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THE STABILITY OF HIGH-TEMPERATURE OXIDES

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Frank Terrance Greene

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THE STABILITY OF HIGH-TEMPERATURE OXIDES

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January 14, 1957

ABSTRACT

I. The Stability of SiO Solid

Equimolar Si-SiO₂ mixtures are investigated by means of high-temperature differential thermal analysis. The heat of fusion of Si is observed in all cases, and is shown to prove the thermodynamic instability of SiO at all temperatures.

II. A Study of the Ultraviolet Bands Attributed to MgO

The ultraviolet spectrum attributed to MgO is investigated by means of intensity change and isotope shift. The responsible species is shown to be an oxide of magnesium.

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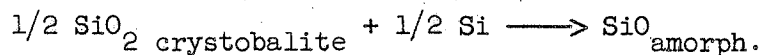
January 14, 1957

I. The Stability of SiO Solid

INTRODUCTION

The first evidence for the existence of silicon monoxide was obtained by Potter in 1907 when he quenched a gas produced over a variety of Si-SiO₂ systems at high temperature and obtained a solid with the empirical composition of SiO.¹ Tone² and Winkler³ had previously obtained a "brown vitreous substance" which was a homogeneous mixture of amorphous Si and SiO₂, but Potter contended on the basis of heat capacity and combustion measurements that his was a different material. The Si-SiO₂ mixture could be obtained by annealing the quenched solid or by a slow cooling of the gas. Subsequent spectroscopic investigations by deGramont and de Watteville,⁴ Jevons,⁵ Saper,⁶ Bonhoeffer,⁷ and Sharma⁸ confirmed the existence of gaseous SiO, and electron and x-ray diffraction work by Inuzuka,⁹ Grube and Speidel,¹⁰ Konig,¹¹ Hass and Scott,¹² Erasmus and Persson,¹³ and Hass,¹⁴ has shown that the material obtained by quenching SiO gas is indeed solid SiO. However, the stability of solid SiO has since remained in doubt, despite the work of a number of investigators.

Brewer and Edwards¹⁵ have reviewed the thermodynamic data for the reaction



The entropy of crystalline SiO at 298°K was estimated to be 8.6 eu by the Latimer method, and then modified to 6.6 eu by analogy with the discrepancy between estimated and measured values for TiO. The randomness entropy for the amorphous form of SiO should not be more than $R \ln 2$, and is taken as 0.9 eu by analogy with the data of Simon and Lange¹⁶ for SiO₂ glass. Thus, a value of 7.3 eu is obtained for amorphous SiO; ΔS_{298}° then equals -0.05 ± 1.0 eu. From the solution measurements by Von Wartenberg,¹⁷ ΔH for the reaction is taken as 0.0 ± 3.0 kcal. The free energy for the above reaction can then be calculated:

$$\begin{aligned} \Delta F_{298}^{\circ} &= \Delta H^{\circ} - T \Delta S^{\circ} \\ &= 0.0 \pm 3.0 + \left(\frac{298.16}{1000} \right) (0.05 \pm 1.0) \\ &= 0.0 \pm 3.0 \text{ kcal.} \end{aligned}$$

Therefore, the results are indecisive at room temperature. The effect of raising the temperature can be determined by estimating a heat capacity for SiO solid. This was done by making Lewis' assumption that C_v for isotropic solids is equal to the same function of $(T/\text{constant})$ and by adjusting the parameters of the experimentally known heat capacity curve for TiO to SiO, using the heat capacity at 338°K determined by Potter.¹ By using this method, we obtained

$$C_p \text{ SiO amorphous} = 10.57 + 2.98 \times 10^{-3}T - 2.72 \times 10^{-5}T^2$$

Using the equation,

$$S_{1200}^{\circ} = S_{298}^{\circ} + \int_{298}^{1200} \frac{C_p}{T} dT$$

we get $S^{\circ}_{\text{cryst. SiO at } 1200^{\circ}} = 22.4 \text{ eu}$, and -- after adding 0.9 eu for randomness entropy -- $S^{\circ} = 23.3 \text{ eu}$. Again using the heat capacity equation, we have

$$\Delta H^{\circ}_{1200^{\circ}} = 1.0 \pm 3.0 \text{ kcal}$$

and

$$\Delta F^{\circ}_{1200^{\circ}\text{K}} = -0.9 \pm 6.6 \text{ kcal.}$$

Once again the result is indecisive. Since the entropy of reaction is increasing with temperature and the heat of reaction is, and will remain, small, SiO solid will become less unstable as the temperature is raised. However, at the melting point of Si the entropy of formation of SiO from liquid Si and solid SiO_2 must become negative because of the large entropy of fusion of Si, and therefore the free energy of formation of SiO solid must become more positive as the temperature is further raised. Therefore, if there is to be a stable SiO phase, it must occur between room temperature and the melting point of Si (1420°C).

