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Kinetics of sulfur transfer from H_2S to $Fe_{1-x}S$

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The rate of sulfur transfer across the gas/solid interface involving $H_2S(g)$ and $Fe_{1-x}S$ surface has been investigated using resistance relaxation measurements at 600°C. The rate of the oxidation reaction incorporating sulfur into $Fe_{1-x}S$ has been found to decrease with sulfur activity (a_S) in the sample as $(a_S)^{-2/3}$, while the rate of the reduction reaction corresponding to sulfur loss is found to increase with the sulfur activity as $(a_S)^{1/3}$. The kinetic finding has been combined with the appropriate defect models for FeS to identify the rate limiting step for the sulfur transfer reaction from H_2S to FeS. Accordingly, the rate limiting step has been identified to be: $H_2S(g) + 2e^- \rightleftharpoons S^{2-}(ad) + H_2(g)$.

Keywords: iron sulfide, resistance relaxation, reaction pathways, non-stoichiometry, rate limiting step, sulfur activity

1. Introduction

In the corrosion of iron by sulfur-containing species, both ionic transport through a sulfide corrosion product barrier and surface dissociation of molecules at the external sulfide surface have been identified as the rate limiting steps [1]. In certain regimes of temperature and environmental chemistry, the diffusion step controls the overall kinetics whereas in other regimes, the surface dissociation reaction, leading to sulfur transfer at the interface in question, is the slow process and controls the overall kinetics. While some studies on the dissociation of sulfur-containing molecules on iron surface have been carried out [2,3], studies on sulfide surfaces in general and iron sulfide in particular have attracted little attention. To this end, our work on the kinetics of sulfur transfer from H_2S across non-stoichiometric surfaces such as $Cu_{2-x}S$ and $Ag_{2+x}S$, using resistance relaxation technique, has been reported [4,5]. The investigation on an iron sulfide surface is reported here.

Iron sulfide has been identified as the corrosion product in the petrochemical industry where carbon steel is widely used as the material of construction in sulfur-containing environments. The kinetics of sulfur transfer from sulfur species to an iron sulfide surface is both scientifically challenging and technologically interesting. Worrell and Kaplan [6] pointed out the relevance of H_2S dissociation kinetics on FeS surfaces and suggested the dissociation of $H_2S(ad)$ and HS(ad) on the iron sulfide surface as the possible rate limiting steps and derived rate equations. Furthermore, these authors alternatively derived the rate equations by taking into consideration the atomic point defects in iron sulfide and electronic species such as electrons. The rate equations in the two cases with and without the incorporation of electronic species were not quite the same but were similar. However, due to a lack of experimental data, Worrell and Kaplan [6] could not carry out a detailed kinetic analysis.

The purpose of the present work is to measure the kinetics of sulfur transfer at the FeS/H_2S interface and to identify the prevailing reaction path. Following the identification of the rate limiting step, rate equations governing the rates of sulfur transfer have been derived.

2. Principle of resistance relaxation technique

The principle of the resistance relaxation technique has been reviewed in our previous study on the kinetics of sulfur transfer at gas/solid interfaces involving $(H_2S + H_2)$ and digenite [4] and $(H_2S + H_2)$ and silver sulfide [5]. The technique consists of measuring changes in the resistivity of a thin sulfide sample upon rapidly changing the sulfur activity at the sulfide surface to a new value. The thickness of the iron sulfide sample is selected such that diffusional processes within the bulk sulfide are very rapid as compared with molecular dissociation at the surface. When this condition is met, the relaxation curve can be analyzed to obtain the rate of molecular dissociation reaction which is equal to the rate of sulfur transfer at the $Fe_{1-x}S$/gas interface.

The above technique can be applied to compounds whose conductivity is a sensitive function of the metal to non-metal ratio. In iron sulfide, for example, the electrical conductivity is increased [6] by increasing sulfur content and this conductivity change is a measure of the sulfur transfer into the sulfide lattice.

