

Electrochemical Investigation of the Commercial Iron Sulfide Stick—Interaction with Complexing Ligands

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The present work aims to examine iron sulfide for its interfacial properties in aqueous media containing different ionic/complexing agents. The primary experimental investigation is the potentiometric response of the commercial iron sulfide stick in various aqueous media supplemented by cyclic voltammetry and UV-visible and IR spectroscopy. The significance of employing the commercial iron sulfide stick is that it is quite stable under ordinary conditions and possesses appreciable conductivity for employing it as an electrode. © 2001 Academic Press

Key Words: commercial iron sulfide stick; iron sulfide; influence of complexing agents on iron sulfide.

1. INTRODUCTION

The interfacial chemistry of pyrite is of great industrial importance. The surface properties of pyrite, particularly its oxidation behavior, have been studied extensively in relation to these industrial applications. A number of excellent review papers on the subject (1–8) have been published. However, there is continuing exploration on the details of the pyrite oxidation processes in alkaline media. Also, studies have not considered in depth the effects of the electrolyte and the “impurities” in the electrolyte on the surface oxidation of pyrites. Further, there is seldom any report on the interfacial chemistry and electrochemistry of iron sulfide (FeS). The silence perhaps has been due to the fact that FeS does not constitute a key component in earthen ores. Still, a study in this direction would prove extremely beneficial and informative. First, such a study would be a veritable scientific curiosity, and second, since FeS is present in meteorites, a transfer of learning would become possible in the future.

2. EXPERIMENTAL

Unless otherwise specified, all chemicals used were Merck extra pure grade products and commercial iron sulfide sticks used for the present study were of BDH make (95% purity).

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Solution UV-visible spectra were recorded using a Cary Varian-13 and also a UV-160A Shimadzu spectrophotometer using 1-cm quartz cells. Fluorescence measurements were made with a Perkin–Elmer MPF 3 and an Aminco-Bowman SPF instrument.

The reaction products were scraped from the surface of the iron sulfide stick whose IR spectra were recorded on a Shimadzu IR408 spectrophotometer using KBr pellets.

Cyclic voltammograms were recorded using a Princeton Applied Research instrument which had the following units: (i) a potentiostat/galvanostat, Model 173, (ii) a current to voltage converter, Model 176, (iii) a universal programmer, Model 175, and (iv) a XY recorder, Model RE008. DC polarograms were recorded on an Elico (Indian) pulse polarograph using a dropping mercury electrode which had the following characteristics: drop time, $t = 6.2$ s per drop in 0.1 M KNO₃; mass of mercury flowing, $m = 0.0013$ kg s⁻¹.

The potentiometric response of iron sulfides in various media has been examined using a Nucleonix digital pH meter in the potentiometric mode; the sensitivity of the instrument was ± 1 mV. A saturated calomel electrode was used as the reference electrode.

A commercial FeS stick wafer was made into an electrode by drilling a small hole, into which a copper lead wire was soldered to give the electrical contact. It was enclosed in an PTFE mount with a circular working electrode area of 0.05-m diameter. The resistance of the FeS sticks was found to be 10 ohm.

3. RESULTS AND DISCUSSION

Elemental analysis carried out by quantification (9) of iron and sulfur showed the commercial iron sulfide to be slightly deficient in iron, having a formula Fe_{0.90}S. The crystal structure is hexagonal as evidenced by SEM pictures (Fig. 1). The crystal structure and chemical composition indicate that commercial iron sulfide could be categorized as hexagonal pyrrhotite, supported by its ferromagnetic behavior (9).

3.1. Response to Tetraborate

Sodium tetraborate is widely used in studies connected with sulfide mineral flotation. Therefore, it was of interest to first

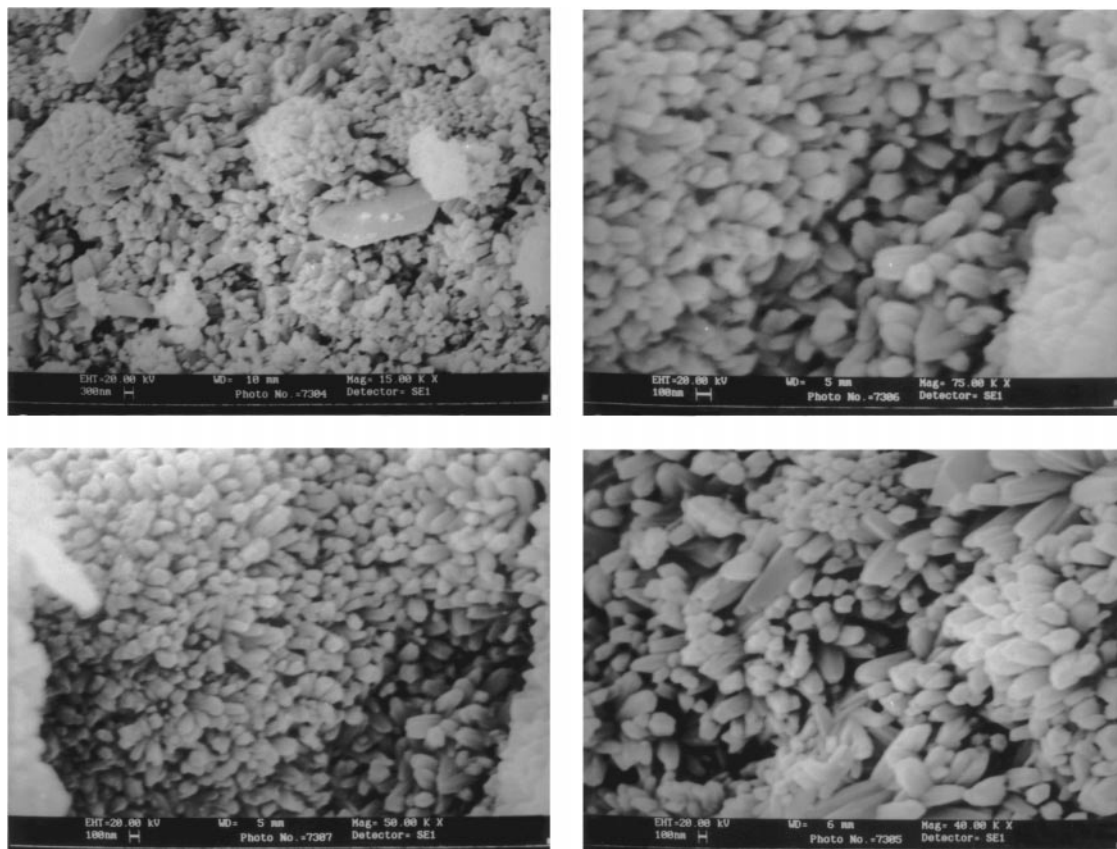
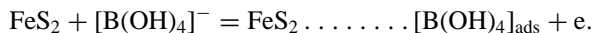


