homologs and some Si_2OF_6 was evolved from reaction of the polymer with the Pyrex container; 160°, mostly SiF_4, higher perfluorosilanes, and Si_2OF_6 evolved.

Discussion

When the SiF_2–H_2S reaction was first investigated, the "diradical" mechanism of SiF_2 reactions seemed well established—with the single exception of the hexafluorobenzene reaction.[2] In accord with this mechanism, one would expect the predominant product of the reaction to be 1,1′,2,2′-tetrafluorodisilanethiol, SiF_2HSiF_2SH. Although this compound is indeed formed in the reaction, it is not the major product—SiF_2HSH and Si_2F_5H are obtained in higher yields. In this regard, the present reaction is analogous to the SiF_2–GeH_4 reaction.[4] Moreover, several other reactions recently studied in this laboratory[6] give rise to major products which contain only one silicon atom. It seems at this point that, among reactions of SiF_2 with inorganic substances, the SiF_2–BF_3 and the SiF_2–benzene reactions in which the products contain at least two silicons should be considered the exception.

The silanethiols produced in this reaction were found to be of limited stability, as have those synthesized in the past. Moreover, as with the fluorosilylgermanes generated in the germane reaction, the stability of the fluorosilanethiols decreases markedly with increasing numbers of silicon atoms. Condensation was evident in the trap-to-trap distillation of the volatiles; each transfer of sample left an intractable viscous liquid or spongy solid on the walls of the trap. It is possible, then, that the compounds $SiF_2H(SiF_2)_nSH$, where $n > 1$, are formed in the reaction but decompose very readily to higher molecular weight species of the form $H(SiF_2)_nS(SiF_2)_nH$ or $(SiF_2)_n$, liberating H_2S. In this respect it is interesting to note that SiF_2HSSiF_2H, the product expected from condensation of SiF_2HSH, was not observed.

It is difficult to ascertain whether or not SiF_3H is a product of the reaction or simply a decomposition product of Si_2F_5H and perhaps higher molecular weight homologs. Si_2F_5H does appear to be a legitimate product; it was often obtained in yields as high as 40% (based on total volatiles) and has been reported as a product in the reaction of SiF_2 with HBr.[13] Consideration of the fact that no compounds such as SiF_3SH or Si_2F_5SH were observed, along with the high yield of pentafluorodisilane, leads to the suggestion that reaction is not a concerted process but that at least two steps are involved. The first is the abstraction of a hydrogen atom from H_2S by an $(SiF_2)_n$ species. The resultant radical may then either attack the thiol radical produced in the first step or may obtain a fluorine atom from an SiF_4 or $(SiF_2)_n$ species. A possible explanation of the dithiol functions observed in the products is that they result from attack of SiF_2 (or Si_2F_4) on H_2S_2, which might in turn be formed from combination of the thiol radicals formed in the first step of the reaction.

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The Melting Curve of Sulfur to 31 kbars

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The melting curve of sulfur has been determined to 31 kbars by the use of the opposed anvil and simple piston–cylinder techniques. Triple points have been found at 9 kbars and 255°, 18 kbars and 344°, and at 20.6 kbars and 375°.

Introduction

The effect of high pressure on the melting temperature of sulfur has been the subject of much inquiry. Tammann,[1] by specific-volume methods, investigated the melting curve of sulfur to a pressure of about 3 kbars. Rose and Mugge,[2] relying on an optical study of the quenched product, determined the liquidus to about 20 kbars and reported what appears to be a definite slope change at about 9.6 kbars at 205°.

Deaton and Blum,[3] using a tetrahedral anvil pressure apparatus setup for differential thermal conductivity analysis, found the melting curve of sulfur to 45 kbars and 700° to be approximately a straight line with a slope of 15°/kbar. Baak,[4] employing an opposed anvil apparatus, determined the melting curve of sulfur to 60 kbars and found it to be concave toward the pressure axis. Paukov, Tonkov, and Mirinskiy,[5] employing a thermal analysis method in conjunction with a "cubic" anvil pressure system, located a maximum in the melting curve of sulfur at approximately 16 kbars and 310°

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and a cusp (or apparent triple point) at 19 kbars at 290°.