The measured conductivity change can be related to an actual sulfur transfer rate across the gas/sulfide interface as follows. If n_{Fe} and n_s are the number of iron and

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sulfur atoms in the sample of $Fe_{1-x}S$, then one can write,

$$\frac{n_s}{n_{Fe}} = \frac{1}{r}\,, \tag{1}$$

where $r = 1 - x$ and x is the iron deficit in $Fe_{1-x}S$.

$$\frac{dn_s}{dt} = \frac{n_{Fe}}{r^2}\frac{dx}{dt}\,. \tag{2}$$

Since x is a function of the sulfur activity, a_S and the electrical conductivity σ,

$$\frac{dn_s}{dt} = \frac{n_{Fe}}{r^2}\frac{dx}{da_S}\frac{da_S}{d\sigma}\frac{d\sigma}{dt}\,. \tag{3}$$

The reaction rate $|\nu|$ is given by $A^{-1}dn_s/dt$ mol cm^{-2} s^{-1}, where A is the reaction area. To obtain a reaction rate, therefore, all the differential quotients on the right hand side of eq. (3) must be known. Of these, $d\sigma/dt$ and $da_S/d\sigma$ can be computed from resistance relaxation data. To obtain dx/da_S, the variation of x with the sulfur activity must be separately established.

3. Experimental procedure

The experimental procedure for the investigations consisted of two parts; first preparing the sulfide sample and second measuring the resistivity of the sulfide in the H_2S/H_2 environment. Starting from an iron foil (0.0025 cm), having a purity of 99.999%, four gold wire contacts were spot-welded on to the iron foil. After annealing in hydrogen for several hours, the iron foil was sulfidized in an H_2S/H_2 atmosphere. The completion of sulfidation was inferred from the attainment of a steady state resistivity. The relaxation measurements were carried out at 600°C. The details of the experimental set-up have been reported elsewhere [4,5]. The resistivity of the sulfide sample was measured by the van der Pauw method [7] which was developed for flat samples with an arbitrary shape.

In the experimental runs to obtain calibration and relaxation curves, the H_2S/H_2 ratio was varied from 1/99 to 1/2. The sulfur activities corresponding to these ratios are within the thermodynamic stability regime of iron sulfide ($Fe_{1-x}S$) at 600°C. The experimental flow rates at 600°C were $\sim$ 75–100 cm^3 min^{-1} (12–18 cm s^{-1}) over a $Fe_{1-x}S$ foil having a surface area of approximately 1.25 cm^2. The thickness of the $Fe_{1-x}S$ foil was measured after each experiment. The relaxation curves in the H_2S/H_2 gas mixture represent a net rate which is a balance of the forward rate (sulfur gain) and the backward rate (sulfur loss). In order to obtain relaxation curves for the loss of sulfur (backward rate), H_2 gas alone was used in the gas stream. After the experiment, the sulfide foil was characterized by X-ray diffraction (using Cu K_α radiation) and scanning electron microscopy.

4. Results

4.1. Relationship between conductivity and equilibrium activity of sulfur

At any point of time, the instantaneous activity of sulfur in the iron sulfide sample can be calculated provided the conductivity–sulfur activity relationship of the sulfide sample is known. Therefore, a calibration curve relating the steady state conductivity of the $Fe_{1-x}S$ foil to the equilibrium sulfur activity (a_S) is first established (figure 1). The sulfur activity in figure 1 and elsewhere is defined with reference to diatomic sulfur gas at 1 atm pressure as the standard state.

4.2. Relaxation measurements in H_2S/H_2 mixtures

For measurements of net reaction rates, the sulfide foil was first equilibrated at a specific H_2S/H_2 ratio. The sulfur activity over the sample was then instantaneously changed by introducing another gas mixture with a different ratio. The resulting change in the resistance was measured until the sulfide foil reached equilibrium with the new ratio of H_2S to H_2. From experience and calculations it has been determined that the new gas mixture composition is established over the sample in about 30–60 s while the relaxation time for equilibration of the foil varies from 10 to 20 min. Figure 2 shows a number of relaxation curves in a stepwise fashion as the H_2S/H_2 ratio is changed from 1/99 to 1/4 . At any specific point in a relaxation curve, the instantaneous sulfur activity in the sulfide can be obtained using the calibration curve in figure 1.