FIG. 1. SEM pictures of a commercial iron sulfide stick under different magnifications. The hexagonal pyrrhotite structure is exhibited.

examine the potentiometric response of FeS to tetraborate. The response is a linear variation with a slope of 54.75 mV (Fig. 2) corresponding to a 1e reaction. This is very interesting because borate has long been considered an inert electrolyte/pH buffer and its reactions with sulfide minerals were completely overlooked. It was Wang who reported for the first time in 1996 (10) that borate can strongly react with the surface of pyrite. From cyclic voltammetry, he showed that the rate-determining step of the reaction is



The obtention of a 1e slope in the present study for the potentiometric response to borate is suggestive of a similar reaction for the commercial FeS stick. In order to confirm this possibility, the cyclic voltammogram of a commercial FeS stick in borate buffer was recorded (Fig. 3). Peak A in the cyclic voltammogram represents the FeS–borate interaction. The linearity of i_p with borate concentration reaffirms that borate buffer cannot be taken as an inert electrolyte (10) for electrochemical studies.

3.2. Reaction with Carbonate in Slightly Alkaline Media

The potentiometric response of the FeS stick to carbonate variation in an alkaline (NaOH) solution of pH 8–9 is shown in

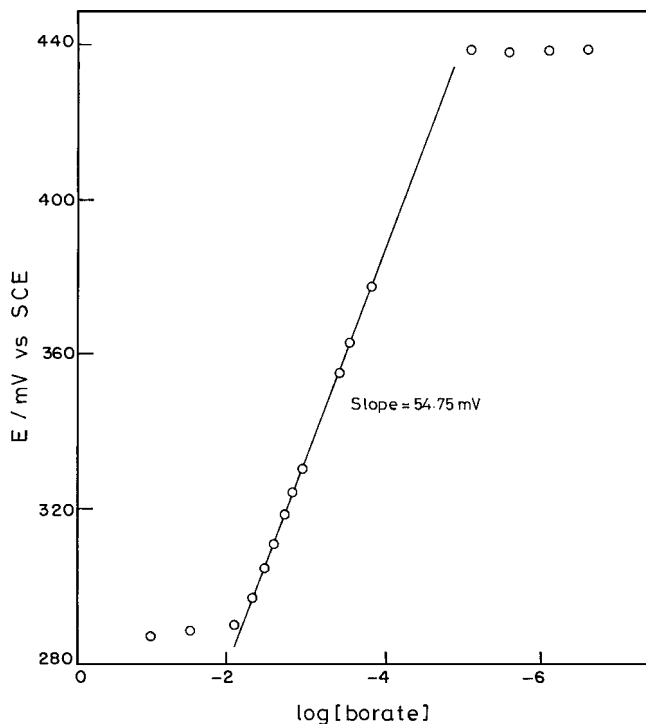


FIG. 2. Potentiometric response of the commercial iron sulfide stick to tetraborate.

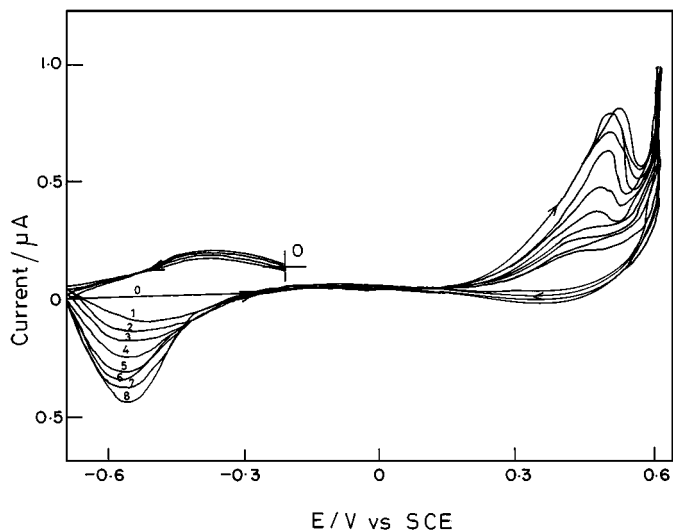


FIG. 3. Cyclic voltammogram of the commercial iron sulfide stick in borate buffer.

Fig. 4. The slope of E vs $[\text{CO}_3]^{-2}$ is 37 mV, a value closer to the value for a $2e$ reaction.

To isolate and identify the reaction products, powdered FeS stick was equilibrated with $\text{Na}_2\text{CO}_3 + \text{NaOH}$ for 74 h under continuous stirring. The solid residue obtained was separated, washed, dried at 383 K, and then analyzed by IR. The IR spectrum (Fig. 5) of the compound exhibits frequencies characteristic of carbonate, indicating that a major component of the residue was a carbonate, which was further confirmed by testing for brisk effervescence with dilute acid.

