

Device for the measurement of sulfur fugacity mountable on the precession camera

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Abstract

A device for measurement of sulfur fugacities of single crystals of sulfides at elevated temperatures was designed for use with a precession camera and successfully employed in studies of pyrrhotite. The device contains the solid-state electrochemical cell Pt, Ag(s)|AgI(s)|Ag₂S(s), S₂(g), Pt and enables simultaneous determination of temperature, sulfur fugacity, and crystal structure. Trial studies confirmed that the stable pyrrhotite structure at 437°, 434°, and 320°C is the 1C type. Measured sulfur fugacities for the crystals are slightly lower than calculated values from earlier data.

Introduction

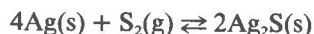
In the course of a study on the Fe-S system (Kissin, 1974; Kissin and Scott, in preparation), we foresaw the need for a technique by which equilibrium sulfur fugacity could be determined at the same time that a single crystal was being X-rayed on a precession camera at high temperature. Such a technique would provide simultaneous measurement of several important variables in condensed sulfide phase equilibria: temperature, sulfur fugacity, and crystallographic structure. A solid-state electrochemical cell, sensitive to sulfur vapor, enables these measurements to be made. Solid-state electrochemical cells have long been used in the field of metallurgy and materials science (for a summary, see Alcock, 1968), but their application to the earth sciences has been relatively recent. Sato (1971) has summarized existing and potential applications.

Theory

The present study made use of the cell:



originally developed by Rheinhold (1934), for which the virtual reaction is:



The voltage, or EMF, of this cell (E), in equilibrium

with sulfur vapor, provides a measure of the fugacity of S₂(g) by means of the following equation:

$$\ln f_{\text{S}_2} = [E - E^\circ(T)](4F/RT) + \ln f_{\text{S}_2}^\circ(T) \quad (1)$$

where $E^\circ(T)$ and $\ln f_{\text{S}_2}^\circ(T)$ are the standard state quantities for S₂(g) in equilibrium with S(l) at a given temperature, F is the Faraday constant, R is the gas constant and T is in Kelvins. Equation 1 can be derived from basic thermodynamic principles [see *e.g.* Sato (1971) and Rickert (1968)], given the following assumptions.

1. The activity of Ag₂S(s) is identical whether in equilibrium with Ag(s) or S(l). This assumption is not strictly valid, as Ag₂S has a small degree of non-stoichiometry (Kracek, 1946; Rau, 1974) although Schneeberg (1973) has shown that the difference in activities is negligible for the temperature range employed here.
2. The electrolyte AgI(s) is a purely ionic conductor, or at least has only a negligible contribution of electronic conduction. The transference number t for AgI, defined by the relation:

$$t(\text{Ag}^+) = \frac{\sigma(\text{ion})}{\sigma(\text{elec}) + \sigma(\text{ion})}$$

where $\sigma(\text{elec})$ is the electronic conductivity and $\sigma(\text{ion})$ is the ionic conductivity, has been shown by Tubandt (1932) to be 1.00 ± 0.01 . More recent work confirms Tubandt's data in that the electronic conductivity, as determined by Ilschner (1958), is many orders of magnitude lower than the total con-

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ductivity, determined by Kvist and Josefson (1968), over a considerable range of temperatures.

Schneeberg (1973), in addition to applying this cell to a variety of sulfidation reactions, has investigated interferences by solid solution of iodine in $\text{Ag}_2\text{S}(\text{s})$ and of sulfur in $\text{AgI}(\text{s})$. He found detectable effects on the cell, although of a magnitude within the precision of his experimental error. Ag_3SI , a stable phase in the $\text{AgI}-\text{Ag}_2\text{S}$ pseudobinary system (Reuter *et al.*, 1967; Takahashi *et al.*, 1967), might interfere with the predicted behavior of the cell and requires further study; however, the stability of Ag_3SI with regard to the decomposition reaction $\text{Ag}_3\text{SI} \rightarrow \text{Ag}_2\text{S} + \text{AgI}$ is unknown (Owens, 1973), and although Ag_3SI was not looked for specifically, neither Schneeberg nor we have encountered a contaminating phase in careful X-ray diffraction and optical studies. Even if Ag_3SI were present in sufficient quantity to form a blocking layer, its $t(\text{Ag}^+)$ at 300°C has been determined to be 0.95 ± 0.01 (Reuter and Hardel, 1966). Its effects on the predicted behavior of the cell would therefore be small and calculable.