To obtain values for the net reaction rate from the relaxation curves, the variation of x (metal deficit) with sulfur activity must also be known (eq. (3)). This relationship is obtained from the work of Fryt, Bhide, Smeltzer and Kirkaldy [8]. A plot of the net reaction rate

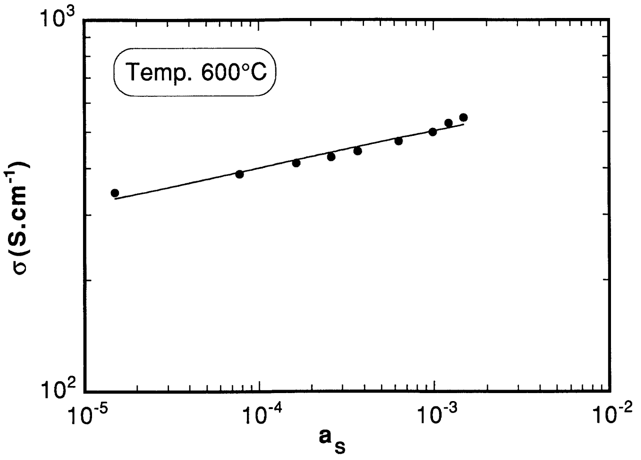

Figure 1. Calibration curve relating the electrical conductivity to the equilibrium sulfur activity of the sulfide sample.

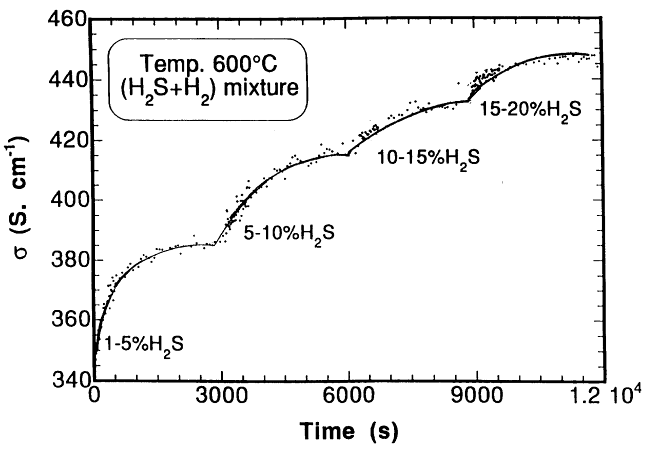

Figure 2. Relaxation curves when the gas mixture is changed from 1–5%, 5–10%, 10–15% and 15–20% H_2S in H_2.

obtained in this manner is shown in figure 3. Figure 4 shows a relaxation curve obtained in pure H_2.

X-ray diffraction analysis of the sulfide reveals the presence of the room temperature phase of iron sulfide (pyrrhotite) as shown in figure 5. Figure 6 shows the typical microstructure of the iron sulfide sample. The morphology of the sulfide reveals a set of two crystal layers divided by a boundary in the middle. This morphology is a consequence of the sulfidation mechanism of iron which involves outward migration of iron ions through the sulfide film. The thickness of the foil is found to be approximately three times that of the starting foil, and is used for computing resistivity by the van der Pauw method [7].

