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DIFFERENTIAL THERMAL ANALYSIS OF THE Si-SiO_2 SYSTEM

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Abstract—An inductively heated differential thermal analysis apparatus has been used to demonstrate that SiO_2 does not react with silicon to form SiO solid at the melting point of silicon. Thus SiO solid must be thermodynamically unstable at all temperatures.

BREWER and EDWARDS[1] have reviewed the properties of SiO and have demonstrated that SiO solid must be thermodynamically unstable at all temperatures below 900°C, although it can exist as a metastable phase at low temperatures. For the reaction $Si(s)+SiO_2(s) = 2SiO(s)$, they have concluded that $\Delta H°$ might be slightly positive and that $\Delta S°$ would be expected to be positive at high temperatures. Thus $\Delta F°$ would be expected to become less positive as the temperature is increased and $SiO(s)$ might become stable with respect to disproportionation at some temperature above 900°C. However at 1415°C, the melting point of silicon, $\Delta H°$ and $\Delta S°$ would surely become negative due to the high heat of fusion of silicon and any further increase in temperature would cause $\Delta F°$ to become more positive. Therefore if there is to be any temperature range of thermodynamic stability for the solid SiO phase, it must become stable below 1415°C.

HOCH and JOHNSTON[2] have presented evidence for an X-ray pattern of SiO at high temperatures, but GELLER and THURMOND[3] have pointed out that the organic cement used in the samples would form silicon carbide and that the observed X-ray pattern is that to be expected for a mixture of SiC and β-crystobalite. Thus there is no clear evidence for the stable existence of a solid SiO phase in the range 900 to 1415°C.

In the present study, an inductively heated differential thermal analysis apparatus[4] has been used to investigate the Si-SiO_2 system. If SiO were to form upon heating a mixture of Si and SiO_2, the heat effect would be expected to be too small to observe. However, if an excess of silica were present, all of the silicon would be consumed if SiO were to form and no heat effect would be expected at the melting point of silicon. On the other hand, if no reaction between Si and SiO_2 took place to form SiO, the large heat of fusion of silicon would be easily detected at 1415°C.

EXPERIMENTAL

The differential thermal analysis (DTA) apparatus described by BREWER and ZAVITSANOS[4] was used for most of this study. The experimental procedures were the same as described by BREWER and ZAVITSANOS for their study of the Ge-GeO_2 system.

The silicon used was obtained from the Electro Metallurgical Division of the Union Carbide and Carbon Co. Spectroscopic analysis indicated a purity of better than 99·9 per cent. The α-quartz form of silica was used because it is the least stable form of silica in the temperature range of interest and thus would furnish the greatest thermodynamic driving force. It contained between 0·01 and 0·1 per cent. Mg and between 0·1 and 1 per cent. Al. The silica was degassed at low pressure at 800°C. A 200 mesh mixture with an over-all composition $SiO_{1.2}$ was used in all runs.

Because of the high vapor pressure of SiO gas in equilibrium with silicon and silica, the samples were sealed in silica glass capsules with thermocouple wells pushed in the sides of the capsules. The thermocouple

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wires had to be of large enough diameter to prevent easy breaking of the wire. To maintain thermal contact, the thermocouple junction was either wedged in the well by a piece of ceramic material or fused into the well with pyrex glass. To insure thermal contact between the sample and the thermocouple well, it was necessary to make the thermocouple well slightly cooler than the rest of the capsule to insure sintering of the sample against the thermocouple well. Because of devitrification of the capsules and segregation of the silicon and silica, the samples were used only once. The maximum temperature of the runs was 1500°C.

A blank run with 0·25 grams silicon gave a good thermal break both on heating and cooling near 1400°C. Mixtures of 0·25 grams silicon with a 50 mole percent excess of silica were heated at a rate of over 100 degrees per minute and at a rate of ten to twenty degrees per minute near the melting point of silicon. Both types of runs gave sharp breaks on heating and cooling with about the same area as for the blank. In a third type of experiment, the sample was maintained just below the melting point of silicon for fifteen minutes before the heating and cooling curves were taken. The same breaks as previously were observed. As noted above, the sample tends to migrate in a temperature gradient due to the high SiO pressure. To confirm that the Si and SiO_2 had maintained sufficiently good contact to undergo reaction if a reaction were possible, a fourth type of experiment was done in which the end of the capsule protruded from the molybdenum block to insure a temperature gradient. From 1/3 to 1/2 of the material transferred to the cooler end of the capsule.