Schneeberg's equation for the evaluation of f_{S_2} , which incorporates his own data for $E^\circ(T)$ and that of Rickert (1968) for $\ln f_{\text{S}_2}^\circ(T)$, was used in our study:

$$\log f_{\text{S}_2} = \frac{1}{T} (20158.6 E - 9099.7) + 3.73 \quad (2)$$

The constants in equation 2 are consistent with values of sulfur fugacity in atmospheres. Schneeberg's Figure 1 illustrates the range of sulfur fugacities (10^{-2} to 10^{-18} atm) and temperatures (178° to 558°C) over which the cell may be used.

Methods

The device incorporating the solid-state electrochemical cell, illustrated in Figure 1, was constructed and successfully employed after considerable experimentation. The manner in which this device was assembled proved to be important to its successful performance.

A Pyrex tube of a size approximately 1.5 mm I.D. \times 3 mm O.D., appropriate for clamping in the goniometer head of the precession camera, was sealed about a thermocouple. The seal was made by carefully melting the glass with a miniature oxygen-natural gas flame. A small hole was cut in the side of the tube with a diamond saw, enabling the thermocouple leads to be passed through to a potentiometer and in series to the controller for the heating element. A sulfide single crystal, in this case synthetic pyrrhotite, was cemented directly to the thermocouple mea-

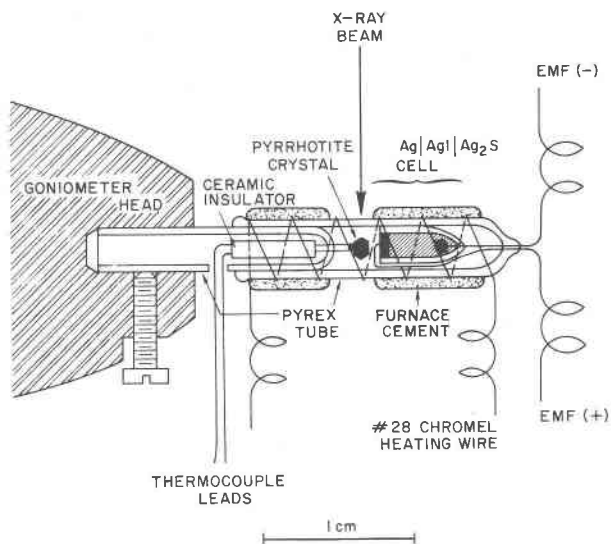


Fig. 1. Schematic top view of the device for measurement of sulfur fugacity mountable on the precession camera.

suring junction and the Pyrex tube was clamped in the goniometer head. The crystal was then oriented on the precession camera. The mounting medium for attaching the crystal was potter's clay. Other cements such as epoxy cement, waterglass, waterglass + powdered alumina mixture, various refractory furnace cements, and litharge cement, advocated by various workers, were also tried but were not suitable. Potter's clay was mixed with water to a pasty consistency and after drying for 24 hr was found to hold the crystal well. The clay strengthened with heating, and expansion and contraction were minimal. The clay also coated the thermocouple junction, protecting it from sulfidization.

The electrochemical cell was constructed next, beginning with welding of platinum wire leads to small pellets of silver and silver sulfide under a nitrogen gas stream. Silver sulfide was synthesized in evacuated silica tubes from silver powder (Johnson, Matthey & Mallory) and sulfur (Electronic Space Products, Inc.), claimed by the manufacturers to be 99.999+% pure. Silver pellets were formed from 99.999+% pure silver shot (ASARCO). The silver pellet with attached lead was placed in a 1.5 mm I.D. \times 2.5 mm O.D. Pyrex tube, and one end of the tube was sealed about the platinum lead. Reagent-grade silver iodide (Johnson, Matthey & Mallory) was then added into the tube.