Bell, England, and Kullerud,[6] utilizing differential thermal analysis methods, determined the melting curve of sulfur to be an almost temperature-independent straight line (up to 20 kbars) differing widely from all other sulfur melting curves reported to date. Susse, Epain, and Vodar,[7] using a belt apparatus and differential thermal analysis, determined the liquidus of sulfur to 90 kbars, finding maxima at 15 kbars at 300° and at 86 kbars at 680° and a cusp at 19 kbars at 290°.

Approximate locations of portions of the melting curve of sulfur may be deduced from data presented by Geller[8] and Sclar, Carrison, Gager, and Stewart.[9] Both papers also report a new quenchable high-pressure phase, with the former reporting two other pressure-induced phases.

Ward and Deaton,[10] using differential thermal conductivity analysis in a piston–cylinder apparatus, determined the melting curve of sulfur to 60 kbars and reported an apparent triple point between rhombic, fibrous, and liquid sulfur at 37 kbars and 410°. They also reported, however, that nucleation of samples with fibrous sulfur changes the triple point to 29 kbars and 380°. (For descriptions of the fibrous form see ref 8 and 9.)

Experimental Section

Apparatus and Techniques.—The apparatus utilized in our study of the liquidus of sulfur included high-pressure differential thermal analysis (up to 1 kbar), a simple piston–cylinder setup of tungsten carbide or steel Bridgman-seal pistons (fitted snugly into a Rêne 41 cylinder), and the opposed anvil system developed originally in their laboratory and described by Dachille and Roy.[11] Analysis was accomplished by optical, petrographic microscope, and X-ray diffraction studies of the product of the thermally quenched samples.

In the case of opposed anvil runs, the melting curve was investigated by the conventional technique consisting of the nickel ring and platinum–10% rhodium foil assembly.

It was found that by using rings having a smaller inner diameter (0.097 cm) than that usually used, the frequency of blowouts could be reduced. Throughout the study of the liquidus, pressure was raised first and maintained for 45 min before temperature was increased at a moderately slow rate (about 5°/min).

Temperatures were measured by chromel–alumel and platinel II thermocouples and are accurate to ±1 to ±2°. Supplementary series of experiments indicated a precision of ±1° at triple points along the liquidus. Pressures are accurate to ±5% in the dta system, ±5–10% in the opposed anvil setup, and ±10% in the piston–cylinder apparatus.

The melting curve of sulfur, determined with the use of the opposed anvil system with the nickel ring–platinum foil assembly, is shown in Figure 1. The curve represents the locus of points at and above which the thermally quenched product, at a given pressure, is discontinuously and substantially different (with respect to physical properties) from the product which is characteristically obtained after quenching at the same pressure, but from the immediately lower temperature. Products which were quenched from below this curve are yellow brittle solids; those quenched from pressures less than 20.6 kbars give an X-ray diffraction pattern at room conditions corresponding to rhombic sulfur; products quenched from between approximately 240° and the liquidus at pressures greater than 20.6 kbars produce an X-ray diffraction pattern at room conditions corresponding to a quenchable high-pressure phase.[8,9]

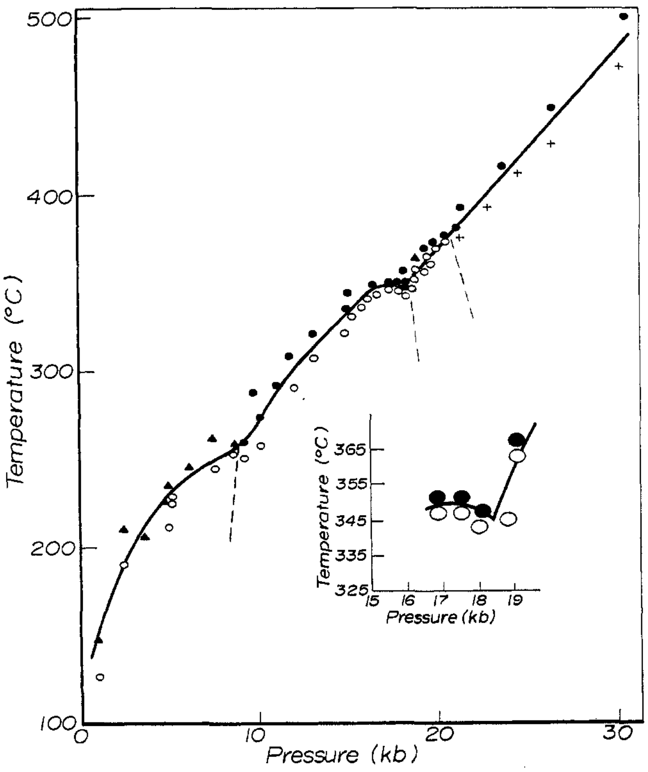

Figure 1.—The melting curve of sulfur to 31 kbars determined with the *opposed anvil* apparatus. The insert represents a second series of runs in the neighborhood of 17 kbars. The products obtained on *thermally quenching* samples from the *p–t* conditions are represented by the following symbols: ○, rhombic sulfur; ▲, slightly stretchable viscous-plastic material; ●, highly stretchable viscous elastic material; +, quenchable high-pressure phase.[8,9]

