Catalysis Letters 27 (1994) 11–25

Kinetics of sulfur transfer from H_2S to digenite ($Cu_{2-x}S$) at 500°C

V.K. Pareek, T.A. Ramanarayanan, J.D. Mumford and A. Ozeckcin

Exxon Research & Engineering Company, Annandale, NJ 08801, USA

Received 3 November 1993; accepted 29 April 1994

The kinetics of sulfur transfer from H_2S to cuprous sulfide (digenite) at 500°C has been established by the resistance relaxation technique. The resistance measurements have been carried out by the van der Pauw method, which uses a four probe configuration. The rate of the forward reaction decreases with the increase in the activity of sulfur in the sulfide (rate $\propto a_S^{-0.55}$) while the rate of the backward reaction is found to be nearly independent of the sulfur activity. Based on these results, the rate limiting step for sulfur transfer reaction to digenite is shown to be: $H_2S(g) + 2e^- = S^{2-}(ad) + H_2(g)$.

Keywords: cuprous sulfide; resistance relaxation; reaction pathways; non-stoichiometry; rate limiting step; sulfur activity

1. Introduction

The mechanism and kinetics of surface reactions involving the dissociation of molecules on solid surfaces are of importance in many technologically important disciplines such as corrosion, catalysis and extractive metallurgy. In many instances of molecular dissociation processes on solid surfaces, the reaction rate can be attributed to one rate-limiting step as shown by a few studies on metal [1], oxide [2] and sulfide [3] surfaces using different experimental techniques such as isotope exchange [4], electrochemical [3] and resistance relaxation [5–7]. In other instances, the reaction pathways are necessarily more involved and the identification of unique pathway is difficult.

The focus of the present work is the study of the dissociation of the H_2S molecules and the transfer of sulfur to non-stoichiometric sulfide surfaces. Cuprous sulfide, digenite, has been selected as a model sulfide surface for study. The understanding of corrosion processes in metal–sulfur interactions has provided the driving force for this study. In the corrosion of metals 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. In certain regimes of temperature and environmental chemistry, the diffusion step controls the overall kinetics, whereas in other regimes the interface reaction is the slow process. Transport processes through non-stoichiometric sulfide films have been reasonably established at high temperatures (>600°C), but only limited information is available at the intermediate and low temperatures. Surface dissociation kinetics of sulfur containing molecules on sulfide surfaces is much less studied and therefore presents an important area of research challenge. The information generated would be critical in providing a quantification of the corrosion processes based on atomistic phenomena. At the same time the understanding of surface reaction kinetics can spill over into other areas such as catalysis.

Kobayashi and Wagner [3] made early attempts to study the dissociation kinetics of H_2S on the $Ag_{2+x}S$ surface by the use of potentiostatic electrochemical techniques. Bechtold [8] as well as Roy and Schmalzried [9] also investigated the same system. These three studies are in disagreement on the nature of the rate limiting step, thus demonstrating the complexity of the study of such interfacial kinetics. There is one study by Worrell and Kaplan [5] on the dissociation of the H_2S molecule on an iron sulfide surface, but a detailed kinetic analysis is lacking in this study. Kobayashi and Wagner [3] also undertook a study of the dissociation of H_2S on cuprous sulfide, but the data could be analyzed only after making some stringent assumptions. All the above results point up the need for a more rigorous study on the dissociation of sulfur containing molecules on sulfide surfaces. The present investigation is designed to address this challenge. Accordingly, the digenite phase of cuprous sulfide, stable above 435°C, has been selected as the first surface for investigation. The phase diagram for the Cu–S system [10] is shown in fig. 1. The digenite phase is seen to exhibit a large non-stoichiometry range from Cu_2S to $Cu_{1.75}S$.

2. Principle of resistance relaxation technique

The resistance relaxation technique has been used for experiments reported in the present study. Many researchers [2,5–7] have described this technique for the study of phase boundary reactions. The technique consists in 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 principle of this method is shown in fig. 2. The top plot indicates a step change in the H_2S/H_2 ratio in the gas phase at time $t = 0$. The bottom graph shows the change in the electrical conductivity of the sample as a function of time resulting from the change in the H_2S/H_2 ratio. A steady state conductivity is finally attained corresponding to the sulfur activity in the new H_2S/H_2 mixture. The thickness of the 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 surface reaction.