A large part of the difficulty in the experimental determination of the stability of SiO solid is that there are few distinguishing physical properties of SiO solid except for the x-ray and electron-diffraction patterns. Brewer and Edwards found that at high temperatures, Si-SiO₂ systems with the over-all composition of SiO showed an anomalous conductivity. This was evidenced by bright bands appearing in Si-SiO₂ resistance elements across which approximately 400 volts was applied. Also, Potter reported and Brewer and Edwards confirmed an anomalously high melting point for SiO composition systems. Both these observations would tend to support the high-temperature stability of SiO, but can be explained otherwise, as is

discussed later. Brewer and Edwards also used a high-temperature x-ray camera up to 900°C and found no evidence of SiO formation in a mixture of Si and SiO_2 . Hoch and Johnston presented data over a wider range that indicated the formation of SiO solid from Si and SiO_2 .¹⁸ However, an organic cement was used as binder, and it was shown by Geller and Thurmond that the reported SiO pattern was undoubtedly due to a mixture of SiC and β -cristobalite.¹⁹

In the study reported here a differential thermal-analysis technique was employed to investigate the Si- SiO_2 system to temperatures above the melting point of silicon. Since ΔH for the reaction $\text{Si} + \text{SiO}_2 \longrightarrow 2\text{SiO}$ is very small, it would be very difficult to detect the heat effect if the reaction took place. However, if the reaction did not take place, the melting of the silicon would produce a very large heat effect in the neighborhood of 1400°C .

EXPERIMENTAL

Materials

The silicon used in this work was obtained from the Electro Metallurgical Division of the Union Carbide and Carbon Company. It was reported on the basis of spectroscopic analyses to be 99.9⁺% pure. The silicon used passed through a standard 200-mesh testing sieve.

Spectroscopic analysis showed that the α -quartz used contained between 0.01 and 0.1% Mg and between 0.1 and 1% Al. It was degassed in a silica-glass crucible under vacuum at 800°C and subsequently passed a 200-mesh standard testing sieve.

Equipment

A high-temperature inductively heated differential thermal analysis apparatus was used as described by Brewer and Zavitsanos.²⁰ Because of the high vapor pressure of SiO gas, whether or not SiO solid was formed, it was necessary to seal the Si-SiO₂ mixtures into quartz capsules. These were provided with thermocouple wells which entered the top of the capsule and went nearly to the bottom. Since the top of the capsule was not covered in the Mo heating element, this arrangement automatically made the well very slightly cooler, so that the Si-SiO₂ mixture would sinter to the wall, insuring good contact. The capsule containing the Si-SiO₂ mixture and an identical blank capsule containing Al₂O₃ were then inserted into a Mo block, which served both as a holder and as a heating element. This was in turn surrounded on all sides by molybdenum radiation shields inside a zircon crucible. Standard Pt-Pt 10% Rh thermocouples were introduced through the shielding by means of ceramic insulators.

Two opposed thermocouples were then set in the two capsules to indicate the differential temperature. Leads from these thermocouples were hooked directly to a Brown recording potentiometer which required 10 mv per full deflection. A second thermocouple was inserted in the molybdenum block and hooked to a Leeds and Northrup No. 8662 potentiometer to record the block temperature. The zircon crucible was then placed in an induction furnace which consisted of a water-cooled pyrex thimble connected to a vacuum line and surrounded by an induction coil powered by an Ajax mercury-gap converter. The recorder showed some noise when the converter was operating, probably owing to the generation of small emf's in the leads, but it was not sufficiently serious to affect the operation.

Procedures

A blank run using 0.25 g of Si was first made to establish the sensitivity of the detecting system. This quantity of Si showed a good break in both the heating and cooling curves in the vicinity of 1400°C . Accurate temperature measurement was not possible in this or most of the succeeding runs, since the rate of heating was usually so great that thermal equilibrium was not established in the block. A smaller rate of heating would probably have made accurate temperature measurements possible, but for this work it was unnecessary.

In Experiment 1, a mixture of 0.25 g Si and 50 mole % excess SiO_2 (corresponding to $\text{SiO}_{1.2}$) was ground in a mortar and pestle, tamped into the silica glass capsules, and sealed. It was then heated rapidly (more than $100^{\circ}/\text{min}$) to about 1500°C . In both the heating and cooling curves a break was observed at a temperature corresponding to the fusion of silicon and containing roughly the same area as that obtained with the blank.

