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A STUDY OF THE $Ge\text{-}GeO_2$ AND $Si\text{-}SiO_2$ SYSTEMS

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August, 1955

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ABSTRACT

The $Ge-GeO_2$ and $Si-SiO_2$ systems have been studied by thermal analysis and the phase diagrams partially worked out.

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The $Ge-GeO_2$ (hexagonal) system has been examined by differential thermal analysis. A sample of 25 mole % GeO_2 absorbed heat at 890°, 950°, and 1000°C and evolved heat upon cooling only at 850°C. At 50 mole % GeO_2, heat absorption was observed at 865°, 925°, and 980°C and heat evolution at 870°C. At 25 mole % GeO_2 heat absorption was observed at 865°C with a small heat effect at 920°, but upon cooling from 1350°C no heat effects were observed. A sample of 89 mole % GeO_2 also supercooled and gave no heat effects upon cooling. X-ray examination of supercooled melts gave no crystalline patterns.

The first heat effect at 870° ± 20°C observed across the entire diagram is clearly the eutectic temperature, in good agreement with Candidus and Tuomi[1] and Thurmond and Trumbore.[2] The second break corresponds to the melting point of germanium or the monotectic temperature. The third break at around 1000°C for some samples may be due to miscibility of the two liquid phases but is probably due to inhomogeneity of the samples. Supercooling and difficulty of maintaining contact between the thermocouple well and the sintered material made accurate temperature measurements difficult. Also cycling of samples caused extensive segregation into metallic and oxide phases owing to their density difference, and best results were obtained on the first heating cycle with well-mixed powders. The previous observations[1,2] in regard to yellow and black supercooled eutectic melts have been confirmed.

Holding of an 89 mole % GeO_2 sample at 920°C for four hours resulted in conversion of hexagonal GeO_2 to tetragonal GeO_2 plus some supercooled liquid. Samples of 89 mole % GeO_2 were heated to 1350°C using hexagonal GeO_2 on one hand and tetragonal GeO_2 on the other. The hexagonal sample gave one break at 833°C, the tetragonal sample

gave only one break at 920°C, and neither sample gave any breaks upon cooling. Both samples yielded a black Ge-rich phase and a yellow amorphous GeO_2 phase. These results confirm Thurmond and Trumbore's conclusions about a higher eutectic temperature for the Ge-GeO_2 (tetragonal) system than for the system with the hexagonal oxide phase. No evidence for a GeO phase is found, and the system is thus of the eutectic type with a miscibility gap for the liquids.

Doubt has recently been cast on the high-temperature x-ray determination of SiO.[3,4] Brewer and Edwards[5] have demonstrated that SiO is unstable below 900°C but would be expected to become increasingly more stable up to the melting point of Si, where the high entropy of fusion of Si would result in reduced stability of SiO upon further increase of temperature. Thus if SiO has any range of stable existence, it must become stable between 900°C and 1420°C. The heat effect upon formation of SiO from Si and SiO_2 would have to be close to zero.[4] Thus no heat effect would be expected upon heating an equimolal mixture of Si and SiO_2 if they reacted to form SiO, while a substantial heat effect would be observed at the melting point of Si if the reaction to form SiO had not taken place. Samples with 50 mole % SiO_2 and 75 mole % SiO_2 using crystalline α-quartz gave no heat effect in the conventional differential thermal analysis apparatus up to 1350°C nor in an inductively heated apparatus using a molybdenum block up to 1480°C. This latter apparatus was not provided with as sensitive a detecting system and difficulty was experienced in the shrinking away of the sintering powder from the thermocouple well, but heatings of pure silicon did give breaks near the melting point of silicon. Further checks are planned with more sensitive equipment. If these results can be confirmed they would indicate that silicon is consumed by a reaction, presumably going to SiO between 900°C and 1480°C. The cooled samples show only patterns due to silicon and α-cristobalite. Crystalline α-quartz heated without silicon under similar conditions remained unchanged.

All samples were heated in silica glass capsules, because of the high vapor pressures of GeO and SiO, with thermocouple wells pushed into the sides of the capsules.

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