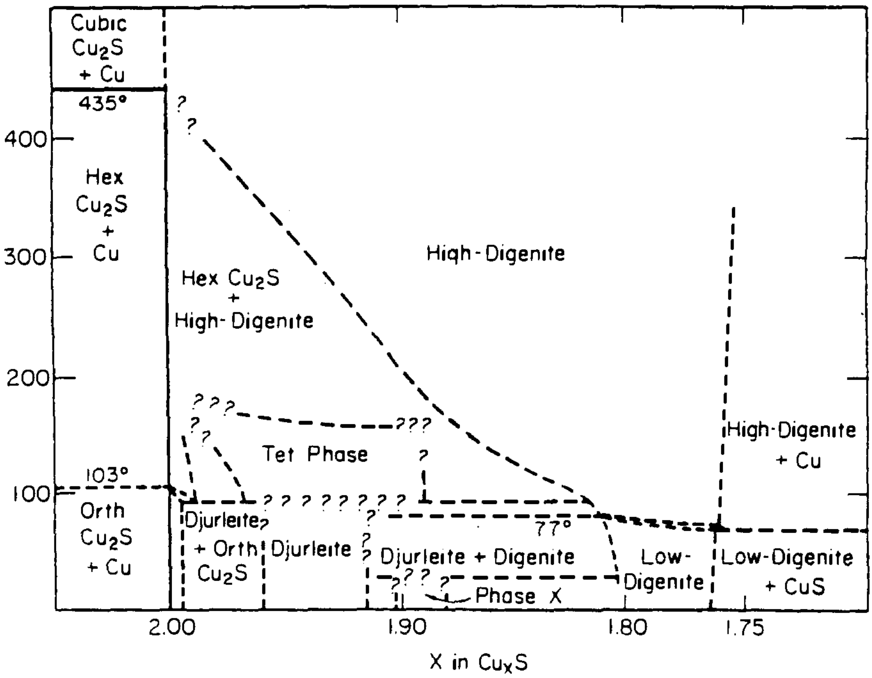

Fig. 1. Phase diagram of Cu–S system.

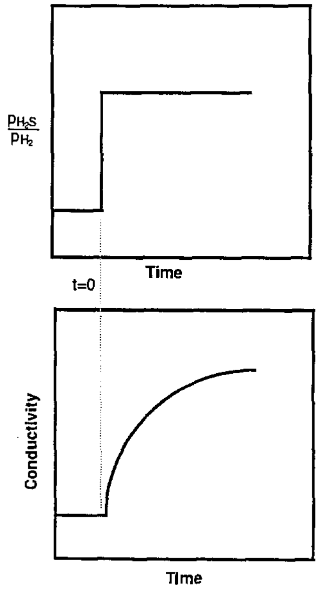

Fig. 2. Principle of the resistance relaxation method.

The above technique can be applied to compounds whose conductivity is a sensitive function of the metal to non-metal ratio. In cuprous sulfide, for example, the incorporation of sulfur into the lattice leads to the formation of negatively charged copper vacancies which are balanced by the creation of electron holes to maintain electrical neutrality. The resulting conductivity change is thus a measure of sulfur incorporation into the sulfide lattice. Fig. 3a illustrates the sulfur transfer process across the $Cu_{2-x}S$/gas interface and creation of copper vacancies and holes in the sulfide sample.

The measured conductivity change can be related to an actual sulfur transfer rate across the gas/sulfide interface as follows. If n_{Cu} and n_S are the number of copper and sulfur atoms in the sample of $Cu_{2-x}S$, then one can write

