

A THERMODYNAMIC ANALYSIS OF THE HIGH-TEMPERATURE VAPORIZATION PROPERTIES OF SILICA

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I. INTRODUCTION

Chemists have long recognized the usefulness of silica (SiO_2) and silicate materials. Continued and increasing interest in high-temperature work has made a review of the vaporization properties of pure silica of particular importance. The present work is both a review and an analysis of the thermochemistry of the vaporization of silica at high temperatures.

A. REVIEW OF VAPOR-PRESSURE AND BOILING-POINT DATA FOR SILICA

Despite man's long use of glass and the abundance of silica on the earth's crust, little accurate vapor-pressure data exist for pure silica at elevated temperatures. The most recent available data on its vapor pressure (14, 56) have all been obtained below 2000°K., but in this review they are shown to agree satisfactorily with vapor pressures which are calculated from other available thermodynamic data.

The tabulated boiling points for silica recorded in various handbooks have values of 2230°, 2590°, and 2950°C. These values have all been traced to earlier work (57, 58, 59). However, these boiling-point determinations can be criticized because of their having been carried out in a reducing atmosphere, and since a reduc-

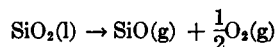
ing atmosphere leads to a higher than expected vapor pressure, the lower boiling points are not considered to represent the properties of the material. Also, the two higher boiling points of 2590° and 2950°C. have been based on a single vapor-pressure determination; i.e., 11 mm. at 2060°C. In their original paper, Ruff and Kenschak (58) stated that this measurement yields 2590°C. as a boiling point. Some nine years later Ruff (57) reinterpreted the earlier data (58) to give a new boiling-point temperature of 2950°C. A review of the earlier extrapolation (58) has indicated that the authors were probably correct the first time in evaluating their data to obtain a normal boiling point of 2590°C. However, the original criticism that their measurement was done under reducing conditions is still valid, and the actual boiling point is probably above 2590°C., as they stated in their original paper (58).

B. THERMODYNAMIC APPROACH USED TO CALCULATE VAPOR-PRESSURE DATA FOR SILICA

In the present paper, various possible reactions that can occur when silica vaporizes have been considered. From available thermochemical data, the free-energy change for each reaction has been obtained as a function of temperature. Hence, equilibrium constants for these

reactions can also be given as functions of temperature. It is then possible to estimate the various species or products present at equilibrium at different temperatures and pressures.

In Section II of this review, the most important reaction involved in the vaporization of silica, namely,



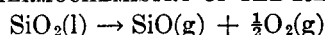
is considered. This reaction is discussed in its entirety, and vapor-pressure relationships are shown based only on this equilibrium. The role of other simultaneous equilibria is discussed in succeeding sections.

Thus, the condensation reaction of SiO(g) is discussed in Section III. That is, it is asked whether the condensation product is SiO(s) or a mixture of silicon and silica. In Section IV, association reactions of SiO(g) which may lead to gaseous dimers, trimers, etc., are discussed. Another factor that can influence the reaction considered in Section II is oxygen dissociation. This reaction is examined in Section V. Another dissociation reaction, that of SiO(g), is reviewed in Section VI. Section VII is devoted to the vaporization of silica via the formation of SiO₂(g). In Section VIII the effect of reducing atmospheres on the vaporization of silica is discussed. Lastly, in Section IX the effects of all the reactions discussed previously are combined to show their relative importance. Also, a final value for the boiling point is calculated and then compared with existing literature values.

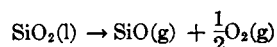
The nomenclature used in this review corresponds in large part with that used in thermochemistry. Thus, ΔH , ΔF , ΔS , and ΔC_p refer to changes in heat content, free energy, entropy, and heat capacity, respectively. The superscript (°) used with the thermodynamic functions indicates that substances are in their thermodynamic standard state. The letters s, l, and g are used to designate solidus, liquidus, and gaseous states of the elements or compounds. For clarity in indicating the type of change being considered, additional subscripts are used. For example, $\Delta H_f; 2000^\circ; \text{SiO}(l)$ refers to the heat of formation of liquid or glassy silica at 2000°K.

Standard units are used: that is, 1 cal. is equal to 4.184 absolute joules, and the gas constant, R , equals 1.987 cal. per degree per mole.

II. THERMOCHEMISTRY OF THE REACTION



The reaction



has been considered by several authors (11, 14, 56) to be the most important reaction occurring when silica decomposes under neutral conditions. The results of the present study are consistent with these earlier findings.

Under oxidizing conditions (i. e., with excess oxygen present) the above reaction can be shifted to the left, so that the formation of SiO gas is repressed.

The equilibrium constant of the reaction and the equilibrium vapor pressure of liquid silica can be obtained by calculation from the heat of reaction and entropy change of the reaction.

A. HEAT OF REACTION

To calculate the heat of reaction, the heat of formation of SiO₂(l) can be subtracted from the heat of formation of the products. Since the heat of formation of the elements is taken to be zero, it is necessary to evaluate the heat of formation of SiO₂(l) and SiO(g) only. For the present case, the temperature range from 2000° to 3000°K. has been considered of primary interest. Because data for this temperature range are not available, it is necessary to use existing data for lower temperatures and to calculate the thermodynamic functions at the higher temperatures by extrapolation.

1. Heat of formation of SiO₂(l)

Before discussing the thermochemical data for silica, a brief literature review (16, 17, 23, 26, 50) of some of its pertinent properties is given below. Structurally, pure silica is a polymorphic material. The vitreous or glassy form of silica is a metastable, undercooled liquid at all temperatures below 1728°C. (2000°K.). The rate of transformation of vitreous silica into the other forms may become measurable above 1000°C. Impurities also affect the rate of transformation. The following are the stability ranges for the various forms of silica:

Form	Temperature Range of Stability
Silica glass.....	$T > 1728^\circ\text{C}.$
β -Cristobalite.....	1728–1470°C. (50)
β -Tridymite.....	1470–870°C. (16, 35, 67)*
β -Quartz.....	870–573°C.
α -Quartz.....	573–

*References 35 and 67 discuss some questions about the stability of tridymite.

The Warren model is generally accepted (44) to represent the short-range order in fused silica glass. Since it is a liquidlike material (8), there is no long-range order greater than about four or five interatomic distances. According to the view of Warren, each silicon atom is surrounded tetrahedrally by four oxygen atoms, and each oxygen atom is shared by two silicon atoms. The silicon–oxygen distance is about 1.6 Å., the oxygen–oxygen distance is 2.65 Å., and the silicon–silicon distance is 3.2 Å.

There is no recognized melting point for fused silica. Since it is a glasslike material, it undergoes a gradual change of viscosity with temperature. A relationship

(51) to express this change of viscosity for the temperature range from 2197° to 2333°K. is

$$\log_{10} \eta = 28,200/T - 7.73 \quad (\eta \text{ in poises})$$

Additional viscosity data obtained for this material yield a somewhat higher viscosity (1).

Fused silica is considered to soften (viscosity $\cong 10^{7.6}$ poises) at 1500°C. (17).

The various crystalline forms of silica do have recognized melting points, as seen below:

Form	Melting Point
	°C.
Cristobalite.....	1728
Tridymite.....	1680
Quartz.....	1610

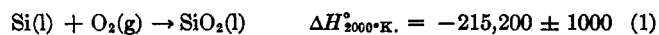
For β -cristobalite a melting point of 1723°C. (1996°K.) is given (50), whereas another reported value is 1728°C. (2001°K.) (16). For convenience, and with negligible error, it has been assumed in the following discussions that 2000°K. is the melting point of silica. It is generally recognized that silica glass is the stable condensed species of SiO₂ above 2000°K. (50). In further discussions, the expressions "SiO₂ (glass)" or "SiO₂(l)" are used interchangeably for temperatures above 2000°K.

Pure fused silica has a density of 2.20 g./cm.³ (17). The molar heat capacity of fused silica given by Kelley (46) for the range from 298° to 2000°K. is

$$C_p = 13.38 + 3.68 \times 10^{-3}T - 3.45 \times 10^{-5}T^2$$

where C_p = heat capacity in calories/mole °K. and T = absolute temperature in °K.

Coughlin (18) has tabulated values for the heat and free energy of formation of silica up to 2000°K. His results are based on the heat of formation data presented elsewhere (40). His data for the heat of formation at 2000°K. are:



In any thermochemical calculation it is desirable to start with the most accurate data available. Referring to equations 1 and 2, it seems preferable to start with equation 2 rather than equation 1, since the heat of formation is given in equation 2 to a greater precision. However, the uncertainty in the heat of fusion of β -cristobalite makes either reaction a suitable starting point. Thus, the difference between equations 2 and 1 is taken to be the heat of fusion of β -cristobalite, $\Delta H_{\text{fusion}} = 2500$ cal./mole. From the entropy data of Kelley (46, 47) a heat of fusion at 2000°K. of 2060

cal./mole is calculated. A value of 3600 cal./mole is quoted by Kubaschewski and Evans (48). The compilation of the National Bureau of Standards (54) gives a value of 1840 cal./mole. The original data quoted by Kelley (45) indicate experimental values for the heat of fusion of cristobalite to be in the range from 1000 to 3700 cal./mole, an average value being 2100 cal./mole. This range in values for the heat of fusion shows why the data for equation 1 are less precise, but still are the best available. Therefore, these data are used for the present calculations.