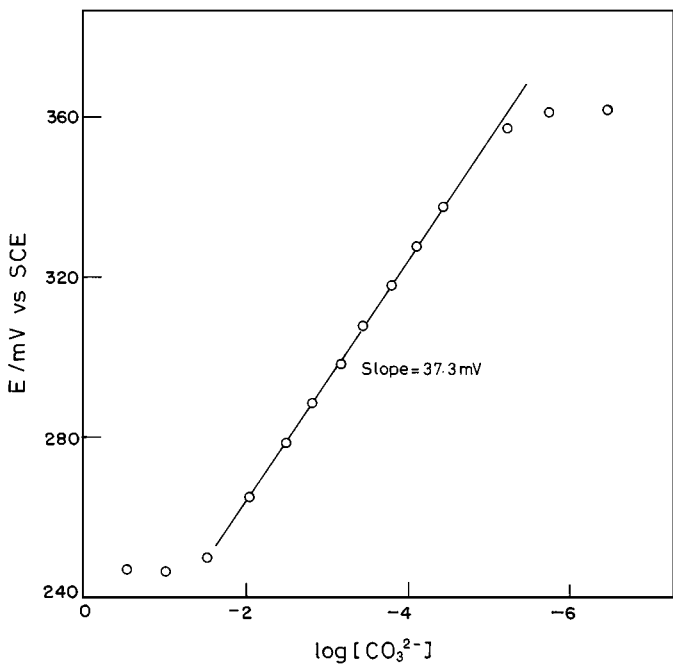


FIG. 4. Potentiometric response of the commercial iron sulfide stick to carbonate in slightly alkaline media.

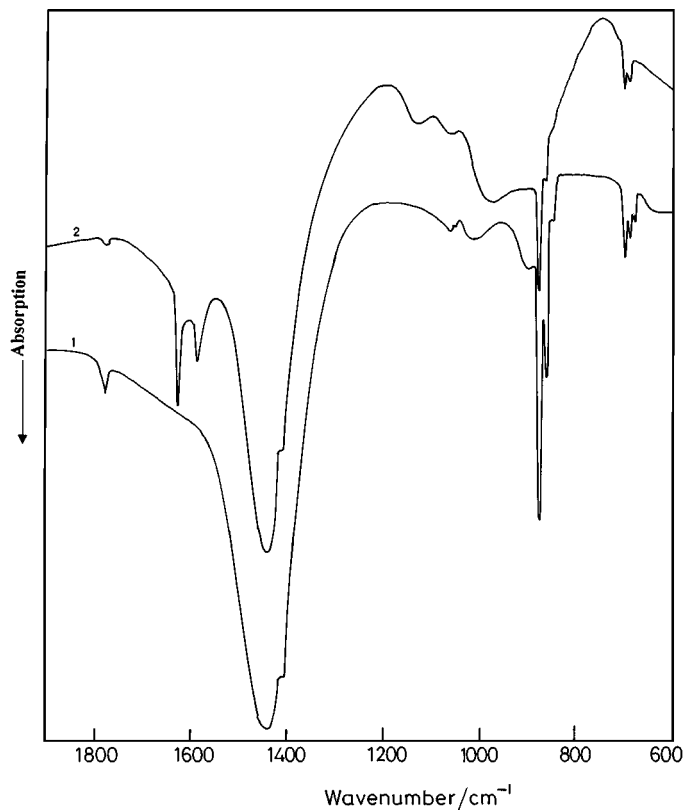
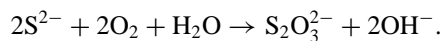


FIG. 5. IR spectra of (1) Na_2CO_3 and (2) the reaction product of the commercial iron sulfide stick with carbonate.

3.3. Interaction of FeS with Na_2S

The potentiometric response of FeS to Na_2S shows a linear variation with two slopes of 33 and 83 mV, respectively (Fig. 6). The first effect of contacting FeS with the Na_2S solution is that the surface of FeS became intensely black. When this blackened FeS was exposed to atmosphere it exfoliated, eventually producing a reddish-brown powder. The powder was very alkaline in nature. IR analysis of the powder showed that it contained considerable quantities of thiosulfate and practically no sulfate (Figs. 7 and 8).

When the blackened FeS was equilibrated with water, a highly alkaline solution ($\text{pH} > 11$) was produced. When the solution was aerated for 6 h and then tested for anions, a positive test for thiosulfate was obtained. The reaction is



Upon contact with a commercial iron sulfide stick, a solution of Na_2S turns dark green immediately. A fresh sample of this solution gave a positive test for iron. The UV spectrum of the solution is distinct from that of sodium sulfide (Fig. 9): the peaks at 365, 300, and 315 nm are indicative of iron; the absorption at 415 nm may characterize the thioferrite group, the presence of which is also indicated by the dark-green color of the

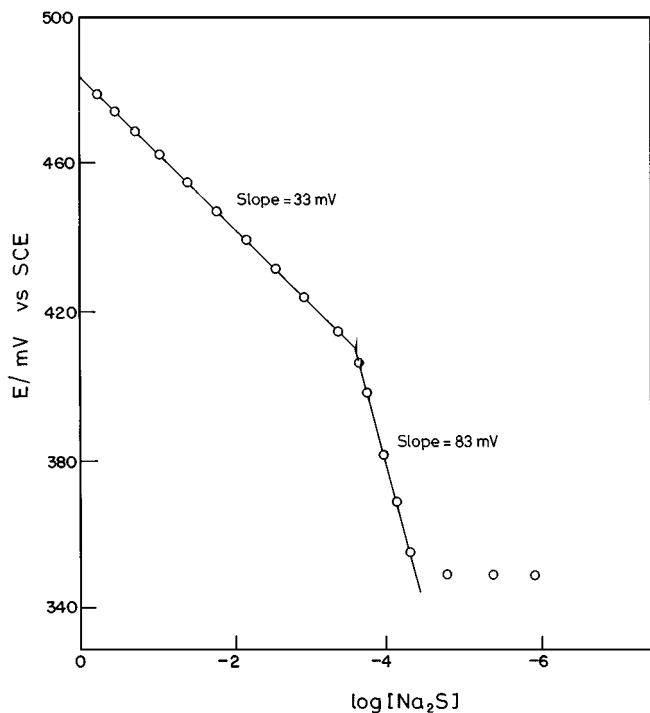


FIG. 6. Potentiometric response of the commercial iron sulfide stick to Na_2S .