$$\frac{n_S}{n_{Cu}} = \frac{1}{2-x} . \tag{1}$$

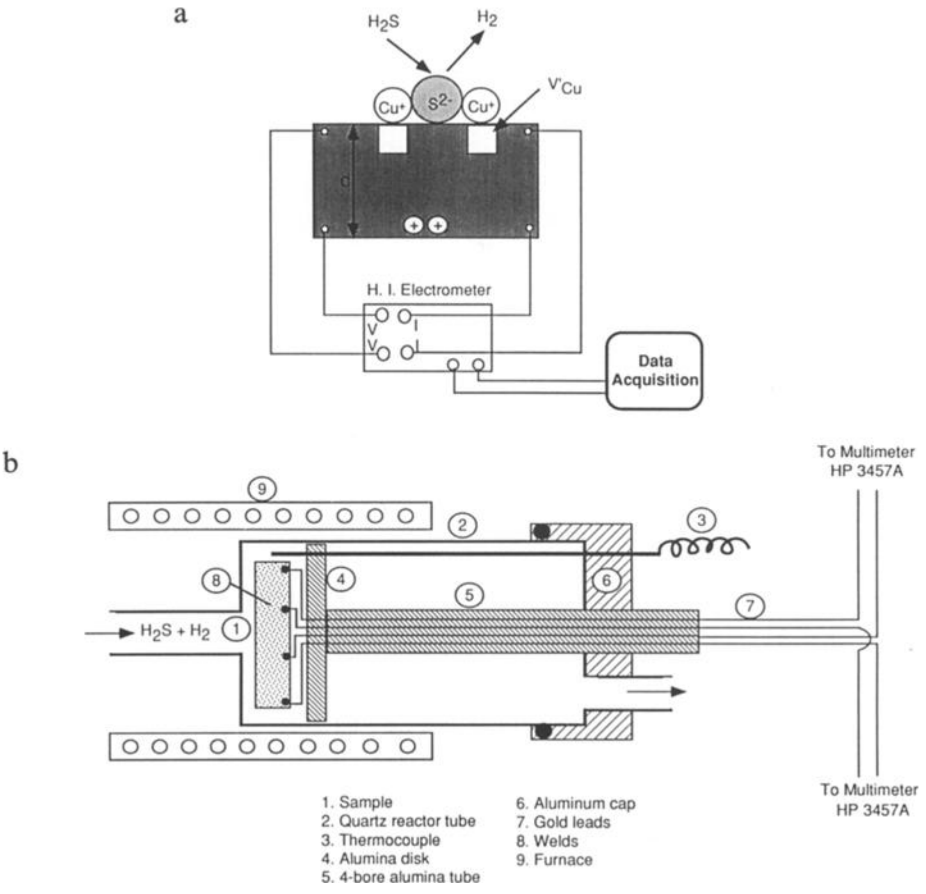

Fig. 3. (a) Schematic diagram showing incorporation of sulfur into $Cu_{2-x}S$. (b) Experimental arrangement for the resistance relaxation measurements.

If sulfur is added to or removed from the sulfide foil, then the rate of change in the number of moles of sulfur is given by

$$\frac{dn_S}{dt} = \frac{n_{Cu}}{(2-x)^2}\frac{dx}{dt} . \tag{2}$$

The rate of sulfur transfer, in accordance with eq. (2), would be proportional to the quantity dx/dt, which can be further broken into measurable parameters as shown below. Since x is a function of the activity of sulfur, a_S, and the electrical conductivity σ is a function of a_S, it can be shown that

$$\frac{dn_S}{dt} = \frac{n_{Cu}}{(2-x)^2}\left(\frac{dx}{da_S}\right)\left(\frac{da_S}{d\sigma}\right)\left(\frac{d\sigma}{dt}\right) . \tag{3}$$

The reaction rate v in mol cm^{-2} s^{-1} is given by $A^{-1}\, dn_S/dt$ mol/cm^2 s, 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 a copper foil (0.0025 cm), having a purity of 99.999%, four gold wire contacts were spot-welded on to the copper foil. The copper foil was held in place by the gold leads as shown in fig. 3b. The four Au leads passed through a 4-bore alumina tube and were connected to a Hewlett Packard high impedance electrometer designed for four probe resistance measurement. An alumina desk was used in the quartz reactor tube to minimize the time required to change from one gas mixture to another by decreasing the effective volume of the gas mixture. A tubular furnace with a 5 cm constant temperature zone was used for the experiment. After a hydrogen anneal at the reaction temperature (500°C) for several hours, the copper foil was sulfidized in an H_2S/H_2 atmosphere. The completion of sulfidation was inferred from the attainment of a steady state resistivity. A schematic arrangement of the experimental set-up is shown in fig. 3b.

The resistivity of the sulfide sample was measured by the van der Pauw method [11] which was developed for flat samples with an arbitrary shape. Four contacts A, B, C, D are made on the sample surface. First, A and B are used as current contacts and the voltage across C and D is measured to compute resistance R_1. In the next measurement resistance R_2 is computed by using B and C as current contacts and measuring the voltage across D and A. The resistivity ρ is computed from the following relationship:

$$\rho = \frac{\pi d}{\ln 2} \frac{R_1 + R_2}{2} f\left(\frac{R_1}{R_2}\right), \tag{4}$$

where f is a function of ratio of R_1 and R_2 only and satisfies the following relationship:

$$\frac{R_1 - R_2}{R_1 + R_2} = f \cosh^{-1}\left(\frac{\exp(\ln 2/f)}{2}\right). \tag{5}$$

Eq. (5) can be simplified for determining values of f, using approximations indicated in ref. [11].

In the experimental runs to obtain calibration and relaxation curves, the H_2S/H_2 ratio was varied from 1/100 to 1/4. The sulfur activities corresponding to these ratios are within the thermodynamic stability regime of cuprous sulfide (digenite). The experimental flow rates at 500°C were $\sim 100\ \mathrm{cm^3/min}$ (17–18 cm/s) over a $Cu_{2-x}S$ foil having a surface area of approximately 1.25 $\mathrm{cm^2}$. The thickness of the $Cu_{2-x}S$ 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) from the sample. In order to obtain relaxation curves for the loss of sulfur (backward rate), H_2 gas alone was used in the gas stream and likewise H_2S alone was used for studying the rate of the forward reaction. After the experiment, the sulfide foil was characterized by X-ray diffraction 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 copper 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 $Cu_{2-x}S$ foil to the equilibrium sulfur activity (a_S) is first established (fig. 4). This curve shows some scatter in the conductivity values from experiment to experiment; therefore, the data from three experiments have been assembled on the same plot and the best fit curve is used as a calibration chart. A variable which strongly influences the conductivity is the metal deficit (x) in the copper sulfide ($Cu_{2-x}S$).

An examination of the Cu–S phase diagram (fig. 1), shows that the range of non-stoichiometry of digenite varies from Cu_2S to $Cu_{1.73}S$ at $\sim$ 500°C. Many investigators have reported the conductivity of cuprous sulfide, but there is poor agreement among different investigators. This is not surprising when one takes into account the fact that the conductivity of the sulfide is critically dependent on the non-stoichiometry which in turn is dependent on the thermodynamic activity of sulfur.