5. Discussion

Diffusion data in iron sulfide have been reported by Fryt, Smeltzer and Kirkaldy [9] and a value of $\sim 4 \times 10^{-7}$ cm^2 s^{-1} has been determined for the chemical diffusion coefficient $\tilde{D}$ at ~ 600°C. An estimate of the time τ required for diffusion of iron through a thickness of 75 μm (sulfide foil) is given by

$$\tau = (37.5 \times 10^{-4})^2/\tilde{D} \approx 35\ \mathrm{s}\,. \tag{4}$$

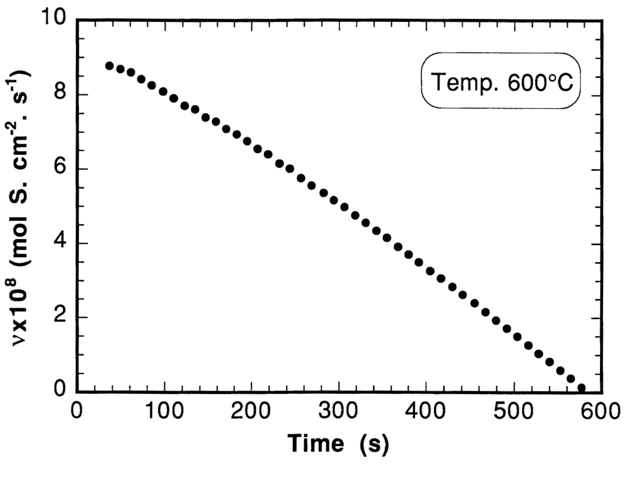

Figure 3. Rate of the net reaction when the concentration of H_2S in the gas mixture is changed from 1 to 50%.

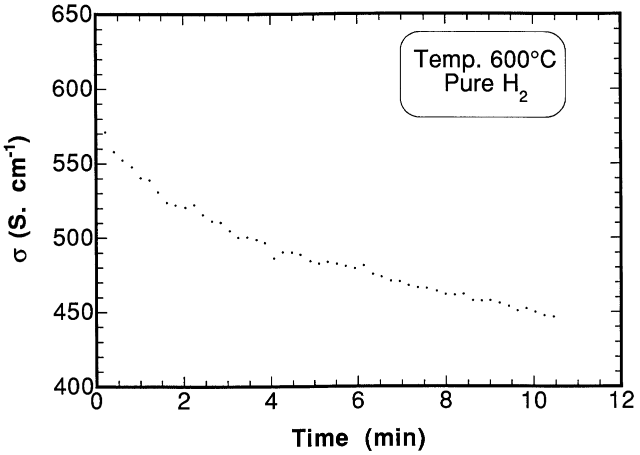

Figure 4. Relaxation curve at 600°C in pure H_2.

As mentioned earlier, the time required for resistance relaxation varies from 10 to 20 min and therefore it can be concluded that the kinetic measurements correspond to the surface reaction without a significant contribution from diffusion.

In considering the rate of the overall sulfur transfer reaction described by

$$H_2S(g) \rightleftharpoons H_2(g) + S \quad (\text{dissolved in } Fe_{1-x}S) \tag{5}$$

sulfur species of different valence states [10], represented by S^{m-} may be proposed to occur as intermediates on the sulfide surface. Depending upon the value of m, many reactions can occur in parallel as represented by the general reaction:

$$H_2S(g) + me' \rightleftharpoons S^{m-}(\mathrm{ad}) + H_2(g) \tag{6}$$

where e′ denotes an electron. Hydrogen molecules have been considered to be involved in the reaction since the experimental rate of the backward reaction has been found to be proportional to the first power of the H_2 partial pressure, as will be shown later.

As stated earlier, depending upon the value of m, different types of sulfur species may be available on the surface and the rate of overall reaction (eq. (6)) is given by

$$\frac{dn_s}{dt} = \sum_{m=0}^{m=2} k_f^{(m)} p_{H_2S} a_e^m - k_b^{(m)} \Gamma_{S^{m-}} p_{H_2}\,, \tag{7}$$

where $k_f^{(m)}$ and $k_b^{(m)}$ are the rate constants for the forward and the backward reactions respectively and m represents the valence state of the adsorbed species. In order to solve eq. (7), the unknown parameters such as activity of electrons (a_e) and concentration of adsorbed species S^{m-} ($\Gamma_{S^{m-}}$) must be eliminated. The equilibration of adsorbed species with the bulk sulfide is described by the