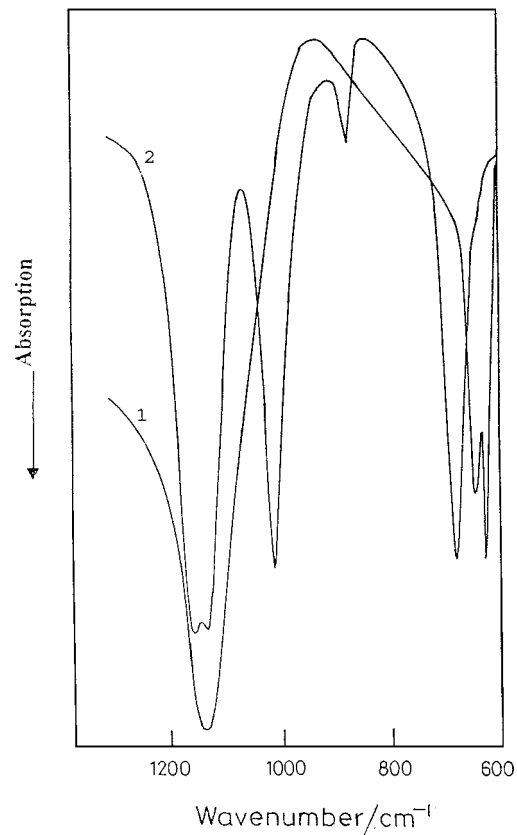


FIG. 8. Infrared spectrum of (1) anhydrous $\text{Na}_2\text{S}_2\text{O}_3$ and (2) the product of FeS with Na_2S .

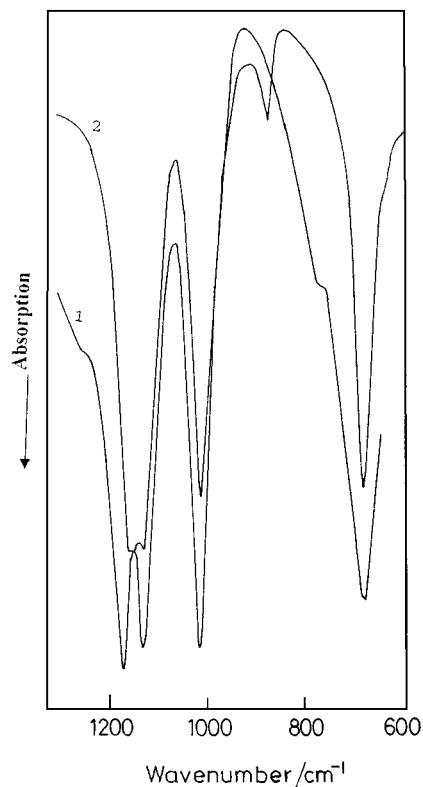


FIG. 7. Infrared spectrum of (1) $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ and (2) the product of FeS with Na_2S .

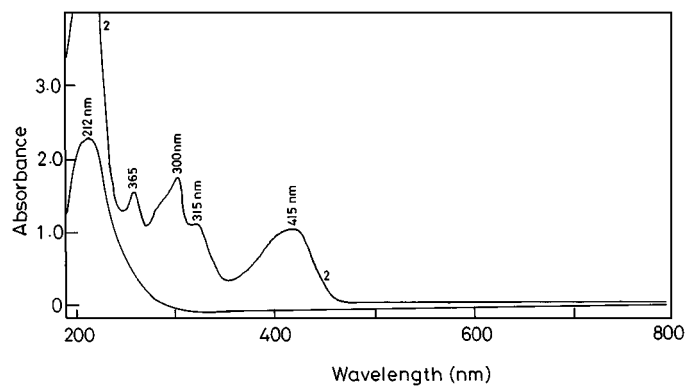


FIG. 9. UV spectrum of Na_2S solution that has been contacted with a commercial FeS stick.

solution. Evidence for the existence of thioferrite, Na_2FeS_2 , comes from the phase equilibrium diagram of the anhydrous Na_2S – FeS system reported by Barnes (11). Further, it is an established fact that soluble thioferrites are formed (12) at $\text{pH} > 8$: in fact, the pH of the Na_2S solution is between 11 and 13, which supports the assumption that a soluble thioferrite is initially formed in the FeS -contacted Na_2S solution. The slope of the plot of E vs $[\text{Na}_2\text{S}]$ is initially 33 mV (Fig. 6), a value closer to 29.58 mV for a $2e$ process, confirming that leaching of the

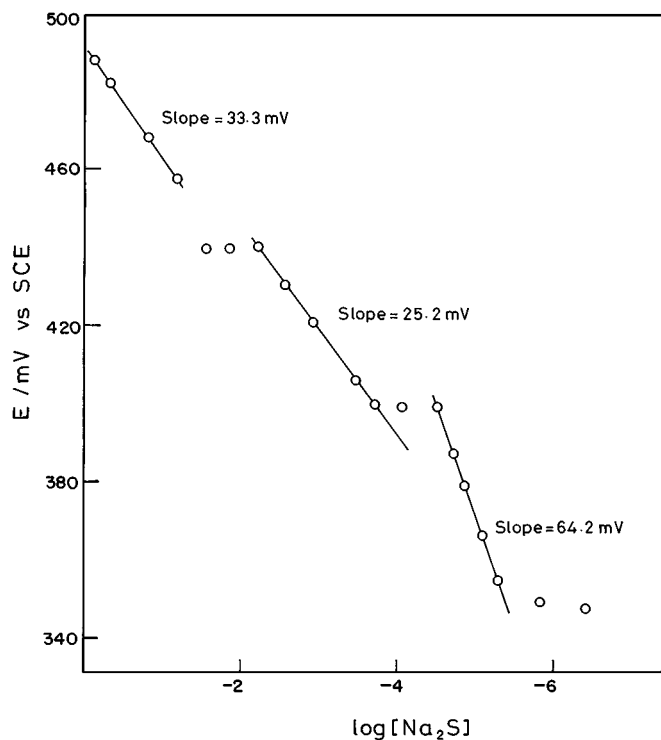
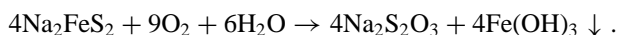


FIG. 10. Potentiometric response of the commercial iron sulfide stick to Na_2S in the presence of carbonate.

electrode material takes place. The FeS-contacted Na_2S solution, upon ageing (1 day), yielded a brownish-red powder, and the solution gave a positive test for thiosulfate. The reaction is



3.4. Interaction with Na_2S in the Presence of Carbonate

The potentiometric response of the FeS stick with Na_2S in the presence of carbonate is shown in Fig. 10. In contrast to the response to Na_2S alone, the response of FeS to Na_2S in the presence of carbonate shows a multistep curve and at least three steps are seen, corresponding to three different processes, the slope values being $2e$, $2e$, and $1e$, respectively.

