *J. Chem. Soc., Faraday Trans. 1* **1983**, *79*, 2961.
(46) Stone, A. T.; Morgan, J. J. *Environ. Sci. Technol.* **1984**, *18*, 450.
(47) Stone, A. T.; Morgan, J. J. *Environ. Sci. Technol.* **1984**, *18*, 617.
(48) Sunda, W. G.; Huntsman, S. A.; Harvey, G. R. *Nature (London)* **1983**, *301*, 234.