The heat of formation at temperatures above 2000°K. can be calculated by means of the Kirchoff relation:

$$\Delta H_T^\circ = \Delta H_{2000}^\circ + \int_{2000}^T \Delta C_p \, dT$$

or

$$\Delta H_T^\circ = \Delta H_{2000}^\circ + (H_T^\circ - H_{2000}^\circ)_{\text{SiO}_2(\text{l})} - (H_T^\circ - H_{2000}^\circ)_{\text{Si(l)}} - (H_T^\circ - H_{2000}^\circ)_{\text{O}_2}$$

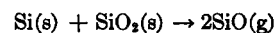
The results of such a calculation at 2000°, 2500°, and 3000°K. are given in table 1. For this calculation, the heat content of SiO₂(l) has been estimated by assuming that its average heat capacity is 1 cal./mole degree greater than that given by Kelley (46) for SiO₂(glass) at 2000°K. That is, $C_p^\circ = 21.66$ has been assumed.

According to Kubaschewski and Evans (48), an estimate of the heat capacity of molten liquids can be obtained by assuming that each atom contributes 7.25 cal./g.-atom °K., for a value of 21.75 cal./mole °K. In a 1952 article (41) the heat capacity of liquid silica was taken to be $C_p^\circ = 24.0$. In the present case, the extrapolation to high temperatures leads to considerable uncertainty in the heat content. The uncertainty in the heat capacity is roughly estimated to be 1 cal./mole degree, thus giving $C_{p\text{SiO}_2(\text{l})} = 21.66 \pm 1.0$.

Sources of data for the calculations of table 1 are given in the table. Rough estimates of the uncertainties in the data have been made. The final values for the heat of formation in the temperature range from 2000° to 3000°K. become more uncertain as the temperature rises because of the uncertainty in the heat capacity of liquid silica in this range.

2. Heat of formation of SiO(g)

The heat of formation of SiO(g) at 298°K. is taken to be $-21,411 \pm 574$ cal. This value is the one recommended elsewhere (11, 22). It is based on a recalculation of the work of Schafer and Hornle (60), who studied the reaction



Other sources of data considered by Brewer and Edwards (11) are given in the table at the top of the following page.

Investigators	Equilibrium Studied	ΔH_{298}° cal./mole
Grube and Speidel (28).....	$H_2(g) + SiO_2(s) \rightarrow H_2O(g) + SiO(g)$	$-15,291 \pm 2000$
Brewer and Mastick (14).....	$SiO_2(s) \rightarrow SiO(g) + \frac{1}{2}O_2(g)$	$-21,159 \pm 2000$
Gel'd and Kochnev (25).....	$Si(s) + SiO_2(s) \rightarrow 2SiO(g)$	$-18,212 \pm 960$
Schafer and Hornle (60).....	$Si(s) + SiO_2(s) \rightarrow 2SiO(g)$	$-21,411 \pm 574$
Tombs and Welch (68).....	$H_2(g) + SiO_2(s) \rightarrow H_2O(g) + SiO(g)$	$-26,004 \pm 2400$ (low-temperature data) $-21,269 \pm 1500$ (high-temperature data)

Brewer and Edwards (11) considered each of the above sources very carefully, and chose the data of Schafer and Hornle (60) as being the best. It should be pointed out that the arguments used (11), which were based on dissociation energies of $SiO(g)$, were fortuitously correct, since more recent data have shown that their values for the heat of sublimation of silicon (88.9 kcal./mole) and for the dissociation energy of $SiO(g)$ (169 kcal./mole) were too low. A later value for the heat of sublimation of monatomic silicon is 105 kcal./mole. This value is based on mass-spectrometer measurements given by Honig (36) and recommended by Stull and Sinke (65). Searcy (61) gives a value of 112 kcal./mole, and Huggins (39) gives 100 kcal./mole for the heat of sublimation. The results of a study of the sublimation of silicon carbide at the University of Chicago (20, 21) led to a value of 113 kcal./mole for the heat of sublimation, a value which is in good agree-

ment with Searcy's value by the same method.

It should also be mentioned that a paper by Baird and Taylor (2) gives a heat of reaction to form silicon carbide from liquid silicon of $-19,250$ cal./mole as compared with earlier values of $-23,300$ cal./mole. Thus, from the results of Drowart, de Maria, and Inghram (20, 21) and of Searcy (61) the heat of sublimation for silicon becomes 116 or 117 kcal./mole.

However, these high values (112 kcal./mole and greater, based on data for the dissociation of silicon carbide) should not necessarily be accepted in preference to Honig's value, which is based on a direct measurement. A further complication in the measurements based on the dissociation of silicon carbide is indicated by Baird and Taylor's statement that silicon carbide becomes unstable relative to liquid silicon and graphite near $2050^{\circ}C$.

For the dissociation energy of $SiO(g)$, Barrow and

TABLE 1
Calculation of heat of formation of $SiO_2(l)$

Function	0°K.	298°K.	2000°K.	2500°K.	3000°K.	Remarks and Sources of Data
$SiO_2(g_{\text{liq}})$:						
1. $H_T^{\circ} - H_{298}^{\circ}$ (cal./mole) ...			$29,010 \pm 580$	$39,840 \pm 1100$	$50,670 \pm 1600$	Data at 2000°K. from Kelley (46) Data at 2500°K. and 3000°K. calculated with help of data in line 2 From C_p° data of line 3 C_p° was chosen to have an average value of 21.66 cal./mole degree in range above 2000°K. This is 1 cal./mole degree over Kelley's value at 2000°K. Uncertainty is estimate
2. $H_T^{\circ} - H_{2000}^{\circ}$ (cal./mole) ...			0	$10,830 \pm 500$	$21,660 \pm 1000$	
3. C_p° (cal./mole °K.)		$C_p^{\circ} = 13.38 + 3.68 \times 10^{-3}T - 3.45 \times 10^{-5}T^{-2}$ for $T = (298-2000^{\circ}K.)$; 2 per cent accuracy	21.66 ± 0.43	21.66 ± 1.0	21.66 ± 1.0	
$Si(l)$:						
4. $H_T^{\circ} - H_{2000}^{\circ}$ (cal./mole) ..			0	3500 ± 70	7000 ± 140	Stull and Sinke (65) (author's estimate is 2 per cent for uncertainty)
$O_2(g)$:						
5. $H_T^{\circ} - H_{2000}^{\circ}$ (cal./mole) ..			0	4583 ± 45	9297 ± 90	Stull and Sinke (65) (author's estimate is 1 per cent for uncertainty)
SiO_2 :						
6. Heat of formation of $SiO_2(l)$ (cal./mole)			$-215,200 \pm 1000$	$-212,453 \pm 1615$	$-210,467 \pm 2230$	Coughlin (18) used data for liquid phase at 2000°K. For 2500° and for 3000°K. $\Delta H_T^{\circ} = \Delta H_{2000}^{\circ} + (H_T^{\circ} - H_{2000}^{\circ})_{SiO_2} - (H_T^{\circ} - H_{2000}^{\circ})_{Si(l)} - (H_T^{\circ} - H_{2000}^{\circ})_{O_2}$

Rowlinson (3) recommend 185 ± 6 kcal./mole. This value agrees with Gaydon's (24) value of 184 ± 23 kcal./mole, but is higher than that given by Herzberg (32) (171 kcal./mole). By calculation from the values of 105 kcal./mole for the sublimation to monatomic silicon, 117.9/2 kcal. for the dissociation of 0.5 mole of oxygen from Stull and Sinke (65), and a heat of dissociation of 185 kcal./mole for SiO(g), a value of $-21,100$ cal./mole is obtained for the heat of formation of SiO(g) at absolute zero. Other possible combinations are shown in table 2.

TABLE 2

Possible heats of formation of SiO(g) at 0°K. from spectroscopic data in kilocalories

$$\Delta H_{f,0}^{\circ} = L_{\text{Si}} + \frac{1}{2}D_{\text{O}_2} - D_{\text{SiO}}$$

L_{Si}	$\frac{1}{2}D_{\text{O}_2}$	D_{SiO}	$\Delta H_{f,0,\text{SiO}}^{\circ}$
88 (22)	58.9 (65)	169 (22)	-22
88 (22)	58.9 (65)	185 (3)	-38.1
100 (39)	58.9 (65)	169 (22)	-10.1
100 (39)	58.9 (65)	185 (3)	-26.1
105 (36)	58.9 (65)	169 (22)	- 5.1
105 (36)*	58.9 (65)	185 (3)	-21.1
112 (61)	58.9 (65)	169 (22)	+ 1.9
112 (61)	58.9 (65)	185 (3)	-14.1

* Indicates a combination of data that agree with thermochemical data.

The data in table 2 show that a wide range of possible values for the heat of formation of SiO can be estimated depending on the choice of the heat of sublimation of silicon and the heat of dissociation of SiO. In view of these uncertainties, it appears that the thermochemical data reviewed by Brewer and Edwards (11, 22) are probably more reliable. Accordingly, their value of $\Delta H_0^{\circ} = -21,695$ cal./mole or $\Delta H_{298}^{\circ} = -21,411 \pm 574$ cal./mole is used.