In order to understand the nature of chemical events that take place in the medium, powdered FeS was equilibrated with $\text{Na}_2\text{S}/\text{Na}_2\text{CO}_3$ for 24 h. The residue thus obtained was washed, dried at 353 K, and analyzed. The IR spectrum (Fig. 11, curve 1) shows frequencies characteristic of organic moieties, particularly of carbonyl/carboxylate functional groups viz., at (cm^{-1}) 1700 (s), 1600 (s), and 1400 (s) (13). When the residue was heat treated at 723 K for 5 h and the IR spectrum recorded, the frequencies characteristic of organic functionalities were absent (Fig. 11, curve 2) and the spectrum exhibited the frequencies characteristic of OH (cm^{-1}) ((1000 (s), 1750 (s)) and sulfate (1000–1150 (s), 600–640 and 500 (m)). The broad absorption at 3500 cm^{-1} is characteristic of bonded OH groups. The EPR

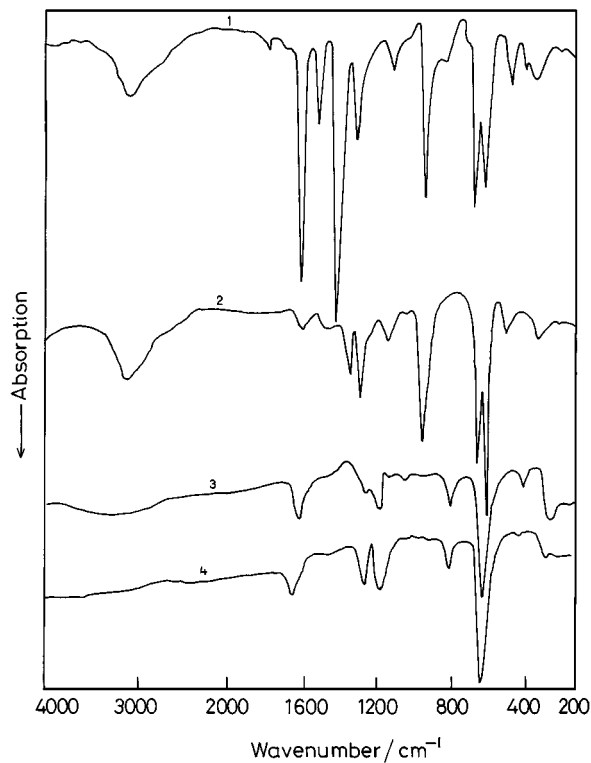


FIG. 11. The IR spectrum of the reaction product of FeS with Na_2S in the presence of the carbonate product (1) heat treated at 523 K (2) and heat treated at 1073 K (3). Curve 4 shows the reaction product of FeS with NaHCO_3 heat treated at 1073 K.

spectrum of the residue at this stage (Fig. 12) shows a g value characteristic of Fe^{3+} . The IR spectrum of the residue that was heat treated at 1073 K shows absorptions that could be associated only with sulfate and oxide groups. The thermogravimetric

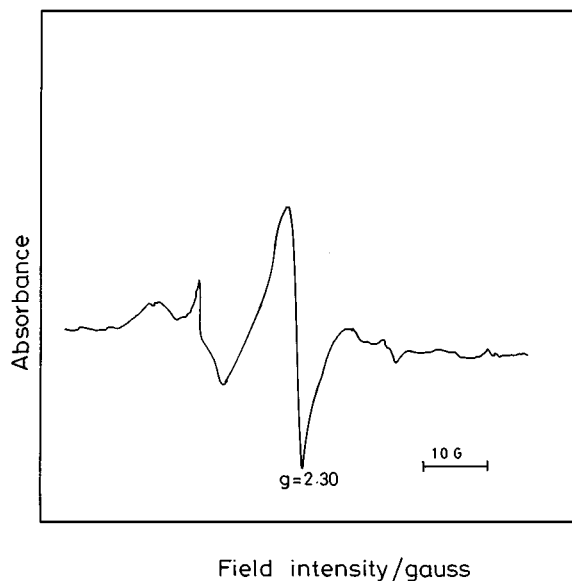


FIG. 12. EPR spectrum of the compound isolated from the FeS– Na_2CO_3 reaction.

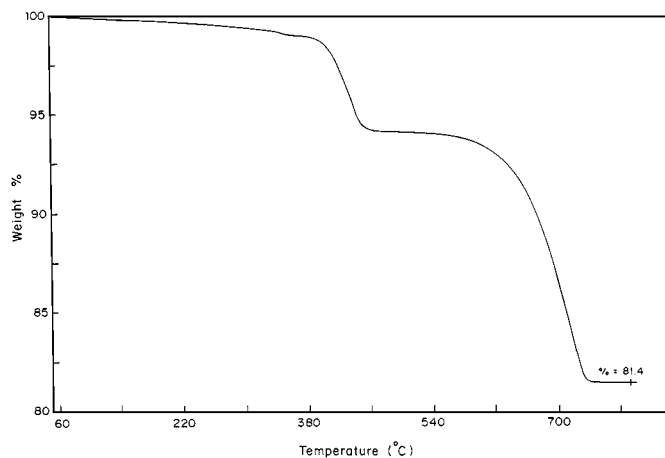
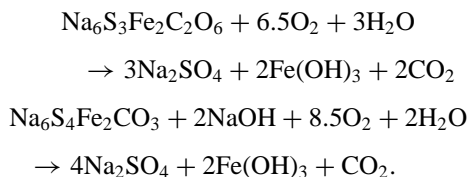


FIG. 13. TGA curve of the product isolated from the reaction of the FeS stick with Na₂S in the presence of carbonate.

