five-line spectrum as reported previously. However, when the five-line species decayed, the spectrum observed was a single line with a width less than the spread of the triplet spectrum observed in ordinary 95% H_2SO_4. Because the line did not have a Lorentzian shape, we believe that it probably consists of unresolved hyperfine structure. Indeed, two equivalent deuterons in the radical would be expected to yield a quintet with one-third the spread of the proton triplet. Because the splitting would be smaller than the line width, an unresolved spectrum would be expected. Thus we believe these results confirm the interpretation that the radical contains two equivalent hydrogen atoms.

The three-line radical was observed to migrate toward the cathode of the transference cell. This result established that the species was positively charged.

The concentration of the three-line species was determined by comparison with the manganese(II) standard and was found to correspond to less than 0.0028 spin per original S_4N_4. Obviously the three-line radical is a relatively unimportant species as far as the overall stoichiometry is concerned.

In summary, the data indicate that the three-line radical is formed in small amounts, probably as one of the decomposition products of the five-line radical. It is positively charged and contains two equivalent hydrogen atoms and at least one sulfur atom. Inasmuch as no nitrogen hyperfine coupling is observed, the radical probably contains no nitrogen atoms, and in view of the fact that the radical forms only in sulfuric acid containing appreciable amounts of water, it seems likely that it is a hydrolysis product containing hydroxyl groups. The high g value and the small hydrogen coupling constant indicate that the radical is probably a π radical. From the available data it is impossible to determine its exact composition or structure.

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Formation and Reversal Kinetics of High-Pressure Sulfur XII

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Sulfur phase XII is in equilibrium with the liquidus at pressures above 20 kbars and may be crystallized at these pressures at temperatures above 200–240°. The rate of crystallization increases by a factor of 1.5–2 for each 10° along an isobar but it decreases with increasing pressure. The activation volume for the transition to XII is about $+2$ cm^3/mol. The very slow rate of formation of XII in the lower temperature region of its apparent stability field renders this phase difficult to detect unless sufficient time is allowed for reaction. For this reason dynamic methods are not successful in locating the lower temperature phase boundary, especially since the enthalpy of transition appears to be small.

Introduction

During a study of the high-temperature high-pressure equilibria displayed in sulfur[1] the authors found evidence for ten new high-pressure phases. Only one of these ten phases could be retained metastably upon quenching to room conditions, but six or more were indicated by quenching to about −30°. The kinetics of the formation of the readily quenchable phase (designated as phase XII) and its metastability both show unusual features and these are reported herein, together with possible explanations for the phenomena.

Earlier, Geller[2] as well as Sclar, Garrison, Gager, and Stewart,[3] publishing almost simultaneously, had reported quite different methods for the preparation of phases which are close to what we call phase XII. Ward and Deaton[4] also reported the synthesis of the same phase. Geller further determined that it crystallizes in the orthorhombic system and that the structure is based on right- and left-handed helical chains of sulfur at least half of which have some disorder about their axes. In the present report we shall call it sulfur phase XII.

Experimental Section

Pressure and temperature were applied in an opposed-anvil system described by Dachille and Roy[5] and calibrated and checked for pressure homogeneity by Myers, Dachille, and Roy.[6] Details of sample assemblies, heating times, and quenching procedures in the sulfur work are given by Vezzoli.[7]

High-purity orthorhombic sulfur (99.999%, prepared by American Smelting and Refining Co.) was used as the starting material and was stored in a vacuum desiccator. The quenched products were examined by using a petrographic microscope, Norelco X-ray diffractometer, and Debye–Scherrer film methods.

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Results

Some indication of the influence of temperature on the rate of formation of phase XII is afforded by the percentage conversion figures shown in various areas within the XII field shown in Figure 1. The field shown for phase XII is based on the results of 100 separate runs, many of which were of 2 or more weeks' duration. The data indicate that the conversion rate increased by a factor of 1.5–2.0 with each 10° increase of temperature along an isobar. The conversion is not necessarily from the orthorhombic sulfur phase I which was charged as the starting material but may be from phases whose fields were traversed in p–T space in the process of achieving p–T conditions in phase field XII. This conclusion is derived from our observations of sharp volume and electrical resistance discontinuities along the interposed boundaries which are taken as being indicative of phase transitions.[1]