It should be noted that the data of table 2 indicate that larger heats of sublimation of silicon require larger heats of dissociation of SiO to give values for the heat of formation which are consistent with the Brewer and Edwards value above. Thus, if a value of 117 kcal./mole for the sublimation of silicon were to be accepted, a heat of dissociation for SiO of 197 kcal./mole would be required to correspond to a heat of formation for SiO of -21.5 kcal./mole. Such a value for the heat of dissociation would be within the range estimated by Gaydon (24) (184 ± 23 kcal./mole).

At this time, therefore, it appears that thermochemical data are to be preferred to spectroscopic data for the heat of formation of SiO(g). Günther (29) recently used the Schafer-Hornle technique, and his data yield a somewhat lower vapor pressure of SiO(g).

A third-law analysis, similar to that already men-

tioned (11, 22), has been performed on Günther's data. For this analysis, entropy and enthalpy data for SiO₂(tridymite) were from Kelley (46, 47), data for silicon were from Stull and Sinke (65), and data for SiO(g) from Brewer and Edwards (11, 22). The heat of formation of SiO₂(tridymite) at absolute zero was taken from Edwards (22). The three temperature ranges studied by Günther yield the following data for the heat of formation of SiO(g) at absolute zero:

Temperature Range °K.	ΔH_0°
1468-1520	-18,918
1329-1439	-17,783
1202-1361	-17,177

These data show a relatively large change with temperature, which may indicate the occurrence of a new reaction. It is also noticed that the high-temperature data (obtained with smallest effusion hole) tend to approach the data of Schafer and Hornle. From an overall standpoint, the data of Schafer and Hornle show less variation of the calculated heat of formation and therefore are preferred.

Having now selected the source data for the heat of formation of SiO(g) at lower temperatures, it is necessary to extrapolate these data to high temperatures, in the range from 2000° to 3000°K. To make such an extrapolation, it is necessary to obtain data for the heat capacity of SiO(g) in this temperature range.

To obtain thermodynamic data for SiO(g), it is necessary to make calculations with spectroscopic data. The methods followed are similar to those described by Mayer and Mayer (52). The molecular weight is taken to be 44.09. Other spectroscopic data have been taken from Herzberg (32). No electronic levels other than the singlet ground state are important in these calculations. The next highest electronic state has a wave number of 42,835 cm.⁻¹, corresponding to $hc\omega/kT = 20.6$ at 3000°K., and $e^{-hc\omega/kT}$ makes a very small contribution to the partition function. For the one vibrational frequency possible in this diatomic molecule, the characteristic frequency ($\omega = \omega_e - 2\omega_e x_e$) is 1230 cm.⁻¹ For the rotational contributions, the moment of inertia is taken to be $I = 38.6 \times 10^{-40}$ g. cm.² The symmetry number is 1, since the atoms of the molecule are dissimilar. Anharmonic corrections to the entropy have been made at the higher temperatures, but they are still quite small.

The results of these calculations are presented in table 3. For comparison purposes, the results of Brewer and Edwards (11, 22) at the lower temperatures have been included and are found to agree with the data here. A further approximate check on these data is indicated by the fact that it has been found that the

TABLE 3
Thermodynamic functions for SiO(g) from spectroscopic data

$\left(\frac{F_T^\circ - H_0^\circ}{T}\right)$	298°K.	2000°K.	2500°K.	3000°K.
	cal./mole °K.	cal./mole °K.	cal./mole °K.	cal./mole °K.
Translation.....	-32.30	-41.76	-42.86	-43.76
Electronic.....	0.00	0.00	0.00	0.00
Vibration.....	0.00	-1.05	-1.34	-1.61
Rotation.....	-11.27	-15.05	-15.49	-15.85
$\left(\frac{F_T^\circ - H_0^\circ}{T}\right)_{\text{net}}$	-43.57	-57.86	-59.69	-61.22
$\left(\frac{H^\circ - H_0^\circ}{T}\right)$	298°K.	2000°K.	2500°K.	3000°K.
	cal./mole °K.	cal./mole °K.	cal./mole °K.	cal./mole °K.
Translation.....	4.965	4.965	4.965	4.965
Electronic.....	0.00	0.00	0.00	0.00
Vibration.....	0.00	1.23	1.36	1.46
Rotation.....	1.987	1.987	1.987	1.987
$\left(\frac{H^\circ - H_0^\circ}{T}\right)_{\text{net}}$	6.955	8.18	8.317	8.412
$S^\circ = \left(\frac{H^\circ - H_0^\circ}{T}\right)_{\text{net}} - \left(\frac{F_T^\circ - H_0^\circ}{T}\right)_{\text{net}}$	50.52	66.04	68.01	69.63
Anharmonic corrections.....	0.00	0.00	0.03	0.04
S_T° (present calculation).....	50.52	66.04	68.04	69.67
S_T° (from Brewer and Edwards (11, 22)).....	50.53	66.02		

heat-capacity term due to vibration at 2000°K. is almost fully excited. Moreover if, for the diatomic gas, it is assumed that translation, rotation, and vibration are contributing fully to the heat capacity at constant pressure, $C_p = 9R/2$. Therefore,

$$S_{3000}^\circ - S_{2000}^\circ = \int_{2000}^{3000} \frac{C_p^\circ dT}{T} \cong 3.62 \text{ e.u.}$$

From the results in table 2, the entropy increment is 3.63 e. u. Calculations with the enthalpy data also lead to

$$H_{3000}^\circ - H_{2000}^\circ = 8876 \text{ cal./mole}$$

giving an average C_p° over this temperature range of 8.876 cal./mole degree. Thus, the data appear to be self-consistent.

With the data from table 3 and additional data for elemental silicon and oxygen from Stull and Sinke (65), it is now possible to calculate the heat of formation of gaseous SiO in the temperature range from 2000° to 3000°K. The results of such a calculation are summarized in table 4.

The calculation is based on the relationship

$$\Delta H_T^\circ = \Delta H_0^\circ + \int_0^T \Delta C_p dT$$

or

$$\Delta H_T^\circ = \Delta H_0^\circ + (H_T^\circ - H_0^\circ)_{\text{SiO(g)}} - (H_T^\circ - H_0^\circ)_{\text{Si}} - \frac{1}{2}(H_T^\circ - H_0^\circ)_{\text{O}_2(\text{g})}$$

To make an estimate of the uncertainty in this calculation, it has been necessary to take into account the accuracy of all the data used in making it. Since Stull and Sinke (65) have not stated the accuracy of their data, an estimate of their accuracy has been made in table 4. To make a partial check on the computation of the heat of formation of SiO(g), the available published data (18, 41) have been tabulated in the second row of the table. The published data for 298° and 2000°K. are in good agreement with the present calculations.

3. Heat of the overall reaction

(a) Calculation of the heat of reaction

In the previous sections, the heats of formation of SiO₂(l) and SiO(g) in the range from 2000° to 3000°K. have been evaluated. Those results can be readily used to calculate the heat of the overall reaction for the vaporization of liquid silica by means of the relation:

$$\Delta H_T^\circ = \Delta H_{f, \text{SiO(g)}}^\circ - \Delta H_{f, \text{SiO}_2(\text{l})}^\circ$$

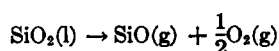
In table 5 the results of such calculations at 2000°, 2500°, and 3000°K. are summarized.

(b) Uncertainty in heats of reaction

It should be noted that uncertainties at 2500° and 3000°K. are less than would be calculated by simple addition of the component uncertainties (see tables 5

and 6). A second set of estimated uncertainties (in parentheses) are 1500 cal. in excess of those not shown in parentheses. Thus, Coughlin (18) gives an uncertainty of 2000 cal. for $\Delta H_{f; SiO(g)}^\circ$ at 298°K., whereas Brewer and Edwards give 574 cal., even though both evaluated the same original data. To make the best estimate of the uncertainties in the heats of reaction obtained above, the sums involved in deriving the values must be considered in detail. It is shown by the following algebraic manipulations that some of the uncertainties cancel out. The remaining terms, which have actually been used in calculating the heat of reaction, can be added without regard to algebraic sign to get the true uncertainty.