analysis (Fig. 13) provides evidence to the above-said transformations. Evidence (11) shows that sulfur-rich FeS yields a slag that could be represented by the formula Na₆S₄Fe₂CO₃ in biological and chemical reactions. On the contrary, a sodium-rich FeS yields a slag of formula Na₆S₃Fe₂C₂O₆. The reactions are

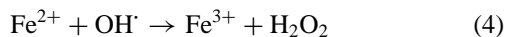
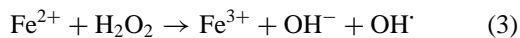
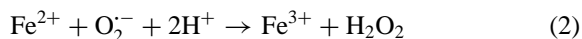
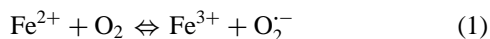


3.5. Interaction of FeS with Phosphate

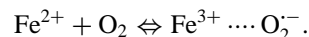
The potentiometric response of FeS to triorthophosphate is shown in Fig. 14. The variation is linear with a 1e slope (56.3 mV). Prolonged contact of the iron sulfide stick with the phosphate solution results in fluorescence emission.

It is known that injection of Fe²⁺ into phosphate buffer gives rise to a flash of light of low intensity with a half-life of about 1 s (14). The intensity is a function of various factors such as the concentration of Fe²⁺ and phosphate and pH and is possibly mediated by traces of carbonate and formate ions.

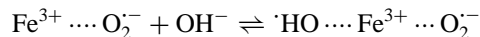
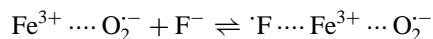
From a study on the effect of superoxide dismutase (SOD) on Fe²⁺-injected phosphate buffer, it was proved that O₂⁻ was responsible for the chemiluminescence, which was destroyed by the addition of SOD (14). The following mechanism for the production of superoxide ions by auto-oxidation of ferrous ions in aqueous solutions was proposed by Weiss (15, 16).



More precisely, step (1) can be represented as



The reverse process leading to the restitution of ferrous ions and O₂ is inhibited in the presence of suitable anions such as F⁻, P₂O₇⁴⁻, or OH⁻, which complex with Fe³⁺.



This type of hydroxylation is rather slow and probably arises from secondary reactions derived from an initial pulse of O₂⁻ giving rise to H₂O₂, which then reacts with metal ions to give the hydroxylating species. Thus Fe²⁺/O₂/phosphate as a system of production of O₂⁻ is now well established (16).

The influence of adding carbonate and formate ions to FeS-equilibrated phosphate solution was studied. It was found that carbonate and formate increased the intensity of fluorescence of the solution (Fig. 15).

The stimulating effect of carbonate/bicarbonate and formate ions on fluorescence emission of FeS-equilibrated phosphate/H₂O₂ medium provides an attractive explanation for the chemiexcitation reactions. Formate ions are known to react with OH[·] radicals and, subsequently, with O₂ to form O₂⁻ and CO₂ (17).

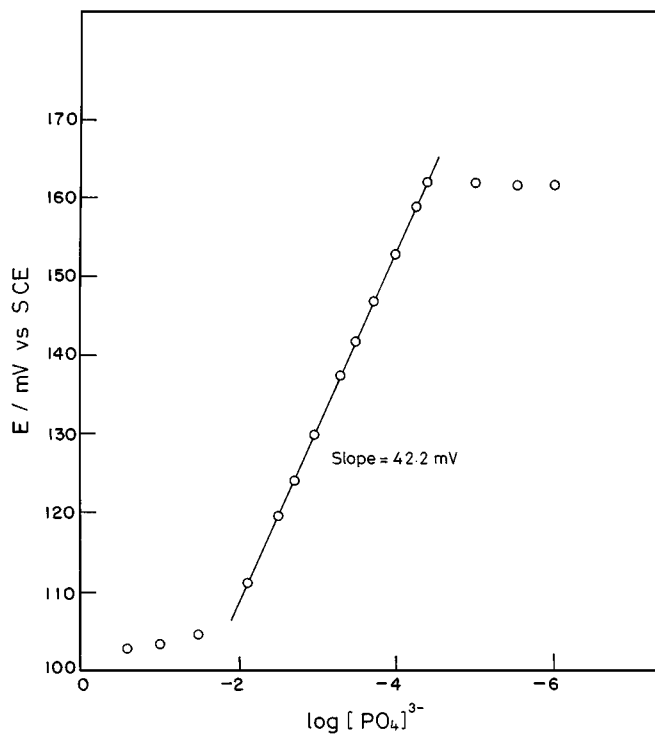


FIG. 14. Potentiometric response of the commercial iron sulfide stick to phosphate.

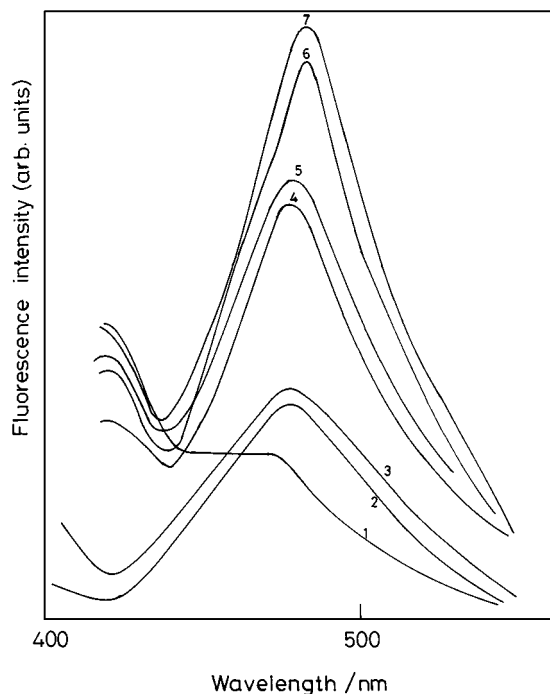
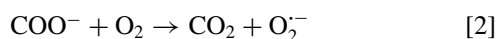


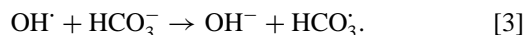
FIG. 15. Fluorescence spectra of (1) FeS + 0.01 M phosphate. (2) FeS + phosphate + H₂O₂. (3) Solution (2) + 0.01 M KOH. (4) FeS + phosphate + H₂O₂ + KCN. (5) solution (4) + 0.01 M KOH. (6) and (7) are, respectively, (1) and (2) with 0.01 M Na₂CO₃ each.