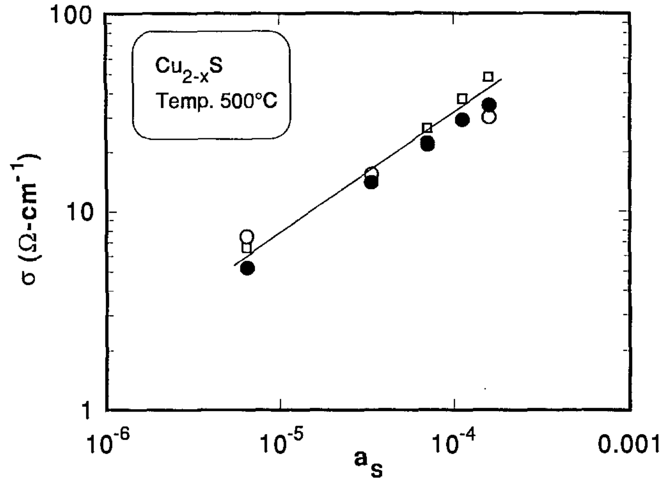

Fig. 4. Calibration curve relating the electrical conductivity to the equilibrium sulfur activity of the sulfide sample.

Thus, for example, if measurements are done under vacuum the stoichiometry of the sample cannot be assumed to be constant. A conductivity value of 60–70 $(\Omega\ \mathrm{cm})^{-1}$ is reported by Abdullaev et al. [12] on vacuum annealed Cu_2S single crystals at 500°C, although no stoichiometry value is mentioned. Several investigators quote a stoichiometry range without discussing how the stoichiometry is actually maintained during the experiment. Thus, Gustavino et al. [13] have reported conductivity varying from ~ 20 to 1000 $(\Omega\ \mathrm{cm})^{-1}$ at 500°C when the stoichiometry varied from Cu_2S to $Cu_{1.88}S$. Kamigaichi [14] has reported very high conductivity values ranging from 1000 to 10 000 $(\Omega\ \mathrm{cm})^{-1}$ when the stoichiometry varied from 1.9 to 1.7 at 500°C. El Akkad et al. [15] have obtained a value of $\sim$ 20 $(\Omega\ \mathrm{cm})^{-1}$ at 400°C for a stoichiometry range of 1.999–1.995. Gillot [16] in his investigations at 500°C has found a conductivity of $\sim$ 100 $(\Omega\ \mathrm{cm})^{-1}$ for cuprous sulfide formed in H_2S and does not mention the stoichiometry. Dumon et al. [17] report a value of $\sim$ 16 $(\Omega\ \mathrm{cm})^{-1}$ at 500°C for the stoichiometry range 2–1.960.

In the present investigation, the stoichiometry of the sample was fixed by the use of an H_2S/H_2 gas mixture. The steady state conductivity corresponding to each sulfur activity was used to establish the calibration curve in fig. 4. The sulfur activity in fig. 4 and elsewhere is defined with reference to pure liquid sulfur 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 particular H_2S/H_2 ratio. The sulfur activity was then instantaneously changed by introducing a new ratio over the sample. The resulting change in the resistance was measured until the sulfide foil is equilibrated with the new ratio of H_2S to H_2.

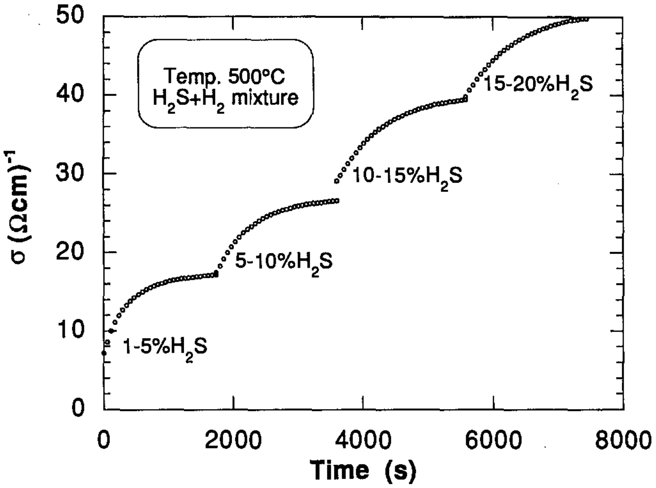

Fig. 5. Relaxation curves when the gas mixture is changed from 1 to 5%, 5 to 10%, 10 to 15% and 15 to 20% H_2S in H_2.

From experience and calculations it has been determined that the new gas mixture is established over the sample in about 30–45 s while the relaxation time for equilibration of the foil varies from 5–30 min. Fig. 5 shows in a step wise fashion a number of relaxation curves as the H_2S/H_2 ratio is changed from 0.01 to 0.25. At any specific point in a relaxation curve, the instantaneous sulfur activity in the sulfide can be obtained using the calibration curve in fig. 4.