Over the pressure range of 2–8.5 kbars, the product which is quenched from just above the liquidus is generally a viscous-plastic material that, if X-rayed immediately, using the diffractometer technique, produces a pattern indicative of an amorphous material.

However, the pattern of rhombic sulfur, with reduced intensities and altered intensity ratios, is obtained with the use of the Debye–Scherrer camera technique, as the noncrystalline phase crystallizes in a few hours at room temperature. This product is *soluble* in CS_2. In the pressure range of 8.5 to about 20.6 kbars (except for pressure near 19 kbars), the quenched product from just above the liquidus is a very viscous and stretchable material that also gives an "amorphous" pattern (on the diffractometer) when X-rayed immediately at room conditions; however, it is *insoluble* in CS_2. Debye–Scherrer diffraction photographs of this product are of rhombic sulfur but with pronounced changes in intensity ratios and show, in addition, a new reflection corresponding to a *d* spacing of 4.52 Å. From near 19 kbars on the liquidus and extending along a narrow *p–t* range to 400° and 10 kbars, the quench product is the same as that obtained from 2 to 8.5 kbars just above the liquidus. Our findings on liquid sulfur pressure are reported elsewhere.[12]

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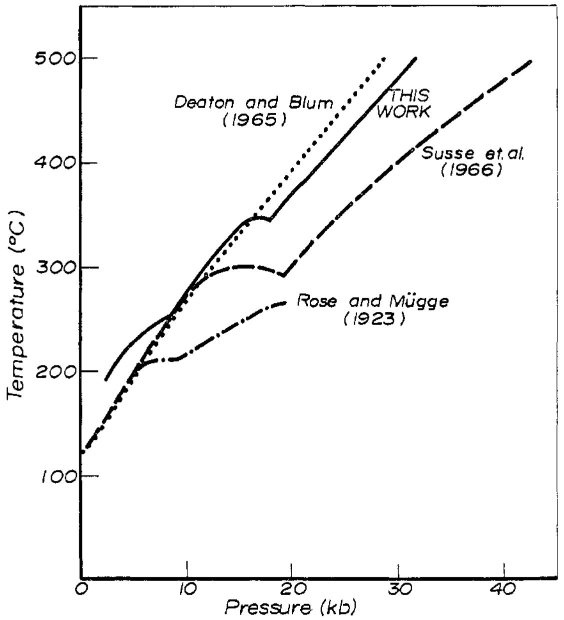

Figure 2.—Comparison of melting curves

At pressures greater than 21 kbars, nickel rings with the small inner diameter (0.097 cm) had to be utilized in order to contain the sample. In this case the sample was insufficient to produce good X-ray diffractometer patterns. However, the products quenched from above the liquidus at pressures exceeding 21 kbars produced the same Debye–Scherrer diffraction pattern and had the same properties as the highly stretchable material which was quenched from above the liquidus and at pressures between 8.5 and 20.6 kbars.

The melting curve, drawn in Figure 1, shows definite cusps at 9 kbars and 255° and at 18 kbars and 344°, a very slight cusp at 20.6 kbars and 375°, and what appears to be a maximum at 17 kbars and 348°. A total of 70 critical quench runs, many spaced only 0.5 kbar apart, was used to delineate the curve up to 31 kbars. Admittedly, the difference in temperature between the maximum at 17 kbars and the cusp at 18 kbars is not much larger than the margin of error in measuring temperature. However, 30 of the 70 runs were made between 17 and 19 kbars, and results were found to be completely consistent. The results of a second series of experiments in this region, also indicating this maximum, are plotted in the insert in Figure 1. A third series gave the same results. Based on all of the data, the precision of the location of the critical features of the melting curve is ±0.5 kbars and ±1–2°.