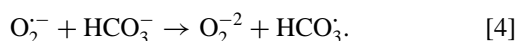
$$K = 2.7 \times 10^{-9} \text{ M}^{-1} \text{ s}^{-1} \quad \text{at pH 4-10}$$



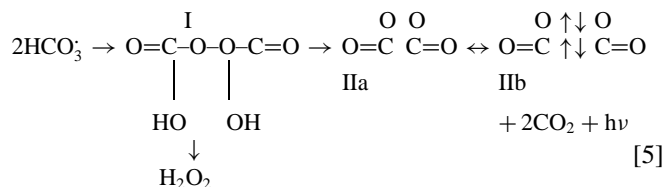
This way, the efficiency of O₂⁻ generation can be doubled. Reaction of OH[·] and O₂⁻ radicals with carbonate/bicarbonate ions leads to the generation of carbonate radicals (18).



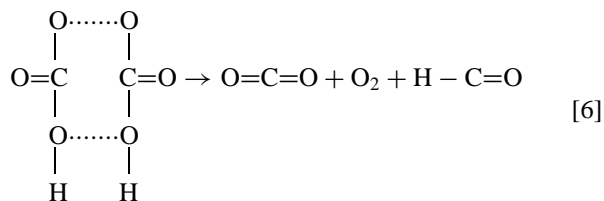
With the second-order rate constant $K = 3.2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ and



Recombination of HCO₃[·] or COO⁻ may generate energy-rich precursors of electronically excited molecules or directly electronic excitation.

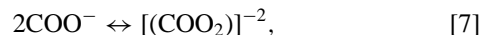


Peroxalate I dissociates to H₂O₂ and dioxetanes IIa and/or IIb, which are considered excited triplet dimers of two CO₂ molecules (19). Spin reversion can be achieved by the emission of radiation of $h\nu$. It can be regarded as a T-S transition enhanced by the neighborhood of the radical electrons. As calculated from the energy balance of the covalent bond's formation and splitting, the last step of the reaction (i.e., Eq. [5]) liberates $\Delta E = E_{2\text{C}=\text{O}} = (E_{\text{C}-\text{C}} + E_{\text{O}-\text{O}}) = 860 \text{ kJ mol}^{-1}$. Another possible mode of recombination and decomposition involves a Russel-like tetraoxide transient complex.

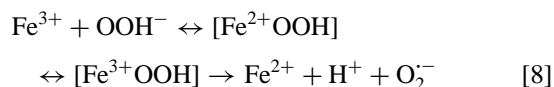


For this mode, the energy difference is $\Delta E = E_{\text{C}=\text{O}} + E_{\text{C}=\text{O}} + E_{\text{C}-\text{H}} - (E_{2\text{C}=\text{O}} + E_{\text{O}-\text{H}}) = 305 \text{ kJ} \cdot \text{mol}^{-1}$, which corresponds to the shortest wavelength, 386 nm.

The recombination of formate ion radicals, e.g., from reaction (1), may generate directly related excited oxalate dianions,



with $\Delta E = 360 \text{ kJ} \cdot \text{mol}^{-1}$ high enough to promote emission with wavelength $\geq 325 \text{ nm}$. Another possibility which cannot be entirely excluded is the formation of the peroxide-ferrous/ferric complex in the conformational out-of-equilibrium state.



Gibbs free energy, ΔG , of the nonequilibrium complex to the equilibrium state of the products should be greater than that calculated from the equilibrium conformational states. This was observed in the fast electron reaction between ferri-complexes and suitable donors (18). Weak emission in the near IR part of the spectrum from the reaction of catalase enzyme and H₂O₂ has been alternatively explained by the forbidden transition in the haem complex (20). The ΔE value for this forbidden transition ($A_{1g} \rightarrow {}^3T_{1g}$) is very close to that observed in the fluorescence spectra corresponding to $\lambda_{\text{max}} = 422 \text{ nm}$.

3.6. Oxygen Reduction in the Presence of FeS

It is well known that the reduction of oxygen at a dropping mercury electrode produces two $2e$ dc waves (Fig. 16). The first $2e$ wave is due to the reduction of oxygen to hydrogen peroxide and the second $2e$ wave is due to the reduction of hydrogen peroxide to water or hydroxide ions, depending on whether the medium is acidic/neutral or alkaline. The

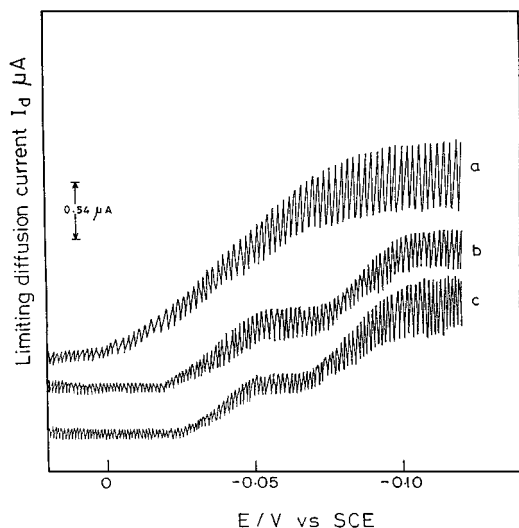
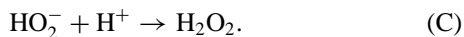


FIG. 16. A dc polarogram for the reduction of oxygen in (a) 0.1 M KNO_3 , (b) FeS-equilibrated 0.1 M KNO_3 , and (c) FeS-equilibrated 0.1 M KNO_3 containing formate.

reduction of $\text{O}_2 \rightarrow \text{H}_2\text{O}_2$ has been shown to occur by the following mechanism (21):



In aqueous media, protonation and subsequent reduction of O_2^- occur instantaneously so that an overall $2e$ dc wave is seen for the reduction in aqueous media.