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 Rau [18]. A plot of the net reaction rate obtained in this manner is shown in fig. 6.

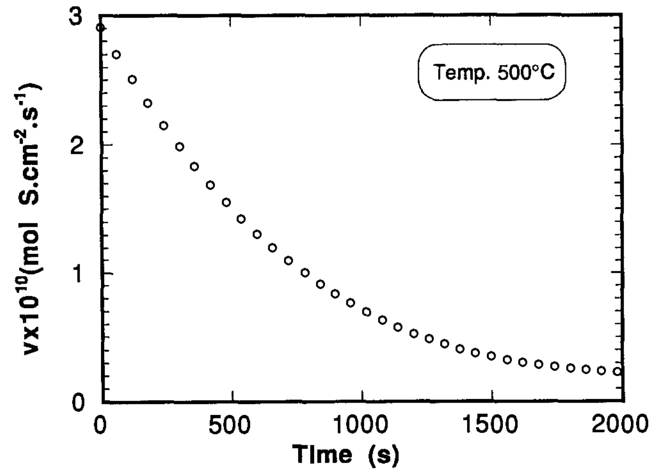

Fig. 6. Rate of the net reaction when the concentration of H_2S in the gas mixture is changed from 10 to 15%.

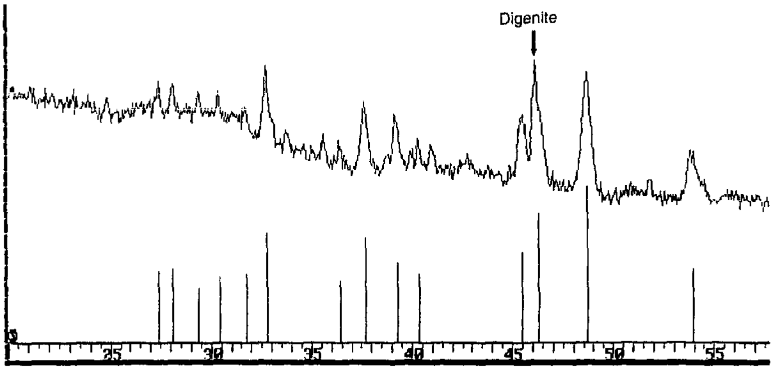

Fig. 7. X-ray diffraction scan of the copper sulfide sample at room temperature, showing characteristic peak of digenite.

At the completion of the kinetic measurements, the copper sulfide sample was characterized by X-ray diffraction and scanning electron microscopy. The X-ray scan reveals the presence of the digenite phase as shown in fig. 7. Fig. 8 shows the typical microstructure of the copper sulfide sample. The thickness of the foil is found to be approximately twice (~ 50 μm) that of the starting foil, and is used for computing resistivity by the van der Pauw method [11]. The morphology of the sulfide reveals two sets of columnar grains divided by a boundary in the middle. This morphology is a consequence of the sulfidation mechanism of copper which involves outward migration of copper ions through the sulfide film.

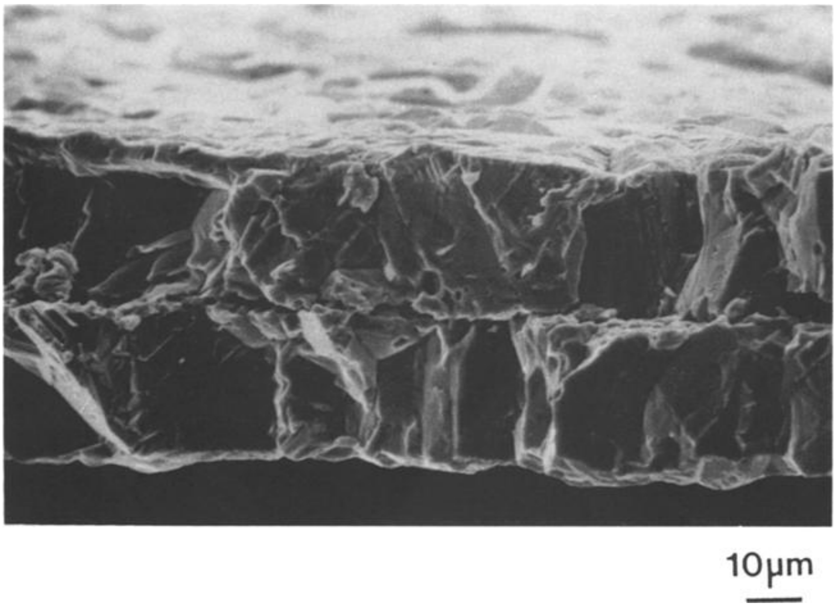

Fig. 8. Scanning electron micrograph of the sulfide after the experiment.