To check the results obtained with the inductively heated DTA apparatus, similar capsules were checked on a conventional platinum wound DTA apparatus to just above the melting point of silicon. The thermal breaks previously obtained were confirmed. X-ray examination of the samples showed the presence of α-quartz and silicon. Under the microscope drops of silicon could be seen. The surface of the quartz crystals appeared to have darkened.

DISCUSSION OF RESULTS

The observation of the heat of fusion of silicon in samples with excess silica demonstrates that the silicon did not react with the silica to form SiO. We know that the SiO solid phase formed by the quenching of SiO gas decomposes rapidly to Si and SiO_2 at much lower temperatures. Therefore, we can assume that SiO solid would have formed rapidly from Si and SiO_2 if it were thermodynamically stable and if there were adequate contact between the phases. Adequate contact was obtained by grinding the materials together and was demonstrated by the experiment with the temperature gradient. In that experiment, the reaction between Si and SiO_2 to form SiO gas was carried out to a very large extent because of the removal of the SiO at the cooler end of the capsule where it disproportionated to Si and SiO_2. Thus it is clear that the Si and SiO_2 can react when a reaction is thermodynamically possible, but they did not react to form solid SiO.

One might argue that this experiment does not exclude the possibility of a stable SiO solid phase that might form at a very slow rate from either Si plus SiO_2 or from SiO gas. No reliable evidence for any SiO phase other than the one obtained by quenching SiO gas is known, and the comparison to be made below with related elements makes such a possibility quite unlikely. An alternate explanation of our observations is that SiO solid did form, but that the melting point and heat of fusion of SiO coincide with those for silicon. This is likewise a very unlikely possibility.

BREWER and EDWARDS[1] have discussed two observations that indicated a reaction between Si and SiO_2. One of these was the apparently high melting point of a mixture of Si and SiO_2 that was reported by POTTER[5] and confirmed by BREWER and EDWARDS. The other is the "thermo-electric" effect reported by BREWER and EDWARDS. In view of the DTA observations, any explanation of these effects by a reaction between Si and SiO_2 must be in terms of reduced oxide that would not require consumption of any appreciable amount of silicon, e.g., $SiO_{1.95}$. EWLES and YOUELL[6] have shown that SiO_2 is reduced to $SiO_{1.999}$ by hydrogen at 750°C. Molten silica would be expected to be reduced even more. Thus one could attribute the apparent high melting point of the Si and SiO_2 mixture to an increase in the viscosity of liquid silica upon slight reduction. The "thermoelectric" effect would likewise be attributed to the effect of reduction upon the electrical properties. It will be necessary to study samples of silica containing small amounts of silicon to verify the above explanations. It might be noted that one attempt to reproduce the "thermal-electric" effect observed by BREWER and EDWARDS using the very pure silicon that is now available was not successful. It may be that the effect is to be attributed to impurities in the silicon. However, only a cursory attempt was made and a more careful study will have to be made. The Si-SiO_2 phase diagram thus has no intermediate solid phases and the two liquid phases are only slightly soluble

in one another. Our results would indicate a slight lowering of the melting point of silicon upon addition of silica, but one would have to insure comparable thermal contacts with Si and with Si-SiO_2 samples to be sure of this effect. We can only say that the lowering is less than 10-20° and undoubtedly much less.

In conclusion, the DTA observations show that the SiO solid prepared by the quenching of SiO gas is metastable and has no temperature range of thermodynamic stability. This is exactly analogous to CO solid prepared by the condensation of CO gas. CO solid is unstable with respect to graphite and solid CO_2 at all temperatures. BREWER and ZAVITSANOS[4] have reviewed the data that demonstrate that GeO solid is likewise metastable and PLATTEEUW and MEYER[7] have recently demonstrated that SnO solid is thermodynamically unstable at all temperatures. Thus in the fourth group of the periodic table from carbon to lead, all of the elements form a stable gaseous molecule MO but only lead forms a stable solid of the composition MO. In the fourth sub-group, the stability of TiO solid is well established, but the available data would indicate that ZrO and ThO solids are thermodynamically unstable at least as pure phases.[8]

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