For the reaction



it follows that

$$\begin{aligned} \Delta H_{reaction}^\circ &= \frac{1}{2}\Delta H_{f; O_2}^\circ + \Delta H_{f; SiO(g)}^\circ - \Delta H_{f; SiO_2(l)}^\circ \\ &= 0 + \Delta H_{f; 0; SiO(g)}^\circ + (H_T^\circ - H_0^\circ)_{SiO(g)} \\ &\quad - (H_T^\circ - H_0^\circ)_{Si(l)} - \frac{1}{2}(H_T^\circ - H_0^\circ)_{O_2(g)} \\ &\quad - \Delta H_{f; 2000; SiO_2(l)}^\circ - (H_T^\circ - H_{2000}^\circ)_{SiO_2} \\ &\quad + (H_T^\circ - H_{2000}^\circ)_{Si(l)} + (H_T^\circ - H_{2000}^\circ)_{O_2(g)} \end{aligned}$$

or

$$\begin{aligned} \Delta H_{reaction}^\circ &= \Delta H_{f; 0; SiO(g)}^\circ - \Delta H_{f; 2000; SiO_2(l)}^\circ + (H_T^\circ - H_0^\circ)_{SiO(g)} \\ &\quad - (H_T^\circ - H_{2000}^\circ)_{SiO_2(l)} - (H_{2000}^\circ - H_0^\circ)_{Si(l)} \\ &\quad + (H_T^\circ - H_{2000}^\circ)_{O_2(g)} - \frac{1}{2}(H_{2000}^\circ - H_0^\circ)_{O_2(g)} \quad (3) \end{aligned}$$

Table 6 shows the magnitude of the uncertainties of the quantities in equation 3. Their sums are taken to

TABLE 4
Calculation of heat of formation of SiO(g) from the elements

Function	0°K.	298°K.	2000°K.	2500°K.	3000°K.	Remarks and Sources of Data
1. Heat of formation of SiO(g) from the elements. (Source data as basis for present calculations) (cal./mole).....	-21,695 ± 574	-21,411 ± 574				Values at 0°K. and 298°K. from Brewer and Edwards (11) and Edwards (22). Based on recalculated data of Schafer and Hornle (60), who had studied the reaction Si(s) + SiO ₂ (s) → 2SiO(g). Brewer and Edwards (11, 22) preferred these data to those of Brewer and Mastick (14). From Coughlin (18) and Humphrey, Todd, Coughlin, and King (41); also based on data of Schafer and Hornle (60)
2. Additional comparative data. Heat of formation of SiO(g) (cal./mole).....		-21,800	-36,700			
3. $\frac{H_T^\circ - H_0^\circ}{T}$ (cal./mole °K.).....			8.18	8.32	8.41	Taken from table 3
4. $(H_T^\circ - H_0^\circ)_{SiO(g)}$ (cal./mole)....			16,400 ± 150	20,800	25,230 ± 250	Error estimated to be 1 per cent Stull and Sinke (65); present estimate 2 per cent
5. $(H_T^\circ - H_{298}^\circ)_{Si(l)}$ (cal./mole)...			21,960 ± 440	25,460	28,960	
6. $(H_T^\circ - H_0^\circ)_{Si(l)}$ (cal./mole).....		769	22,729 ± 460	26,299 ± 520	29,729 ± 594	Stull and Sinke (65) give $(H_{298}^\circ - H_0^\circ)$
7. $(H_T^\circ - H_{298}^\circ)_{O_2(g)}$ (cal./mole)...			14,148 ± 140	18,731 ± 180	23,445 ± 230	Stull and Sinke (65)
8. $(H_T^\circ - H_0^\circ)_{O_2}$ (cal./mole).....		2075	16,223	20,806	25,520	Stull and Sinke (65) give $(H_{298}^\circ - H_0^\circ)$
9. $\frac{1}{2}(H_T^\circ - H_0^\circ)_{O_2}$ (cal./mole).....			8111 ± 80	10,403 ± 100	12,760 ± 125	
10. Final preferred values of heat of formation of SiO(g) (cal./mole).....	-21,695 ± 574	-21,411 ± 574	-36,135 ± 1264	-37,527 ± 1394	-38,954	$\Delta H_T^\circ = \Delta H_0^\circ + (H_T^\circ - H_0^\circ)_{SiO} - (H_T^\circ - H_0^\circ)_{Si} - \frac{1}{2}(H_T^\circ - H_0^\circ)_{O_2}$ = Row 1 at 0°K. + Row 4 - Row 6 - Row 9

TABLE 5

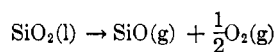
Heat of the reaction $\text{SiO}_2(\text{l}) \rightarrow \text{SiO}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$

	2000°K.	2500°K.	3000°K.
	<i>cal./mole</i>	<i>cal./mole</i>	<i>cal./mole</i>
$\Delta H_f^\circ; \text{SiO}(\text{g})$	-36,135 ± 1264 or (± 2764)	-37,527 ± 1394 or (± 2894)	-38,954 ± 1543 or (± 3043)
$\Delta H_f^\circ; \text{SiO}_2(\text{l})$	-215,200 ± 1000	-212,453 ± 1615	-210,467 ± 2230
$\Delta H_{\text{reaction}}^\circ$	179,065 ± 2264 or (± 3690)	174,926 ± 2834 or (± 4260)	171,513 ± 3409 or (± 4835)

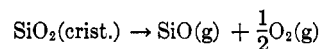
be the true uncertainty. At 3000°K. it is seen that about half of the error arises from the thermochemical data for the heats of formation of the reference materials. However, the other determinations of the heat of formation of SiO(g) as quoted by Brewer and Edwards (11, 22) indicate a possible spread of a few thousand calories per mole. Hence it is possible that the uncertainty in $\Delta H_f^\circ; \text{SiO}(\text{g})$ may be larger than 574 cal./mole. If this uncertainty is 2000 cal./mole, as chosen by Coughlin, then the resultant uncertainty in the overall heat of reaction at 3000°K. is about 5000 cal./mole. The 2000 value for the uncertainty of the heat of formation of SiO(g) may be more reasonable than the 574 value, since the values of other experimenters have had a wider spread than 574 cal. The other large uncertainty contributions arise from the estimation of data for the heat capacity of liquid silica and liquid silicon.

(c) Comparison of heat of reaction data with directly determined data

The previous calculation of the heat of the reaction



has been indirect. Now, it may appear preferable to use heat of reaction data which are based on this reaction directly. However, directly determined data, such as those of Brewer and Mastick (14) and recalculated by Brewer and Edwards (11, 22), give a greater uncertainty in the final heat of reaction. For example, these authors give $\Delta H_0^\circ = 186,578 \pm 2700$ cal./mole for the reaction



As a check on the earlier calculations and to show that the Brewer-Mastick work is more uncertain, it is possible to calculate ΔH_T° for the first reaction above, using the direct data of Brewer and Mastick in the following manner:

$$\Delta H_T^\circ = \Delta H_0^\circ + (H_T^\circ - H_0^\circ)_{\text{SiO}(\text{g})} + \frac{1}{2}(H_T^\circ - H_0^\circ)_{\text{O}_2(\text{g})} - (H_T^\circ - H_0^\circ)_{\text{SiO}_2(\text{l})}^1$$

Values of $(H_T^\circ - H_0^\circ)_{\text{SiO}(\text{g})}$ and $(H_T^\circ - H_0^\circ)_{\text{O}_2(\text{g})}$ have already been obtained and are listed in table 4. The heat

¹ $(H_T - H_0)_{\text{SiO}_2(\text{l})}$ is referred to cristobalite at 0°K.

TABLE 6

Summary of component uncertainties of the heat of reaction

Uncertainties	2000°K.	2500°K.	3000°K.
	<i>cal./mole</i>	<i>cal./mole</i>	<i>cal./mole</i>
$\Delta H_f^\circ; \text{SiO}(\text{g})$	± 574 (2000)†	± 574 (2000)†	± 574 (2000)†
$\Delta H_f^\circ; \text{SiO}_2(\text{l})$	± 1000	± 1000	± 1000
$(H_T^\circ - H_0^\circ)_{\text{SiO}(\text{g})}$	± 150	± 200	± 250
$(H_T^\circ - H_{2000}^\circ)_{\text{SiO}_2(\text{l})}$	0	± 500	± 1000
$(H_{2000}^\circ - H_0^\circ)_{\text{Si}(\text{l})}$	± 460	± 460	± 460
$\frac{1}{2}(H_T^\circ - H_0^\circ)_{\text{O}_2(\text{g})}^*$	± 80	± 100	± 125
	± 2264 (3690)†	± 2834 (4260)†	± 3409 (4835)†

* Combined uncertainty of the last two terms of equation 3 used.

† Coughlin's estimate of uncertainty in $\Delta H_f^\circ; \text{SiO}$ (in parentheses) is greater than that of Brewer and Edwards and results in a larger uncertainty for the heat of reaction (in parentheses).