Confirmation of the existence of the three cusps was found in a study of the polymorphism of sulfur,[13] with the determination of phase transition boundaries consistent with the approximate locations of triple points at the cusps.

In the opposed anvil apparatus, the melting curve could not be adequately studied at pressures exceeding 31 kbars because at temperatures above 500° the nickel in contact with the sulfur reacted to form Ni_3S_2.

Samples which were quenched from *p–t* conditions corresponding to the solid–liquid boundary gave spotty Debye–Scherrer patterns. Since at these conditions the solid and liquid coexist in equilibrium, the spotty patterns were indicative of the presence of numerous well-formed crystals. Furthermore, microscopic examination of products which were quenched from the solid–liquid boundary at pressures less than 20.6 kbars revealed euhedral crystals having clean, straight extinctions. On the other hand, microscopic examination of products quenched from below our melting curve (but above the liquidus as reported by Bell, *et al.*) showed them to be very fine-grained solids exhibiting no distinct crystals—similar in appearance to products from all other solid-phase regions other than that of the quenchable high-pressure phase.

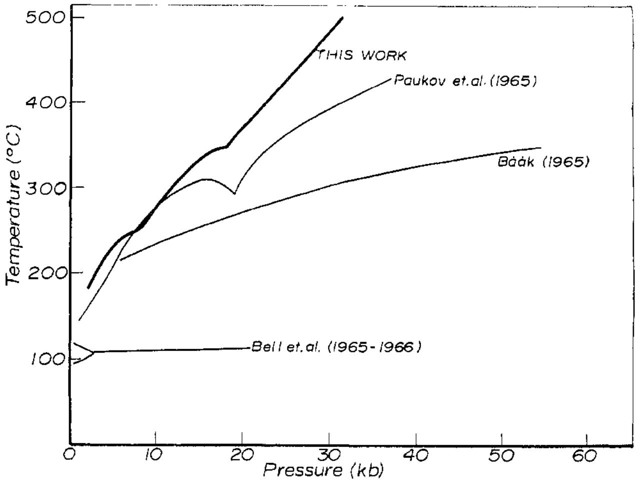

Figure 3.—Comparison of melting curves.

In order to make it possible to apply the Clausius–Clapeyron equation to any point on the liquidus, empirical equations were derived, capable of describing the curve in each smooth interval within an accuracy of 1%.[14]

The presence of the maximum in the liquidus at 17 kbars at 348° indicates that at these conditions the change in volume upon melting is zero. Deaton and Blum[3] gave two "explanations" for the presence of a maximum in a melting curve: first, an increase in the coordination of the liquid as a function of pressure to give rise to the required condition that the density of the liquid exceeds that of the solid at pressures beyond the maximum on the curve, and, second, the existence of a solid–solid boundary intersecting the melting curve at the maximum. We have found no evidence to affirm the existence of such a boundary and would therefore favor the first explanation, especially in light of the major structural changes we have noted in liquid sulfur at high pressures.[12]

Melting at approximately constant volume could be the result of the liquid having a very efficient packing arrangement over a short range in the neighborhood of the maximum. Alternatively, at the maximum, crystalline sulfur may be melting to an equilibrium concentration of two liquid allotropes or two different polymers of a density equal to that of the solid phase. However, our study of liquid sulfur[12] indicates that, at the maximum at 17 kbars, sulfur melts to a single liquid.

In Figures 2 and 3 the melting curve determined from the results obtained with our regular opposed anvil technique is compared with seven curves for the melting of sulfur reported by others. The wide divergence among all of these results, in the absence of any calibration data concerned specifically with pressure and temperature of the sulfur *in situ*, clearly indicates that many factors may be responsible. These factors would include the nature of the starting material, types of pressure systems used, and details of technique and sample configuration.

It is hardly likely that differences in purity of the sulfur which was used in the several investigations could be responsible for the significantly different melting curves. The molal freezing point lowering of sulfur at atmospheric pressure is of the order of 33°. This would hardly begin to explain the wide differences in the melting curves reported by the various workers without having grossly impure sulfur or an inordinately high increase of the cryoscopic constant with pressure. At a pressure of 20 kbars these differences vary from about 10 to almost 300°. As far as we know, all workers started with rhombic sulfur, thereby avoiding the influence of metastable forms.

