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The Kinetics of the Dissolution of Monoclinic Pyrrhotite in Aqueous Acidic Solutions

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Using the rotating disc method, the rates of dissolution of natural monoclinic pyrrhotite, $FeS_{1.14}$, in oxygen-free aqueous solutions $S([H^+] = 0.1, [Na^+] = 0.9, [ClO_4^-] = 1.0\,mol\,kg^{-1})$ were determined. In the temperature range 40-90 °C the dissolution reaction occurs under kinetic control; the activation energy being $14 \pm 1\,kcal\,mol^{-1}$ ($59 \pm 5\,kJ\,mol^{-1}$).

(Keywords: Dissolution; Kinetics; Pyrrhotite; Rotating disc)

Die Kinetik der Auflösung von monoklinem Pyrrhotin in sauren wäßrigen Lösungen

Die Auflösungsgeschwindigkeit von natürlichem monoklinen Pyrrhotin, $FeS_{1.14}$, wurde in sauerstofffreien Lösungen $S([H^+] = 0.1, [Na^+] = 0.9, [ClO_4^-] = 1.0\,mol\,kg^{-1})$ mit Hilfe der Methode der rotierenden Scheibe bestimmt. Im Temperaturbereich von 40—90° erfolgt die Auflösungsreaktion kinetisch kontrolliert, wobei eine Aktivierungsenergie von $14 \pm 1\,kcal\,mol^{-1}$ ($59 \pm 5\,kJ\,mol^{-1}$) gefunden wurde.

Introduction

The process of dissolution of iron sulphides in acidic electrolyte solutions has been examined by several authors[1–5]. *Tewari* and *Campbell*[1] have studied the kinetics of dissolution of powdered iron-sulphide (FeS, troilite) by means of the rotating disc method. In oxygen free solutions of sulphuric acid, at 25 °C and $[H^+] = 1.14 \cdot 10^{-3}\,mol\,kg^{-1}$ the rates of dissolution depended slightly on the square root of frequency, $f^{1/2}$, of revolutions of the disc (r.p.s.). Consequently it was concluded that the process occurs in the mixed kinetic region[1].

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However, preliminary experiments carried out in this laboratory showed that the rates of dissolution of monoclinic pyrrhotite, $FeS_{1.14}$, were not well reproducible when electrodes made of pressed powder were used. After each experiment sulphur was observed on the surface of the electrodes. Therefore it was concluded that in this case hydrogen sulphide was oxidized to sulphur by oxygen occluded in the porous electrode. Much better results were obtained when the electrodes were prepared from a monolithic mineral.

The reaction leading to dissolution of iron sulphide in oxygen free acidic electrolytes can be written as:

$$FeS_{(s)} + 2\,H^+_{(aq)} \rightleftharpoons Fe^{2+}_{(aq)} + H_2S_{(g)} \tag{1}$$

The aim of this work was to continue a previous investigation of the solubility of $FeS_{1.14}$[6] by a kinetic study of reaction (1) using a disc electrode of natural monolithic monoclinic pyrrhotite. A kinetic control was established in a wide range of temperature; respective rate constants and the activation parameters were evaluated.

Experimental

The starting material was natural monoclinic pyrrhotite (from Orawitza/Banat region). X-ray-fluorimetry showed the following contents of impurities: Cr 0.01, Mn 0.06, Cu 0.24, Zn 0.80%. X-ray analysis indicated that the sample consisted of comparatively pure monoclinic pyrrhotite (X-ray pattern agreed with ASTM 17-200).

The iron content was determined using the *Arnold* method[7]. The mole fraction of Fe was found to be $x_{Fe} = 0.4688$.

From the material described above, disc electrodes were cut out by a diamond saw. The geometrical surfaces of the electrodes were: 7.79 cm^2 for experiments at 40, 50 and 60 °C, and 2.83 cm^2 for experiments at 90 °C.

The pyrrhotite electrodes were cemented into teflon holders, fitted to the shaft of the rotating system. Rotational speeds were measured with a stroboscope.

A thermostated vessel made of glass was used, maintaining the temperature constant within ± 0.2 °C. Before each experiment the surface of the disc was polished with a fine emery paper, rubbed with filtrating paper, put into the vessel and immediately afterwards the experiment was started.