TABLE 7

Entropy change for the reaction $\text{SiO}_2(\text{l}) \rightarrow \text{SiO}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$

	2000°K.	2500°K.	3000°K.	References
$\frac{1}{2}S_{\text{O}_2}^{\circ}(\text{g})$ (e. u.).....	32.11 ± 0.02	33.13 ± 0.02	33.99 ± 0.03	(65)
$S_{\text{SiO}(\text{g})}^{\circ}$ (e. u.).....	66.04 ± 0.1	68.04 ± 0.1	69.67 ± 0.1	Table 3
$S_{\text{SiO}_2(\text{l})}^{\circ}$ (e. u.).....	41.07 ± 0.6	46.13 ± 0.8	50.03 ± 1.0	(46, 47) at 2000°K.; calculated using $C_p^{\circ} = 21.66$ cal./mole °K. for $T > 2000^{\circ}\text{K}$.
ΔS° (e. u.).....	57.08 ± 0.7	55.04 ± 0.9	53.63 ± 1.1	
$T\Delta S^{\circ}$ (cal./mole).....	114,160 ± 1400	137,600 ± 2250	160,890 ± 3300	

content of liquid silica relative to cristobalite at 0°K. can be obtained from the relation

$$(H_T^{\circ} - H_0^{\circ})_{\text{SiO}_2(\text{l})} = (H_T^{\circ} - H_{2000}^{\circ})_{\text{SiO}_2(\text{l})} + \Delta H_{\text{fusion of cristobalite}}^{\circ} + (H_{2000}^{\circ} - H_{298}^{\circ})_{\text{crist.}} + (H_{298}^{\circ} - H_0^{\circ})_{\text{crist.}}$$

which can be evaluated as follows:

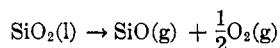
$(H_T^{\circ} - H_{2000}^{\circ})_{\text{SiO}_2(\text{l})}$	21,660 ± 1000 cal./mole (from table 1)
$\Delta H_{\text{fusion}}^{\circ}$	2500 ± 500 cal./mole (see earlier discussion)
$(H_{2000}^{\circ} - H_{298}^{\circ})_{\text{crist.}}$	28,120 ± 600 cal./mole (46)
$(H_{298}^{\circ} - H_0^{\circ})_{\text{crist.}}$	1667 ± 50 cal./mole (22)
$(H_T^{\circ} - H_0^{\circ})_{\text{SiO}_2(\text{l})}$ referred to cristobalite at 0°K.	53,947 ± 2150 cal./mole

Substituting the total value into the expression for ΔH_T° , the value $\Delta H_{3000}^{\circ} = 170,621 \pm 5225$ cal./mole is obtained.

This value of the heat of reaction agrees well with the previous value of $\Delta H_{3000} = 171,513 \pm 3400$ cal./mole. However, the earlier data of table 5 have a smaller uncertainty and are used for subsequent calculations.

4. Total heat of decomposition

The total heat that can be absorbed by fused silica when it decomposes at 3000°K. by the reaction



is next computed.² This computation is of interest in ablation calculations of the type discussed in the literature (5). The calculation follows:

² Assuming that fused silica is originally at room temperature.

TABLE 8

Free-energy change for the reaction $\text{SiO}_2(\text{l}) \rightarrow \text{SiO}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$

	2000°K.	2500°K.	3000°K.
ΔH° (cal./mole).....	179,065 ± 3700	174,926 ± 4300	171,513 ± 4800
$-T\Delta S^{\circ}$ (cal./mole).....	-114,160 ± 1400	-137,600 ± 2250	-160,890 ± 3300
ΔF° (cal./mole).....	64,905 ± 3000	37,326 ± 3500	10,623 ± 4000

$(H_{2000}^{\circ} - H_{298}^{\circ})_{\text{SiO}_2(\text{glass})}$	29,010 cal./mole (46)
$(H_{2000}^{\circ} - H_{2000}^{\circ})_{\text{SiO}_2(\text{l or glass})}$	21,660 cal./mole (table 1)
ΔH_{3000}° for $\text{SiO}_2 \rightarrow \text{SiO}(\text{g}) + \frac{1}{2}\text{O}_2$	171,513 cal./mole (table 5)
Total heat of decomposing SiO_2 (glass) at 3000°K. starting from 298°K.....	222,183 cal./mole

B. ENTROPY CHANGE

Stull and Sinke (65) give the absolute entropy of $\text{O}_2(\text{g})$. In table 3 the entropy data for $\text{SiO}(\text{g})$ are given. Kelley (47) gives the entropy of $\text{SiO}_2(\text{glass})$ at 298°K. as $S_{298}^{\circ} = 11.2 \pm 0.4$ e. u. For higher temperatures he (46) gives $S_{2000}^{\circ} - S_{298}^{\circ} = 29.87$ e. u. Thus, $S_{2000}^{\circ} = 41.07$ e. u. To obtain entropy data for $\text{SiO}_2(\text{l})$ above 2000°K., the estimated heat-capacity data ($C_p^{\circ} = 21.66$ cal./mole degree) have been used. The results of these calculations are shown in table 7.

C. FREE-ENERGY CHANGE

The heat of reaction and the entropy change having been obtained in the previous sections, it is now possible to calculate the free-energy change from the relation:

$$\Delta F^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$

The results of this calculation are shown in table 8.

For ΔH° the uncertainties represent maximum estimates. In estimating the uncertainties in ΔF° from the data in table 5, the uncertainties of ΔH° and $T\Delta S^{\circ}$ do not add algebraically. Actually, those uncertainties cancel in part by the use of consistent heat-capacity data as discussed in the following paragraphs, so that the value given at 3000°K. is probably good to about ±4000 cal./mole, depending again on the uncertainty of the heat of formation of $\text{SiO}(\text{g})$.

The variation of the above free-energy data with

temperature can be represented with sufficient accuracy by a straight line such as

$$\Delta F_T^\circ = 173,000 - 54.2T \text{ (cal./mole)} \quad (4)$$

which is valid for the temperature range from 2000° to 3000°K. and accurate to ± 4000 cal./mole at 3000°K. The values from this equation fit the calculated points of table 8 sufficiently well so that it can be used for the sake of simplicity in these applications. This linear equation can also be used to extrapolate slightly beyond the temperature range of the data (2000–3000°K.).

In assessing the accuracy of the free-energy expression which has been obtained, a heat capacity for liquid $\text{SiO}_2(\text{l})$ of 20.66 cal./mole °K. instead of the 21.66 cal./mole °K. as in the earlier calculations may be taken as a second trial. With such a value for the heat capacity, the heat of formation of $\text{SiO}_2(\text{l})$ at 3000°K. would be $\Delta H_{3000}^\circ = -211,467$ (instead of $-210,467$) cal./mole. In table 5, use of this value of $\Delta H_{3000}^\circ; \text{SiO}_2(\text{l})$ will raise the heat of the reaction to

$$\Delta H^\circ \left(\text{SiO}_2(\text{l}) \rightarrow \text{SiO}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \right) = 172,513 \text{ cal./mole}$$

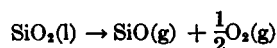
(instead of 171,513). Next, from table 7 it can be seen that the entropy of $\text{SiO}_2(\text{l})$ would be lowered by the use of the smaller C_p value by an amount equal to $\Delta S_{\text{SiO}_2(\text{l})}^\circ = 0.41$ e. u. This would make $\Delta S_{\text{SiO}_2; 3000^\circ\text{K.}}^\circ = 49.62$ e. u. (instead of 50.03 e. u.). Consequently, the ΔS° of reaction at 3000°K. would be increased to 54.04 e. u. (instead of 53.63 e. u.), and $(T\Delta S^\circ)_{3000^\circ\text{K.}} = 162,120$ cal. (instead of 160,890). The corresponding free-energy value is $\Delta F_{3000^\circ\text{K.}}^\circ = 10,393$ cal./mole instead of the 10,623 obtained with $C_p^\circ = 21.66$ cal./mole °K. or a decrease below the previous value of 230. The lower C_p° value for silica indicates a slightly increased vapor pressure.

It is seen from the above discussion that the free energy does not change too rapidly with changes in the value of the heat capacity of liquid silica, although its components, the heat of reaction and the entropy, do.

To estimate the accuracy of the free-energy functions, a reconsideration in detail is needed of how they have been calculated. The discussion is based on the fundamental definition:

$$\Delta F = \Delta H - T\Delta S$$

In considering the reaction



it should be noted that at 2000°K. the free-energy change is accurate to about ± 3000 cal./mole. This uncertainty is estimated from Coughlin's table (18). Of this uncertainty, about 2000 cal./mole is associated with contributions from the formation of $\text{SiO}(\text{g})$, and 1000 cal./mole is associated with the formation of liquid

silica. To make a rough estimate of the errors to be expected at higher temperatures, the fundamental equation can be modified to obtain

$$\begin{aligned} \Delta F^\circ &= \Delta H_{2000}^\circ + \int_{2000}^T \Delta C_p^\circ dT - T \left(\Delta S_{2000}^\circ + \int_{2000}^T \frac{\Delta C_p^\circ dT}{T} \right) \\ &= \Delta H_{2000}^\circ - 2000 \cdot \Delta S_{2000}^\circ - (T - 2000) \Delta S_{2000}^\circ \\ &\quad + \int_{2000}^T \Delta C_p^\circ dT - T \int_{2000}^T \frac{\Delta C_p^\circ dT}{T} \quad (5) \end{aligned}$$

If the first two terms of equation 5 are designated as ΔF_{2000}° and the variable of integration T is replaced by τ , the dummy variable (to avoid confusion with the T used as the limit of integration), then

$$\begin{aligned} \Delta F^\circ &= \Delta F_{2000}^\circ - (T - 2000) \Delta S_{2000}^\circ + \int_{2000}^T \Delta C_p^\circ d\tau - T \int_{2000}^T \frac{\Delta C_p^\circ}{\tau} d\tau \\ &= \Delta F_{2000}^\circ - (T - 2000) \Delta S_{2000}^\circ + T \int_{2000}^T \left(\frac{\Delta C_p^\circ}{T} - \frac{\Delta C_p^\circ}{\tau} \right) d\tau \end{aligned}$$

is obtained.