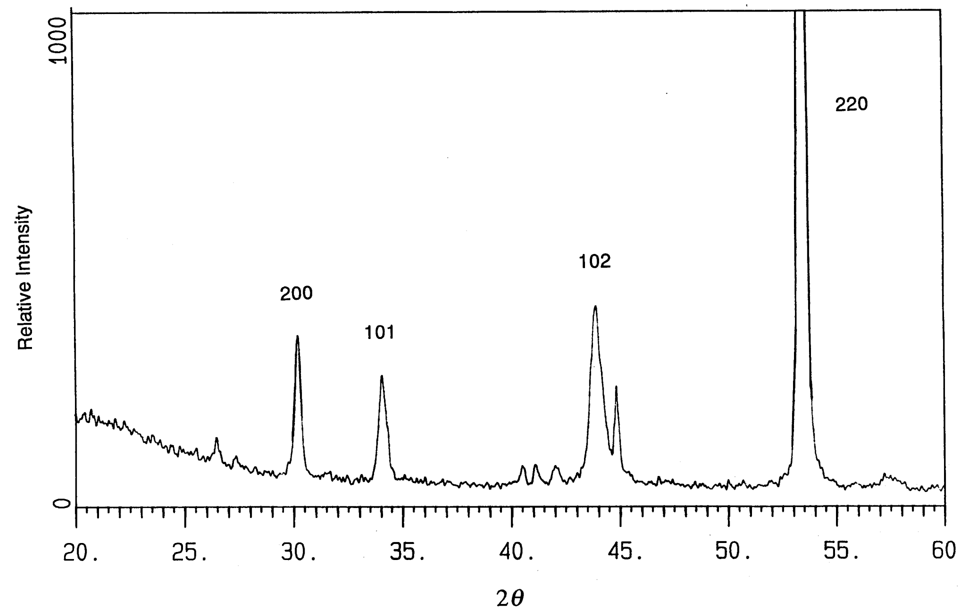

Figure 5. X-ray diffraction scan (Cu K_α radiation) of the iron sulfide sample at room temperature, showing characteristic peaks of $Fe_{1-x}S$.

following sequential reactions. Firstly, the adsorbed species transfer their charge as per reaction,

$$S^{m-}(ad) \rightleftharpoons S(ad) + me' \tag{8}$$

Secondly, the adsorbed species take a position in the lattice by creating (or eliminating) an appropriate lattice defect,

$$S(ad) \rightleftharpoons V_{Fe} + S_S \tag{9}$$

Finally, lattice defects equilibrate with other defects in the lattice,

$$V_{Fe} + 2e' \rightleftharpoons V''_{Fe} \tag{10}$$

The defects are represented by the Kröger–Vink notation. In Köger–Vink notation [11], charges on defects are determined relative to the perfect lattice as opposed to the notation of actual charges on the defect species. From eqs. (8)–(10), the value of $\Gamma_{S^{m-}}$ can be calculated as

$$\begin{aligned}\Gamma_{S^{m-}} &= K_8\Gamma_S a_e^m = K_8K_9[V_{Fe}]a_e^m \\ &= K_8K_9K_{10}[V''_{Fe}]a_e^{m-2},\end{aligned} \tag{11}$$

where K_8, K_9 and K_{10} are equilibrium constants for reactions (8)–(10). If we assume that the majority of charged defects in $Fe_{1-x}S$ are V''_{Fe}, then the approximate electroneutrality condition can be written as

$$2[V''_{Fe}] \approx p \propto n^{-1} \propto a_e^{-1}, \tag{12}$$

$$\frac{dn_s}{dt} = \sum_{m=0}^{m=2} k_f^{(m)} p_{H_2S} a_e^m - k_b^{(m)} a_e^{m-3} p_{H_2}, \tag{13}$$