Stock solutions of perchloric acid and sodium perchlorate were prepared from $HClO_4$ (70–72% p.a. Merck) and $NaClO_4 \cdot H_2O$ ("Baker analyzed" Reagent) respectively and analyzed by conventional methods.

These stock solutions were mixed on a weight basis to give solutions $S([H^+] = 0.1,\ [Na^+] = 0.9,\ [ClO_4^-] = 1.0\,\mathrm{mol\,kg^{-1}})$. All solutions used were flushed with nitrogen (99.999%) for 15 h before starting the experiments. During the experiments reentering of oxygen was prevented by a continuous flow of nitrogen. Evaporation and condensation rates were kept low by passing the incoming and leaving gas through equally sized and cooled condensers. During each run periodically 6 samples of the solution were taken and the total iron ion concentration was determined photometrically with *o*-phenanthroline.

Results and Discussion

The amount of iron dissolved, Δn_{Fe} (mol m^{-2}), from the monoclinic pyrrhotite disc was found to be a linear function of time for experiments lasting 6 h at 40, 50 and 60 °C and 1.5 h at 90 °C. Typical examples of experimental data at 90 °C are shown in Fig. 1.

The slopes of the straight lines Δn_{Fe} vs. time gave rates of dissolution of monoclinic pyrrhotite. These rates were further studied as a function of the square root of frequency of revolutions of the disc (Table 1).

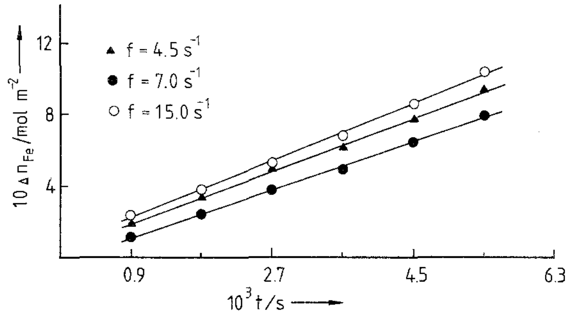

Fig. 1. Plot of amount of iron dissolved from monoclinic pyrrhotite vs. time in oxygen-free aqueous solutions S([H$^+$] = 0.1, [Na$^+$] = 0.9, [ClO$_4^-$] = 1.0 mol kg^{-1}) at 90 ± 0.2 °C. The symbols refer to the values of disc r.p.s.

As can be seen in Table 1, in the temperature range 40-90 °C the rates of dissolution of monoclinic pyrrhotite remain constant within experimental error when the square root of the angular velocity of the disc is varied. This implies that dissolution according to reaction (1) occurs in the kinetic control region, i.e. the rate of transport of reactants in the solution is at least one order of magnitude greater than the rate of chemical reaction[8–10].

According to literature data[1] reaction (1) is of first order with respect to hydrogen ion concentration. This was confirmed experimentally at 60 °C using a monoclinic pyrrhotite disc and a solution S_1 ([H$^+$] = 0.01, [Na$^+$] = 0.99, [ClO$_4^-$] = 1 mol kg^{-1}), the rate of dissolution being $(3.6 \pm 0.4) \cdot 10^{-6}$ mol m^{-2} s^{-1}. Thus equation (2) describes the rate of the reaction examined:

$$j_{\mathrm{Fe}} = k_f\,[\mathrm{H}^+] \qquad (2)$$

Table 1. *The rate of dissolution of monoclinic pyrrhotite in oxygen free aqueous solutions*, $S([H^+] = 0.1, [Na^+] = 0.9, [ClO_4^-] = 1.0\,\mathrm{mol\,kg^{-1}})$ *at different temperatures and angular velocities of the disc*[a]

T/K	$f^{1/2}/\mathrm{s}^{-1/2}$	$10^5 j_{\mathrm{Fe}}/\mathrm{mol\,m^{-2}\,s^{-1}}$	$10^5 \bar{j}_{\mathrm{Fe}}/\mathrm{mol\,m^{-2}\,s^{-1}}$[b]
313.15	1.1	0.844	(0.778 ± 0.110)
	1.1	0.778	
	2.1	0.850	
	2.7	0.867	
	3.9	0.572	
	3.9	0.756	
323.15	1.1	1.72	(1.96 ± 0.10)
	1.1	1.94	
	2.1	1.97	
	2.7	1.86	
	3.9	1.89	
	3.9	1.78	
333.16	1.1	2.86	(2.75 ± 0.15)
	1.1	2.71	
	2.1	2.67	
	2.7	2.67	
	3.9	2.99	
	3.9	2.60	
363.16	1.5	18.4	(17.6 ± 1.3)
	2.1	17.1	
	2.7	15.3	
	2.7	18.7	
	3.9	17.8	
	3.9	18.4	

[a] $\omega = 2\pi f$ where: ω angular velocity of the disc; f frequency of revolutions of the disc.