In order to obtain good electrical connection and mechanical coherence between the electrodes and electrolyte, it was found desirable to melt the silver

iodide electrolyte about the electrodes. This was accomplished by placing the small Pyrex tube and its contents in a simple furnace consisting of a larger-diameter Pyrex tube heated by a resistance coil whose temperature was controlled by a variable transformer. Temperature was measured with a thermocouple to which the tube containing the silver iodide and silver pellet was attached. The coil was heated to just above the melting point of silver iodide (558°C), whereupon the pellet of silver sulfide was placed on top of the molten silver iodide, where it stuck fast on cooling. During the heating operation a stream of nitrogen was passed through the furnace tube in order to prevent oxidation of the cell components. The heating coil was then cooled slowly to room temperature over about one-half hour in order to minimize strain on the cell. The electrochemical cell was carefully inspected for defects such as poor welding of the platinum leads or cracks in the silver iodide electrolyte.

The final step in the construction of the device was the sealing of an outer encapsulating Pyrex tube (4 mm I.D. × 5 mm O.D.) which held both the crystal and the electrochemical cell under a vacuum. A Pyrex tube, with the electrochemical cell inserted, was passed over the crystal so that it touched the walls of the tube held in the goniometer head. The encapsulating tube was then welded with the miniature oxygen-natural gas flame to the tube held in the goniometer head. Vacuum was applied to the opposite end of the encapsulating tube, and the tube was sealed with the miniature flame about the platinum leads of the electrochemical cell. A heating element of No. 28 chromel wire was coiled uniformly about

Table 1. Results of high-temperature experiments using the solid-state electrochemical cell. In all cases NA-type pyrrhotite with $N_{FeS} = 0.9464$ was used as the starting material. Sulfur fugacities are in atm.

| | $T(^{\circ}C)$ ± 1.0 | $\log f_{S_2}(\text{meas})^*$ | $\log f_{S_2}(\text{calc})^{**}$ | equil. time | high- T structure |
|--------------|-----------------------------|-------------------------------|----------------------------------|-------------|---------------------|
| Experiment 1 | 437.0 | -8.42(15) | -7.23 | 3 days | 1C |
| | 434.0 | -8.51(15) | -7.30 | | |
| Experiment 2 | 320.0 | -10.99(18) | -10.34 | 2 days | 1C |
| | 320.0 | -11.01(18) | -10.34 | | |
| | 320.0 | -10.94(18) | -10.34 | | |
| Experiment 3 | 320.0 | -11.41(18) | -10.34 | 9 days | 1C |

*Experimental values from this study calculated from Schneeberg's (1973) equation 2. Parenthesized figures represent the estimated standard deviation (*esd*) in terms of least units cited for the value to their immediate left, thus -8.42(15) indicates an *esd* of 0.15.

**Calculated values from equation 8 of Toulmin and Barton (1964) at the indicated temperatures.

Table 2. Comparison of $\log f_{S_2}$ values (in atm) along the pyrite-pyrrhotite equilibrium curve from this study, Schneeberg (1973), Scott and Barnes (1971), and Toulmin and Barton (1964)

| $T(^{\circ}C)$ ± 1 | $\log f_{S_2}$ (atm) | | | |
|---------------------------|----------------------|-----------|------|-------|
| | (1) | (2) | (3) | (4) |
| 460 | -5.26(06) | — | -5.4 | -5.5 |
| 438 | — | -5.78(13) | -5.9 | -6.2 |
| 413 | -6.54(09) | — | -6.6 | -6.9 |
| 401 | — | -6.90(11) | -7.0 | -7.3 |
| 367 | — | -8.30(11) | -8.1 | -8.5 |
| 364 | -7.84(08) | — | -8.2 | -8.6 |
| 324 | — | -9.82(12) | -9.9 | -10.2 |

(1) This study: means of several measurements. Parenthesized figures are estimated standard errors (S.E.) of the means in terms of least units cited for the value to their immediate left, thus -5.26(06) indicates an S.E. of 0.06.

(2) Means of two values at each temperature obtained from sulfur-rich and sulfur-poor starting materials, as reported in Table 5 of Schneeberg (1973). Parenthesized figures have the same significance as in (1).

(3) Taken from the smoothed curve of Scott and Barnes' (1971) Figure 4 for the temperatures reported by Schneeberg (1973) and this study.

(4) Taken from the smoothed curve derived from Toulmin and Barton's (1964) Table 5 for the temperatures reported by Schneeberg (1973) and this study.

the encapsulating tube and cemented in place with Sauereisen No. 33 sealing cement, leaving a window for the X-ray beam, and allowed to dry for 24 hr.