However, in the present study it was possible to observe the splitting of the single $2e$ dc wave into two $1e$ waves (Fig. 15) in a phosphate buffer (pH 8) that has been equilibrated with FeS. Further, whenever formate or carbonate was added to the medium, the i_d of the $\text{O}_2^- \rightarrow \text{H}_2\text{O}_2$ reduction wave was much higher than that calculated from the concentration of dissolved oxygen, showing that O_2^- was also generated by chemical means in the medium.

3.7. Interaction with Ferricyanide

The potentiometric response of the FeS stick to $\text{K}_3[\text{Fe}(\text{CN})_6]$ is shown in Fig. 17. The variation is linear with a slope of 63 mV.

In order to understand the nature of the chemical reaction that takes place between FeS and ferricyanide, the absorption spectra of the solution were recorded. The absorption spectrum of $\text{K}_3[\text{Fe}(\text{CN})_6]$ (Fig. 18) shows three high-intensity bands at 260, 304, and 425 nm, which are to be attributed to ligand metal charge transfer transitions involving the t_{2g} "metal orbitals." Ligand field bands appear as shoulders at 396, 322, and 282 nm in agreement with the literature data (22, 23).

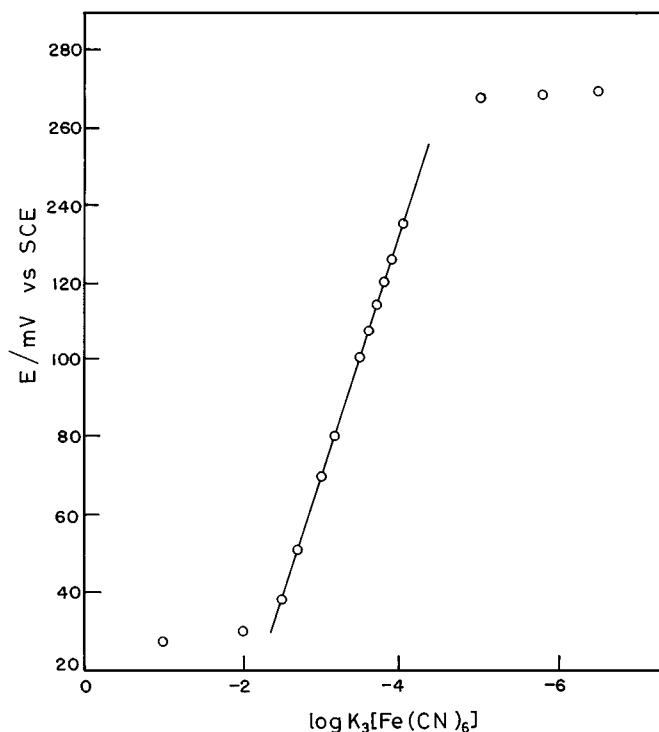


FIG. 17. Potentiometric response of the commercial FeS stick to ferricyanide.

A solution of potassium ferricyanide that has been shaken with FeS shows certain changes in the spectral band (Fig. 18). The decrease of absorbance at 425 and 304 nm, the increase at 260 nm, and the isobestic point at 283 nm indicate the transformation of $\text{K}_3[\text{Fe}(\text{CN})_6]$ into a different chemical species.

The ferricyanide ion $[\text{Fe}(\text{CN})_6]^{4-}$ shows two moderately weak band at 320 and 270 nm. The band can be attributed to the spin-allowed ligand field transition (22).

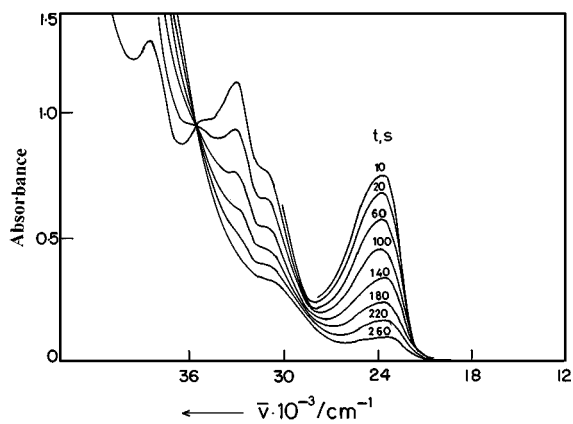
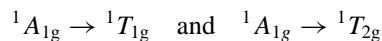


FIG. 18. UV spectrum of ferricyanide solution that has been contacted with a commercial FeS stick.

At longer wavelengths (422 nm) there is a very low absorption assigned to the $^1A_{1g} \rightarrow ^3T_{1g}$ spin forbidden ligand field transition (23).

A possibility that can be foreseen is the conversion of ferricyanide to ferrocyanide. However, it is important to check whether this reaction was reversible, i.e., to exclude side reactions such as (e.g.) exchange of the CN^- ligand for H_2O or H_2O_2 (a product of O_2^-).

In fact, the system appears to be a reversible one, at least within the limits of sensitivity of the spectrophotometric method as inferred from the following data (Fig. 18).

1. The isobestic point is persistent.

2. There is equivalence of the intensity increase at 260 nm to the intensity decrease at 425 nm.

3.8. Detection of Sulfur on the Electrode Surface

In most of the studies carried out in the present work, sulfur was invariably an initial product on the FeS surface. This was observed by UV examination of the chloroform extract of the product formed on FeS, during the initial 5-min contact with reactive species. Sulfur exhibits a characteristic UV spectrum with a λ_{max} of 213 nm (24).

4. CONCLUSION

In the present work electroanalytical techniques have been employed to study the interfacial properties of FeS (commercial iron sulfide stick) in various salt/complexing media. The results have indicated that, except nitrate, all other ions are active toward FeS. Cyclic voltammetric data have confirmed that borate buffer, which is generally used as an inert medium for the froth flotation of sulfide minerals, is electrochemically active toward FeS. A phosphate solution that has been equilibrated with FeS gives fluorescent emission. Ferricyanide appears to be converted into ferrocyanide by FeS. Further, FeS is seen to stabilize reactive oxygen intermediates during polarographic reduction of oxygen to hydrogen peroxide. Overall, several interesting results have been obtained in the present study which have aided newer knowledge of the chemistry and electrochemistry of the commercial iron sulfide stick.

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