The uncertainty in ΔF_{2000}° is ± 3000 cal./mole according to the earlier estimate. Since the value of $\Delta S_{2000}^\circ = 57.08 \pm 0.7$ e. u., the uncertainty in the second term at 3000°K. is ± 700 cal./mole. The last integral would also contribute to the overall uncertainty if ΔC_p° for the reaction were in error. For the present case, a rough order of magnitude of this uncertainty may be calculated, if it is noted that C_p° for $\frac{1}{2}\text{O}_2 \cong 4.5$ cal./mole degree, $C_{p_{\text{SiO}}}^\circ \cong 9.0$ cal./mole degree, and $C_{p_{\text{SiO}_2}}^\circ = 21.66$ cal./mole degree. Hence, $\Delta C_p^\circ \cong -8.0$ cal./mole degree. The most likely source of error in ΔC_p° is $C_{p_{\text{SiO}_2}}^\circ$. If this error were 1 cal./mole degree, so that actually $C_{p_{\text{SiO}_2}}^\circ = 20.66$ and $\Delta C_p^\circ = -7.0$, then the total error would amount to an additional 220 cal./mole. Thus at 3000°K., the uncertainties in ΔF° add up to 3920 or 4000 cal./mole.

As a further check on the free-energy equation obtained, the values of the free energy at 2000°K. can be compared with those tabulated by Coughlin (18). He gives

$$\Delta F_{2000; \text{SiO}(\text{g})}^\circ = -59,200 \text{ cal./mole}$$

and

$$\Delta F_{2000; \text{SiO}_2(\text{l})}^\circ = -123,900 \text{ cal./mole}$$

from which there is for the reaction $\text{SiO}_2(\text{l}) \rightarrow \text{SiO}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$, the free-energy change

$$\Delta F_{2000}^\circ = 64,700 \pm 3000 \text{ cal./mole}$$

This value compares favorably with the value of 64,600 cal./mole, which is based on the empirical equation 4.

The free-energy data obtained by the present calculations are plotted in figure 1. The empirical equation has been extrapolated above 3000°K., which can be

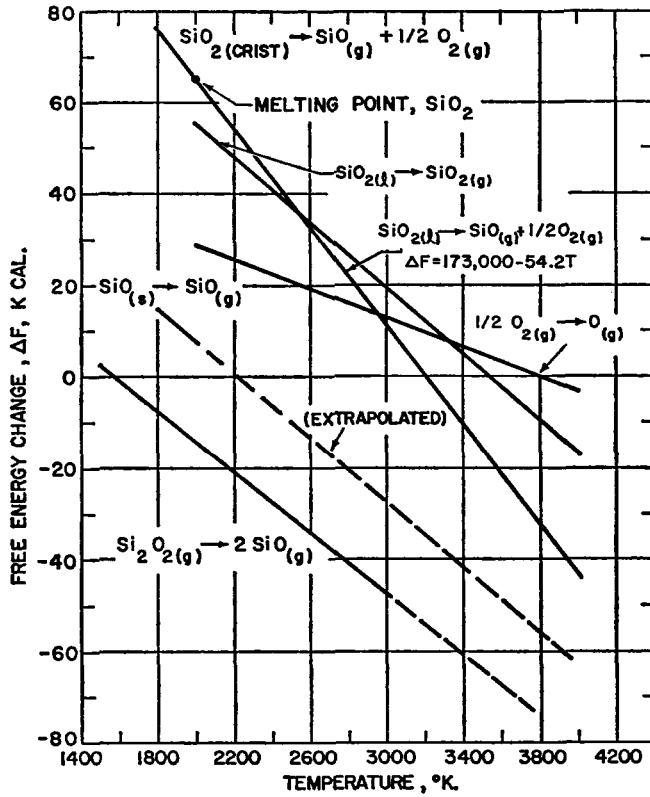


FIG. 1. Free-energy changes of reactions in the decomposition of silica.

safely done over a narrow temperature range, and will be a fair approximation at higher temperatures. From the expression

$$\Delta F^\circ = \Delta H^\circ - T\Delta S^\circ$$

with a reference temperature of 3000°K.,

$$\Delta F_T = \Delta H_{3000}^\circ + \int_{3000}^T \Delta C_p^\circ dT - T\Delta S_{3000}^\circ - T \int_{3000}^T \frac{\Delta C_p^\circ dT}{T} \quad (6)$$

where ΔC_p° is equal to the change in heat capacity of the reaction considered, i. e.,

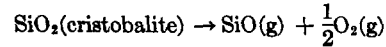
$$\Delta C_p^\circ = \frac{1}{2}C_{pO_2}^\circ + C_{pSiO}^\circ - C_{pSiO_2(l)}^\circ$$

For small temperature intervals, the second and fourth terms in the free-energy equation 6 will cancel, thus justifying the extrapolation:

$$\Delta F_T^\circ = \Delta H_{3000}^\circ - T\Delta S_{3000}^\circ$$

For temperatures below 2000°K., where solid silica is the stable phase, the data of Coughlin (18) for cristobalite have also been plotted in figure 1. In this case, his tabulated free energies of formation for SiO_2 and $SiO(g)$ can be subtracted and used directly.

It is also possible to develop an empirical free-energy equation for the immediate range below 2000°K. by the use of entropy data. For example, for the reaction



$$S_{\text{cristobalite}; 2000} = S_{298}^\circ + (S_{2000}^\circ - S_{298}^\circ) = 40.04 \text{ e.u.} \quad (46, 47)$$

$$\frac{1}{2}S_{O_2; 2000}^\circ = 32.11 \text{ e.u.}$$

$$S_{SiO; 2000}^\circ = 66.04 \text{ e.u.}$$

and

$$\Delta S_{2000}^\circ = S_{SiO}^\circ + \frac{1}{2}S_{O_2}^\circ - S_{SiO_2}^\circ = 58.11 \text{ e.u.}$$

Using this value of the entropy change at 2000°K. a curve can now be fitted through the 2000°K. point, since $\Delta F_{2000}^\circ = 64,600$ cal./mole from equation 4. Hence,

$$\Delta F^\circ = 180,800 - 58.11T \quad (\text{cal./mole for } 1800 < T < 2000^\circ\text{K.}) \quad (7)$$

Relation 7 gives $\Delta F_{1800}^\circ = 76,200$ cal./mole and $\Delta F_{1900}^\circ = 70,390$ cal./mole. These values can be compared with values calculated from Coughlin's data (18); i. e.,

$$\Delta F_{1800}^\circ = 76,450 \text{ cal./mole}$$

and

$$\Delta F_{1900}^\circ = 70,650 \text{ cal./mole}$$

This good agreement increases the confidence in the data and calculations.

D. EQUILIBRIUM CONSTANT

For the evaluation of the equilibrium constant, K , corresponding to the reaction that is the subject of Section II, the usual relation $\Delta F^\circ = -RT \ln K$ can be modified to give

$$\log_{10} K = \frac{-\Delta F^\circ}{2.303RT} = \frac{-\Delta H^\circ}{4.57T} + \frac{\Delta S^\circ}{4.57}$$

or, for the present case,

$$\log_{10} K = \frac{-37,900}{T} + 11.85$$

This equilibrium constant has been plotted in figure 2 as a function of $1/T$. It can be seen that at higher temperatures the equilibrium constant becomes larger.

E. EQUILIBRIUM VAPOR PRESSURE

1. Expression for equilibrium constant

In the range from 2000° to 3000°K. it has been shown that the standard free energy of the reaction $SiO_2(l) \rightarrow SiO(g) + \frac{1}{2}O_2(g)$ can be represented as a function of temperature by

$$\Delta F_T^\circ = 173,000 - 54.2T$$

This function is related to the equilibrium constant by the conventional definition,

$$\Delta F_T^\circ = -RT \ln K = -RT \ln \frac{a_{SiO(g)} a_{O_2(g)}^{1/2}}{a_{SiO_2(l)}}$$

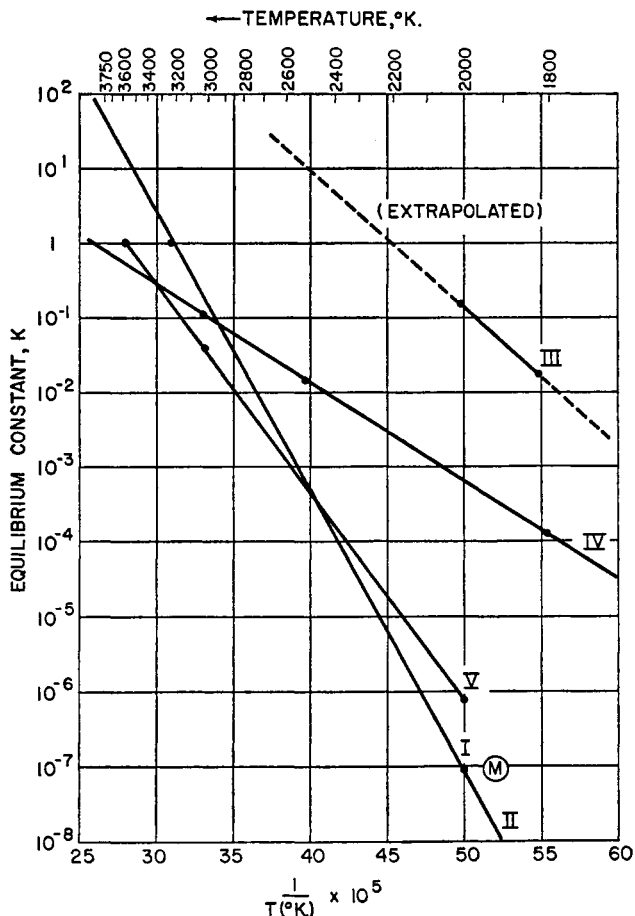
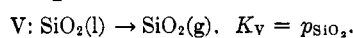
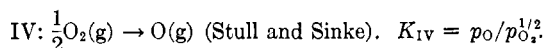
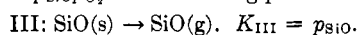
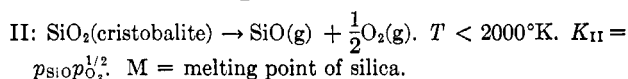
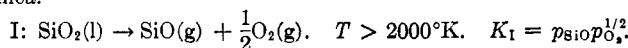


FIG. 2. Equilibrium constants of decomposition reactions of silica.



where a_i = activity of component (or the fugacity in the case of gaseous components) and i = $\text{SiO}(\text{g})$ or $\text{O}_2(\text{g})$ or $\text{SiO}_2(\text{l})$.