In order to prevent breakage of wires during operation of the precession camera, all leads from the device were wound in spiralling loops. The heating coil was powered and controlled by a carefully calibrated Thermo Electric Model 3142200 solid-state controller, which was modified for 20 V maximum output in order to provide maximum sensitivity of control. The thermocouple leads to the controller were run in series to a Leeds and Northrup Model 8690 millivolt potentiometer for accurate temperature measurement. Cell EMF's were measured on an Orion Model 811 digital voltmeter wired in series with a strip-chart recorder. Thermal gradients were not evaluated in detail; however, they are believed to be negligible owing to the small thermal mass of the system and the nearness of the crystal to the electrochemical cell.

Before applying heat to the device, a precession photograph of the crystal was made as a basis for comparison with the high-temperature photographs. Unfiltered Mo radiation was used in order to obtain photographs through the Pyrex tubing within a reasonable time. After heating the device to the desired temperature, the orientation of the crystal was rechecked. Once a steady EMF was obtained from the cell, the high-temperature precession photograph was taken. Exposures of 24 hr were generally necessary

because of the weak intensities of the X-ray reflections being sought and the high absorption of X-rays by the glass.

Results

Three successful experiments employing the device were conducted, the results of which are in Table 1. The same starting material was used in all three cases, NA-type pyrrhotite, using the terminology of Nakazawa and Morimoto (1970, 1971), synthesized hydrothermally at 435°C in a manner described elsewhere (Kissin, 1974; Kissin and Scott, in preparation). The composition of the crystals was 47.322 *esd* 0.061 atomic percent Fe, as determined by the d (10 $\bar{1}2$) vs. composition relation of Yund and Hall (1969). The crystals were tabular and euhedral with a maximum dimension of 1 mm. Sharp diffractometer peaks obtained from bulk samples and sharp diffraction spots in precession photographs are evidence that the crystals were unzoned. Their small size precluded formation of surficial zoning effects during runs with the electrochemical cell.

The high-temperature precession photographs indicated that the pyrrhotite structures were of the 1C type of Nakazawa and Morimoto (1970, 1971), confirming earlier results of Corlett (1968), Sugaki *et al.* (1977), and Nakazawa and Morimoto. These workers found the 1C type pyrrhotite to be unquenchable, a result also confirmed in the present study.

The measured $\log f_{S_2}$ values from our experiments in Table 1 are consistently lower than those predicted by Toulmin and Barton's (1964) equation 8, which related f_{S_2} , T , and pyrrhotite composition. Although the differences are small (0.6 to 1.2 orders of magnitude), they are nevertheless significant. In a related study (see also Kissin, 1974), we have used the electrochemical cell in a standard tube furnace in the manner described by Schneeberg (1973) to measure f_{S_2} for a segment of the pyrite-pyrrhotite buffer curve. Table 2 compares our f_{S_2} values with those of Schneeberg (1973), Scott and Barnes (1971) who computed their f_{S_2} 's from Fe-Zn-S equilibria, and Toulmin and Barton (1964) who used the electromotive force method. The results of Scott and Barnes, Schneeberg, and our study are in excellent agreement but give values of f_{S_2} that are slightly higher than those determined by Toulmin and Barton. Note that this disagreement with respect to the pyrite-pyrrhotite data of Toulmin and Barton in Table 2 is in the opposite sense from that for the pyrrhotite isopleth in Table 1.

Conclusions

The device for measurement of sulfur fugacity mountable on the precession camera provides a means of simultaneously measuring in sulfides all variables pertinent to condensed phase equilibria. This capability is invaluable in the study of minerals such as pyrrhotite in which high-temperature structures are unquenchable. Such behavior is a complicating factor in many sulfide systems. The first model of the device described here is crude and difficult to construct; however, with a more sophisticated design, it should prove to be a valuable research tool.

On the basis of our experimental data for one pyrrhotite composition, equation 8 of Toulmin and Barton (1964) relating pyrrhotite composition to f_{S_2} and T appears to give values that are somewhat too high. From other sources, their estimates of f_{S_2} below 450°C for the pyrite + pyrrhotite solvus appear to be slightly too low. The discrepancies are small, and may be due in part to differences in standard-state thermodynamic data that were chosen. Nevertheless, because of the importance of the Fe-S system, refinement of the f_{S_2} - T - X relationships perhaps using a device such as ours is desirable.

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