5. Discussion

Diffusion data in digenite have been compiled by Mrowec and Przybylski [19] and a value of $2 \times 10^{-3}\ \mathrm{cm^2/s}$ has been indicated for the chemical diffusion coefficient $\tilde{D}$ at 500°C. An estimate of the time t required for diffusion of copper through a thickness of 50 μm (sulfide foil) is given by

$$t = (50 \times 10^{-4})^2/\tilde{D} \approx 0.01\ \mathrm{s}.$$

As mentioned earlier, the time required for resistance relaxation varies from 5–30 min and therefore it can be concluded that the kinetic measurements correspond to the surface reaction without any contribution from diffusion.

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

$$\mathrm{H_2S(g) = H_2(g) + S\ (dissolved\ in\ Cu_{2-\mathit{x}}S)} \tag{6}$$

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

$$\mathrm{H_2S(g)} + m\mathrm{e^-} = \mathrm{S}^{m-}\mathrm{(ad)} + \mathrm{H_2(g)}, \tag{7}$$

where e^- denotes a negative charge.

Hydrogen molecules have been considered to be involved in the reaction since the rate of backward reaction has been found to be proportional to the first power of the H_2 partial pressure, as will be shown later. The equilibration of adsorbed sulfur species with the bulk crystal is described by the sequential steps:

$$\mathrm{S}^{m-}\mathrm{(ad)} = 2\mathrm{V_{Cu}^{+}} + \mathrm{S_s^{2-}} + m\mathrm{e^-} \tag{8}$$

$$\mathrm{V_{Cu}^{+} = V_{Cu}^{0} + h^{+}} \tag{9}$$

$$\mathrm{V_{Cu}^{+} + V_{Cu}^{0} = V_{Cu}^{0}V_{Cu}^{+}\ (vacancy\ complex)}, \tag{10}$$

where V_{Cu}^{+} and V_{Cu}^{0} denote vacancies of Cu in the digenite lattice having one plus and zero charge respectively, and h^+ denotes a positive electron hole. S_s^{2-} denotes a sulfur ion having two negative charges in the digenite lattice.

Since $Cu_{2-x}S$ is a p-type semiconductor and exhibits hole conductivity, electrons and holes in general have been considered to participate in the reaction steps involving the ionization of species. The adsorption and desorption of gaseous molecules at elevated temperatures are generally quite rapid, therefore reaction steps involving adsorption of H_2S and desorption of H_2 have not been considered. A rate equation based on the assumption that the set of reactions represented by (7) is the rate limiting, will now be derived.

As stated earlier, depending upon the value of m different types of sulfur species may be available on the surface and the overall rate as per reaction (7) is given by

$$\frac{dn_S}{dt} = \sum_{m=0}^{m=2} (k_f^m p_{H_2S} a_{e^-}^m - k_b^m \Gamma_{S^{m-}} p_{H_2}) , \tag{11}$$

where k_f and k_b are the rate constants for the forward and the backward reaction respectively in step (7) and Γ_i denotes the surface concentration of the ith adsorbed species.

While reaction (7) is rate controlling, the reactions (8)–(10) are in equilibrium and we can write equilibrium relations involving activities of products and reactants for these reactions. Thus, from reaction (8), we can write

$$\Gamma_{S^{m-}} = [V_{Cu}^{+}]^2 a_{e^-}^m . \tag{12}$$

Substituting the value of $\Gamma_{S^{m-}}$ from eq. (12) into eq. (11),

$$\frac{dn_S}{dt} = \sum_{m=0}^{m=2} (k_f^m p_{H_2S} a_{e^-}^m - k_b^m [V_{Cu}^{+}]^2 p_{H_2}) . \tag{13}$$

The equilibrium involving ionic defects and electronic species in $Cu_{2-x}S$ has been solved by Rau [18] and his results can be used for the analysis of the present data. An extension of Rau's analysis [#1] of the defect structure of $Cu_{2-x}S$ leads to the following relationships for the vacancies and electrons:

$$V_{Cu}^{+} \propto a_S^{0.36} , \tag{14}$$

$$a_{e^-} \propto a_S^{-0.31} . \tag{15}$$

Eq. (13) can be simplified by using eqs. (14) and (15). Thus,

$$\frac{dn_S}{dt} = \sum_{m=0}^{m=2} (k_f^m p_{H_2S} a_S^{-0.31m} - k_b^m a_S^{0.72} a_S^{-0.31m} p_{H_2}) . \tag{16}$$

Eq. (16) is the final rate equation in terms of measurable parameters and represents the most general case of the dissociation of H_2S on $Cu_{2-x}S$ surface. Based on experimental results for the net reaction rate (fig. 6), a value for m cannot be obtained. In an attempt to define the value for m, the rate of the backward reaction alone was measured.