[b] Errors quoted are standard deviations.

where j_{Fe} is the rate of dissolution of the pyrrhotite, k_f is the rate constant for the forward reaction [according to Equ. (1)], and $[H^+]$ is the hydrogen ion concentration in the bulk of the solution. When Equ. (2) is applied to experimental data of Table 1 and 2 the units of concentration have to be changed to mol m^{-3}.

In order to determine the activation energy the rate constants of reaction (1) were calculated from equation (2). At each temperature the hydrogen ion concentration was calculated using the corresponding density. The density of the solution S was determined using the Paar Digital Density Meter and found to be 1.0713 g/cm^3 at 18 °C. Assuming that the density of the solution is the same function of temperature as

Table 2. *Data for the determination of the activation energy of reaction (1)*

$10^3 T^{-1}/K^{-1}$	$10^2[H^+]/mol\,dm^{-3}$	$k_f/m\,s^{-1}$	$\log k_f$
2.753	9.206	$1.91 \cdot 10^{-6}$	—5.72
3.002	9.377	$2.93 \cdot 10^{-7}$	—6.53
3.094	9.423	$1.97 \cdot 10^{-7}$	—6.70
3.193	9.463	$8.22 \cdot 10^{-8}$	—7.09

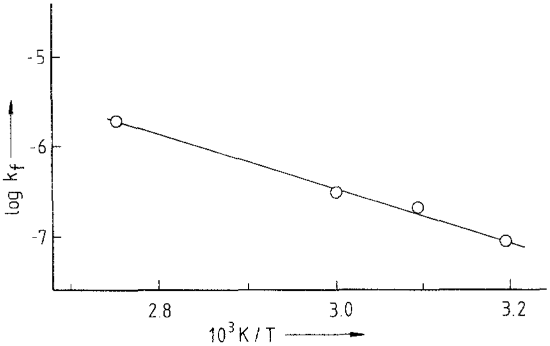

Fig. 2. *Arrhenius* plot for the dissolution of monoclinic pyrrhotite in oxygen-free aqueous solutions S ($[H^+] = 0.1$, $[Na^+] = 0.9$, $[ClO_4^-] = 1.0\,mol\,kg^{-1}$)

the density of pure water[11], the molarities of H^+-ions at temperatures 40, 50, 60 and 90 °C were calculated. All data for the determination of the activation energy are summarized in Table 2, and the respective *Arrhenius* plot is shown in Fig. 2.

The activation energy of the dissolution of monoclinic pyrrhotite determined from the plot presented in Fig. 2 is equal to $14 \pm 1\,kcal\,mol^{-1}$. The value of the activation energy of reaction (1) obtained for another iron sulphide (hexagonal troilite) by *Tewari* and *Campbell*[1] was equal to $17 \pm 2\,kcal/mol$.

Summarizing open-circuit measurements of dissolution rates of monoclinic pyrrhotite in oxygen-free aqueous solutions S ($[H^+] = 0.1$, $[Na^+] = 0.9$, $[ClO_4^-] = 1.0\,mol\,kg^{-1}$) it should be emphasized that rate constants of reaction (1) used for the determination of the activation energy originated from the kinetic control region only. The activation energy reported by *Tewari* and *Campbell*[1] was calculated from rate constants without separating contributions from the kinetic and mixed control region respectively.

In order to keep activity coefficients of the H^+-ions constant we used sodium perchlorate as supporting electrolyte.

With discs made of monolithic minerals complications arising from the desintegration of powdered samples can be effectively avoided.

The induction period, which is usually observed during dissolution of sulphides, was negligible in these measurements as compared to the intervals of sampling.

Finally, it ought to be mentioned that there is a large influence of the chemical composition of semiconductor sulphides on their properties, consequently the results obtained are not necessarily applicable for other iron sulphides.

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