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The matter of apparatus is more complicated for, as mentioned earlier, three major families were used by the various workers: opposed anvils; multianvils or piston–cylinders utilizing solid pressure-transfer media surrounding the sample; and gas-pressured apparatus. In our work with other types of apparatus or with modified techniques using opposed anvils we have found some indications of cause for discrepancies in results. For example, while our piston–cylinder data generally fitted the curve shown in Figure 1 up to a limiting pressure of about 13 kbars, the cusp in this portion of the curve was apparently lowered both in pressure and temperature. Our interpretation of this behavior is that on approaching the *p–t* conditions of the cusp, the boundary of a very rapid solid–solid transition had to be crossed at which time the sample–apparatus complex responded with an exaggerated volumetric change or "blowout."

Another example was found in the results we obtained on using a modified sample wafer assembly with the opposed anvils. In this series of runs the enclosed platinum–rhodium foils were omitted and instead the faces of the anvils and nickel ring were coated with an abrasive (rouge). The melting curve up to 23 kbars obtained with this procedure was displaced in the up-pressure direction and showed some unusual features. This behavior is attributed to the fact that the use of the abrasive in effect made the containing ring more rigid than in normal usage, so that it could support a greater proportion of the load force and, in general, would be less compliant to volumetric changes of the sample.

Data and further discussion concerning these two examples will be found in ref 14, as will a consideration of the marked deviations of the melting curves of Baak and Bell, *et al.*, from the others shown in Figures 2 and 3.

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An Investigation of the Structure of the Disulfite Ion in Aqueous Solution Using Raman and Infrared Spectroscopies

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The species formed upon preparing saturated solutions of sodium and potassium disulfites ($Na_2S_2O_5$ and $K_2S_2O_5$, respectively) have been studied using Raman and infrared (4000–200 cm^{-1}) spectroscopies. These studies are supplemented by an examination of the corresponding solid salts by both techniques. Fifteen lines which are attributable to the disulfite ion appear in the Raman and infrared spectra, and nine of the Raman lines are found to be polarized. These measurements indicate an assignment of this ion to the C_s point group, consistent with its formulation as an asymmetrical species containing a S–S bond in contradiction to earlier vibrational investigations by Simon and coworkers.[2] There is some evidence for the existence of the hydrogen disulfite ($HS_2O_5^-$) ion. Also, Raman spectra of the sulfite ion (sodium salt) indicate that the degeneracies of the E modes at *ca.* 930 and *ca.* 470 cm^{-1} are removed in concentrated aqueous solution.

In a fundamental review of problems in the hydration of ions in solution, Taube[3] noted the incongruity between the symmetrical $O_2SOSO_2^{2-}$ structure proposed for the disulfite ion on the basis of Raman data[2] and the asymmetrical one, $O_3SSO_2^{2-}$, assigned from a complete X-ray determination by Lindqvist and Mortsell,[4] confirming an earlier study by Zachariasen.[5] Although Raman spectra were obtained for both the solid and concentrated aqueous solutions,[2] structural conclusions were based primarily on the solution measurements. The case for a definitive assignment of structure for this ion in aqueous solution is generated by Woolfolk's bacterial studies,[6] which indicate that disulfite is the metabolized species in assimilatory sulfite reduction with dithionite ($S_2O_4^{2-}$) formed as an intermediate in a reversible initial step. Similarly, the dithionite–disulfite equilibrium is of probable significance in adenosine triphosphate dependent hydrogen evolution[7,8] and $Na_2S_2O_4$-supported nitrogen fixation[8] by extracts of *Clostridium pasteurianum*, as well as in the reduction of tetrahydroporphyrin by sulfite and dithionite.[9] Although a rearrangement to the oxygen-bridged species in solution is possible, this would represent one of the more drastic departures from solid structure upon dissolution, and it would be difficult to formulate a biological mechanism for sulfite reduction[6] incorporating the symmetrical structure.[10,11]

Experimental Procedures

Reagent grade sodium disulfite (J. T. Baker) and potassium disulfite (Fisher) were used without further purification in preparation of saturated solutions. The disulfite concentration was approximately 2.5 *F*. Saturated solutions of sodium sulfite (J. T. Baker) were similarly prepared. Below pH 3.0 the solutions evolved sulfur dioxide and a previously noted yellow color[12] developed, preventing measurement of a Raman spectrum using the 4358-Å mercury line. Above pH 8.0 the spectrum is characteristic of sulfite ion as the predominant species. The spectrum of the solution was measured at several acidities within

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