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Author
Meyer, B.

Publication Date
1979-07-01
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B. Meyer, L. Peter and M. Ospina

July 1979

Prepared for the U. S. Department of Energy under Contract W-7405-ENG-48
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GEOCHEMICAL AND COSMOCHEMICAL CYCLES INVOLVING SULFUR, SULFIDE, SULFITE AND SULFATE

B. Meyer, L. Peter and M. Ospina

Department of Chemistry
University of Washington
Seattle, Washington 98195

and

Molecular and Materials Research Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

ABSTRACT

Raman spectra of aqueous systems containing sulfur dioxide, elemental sulfur and sulfate indicate that the equilibrium between these species is catalyzed by elemental sulfur. Therefore, dynamic equilibrium can be expected under conditions prevalent on Venus, on Io and in epigenic sulfur deposits.

Sulfur, sulfuric acid, sulfur dioxide and water are in contact with each other in a variety of systems such as planetary atmospheres (Knollenberg, 1979; Nelson, 1978; Oyama, 1979; and Stewart, 1979), bio-epigenic sulfur deposits (Rucknick, 1979) as well as in industrial SO_2 recovery systems in coal burning power plants (Meyer, 1977).

The reactions and equilibria between elemental sulfur, sulfur dioxide, sulfuric acid and water can be summarized in two over-all equations:

\[
3\text{SO}_2 + 2\text{H}_2\text{O} \rightleftharpoons 2\text{H}_2\text{SO}_4 + \frac{1}{n} \text{S}_n \quad \text{Eq. I}
\]

\[
\frac{1}{n} \text{S}_n + 4\text{H}_2\text{O} \rightleftharpoons 3\text{H}_2\text{S} + \text{H}_2\text{SO}_4 \quad \text{Eq. II}
\]

At room temperature pure liquid SO_2 in contact with water is stable for many years. Likewise, elemental sulfur, water and sulfuric acid do not readily react. However, contrary to the widely held belief, this sulfur system is not inert. Priestley, 1970, heated sulfur dioxide in a sealed tube and observed the reaction over a period of several months and observed crystals which he identified as elemental sulfur. Boehm, 1882, studied reaction Eq. II. Bichowsky, 1922, studied both systems carefully and discovered that the reactions are reversible. Despite its importance and practical applications, the chemistry of this system has not been studied in more than half a century, even though Thode's pioneering work on isotope fractionization (Monster, 1965) stimulated interest among earth scientists (Ellis, 1971; Dana, 1966; Dana, 1971; and Robertson, 1973). Unfortunately, thermodynamics are only of limited help, because of the uncertainty about the variety of states in which the various sulfur species can appear. We report here some qualitative data based on experiments in which we used high purity elemental sulfur and in situ observation techniques. Neither was available to earlier authors.

At room temperature, we confirm that the pure chemicals in reaction (I) do not react noticeably over a period of at least five years. However, in the presence of ammonia or other suitable catalysts, reaction commences within weeks (Meyer, 1979), elemental sulfur precipitates from tubes containing sulfur dioxide within one to three years, and the resulting
solution contains dithionate and other sulfur oxyacids as transient species, in addition to sulfate which constitutes the most stable end product. Figure 1a shows the Raman spectrum of the aqueous phase in a sealed pyrex tube 6 mm diam. x 6 cm containing 0.2 ml. H₂O and 0.2 ml liquid sulfur dioxide at 25°C after it was heated for 27 hrs at 80°C. The liquid remained clear and colorless. The broad peaks at 470 cm⁻¹ and 800 cm⁻¹ are characteristic for colloidal sulfur; the weak shoulders at 980 cm⁻¹ and 1,050 cm⁻¹ are due to sulfate and bisulfate, respectively. The strongest peak at 1,144 cm⁻¹, due to unreacted sulfur dioxide, is not shown. The Raman band intensities can be evaluated by comparison with the internal water standard (Meyer, 1979) and correspond to 0.25 M sulfate and 0.30 M bisulfate solutions. Our observations are consistent with Bichowsky's equilibrium studies (Bichowsky, 1922), however, we have found that at 80°C reaction (I) proceeds about halfway in one day or less, while Bichowsky observed that at 312°C equilibrium in the opposite direction required at least three to seven days.