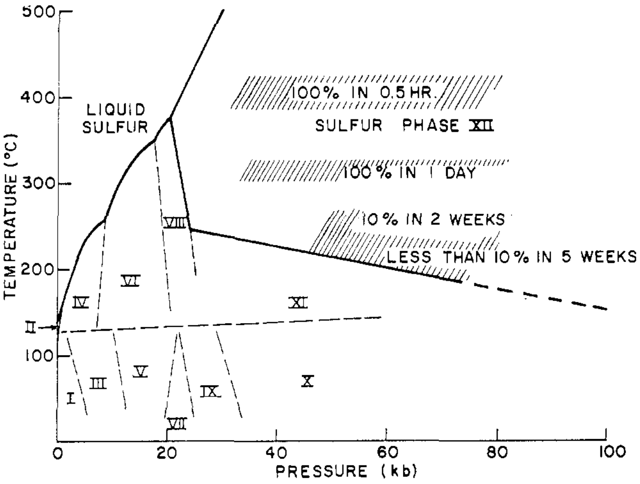

Figure 1.—The apparent phase field of sulfur XII, with fields for other crystalline phases sketched in. The percentage figures refer to the amount of XII relative to orthorhombic sulfur (I) in the quench product as determined from the intensities of their major X-ray diffraction maxima corresponding to 4.04 and 3.85 Å, respectively.

Figure 2 shows the effect of pressure on the rate of crystallization of phase XII at 305 ± 2° for pressures of 30, 50, and 70 kbars. The X-ray method that was utilized for estimating the amounts of the phases present was not sufficiently sensitive to permit any conclusions about crystallization at low product phase concentration. However, the inhibiting effect of pressure on the formation of sulfur phase XII is obvious. This pressure effect remained noticeable up to a temperature of about 350°, above which the conversion was almost complete within 0.5 hr at all pressures investigated. There is also an indication that induction of nucleation and the rate of early crystal growth may be strongly influenced by pressures of 70 kbars but this matter was not further pursued.

The data shown in Figure 2 fit first-order kinetics curves of the form $dc/dt = -kc$. According to transition-state theory, the volume of activation for a polymorphic reaction, ΔV^*, may be calculated from the relation $d \ln k/dp = -\Delta V^*/RT$. From the data in Figure 2, ΔV^* is found to be positive and of the order of 2 cc/mol. The positive ΔV^* is a reflection of structural changes and bonding processes and may eventually provide an insight into the mechanisms of the reaction.

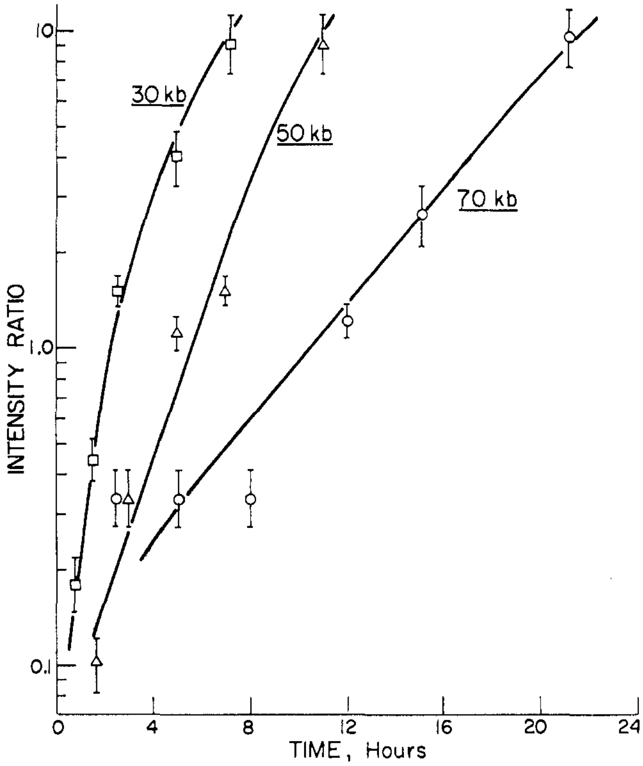

Figure 2.—The intensity ratio of the major X-ray diffraction maxima of sulfur XII relative to sulfur I *vs.* time in the quench product for a series of runs at 305° and 30, 50, and 70 kbars.