5.1. 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. Furthermore, the hydrogen partial pressure can be varied by

---

[#1] Rau in his analysis follows the Kroger–Vink notation to denote the charged defect species. In Kroger–Vink notation charges on defects are determined relative to the perfect lattice as opposed to the notation of actual charges, followed in the present work. Accordingly V_{Cu}^{+} and S_s^{2-} in the present work are designated V_{Cu}^{x} and S_s by Rau.

dilution with argon. The experimental results are shown in figs. 9a and 9b. The backward rate is seen to be proportional to the partial pressure of H_2 and to $a_S^{0.025}$. By setting $p_{H_2S} = 0$, eq. (16) can be written as

$$\frac{dn_S}{dt} = \sum_{m=0}^{m=2} (k_b^m a_S^{0.72} a_S^{-0.31m} p_{H_2}) . \tag{17}$$

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

$$\frac{d\log(\text{rate})}{d\log a_S} = 0.72, 0.41 \quad \text{or} \quad 0.1 . \tag{18}$$

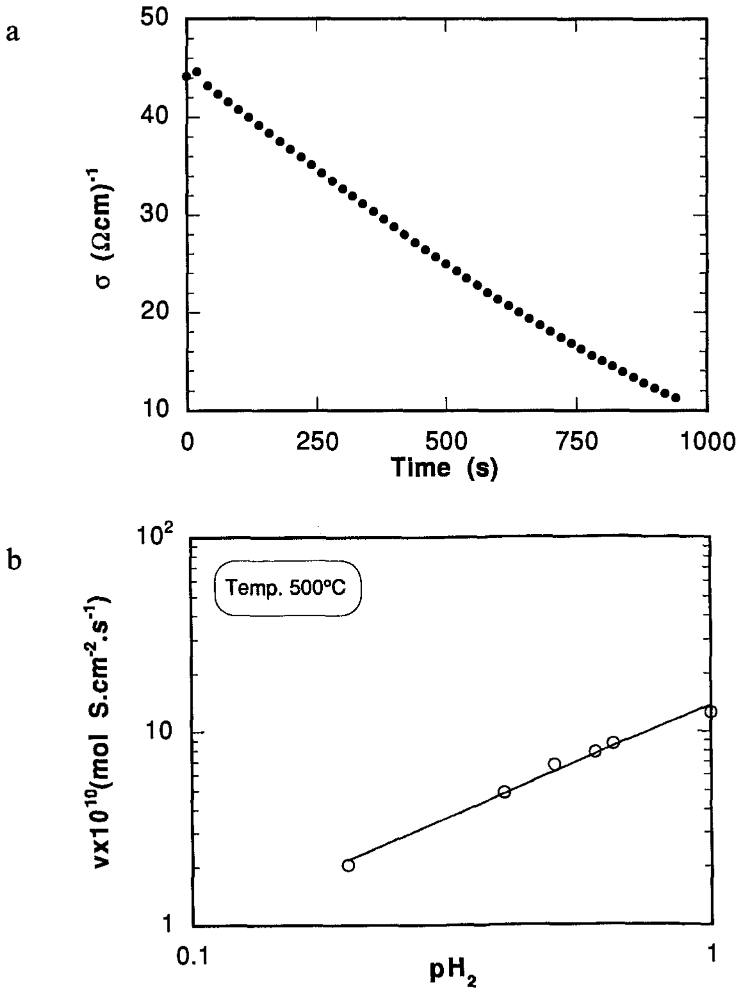

Fig. 9. (a) Relaxation curve at 500°C in pure H_2. (b) Rate of sulfur loss as a function of p_{H_2} in Ar and H_2 gas mixtures.

The rate of the backward reaction as a function of sulfur activity is plotted in fig. 9. The value of the slope of the backward reaction rate curve is 0.025 which is closest to 0.1 in eq. (18). This corresponds to the value of $m = 2$. The rate limiting step then can be defined, based on the backward reaction as

$$H_2 + S^{2-}(\text{ad}) = H_2S + 2e^- . \qquad (19)$$

It can be stated that the rate of sulfur transfer in $Cu_{2-x}S$ is controlled by the species S^{2-}(ad). For reversible reactions, the rate controlling step will be the same for the forward and the backward reactions.

Kobayashi and Wagner [3] have reported on the rate of the backward reaction (removal of sulfur) on cuprous sulfide (chalcocite) at 385°C and concluded that the rate limiting step is reaction (19). However, they investigated a different phase of cuprous sulfide and used the following assumptions for arriving at the rate limiting step:

(a) The surface concentration of adsorbed species S^{2-}(ad) is constant.

(b) Surface coverages of adsorbed species S^-(ad) and S(ad) are low.

In the present analysis these assumptions have been relaxed. Furthermore the assumption that S^{2-}(ad) concentration is constant will lead to the wrong dependence of the forward reaction rate on the sulfur activity as described below.

5.2. WHEN $p_{H_2} = 0$ AND $p_{H_2S} = p(\text{total})$

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 is shown by the uppermost line in fig. 10. To test the internal consistency of the model, the forward reaction rate was also measured by setting $p_{H_2} = 0$ in the gas mixture. The experimental points are seen to be in excellent agreement with the calculated line (fig. 10). The forward rates obtained in H_2S alone were corrected for dilution of the gas phase.