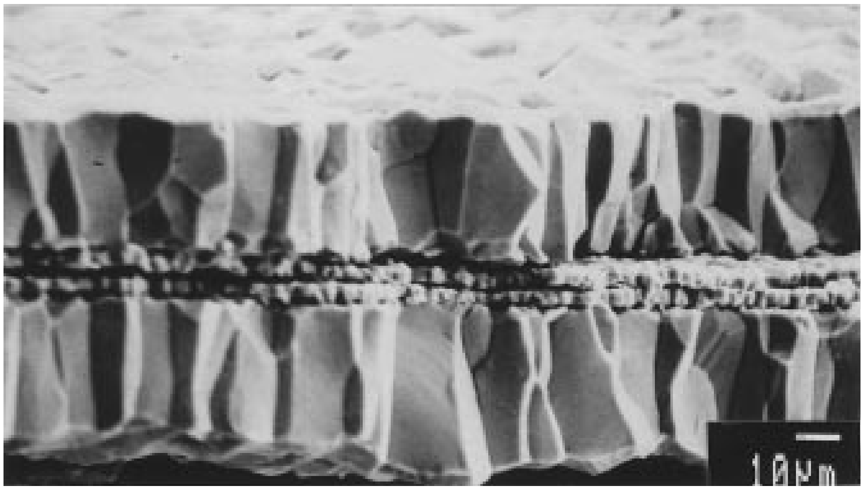

Figure 6. Scanning electron micrograph of the sulfide after the experiment.

where the concentration of electrons is expressed as n.

Eq. (13), is the final rate equation which represents the most general case of the dissociation of H_2S on an $Fe_{1-x}S$ surface. The activity of electrons as a function of sulfur activity can be expressed as

$$a_e \propto (a_S)^{1/\alpha}, \tag{14}$$

where α can take different values depending upon the internal defect structure in iron sulfide. Using eq. (14), eq. (13) can be rewritten as,

$$\frac{dn_S}{dt} = \sum_{m=0}^{m=2} k_f^{(m)} p_{H_2S} a_S^{m/\alpha} - k_b^{(m)} a_S^{(m-3)/\alpha} p_{H_2}. \tag{15}$$

Based on experimental results for the net reaction rate (figure 3), a value for m cannot be obtained. In an attempt to define the value for m, the rate of the backward (reduction) reaction was measured separately.

5.1. Kinetics of backward reaction when $p_{H_2} = p(total)$ and $p_{H_2S} = 0$

The backward reaction rate can be separately measured by having only H_2 in the reaction stream. The experimental results are shown in figures 7 and 8. Furthermore, the hydrogen partial pressure can be varied by dilution with argon. The backward rate is seen to be proportional to the partial pressure of H_2 (figure 8) and to $a_S^{(0.33\pm0.04)}$ (figure 7). By setting $p_{H_2S} = 0$, eq. (15) can be written as

$$\left|\frac{dn_S}{dt}\right| = \sum_{m=0}^{m=2} k_b^{(m)} a_S^{(m-3)/\alpha} p_{H_2}. \tag{16}$$

If one of the reactions corresponding to $m = 0$, 1 or 2 prevails, the slopes of the log–log plots between rate and a_S will have a value as follows:

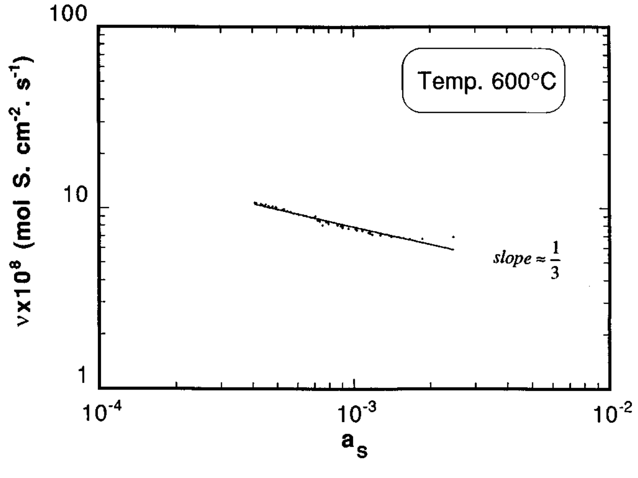

Figure 7. Rate of sulfur loss in pure H_2.