It seemed inadvisable to use a capsule more than once, as the capsule showed some devitrification and deformation. Also, when the capsules were broken open, very fine drops of Si were visible under magnification (and occasionally to the naked eye), so that further segregation was feared. The quartz crystals appeared darkened when compared with unsintered material, though it was difficult to tell whether they were coated or had dissolved some of the silicon, since the material still appeared homogeneous after being crushed.

In Experiment 2, capsules were prepared as in Experiment 1, and heated slowly to about 1500°C (10° - 20° /min at the higher temperatures). Reversible breaks were observed as before.

Experiment 3 was carried out as Experiments 1 and 2 except that the temperature was held just below the melting point of Si for about 15 minutes. Breaks were observed as before.

In Experiment 4 the capsule was made longer, so that it just protruded above the top of the block. Heating was carried out approximately as in Experiment 1. When the capsule was broken open, it was observed that about $1/3$ to $1/2$ of the material had collected in the cooler end of the tube.

The principal difficulties that occurred in these experiments were thermocouple failure and loss of contact between the thermocouple and well. The first seemed to be due mainly to small mechanical strains which caused the thermocouple wire to part as the softening point of Pt was approached. Difficulty ceased when larger-diameter wires were used. Several methods were attempted to prevent loss of contact between the thermocouple well and the thermocouple. The more successful

expedients included wedging the thermocouple in with a piece of ceramic, or adding powdered pyrex to provide contact or by prefusing the thermocouple in place. With the heavier wire later used it was found that enough pressure could be applied through the insulator to hold the thermocouples firmly in place.

To check the results from the induction-heated DTA, similar capsules were made and checked on a conventional differential thermal analysis apparatus with Pt windings. The break due to the fusion of Si was observed as before at about 1400°C.

Samples from several of the runs were x-ray-analyzed. In these samples only α -quartz and silicon were reported.

DISCUSSION OF RESULTS

From the observation of the heat of fusion of silicon, it is evident that the silicon was not consumed by a reaction and that SiO did not form. Since SiO solid decomposes rapidly to Si and SiO₂, even at much lower temperatures, it might be expected that the reverse reaction would also be rapid. Even if the reaction were slow, it would be expected to go to completion in the time allowed in Experiment 3 if the contact between the two solid phases were good. Good contact was insured by the use of very fine particles, by grinding the materials together to obtain intimate contact, and by careful packing into the capsules. That good contact did exist was demonstrated in Experiment 4, in which Si and SiO₂ reacted readily to form SiO gas, which condensed and disproportionated at the cooler end of the tube, transferring a large fraction of the material in the course of one of the shorter runs. Alpha-quartz was used as a starting material because it is the least stable of the forms of SiO₂ and consequently would furnish the largest driving force for the reaction to form SiO. Since SiO solid is not stable with respect to α -quartz and Si, it would not be stable with respect to any other form of SiO₂. Further evidence that no reaction took place is that only α -quartz was found in the sintered material. If a reaction had taken place, one would expect that the resultant SiO would have disproportionated to a more stable form of SiO₂. Thus, there appears to be no question that a reaction would have taken place if it could, that it did not take place at the melting point of silicon, and therefore that SiO must be unstable at all temperatures as noted in the Introduction. It is, of course, possible that some other

yet unknown phase of SiO, other than the metastable phase obtained by condensation of SiO gas, might exist which would form only extremely slowly from SiO₂ and Si.

The anomalous behavior in the melting point of Si and SiO₂ mixtures mentioned previously could be accounted for as an increase in the viscosity of SiO₂ in which silicon is dissolved. The electrical anomaly reported by Brewer and Edwards¹⁵ could be accounted for similarly by Si dissolving in the SiO₂ phase and increasing its conductivity. Consequently, the various anomalies that seemed to support the existence of an SiO phase are probably the result of a small solubility of Si in SiO₂. That such a solid solution exists is further indicated by the microscopic appearance of the SiO₂ sintered with Si. Possibly a situation occurs that is analogous to the SiO_{1.999} produced by Ewles and Youell by reduction of SiO₂ with H₂.²¹

II. A STUDY OF THE ULTRAVIOLET BANDS ATTRIBUTED TO MgO

INTRODUCTION

The green $^1\Sigma \longrightarrow ^1\Sigma$ transition at about λ 5000 for gaseous MgO has been known for quite some time. Only recently, however, Barrow and Crawford²² reported a very complex ultraviolet band system obtained in absorption in flames and attributed to MgO or some related species. They measured a number of band heads, but did not have sufficient resolution to attempt a vibrational analysis. Verhaeghe²³ grouped the bands into several sequences, but was unable to proceed further. Brewer and Porter²⁴ obtained the bands from several sources, but even in the second order of a 21-ft grating the resolution was insufficient to permit analysis. In the absence of analysis, the species responsible for the band system has so far been in doubt.