When $p_{H_2} = 0$, from reaction (7), the forward reaction rate can be written as

$$\frac{dn_S}{dt} = \sum_{m=0}^{m=2} k_f^m p_{H_2S} a_S^{-0.31m} . \qquad (20)$$

Inserting $m = 2$, the rate equation becomes:

$$\frac{dn_S}{dt} = k_f^2 p_{H_2S} a_S^{-0.62} . \qquad (21)$$

The experimental rate curves show slopes of a value of -0.55 ± 0.07, in reasonable agreement with -0.62. The overall rate in mol cm^{-2} s^{-1} for the molecular dissociation of H_2S on digenite is thus given by

$$v = (1.2 \pm 0.11) \times 10^{-9} p_{H_2S} a_S^{-(0.55 \pm 0.07)} - (6.8 \pm 0.11) \times 10^{-8} a_S^{0.025} p_{H_2} . \qquad (22)$$

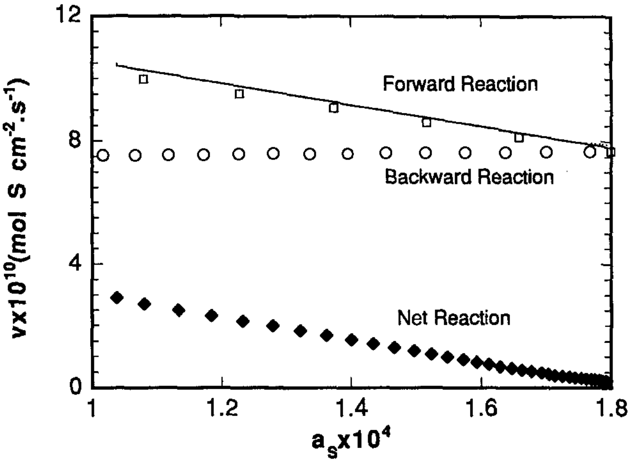

Fig. 10. Summary of the reaction kinetics at 500°C.

If the concentration of the surface species S^{2-} is assumed to be constant, as was done by Kobayashi and Wagner for H_2 oxidation reaction on chalcocite, then the forward rate should vary as a_S^{-1}. Such a dependence would be inconsistent with the results of the present study.

6. Summary

The kinetics of sulfur transfer from H_2S to digenite at 500°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 forward reaction is shown to vary as $a_S^{-0.55}$ while that of the backward reaction is nearly independent of the sulfur activity and proportional to the first power of hydrogen pressure. The results are consistent with the defect model for $Cu_{2-x}S$ proposed by Rau.

Acknowledgement

The authors wish to acknowledge many useful suggestions by Dr. S. Ling.

References

[1] H.J. Grabke and E.M. Muller, Scripta Metall. 14 (1980) 159.
[2] V.S. Stotz, Ber. Bunsenges. Phys. Chem. 70 (1966) 37.
[3] H. Kobayashi and C. Wagner, J. Chem. Phys. 26 (1957) 1609.
[4] H.J. Grabke, Ber. Bunsenges. Phys. Chem. 69 (1965) 48.

[5] W.L. Worrell and H.I. Kaplan, in: *Heterogeneous Kinetics at Elevated Temperatures*, eds. G.R. Belton and W.L. Worrel (Plenum Press, New York, 1970).
[6] C. Wagner, in: *Molecular Processes in Solid Surfaces*, eds. E. Drauglis, R.D. Gretz and R.I. Jaffe (McGraw-Hill, New York, 1969).
[7] H.G. Grabke and G. Horz, Ann. Rev. Mater. Sci. 5 (1977) 155.
[8] E. Bechtold, Ber. Bunsenges. Phys. Chem. 69 (1965) 328.
[9] P. Roy and H. Schmalzried, Ber. Bunsenges. Phys. Chem. 71 (1967) 200.
[10] G. Smith and M.A. Clevinger, eds., *Phase Diagrams for Ceramists*, Vol. 5 (The American Ceramic Society, Westerville, 1983).
[11] L.J. van der Pauw, Philips Res. Rep. 13 (1958) 1.
[12] G.B. Abdullaev, Z.A. Aliyaroa, E.H. Zamanova and G.A. Asadov, Phys. Stat. Sol. 26 (1968) 68.
[13] F. Guastavino, H. Luquet, J. Bougnot and M. Savelli, J. Phys. Chem. Solids 36 (1975) 621.
[14] T. Kamigaichi, J. Sci. Hiroshima Univ. A 16 (1952) 325.
[15] F. El Akkad, B. Mansour and T. Hendeya, Mater. Res. Bull. 16 (1981) 535.
[16] B. Gillot, Mater. Chem. 7 (1982) 35.
[17] P.A. Dumon, A. Lichanot and S. Gromb, J. Chim. Phys. Physico-Chimie Biol. 71 (1974) 407.
[18] H. Rau, J. Phys. Chem. Solids 28 (1967) 903.
[19] S. Mrowec and K. Przybylski, High Temp. Mater. Proc. 6 (1984) 1.