With the exception to be noted, the reversal of XII could not be achieved under the p–T conditions in any other solid-phase field. We have found, however, that by preparing sulfur XII at 45 kbars and 320° and then lowering both pressure and temperature slowly in several small steps (decreasing pressure first, then temperature, etc., along a path which would avoid crossing the liquidus) a product was obtained which produced an X-ray pattern similar to that of the sulfur phase reported by Baak[8] having a major reflection at 3.66 Å. This product may be a metastable single phase or a mixture of metastable phases and is not represented in Figure 1.

Discussion

Some evidence for a transition in sulfur to a phase showing metallic conduction has been found at pressures from 100 to 300 kbars.[9] Deaton and Blum[10] predicted that sulfur would undergo a transformation under pressure from a ring-type to a chain-type structure prior to a transformation to the metallic state. According to Geller[2] the sulfur phase we call XII is constructed of helical chains of period ten atoms in contrast to the stable atmospheric pressure crystalline

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forms of orthorhombic and monoclinic sulfur which are based on eight-membered puckered ring molecules.[11,12] Hence phase XII has a structure very similar to the spiraling zigzag chains of selenium and tellurium[13] and represents one step in the sequence predicted by Deaton and Blum.[10]

The failure to reverse the XII phase of sulfur near its solid–solid boundaries and its persistence as a metastable phase at atmospheric conditions appear to be properties consistent with the radical reconstructive change in structural building units. If in the close-packed helical chain structure of sulfur XII the second nearest neighbor distance is appreciably shorter than the van der Waals diameter $2R(d)$ of the atoms [as is the case for selenium and tellurium[14]], then there would be a high probability for the existence of secondary bonds. The term secondary bonds is used in the sense of attraction based on second nearest neighbor interactions or more distant ones. Hence in the case of close-packed chains, secondary bonding would refer to attractive interactions other than covalent bonding. Von Hippel,[15] discussing the structure of selenium and tellurium, states that chain structures, once formed, are interlinked by so many secondary bonds that the chains in general cannot revert to ring molecules. It should be noted that hexagonal selenium, based on spiral chains, is more stable under all conditions than monoclinic selenium which is based on Se_8 rings.

Similar structural factors certainly apply in the case of sulfur XII relative to sulfur I where a close-packed chain → octameric ring polymorphic transition would have to take place. The structures of phases in fields neighboring that of XII are not known. There is, however, a feature of the phase diagram which invites a very tentative suggestion about the basic building units of these phases. It is known that scission of the octameric rings of sulfur at atmospheric pressure occurs at about 119°. We have found a series of transitions which extends from about 1 kbar at 120° to 56 kbars at 140° which may be associated with a ring scission process that is only slightly pressure dependent. If this is in fact more than a coincidence, then the phases on the lower temperature side of the boundaries would be constituted of the ring molecules, while those at higher temperature (with the exception of II) would be based on chains, with phase XII having the most complex and close-packed chain structure in the series.

Interpretations of the data shown in Figures 1 and 2 may resolve apparent discrepancies among the results of various workers. For example, Baak's sulfur phase diagram[8] showed that the phase producing a single X-ray diffraction reflection at 4.04 Å was not formed at temperatures lower than about 350°. Since conditions of synthesis as well as the characteristic d spacing indicate that this phase is related to sulfur XII, it is felt that Baak was not able to form it at temperatures between 250 and 340° because sufficient time had not been allowed.

Further, dynamic methods used in the study of sulfur in the p–T region of phase XII have yielded results at variance with those from the static phase equilibrium and synthesis procedures. Differential thermal analysis[16] and thermal analysis[17] experiments did not reveal any evidence of a solid-state transformation to phase XII. The more sensitive procedure of differential thermal conductivity analysis by Ward and Deaton,[4] however, did show discontinuities in this pressure region but at a temperature of 400°.

It is clear that solid–solid transitions to XII are slow at the lower temperatures of the apparent stability field and, further, that the enthalpies of transition must be small. Both these features are manifestations of mechanisms of structural changes. If the "infinite," close-packed chain structure of XII were to be formed directly from packed octameric rings, the net change in the strong covalent bonding would be low and the net changes in the relatively weak van der Waals bonding may or may not dominate the enthalpy of transition. However, it is more likely that the phases neighboring XII are also based on long chains but with a lesser degree of close packing. In this case the enthalpy of transition would definitely be dominated by van der Waals bonding forces associated with the degree of close packing and would tend to be small.

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