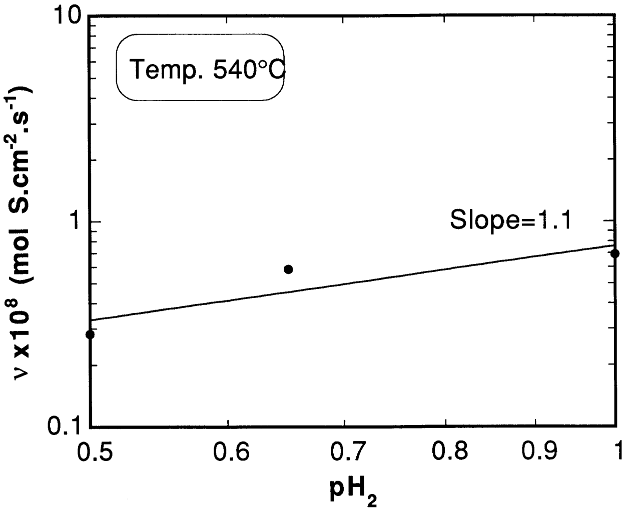

Figure 8. Rate of sulfur loss as a function of p_{H_2} in Ar and H_2 gas mixtures.

$$\frac{d\log(\text{rate})}{d\log a_S} = -\frac{3}{\alpha}, -\frac{2}{\alpha}, -\frac{1}{\alpha}. \tag{17}$$

Worrell and Kaplan [6] for their kinetic analysis on the dissociation of H_2S on iron sulfide had assumed α to be -2.5. From the simple defect model mentioned above, the value of α works out to be -3. Using $\alpha = -3$, the slope of log(rate) as a function of log(a_S) is expected to be 1, 0.67 or 0.33 depending upon whether the value of m is 0, 1 or 2 respectively. The rate of the backward reaction as a function of sulfur activity is plotted in figure 7 and the slope of the backward reaction rate curve is (0.33 ± 0.04) which indicates that the value of m is 2. Thus, based on the slope of the backward reaction rate as a function of sulfur activity a_S, the rate limiting step then can be identified as

$$H_2(g) + S^{2-}(ad) \rightleftharpoons H_2S(g) + 2e' \tag{18}$$

It can thus be stated that the rate of sulfur transfer in iron sulfide at 600°C is controlled by the species S^{2-}(ad). The kinetics of the backward reaction alone is given by

$$\nu_b = 0.85 \times 10^{-8} (a_S)^{1/3} p_{H_2} \text{ mol S cm}^{-2} \text{ s}^{-1} \tag{19}$$

For reversible reactions, the rate controlling step will be the same for the forward and the backward reactions. However, this can also be established separately as described below.

5.2. Kinetics of forward reaction from net rate and backward rate

The rate of the forward reaction can be obtained by addition of the backward rate to the net reaction rate. The calculated forward reaction rate by this method, is shown by the uppermost line in figure 9 and is given by

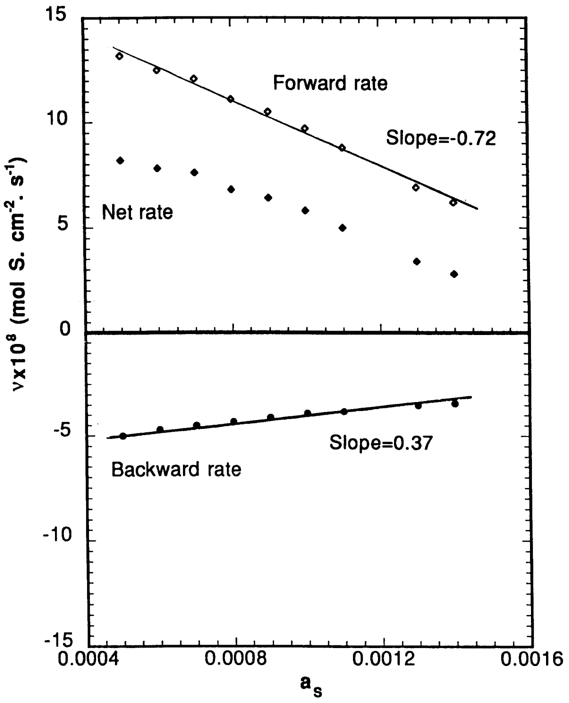

Figure 9. Summary of the reaction kinetics at 600°C.