2. Simplification of equilibrium constant

For liquid silica the usual assumption is made that the activity is unity; i. e., any solution effects of $\text{SiO}(\text{g})$, $\text{O}_2(\text{g})$, or other equilibrium species in SiO_2 are considered negligible.

For the gaseous components, it is reasonable to replace the activities by partial pressures of the species being considered as long as the gases do not deviate markedly from the perfect gas laws. This assumption is valid at low pressures and high temperatures. For oxygen (fugacity = 48 atm. at a pressure of 50 atm. and 0°C . (27); critical temperature, $T_c = 154.3^\circ\text{K}$.; critical pressure, $P_c = 49.7$ atm.) at 50 atm. and

2000°K ., the reduced temperature is $T_r = T/T_c = 12.95$, and the reduced pressure is $p_r = p/p_c = 0.995$. For this case, $f/p = 1.0+$ by reference to the Hougen and Watson charts (38), and the fugacity is essentially equal to the pressure.

For $\text{SiO}(\text{g})$, whose condensed properties are practically unknown, very rough approximations must be used to estimate p_c and T_c . Some empirical rules can be used in this case (33). Using the condition that the melting temperature is $\frac{2}{3}T_c$, and the fact that Edwards (22) states that the melting point of SiO must be greater than 1975°K ., T_c is calculated to be approximately 5000°K .. To estimate the molar volume at the critical point, $\bar{V}_m^{\text{sol}} = 0.321\bar{V}_c$. According to Edwards (22), the density of solid SiO is about 2.15 g./cm.³ (20.5 cm.³/mole). Making the assumption that the molar volume of SiO at its melting point is equal to the molar volume (20.5 cm.³/mole) given by Edwards, a molar volume is found at the critical point of $\bar{V}_c = 64.0$ cm.³/mole. Finally, from the fact that many molecules have a compressibility factor of 0.292 (33), p_c is found to be equal to 1870 atm. At 50 atm. and 2000°K ., $p_r = 0.0267$ and $T_r = 0.4$. Again, estimating from the Hougen and Watson chart, it is found that $f/p \cong 0.95$. In view of the uncertainties involved in the above calculations, the results must be considered very approximate. However, they do indicate that in the pressure range of interest (from 1 to 50 atm.) and from 2000° to 3000°K ., the gas will behave ideally. For future considerations, pressures will be used instead of fugacities.

3. Vapor-pressure relation under neutral conditions

Using the simplifying assumptions discussed above, the final equations obtained are:

$$\Delta F_T^\circ = -RT \ln p_{\text{SiO}}p_{\text{O}_2}^{1/2} = -RT \ln K_{\text{eq}}$$

or

$$p_{\text{SiO}}p_{\text{O}_2}^{1/2} = e^{-\Delta F^\circ/RT} = e^{-173,000/RT} e^{54.2/R} \quad (8)$$

Under neutral conditions $p_{\text{SiO}} = 2p_{\text{O}_2}$ and

$$p_{\text{SiO}} = e^{18.41(1-3160/T)} \quad (9)$$

The vapor-pressure data for equation 9 are presented as the upper curve in figure 3. It gives a partial pressure of 0.667 atm. for $\text{SiO}(\text{g})$ at 3085°K ., (boiling point under neutral conditions, neglecting other reactions). It should also be noted that

$$p_{\text{total}} = 1.5p_{\text{SiO}} = 1.5e^{18.41(1-3160/T)} \quad (10)$$

The vapor pressure of $\text{SiO}(\text{g})$ in equilibrium with condensed silica is plotted for a large temperature range in figure 4. The principal curve in this figure is based on the single reaction given and neglects all other equilibria.

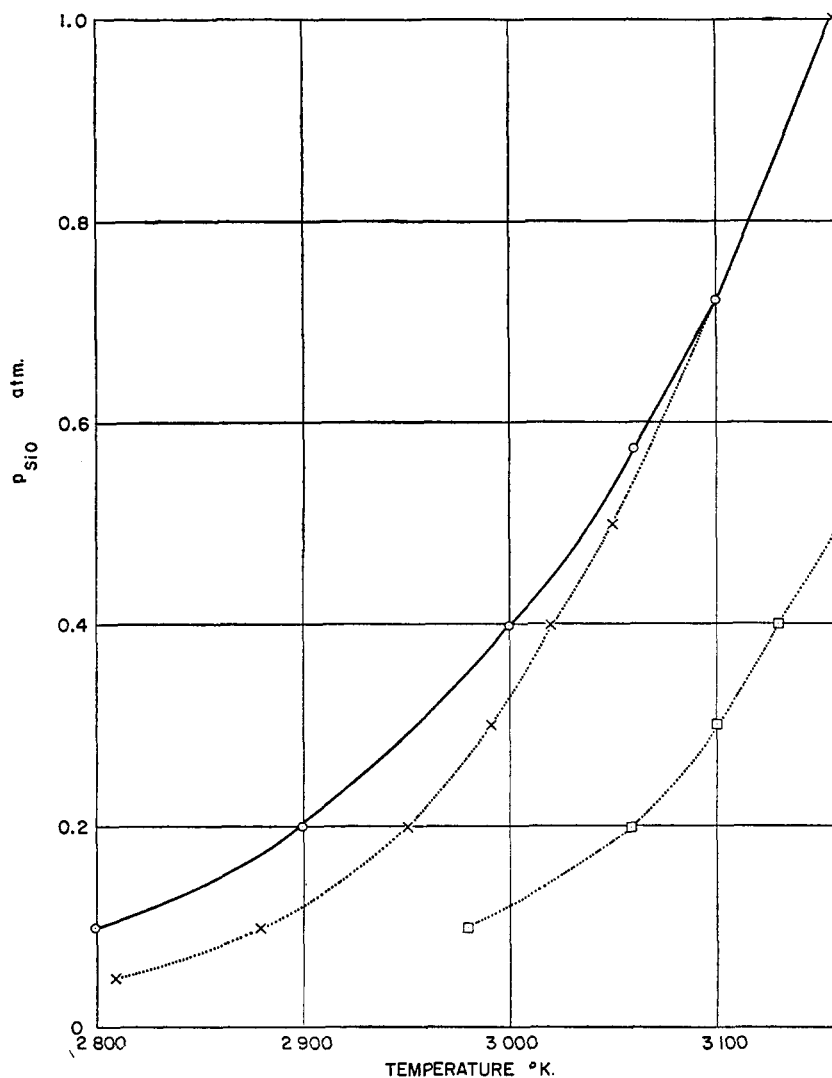


FIG. 3. Linear plot of partial pressure of $\text{SiO}(\text{g})$ near 3000°K . (neglecting the dissociation of oxygen).

Neutral conditions:

$$p_{\text{SiO}} = e^{18.41(1-3160/T)}, \quad \odot, p_{\text{SiO}} \text{ from this equation.}$$

Oxidizing conditions:

$$p_{\text{SiO}} (p_{\text{total}} + p_{\text{SiO}})^{1/2} = e^{28.0(1-3110/T)}, \quad \times, p_{\text{SiO}} \text{ for } p_{\text{total}} = 1 \text{ atm. } \square, p_{\text{SiO}} \text{ for } p_{\text{total}} = 10 \text{ atm.}$$

4. Vapor-pressure relation in air³

For the case of silica decomposing in the presence of air, and assuming a constant total pressure,

$$p_{\text{N}_2} = 4(p_{\text{O}_2} - \frac{1}{2}p_{\text{SiO}})$$

and

$$p_{\text{total}} = p_{\text{N}_2} + p_{\text{SiO}} + p_{\text{O}_2} = 5p_{\text{O}_2} - p_{\text{SiO}} = \text{constant}$$

From the relation (equation 8) for $p_{\text{SiO}} p_{\text{O}_2}^{1/2}$,

$$p_{\text{SiO}} (p_{\text{total}} + p_{\text{SiO}})^{1/2} = e^{28.0(1-3110/T)}$$

These data have been plotted in figures 3 and 4 for the two cases $p = 1 \text{ atm.}$ and $p = 10 \text{ atm.}$

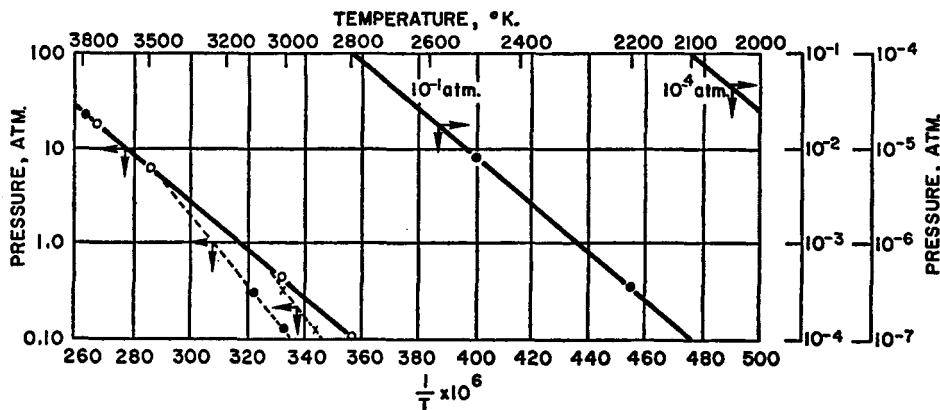
³ In this discussion the composition of air is approximated as 80 per cent nitrogen and 20 per cent oxygen.

