The Kinetics of $\text{S}^{35}$ Exchange between $\text{SO}_2/\text{CO}/\text{CO}_2$ Gas Mixtures and Copper Sulfide Melts at 1523 K

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The kinetics and mechanisms of oxidation of copper sulfide melts have been investigated using a radioisotope exchange technique. Copper sulfide melts were doped with $\text{S}^{35}$. The transfer of the radioisotope between the melt and $\text{SO}_2/\text{CO}/\text{CO}_2$ gas mixtures in chemical equilibrium with the melt was monitored by analyzing the changes in radioactivity of the gas. Analysis of the results indicates that the rate-limiting chemical reaction involves the formation of an activated complex $\text{SO}_2$, and the rate of exchange of the sulfur isotope at 1523 K is described by the relationship $R = 6.4(\pm 2) \frac{P_{\text{co}}}{P_{\text{co}_2}} \frac{P_{\text{so}_2}}{\text{g atom S} \text{ m}^{-2} \text{ s}^{-1}}$.

I. INTRODUCTION

The reaction of oxygen with metal sulfide melts is the basis of production of a number of base metals from their sulfides. While much is known of the equilibrium thermodynamics of these systems, the kinetics of the chemical reactions involved have yet to be characterized. The high utilization of oxygen in industrial copper converters indicates that these reactions are fast compared with transport processes in the gas or melt. This view has been confirmed in laboratory studies in which melts are suspended in flowing gas streams,\textsuperscript{[1]-[6]} gas jets are directed at the surfaces of the melts,\textsuperscript{[7]} and sulfides are mixed with molten oxides.\textsuperscript{[8]}

The above techniques are dynamic experiments in that they involve the net removal of sulfur from the system, for example, through the overall reaction

$$\text{Cu}_2\text{S} (l) + \text{O}_2 (g) \rightarrow 2\text{Cu} (l) + \text{SO}_2 (g) \quad [1]$$

The approach taken in the present study is significantly different from those quoted above in that the melt and the gas phase are in chemical equilibrium. Under these conditions, there is no net sulfur removal from the system but, rather, the transfer of labeled sulfur species, in the form of $\text{S}^{35}$ radioisotope, from the melt to the gas phase. The kinetics of the reaction are followed by measuring the rate of transfer of labeled species to the gas phase. Sulfur-35 is a 100 pct $\beta$ emitter,\textsuperscript{[9]} having a half-life of 87.4 days. The change in concentration of $\text{S}^{35}$ atoms in the gas phase can therefore be followed using a suitable radiation detector device, in this case, a Geiger-Müller (G-M) tube. The oxygen potentials of the gas mixtures were controlled by using mixtures of CO and CO$_2$.

II. EXPERIMENTAL

A. Materials

The high-purity nitrogen, sulfur dioxide, and carbon dioxide gases used in these experiments were passed through packed columns of silica gel, DRIERITE,* and magnesium perchlorate to remove water vapor. Carbon monoxide gas was produced in the laboratory by passing dry carbon dioxide through a bed of packed carbon held at 1523 K. Residual carbon dioxide in the carbon monoxide was removed by passing the gas through ASCARITE.** Sulfur-35 was obtained from Amersham International Ltd. (Amersham, United Kingdom) as rhombic crystalline sulfur at an initial activity of 200 M Bq.

Copper sulfide, $\text{Cu}_2\text{S}$, was prepared by placing stoichiometric quantities of high-purity copper (Leico, 99.999 pct) and sulfur (Aldrich, 99.999 pct) powder, containing the $\text{S}^{35}$, in a VYCOR\textsuperscript{*} tube. The tube was evacuated to approximately $10^{-3}$ bar using a rotary pump and then sealed. The ampoule was heated gradually to 873 K and held at that temperature for three days before cooling again to room temperature.

B. Apparatus

The apparatus used in the experiments is shown schematically in Figure 1. The $\text{Cu}_2\text{S}$ containing the $\text{S}^{35}$ radioisotope was held in a recrystallized alumina crucible (10-mm ID × 25-mm height) and placed in a 19-mm-ID recrystallized alumina reaction tube. The CO/CO$_2$/SO$_2$ gas mixtures were directed at the surface of the sulfide melt by passing them through a 5-mm-ID alumina tube held 3 mm above the melt surface. To minimize the gas volume in the system, the bottom half of the 750-mm-long reaction tube was filled with castable alumina cement. The brass water-cooled furnace ends were gold-plated on their internal surfaces to minimize any reaction with the gas mixtures. The gas delivery tube at the top

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*VYCOR is a trademark of Corning Glass Works, Corning, NY.