$$\frac{dn_S}{dt} = \sum_{m=0}^{m=2} k_f^{(m)} p_{H_2S} a_S^{m/\alpha} . \tag{20}$$

Choosing the value of α and m that we used to satisfy eq. (17), the forward rate equation becomes:

$$\frac{dn_S}{dt} = k_f^{(2)} p_{H_2S} a_S^{-2/3} . \tag{21}$$

The rate curve for the forward reaction derived from net rate and backward rate shows a slope $-(0.66 \pm 0.06)$, in reasonable agreement with $-2/3$, expected from eq. (21). Hence, the rate of the forward reaction is given by

$$\nu_f = 0.12 \times 10^{-8} (a_S)^{-2/3} p_{H_2S} . \tag{22}$$

5.3. Overall rate equation

It is evident from the above that the analysis to identify the rate limiting step utilizes the experimentally observed sulfur activity and p_{H_2} dependence in conjunction with the equilibria involving various bulk and surface species. While the rate equation for the backward reaction is developed by appropriately varying the experimental parameters, the rate equation for the forward reaction is derived from rates of the net reaction and the backward reaction. The overall rate for sulfur transfer expressed in mol cm^{-2} s^{-1} is given by

$$\nu = (1.2 \pm 0.15) \times 10^{-9} (a_S)^{-2/3} p_{H_2S} - (0.85 \pm 0.1) \times 10^{-8} (a_S)^{1/3} p_{H_2} \quad \text{mol S cm}^{-2}\,\text{s}^{-1} . \tag{23}$$

6. Summary

The kinetics of sulfur transfer from H_2S to $Fe_{1-x}S$ at 600°C has been established. The rate limiting step is shown to involve S^{2-}(ad) species as the intermediary on the sulfide surface. The rate of the forward reaction is shown to vary as $a_S^{-2/3}$ while that of the backward reaction follows $a_S^{1/3}$ dependence and is proportional to the first power of hydrogen partial pressure. The results are consistent with the assumed defect model for $Fe_{1-x}S$.

References

[1] W.L. Worrell and E.T. Turkdogan, Trans. TMS-AMIE. 242 (1968) 1673.
[2] H.G. Grabke, Mater. Eng. 42 (1980) 91.
[3] J. Oudar, Mater. Eng. 42 (1980) 101.
[4] V.K. Pareek, T.A. Ramanarayanan, J.D. Mumford and A. Ozekcin, Catal. Lett. 27 (1994) 11.
[5] V.K. Pareek, T.A. Ramanarayanan and J.D. Mumford, J. Electrochem. Soc. 142 (1995) 1784.
[6] W.L. Worrell and H.I. Kaplan, in: *Heterogeneous Kinetics at Elevated Temperatures*, eds., G.R. Belton and W.L. Worrell (Plenum Press, New York, 1970) p. 113.
[7] L.J. van der Pauw, Philips Research Reports 13 (1958) 1.
[8] E.M. Fryt, V.S. Bhide, W.W. Smeltzer and J.S. Kirkaldy, J. Electrochem. Soc. 126 (1979) 683.
[9] E.M. Fryt, W.W. Smeltzer and J.S. Kirkaldy, J. Electrochem. Soc. 126 (1979) 673.
[10] H. Kobayashi and C. Wagner, J. Chem. Phys. 26 (1957) 1609.
[11] F.A. Kröger, *The Chemistry of Imperfect Crystals* (North-Holland/Wiley, Amsterdam/New York, 1964).