Brewer and Porter showed that the molecule responsible for the bands contained one Mg and one O per molecule by comparing the intensity of the green bands with the integrated intensity of the ultraviolet bands at varying activities of MgO. Consequently, the principal species must be either MgO itself or a product of the reaction of MgO with some species common to the flame, arcs, and carbon tube furnace in which the bands were found. Since hydrogen -- either as the gas or in water -- is present in all three sources, it is possible that the unknown molecule could be the MgOH radical as suggested for some of the alkaline earths by James and Sugden²⁵ and demonstrated by Gaydon²⁶ and Lagerqvist and Huldt²⁷ for calcium, strontium, and barium. If this is the case, then the bands ought to show an increase in intensity with H_2 pressure and also an isotope shift with D_2 .

EXPERIMENTAL

The methods described by Porter were followed. Baker and Adamson special reagent MgO was degassed at 1200°C in vacuo, and placed on a tungsten liner which was then placed inside a tantalum liner and inserted in the King type graphite-tube furnace used by Porter. The furnace was operated at temperatures ranging from 2250° to 2300°C . The light from the hot gases was focused on the slit of a 3-meter grating equipped with the photomultiplier and recorder described by Phillips.²⁸ All-quartz optics were used. Temperatures were read by a Leeds and Northrup optical pyrometer.

The furnace was first degassed by heating and pumping, and by sweeping out with argon. Some degassing was observed even after repeated treatment. The degassed MgO was inserted and the furnace brought to temperature in about 1/2 atmos of argon.

The furnace was then shut off and evacuated to remove any further water vapor introduced. Argon, at about 5 cm pressure, was bled into the furnace and the furnace brought back to temperature. The ultraviolet and green bands were then traced in a quick sequence several times until the same intensities were reproduced and thermal equilibrium assured. Regardless of the efforts made to reduce the H_2 and water pressure, the bands remained strong. Hydrogen was then added in about 10-cm increments and the procedure repeated. Constancy of temperature was assured by the reproducibility of the green bands under various pressures. The total integrated intensity of the ultraviolet bands was found to vary approximately directly with the square root of the hydrogen pressure. Since it was uncertain whether the intensity of

the bands was changing or a continuum was being "built up" under the bands, the experiment was repeated with argon in place of hydrogen. The argon was found to produce a very similar effect. The hydrogen experiment was then repeated, but this time the ratio of the total band intensity to the continuum was taken in the region λ 4000. Although this ratio was found to vary with hydrogen pressure, the variation was much smaller. At the time of the experiment, abnormal difficulty was being encountered with temperature gradients in the furnace and the MgO did not last sufficiently long for a series of values to be obtained. Also, there was probably more than the usual uncertainty in the temperature. Therefore, this experiment contains a rather high uncertainty.

As a further check, the experiment was repeated using pure hydrogen in one experiment and an equal pressure of pure argon in a second experiment. The resulting tracings could almost be superimposed.

A similar King furnace was set up and the light focused on the slit of a 21-ft grating with a dispersion of 1.34 A/mm. The band system was photographed on II-0 and 103 a0 plates. The MgO was found to last about 30 minutes at 2270°C. This gave a badly underexposed but still readable plate. Runs were made with the furnace containing about 0.2 atmos of H₂ and D₂. All the bands reported by Porter in thermal emission were observed. No shift of any of the bands was observed.

DISCUSSION OF RESULTS

Evidently, the molecule contains no hydrogen, as an intensity change upon replacement of hydrogen by argon would have occurred as well as an isotope shift with the deuterium. It would appear that the intensity changes result from some sort of pressure effect. Broadening of the atomic Mg lines in the region 3825-3840 A or of the associated Mg_2 bands reported by Soulen, Sthapitanonda, and Margrave,²⁹ would seem to be the cause of the change of intensity upon increase of either the H_2 or A pressure.

The unknown molecule must be an oxide, because it contains no hydrogen, and mass-spectrometer analysis of King furnace gases show N_2 and CO to be the only other constituents present in any quantity. From the work of Brewer and Porter, it would appear that this oxide must be principally monomeric MgO. Some question on the validity of Brewer and Porter's conclusions might arise from the fact that the intensities of the ultraviolet bands measured include the Mg_2 continuum. Since their work was done at constant pressure, this would have no effect unless the Mg concentration varied considerably.

There is the possibility that the band system arises from an impurity in the Mg and MgO used. It is unlikely that any impurity is present in sufficient amount to produce such a high intensity of emission.

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