Fig. 1. Raman spectra of sulfur systems: (a) SO₂ and H₂O after 27 hours at 80°C, (b) elemental sulfur and water after 24 hours at 190°C, (c) elemental sulfur, SO₂ and H₂O after 12 hours at 120°C, and (d) SO₂ and water with 0.1 M BaCl₂ after 12 hours at 25°C.
According to earlier work (Bichowsky, 1922) reaction (II) takes sixty days to reach equilibrium at 260°C. However, using high purity sulfur, we observed already after 24 hrs at 190°C the Raman spectrum in Figure 1b. The main peaks correspond to 0.01 M sulfate (SO_4^{2-}) and 0.03 M bisulfide (HS^{-1}). Upon further heating, the concentration of sulfuric acid does not increase rapidly, but hydrogen sulfide disappears, probably because sulfuric acid and elemental sulfur enter reaction (I), and the resulting sulfur dioxide consume hydrogen sulfide yielding elemental sulfur. The latter reaction is well known and was first described by Wackenroder, 1846. It involves the formation of intermediate species in intermediate oxidation states, including thiosulfate, tetrathionate, and other polythionates which are not stable under our conditions (Meyer, 1977). The existence of hydrogen sulfide in reaction (II) suggests that hydrogen sulfide might also occur as an intermediate in reaction (I). Unfortunately, this cannot be easily verified, because of the above mentioned Wackenroder reaction.

In further experiments, we added elemental sulfur to the reagents in reaction (I). Figure 1c shows the Raman spectrum of this system after it was kept for 12 hrs at 120°C. The peaks at 1,050 cm^{-1} and 980 cm^{-1} correspond to 1 M HSO_4^{-} solution and 0.2 M sulfate. Obviously, this reaction is far faster than with SO_2 and water alone, as observed in the experiment shown in Figure 1a. We observed the behavior of this system over a range of temperatures between 20°C and 200°C, and conclude that it is catalyzed by solid as well as liquid elemental sulfur. We do not understand the mechanism, but the affinity between sulfur dioxide and elemental sulfur is consistent with our earlier observation that the solubility of elemental sulfur in SO_2 exhibits unusual temperature dependence (Meyer, 1971). The solubility and catalysis effects are both difficult to measure quantitatively, because sulfur undergoes a phase transition at 95°C and changes its allotropic composition above the melting point at 124°C. The catalysis appears to be inhibited by a factor of four in 1 M HCl, but this effect is due to the fact that HCl reduces the solubility of SO_2 in water.

In the last set of experiments we sealed SO_2 in a tube containing 0.1 M BaCl_2. The solution promptly clouded at room temperature due to the formation of BaSO_3 which slowly precipitated. Figure 1d shows the Raman spectrum of the suspension after 9 hrs. The strongest peak at 960 cm^{-1} is due to barium sulfite. The peaks at 800, 490 and 460 cm^{-1} are due to orthorhombic elemental sulfur. The peak at 980 cm^{-1} corresponds to sulfate. Since barium sulfate has a solubility product (Cohen, 1940) of about 10^{-10}, our observation indicates that the sulfate ion concentration reaches at least 10^{-9} M in our system.

Our experiments show that the ubiquitous reactions (I) and (II) can proceed over a wide range of temperatures, and thus can take a dynamic role wherever elemental sulfur and sulfuric acid or sulfite and water are present. The Pioneer experiments (Knollenberg, 1979; Oyama, 1979; Stewart, 1979) have recently indicated that in the upper cloud layer in the atmosphere of Venus at 13°C, sulfuric acid (Knollenberg, 1979) and sulfur dust are present. In lower, hotter levels, 30 miles above the ground, sulfur dioxide (Oyama, 1979; Stewart, 1979) and water vapor at about 200°C are present. Our work suggests that under these conditions, a dynamic chemical equilibrium between the atmospheric layers can be expected. As a further example, the Voyager Project shows that active volcanoes exist on Io and that its surface contains elemental sulfur (Nelson, 1978). Again, the temperature of the effluents is high enough to enhance equilibrium among reaction products before they are condensed on the cold surface. Finally, it is quite possible that reactions (I) and (II) can participate in the formation of sulfur deposits under conditions found in bio-epigenic deposits.
Further study of these systems seems highly desirable, and would also directly benefit terrestrial pollution abatement processes, because the same chemicals occur in the liquor of several abatement systems used for capturing sulfur dioxide from coal burning electric power plants. In those systems a recurring key problem is the unreliable kinetics of conversion of sulfur (IV) to sulfate and/or elemental sulfur. It is amazing how little progress has been made in understanding the mechanism and the catalysis of reactions (I) and (II) since Priestley, 1970, or Wackenroder, 1846.

ACKNOWLEDGMENT

This work was partly supported by a contract from the Morgantown Energy Technology Center, U.S. Department of Energy.

REFERENCES


This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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