**DRIERITE is a trademark of Drierite Company, Xenia, OH.

**ASCARITE is a trademark of Thomas Scientific, Swedesboro, NJ.

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of the furnace and the alumina thermocouple sheath at the bottom were held in place by ethylene propylene (EPDM) O-ring seals.

The gas lines were constructed from glass joined with polyvinyl chloride (PVC) tubing. The losses of SO₂ by diffusion through the PVC were shown to be negligible over the period of the experimental times studied. By using glass taps, it was possible to pass gas mixtures directly through the system to the waste gas or to recirculate them in a closed system over the melt surface. Recirculation was achieved using a "Dynavac GK-12-02-M" magnetically coupled pump having gold-plated inlet tubes, a TEFLON chamber, and graphite pistons. The use of the magnetically coupled impeller ensured that the system was completely sealed from the outside atmosphere; hence, the radioactive gas mixture was readily retained in the system, and the gas composition was not altered during this mode of operation.

The radioactive S³⁵ in the gas phase was monitored using a Phillips/Mullard ZP1430 Geiger-Muller (G-M) Tube. The G-M tube was sealed with O-rings into a glass measuring chamber such that the mica window of the detector was in direct contact with the gas phase. Counting of the radioactive "pulses" was carried out using a PHILIPS* 4251 counter/ratemeter.

C. Experimental Procedure

A weighed charge of copper sulfide containing S³⁵ in an alumina crucible was placed in the reaction furnace at room temperature, and the system was thoroughly flushed with dried high-purity nitrogen. A background count of the G-M tube was taken at this point. The sample was then heated to 1523 K in a stagnant nitrogen atmosphere. A controlled CO/CO₂/SO₂ gas mixture was then allowed to flow through the system until a steady count rate was recorded by the G-M tube on the exit gas. The gas was then assumed to have reached equilibrium with the melt in the reaction furnace. At this stage, the gas flow was shut off, and the gas mixture within the system was recirculated at a flow rate of 500 ml min⁻¹.

The change in the concentration of S³⁵ in the gas mixture was then monitored using the G-M tube and counter until isotopic equilibrium was achieved; i.e., no change in count rate was observed with time. This "endpoint" was taken when three successive 400- or 1000-second counts were within one standard deviation of each other (i.e., the square root of the count). The counting chamber was then flushed with nitrogen, and background counts were again taken.

Provided sufficient radioactive material remained in the melt, the experiment was then repeated using the procedure outlined above. After experiments were completed, the sample was cooled in the furnace under stagnant nitrogen and then removed and weighed.

The raw count data were corrected for the background and counter dead time.

The total moles of gas in the recirculating system during the experiments were determined by filling the system, while the furnace was at temperature, with pure SO₂. This gas was then flushed out with nitrogen into a weak hydrogen peroxide solution to form sulfuric acid. The acid was then titrated against a base, and the total number of moles of SO₂, and hence the moles of gas, present in the system was calculated.

III. BACKGROUND THEORY

The overall reaction involving the transfer of labeled sulfur species S* between the melt and the gas can be expressed as

$$\text{SO}_2 (g) + S^* (\text{melt}) \rightarrow S (\text{melt}) + S^*O_2 (g) \quad [2]$$

The system is in chemical equilibrium with respect to both sulfur and oxygen species, and it is assumed that isotopic differences do not affect the exchange reaction. Also, the quantity of sulfur in the melt is much larger than that in the gas phase.

Provided that the relative concentrations of labeled species are low, it has been demonstrated[10,11] that the rate of isotope equilibration is always first order with respect to the fractions of labeled species. Thus,

$$\frac{dF_{SO_2}}{dt} = AR(F_{SO_2}^{eq} - F_{SO_2}^*) \quad [3]$$

where $n_{SO_2}$ is the total number of moles of SO₂ in the system, $F_{SO_2}^{eq}$ is the fraction which would be in isotopic equilibrium with the melt at any instant, A is the area of the melt/gas interface, and $R$ is the total rate of exchange of sulfur atoms per unit area. Kinetic isotope effects can reasonably be ignored at the atomic mass of sulfur.

If the only sulfur-containing species are SO₂ molecules and the matte, and initially only the matte contains