It can be seen from the above equations that the presence of the oxygen suppresses the formation of $\text{SiO}(\text{g})$. It should also be emphasized that the data here assume only the reaction $\text{SiO}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$ to be important. Dissociation of oxygen has been neglected but is included in later discussions. Nitrogen is considered to be an inert gas. If this assumption is incorrect, then the present case should be considered as a mixture of oxygen plus some other undefined gas which is inert.

5. Vapor-pressure relation below 2000°K .

For temperatures below 2000°K . the relation for the vapor pressure, p_{SiO} , must be modified. Using the relation $\Delta F^\circ = 180,800 - 58.11T$ for ($1800^\circ\text{K} < T < 2000^\circ\text{K}$),

$$p_{\text{SiO}} = e^{19.72(1-3075/T)}$$



Reaction: $\text{SiO}_2(\text{l}) \rightarrow \text{SiO}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$ for $T > 2000^\circ\text{K}$.

Neutral conditions: —, p_{SiO} for the relation

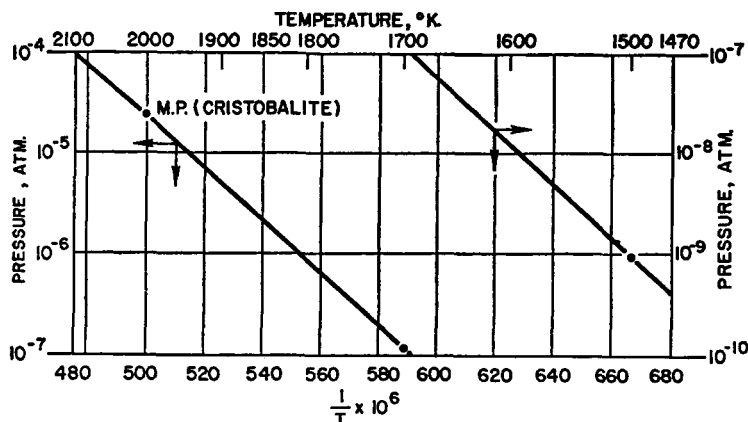
$$p_{\text{SiO}} = e^{18.41(1-2160/T)}$$

○, p_{SiO} are four representative values from Section IX,B, corrected for the dissociation of oxygen.

Oxidizing conditions: For the relation

$$p_{\text{SiO}} (p_t + p_{\text{SiO}})^{1/2} = e^{28.0(1-2160/T)}$$

×, p_{SiO} for $p_t = p_{\text{N}_2} + p_{\text{O}_2} + p_{\text{SiO}} = 1 \text{ atm}$. ●, p_{SiO} for $p_t = 10 \text{ atm}$.



Reaction: $\text{SiO}_2(\text{s}) \rightarrow \text{SiO}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$ for $T < 2000^\circ\text{K}$. —, p_{SiO} for neutral conditions, using Coughlin's tables (18).

FIG. 4. Logarithmic plots of partial pressure of $\text{SiO}(\text{g})$ over extended temperature range (neglecting dissociation of oxygen).

A curve for this function has been plotted in figure 5 over the temperature range from 1800° to 2000°K .

6. Comparison of calculated data with experimental values

For comparison purposes, the available experimental data have also been plotted in figure 5. The effusion-cell measurements of Brewer and Mastick are seen to agree well with the calculated data. The mass-spectrometric measurements of Porter, Chupka, and Inghram (56) are high by a factor of about 6. They indicated that their absolute values of pressures could be in error by a factor of 2 or 3. A point of possible uncertainty in their work is the fact that they used some older vapor-pressure data from Brewer (9). They had calibrated

their equipment by assuming that $p_{\text{Ag}^{107}} = 1 \times 10^{-6}$ atm. at 1245°K ., and that $p_{\text{Au}} = 2 \times 10^{-5}$ atm. at 1750°K .. However, more recent work by Honig (37) gives values of 1.85×10^{-6} atm. for Ag^{107} and 7.9×10^{-5} atm. for Au. All observed pressures of the various species are then increased for the appropriate temperature range by the ratios 1.85/1 and 7.9/2. It is not completely clear that the pressures should be increased by this much, since Porter, Chupka, and Inghram (56) state that they checked their calibration by the vaporization of a weighed amount of silver or gold.

To compare their data further with the present results, table 9 shows the free-energy data calculated from their observed vapor pressures. It is seen that

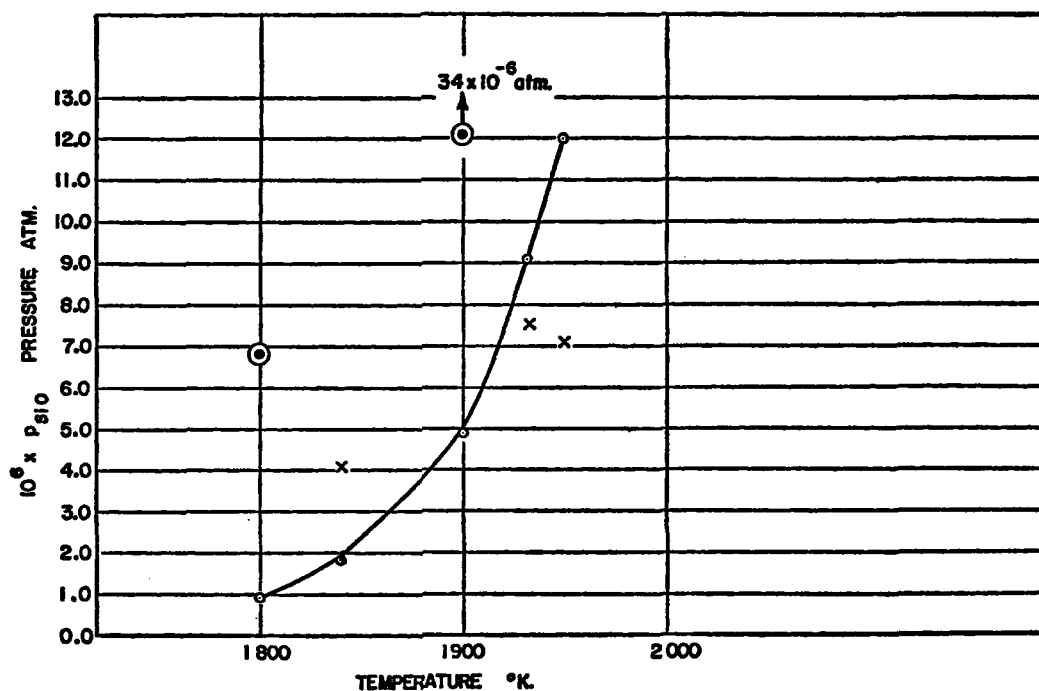


Fig. 5. Comparison of calculated partial pressures of SiO(g) in equilibrium with cristobalite with experimental data for the range from 1800° to 2000°K. O, calculated from the relation

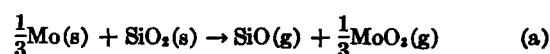
$$P_{\text{SiO}} = e^{19.73(1-2675/T)}$$

X, experimental points of Brewer and Mastick (effusion cell) for neutral conditions. O, experimental points of Porter, Chupka, and Inghram (mass-spectrometer) for quoted neutral conditions, but their data indicated actual reducing conditions.

their results are in good agreement with the free-energy data of this paper. It should also be noted that their reaction does not correspond to stoichiometric conditions. They apparently did not have neutral conditions. The free-energy data based on recalculated vapor pressures are less in agreement with the calculated free-energy curve given in figure 1. Further evidence that the mass-spectrometer data as originally reported (56) are probably preferable will be produced when the dissociation of oxygen is considered in a following section.

Inuzuka and Ageha (43) have reported some additional vapor-pressure data for silica. They give a vapor pressure of 1.1×10^{-7} atm. for silica at 1200°C. (1473°K.). They used a "Mo and W wire" to heat a fused silica tube and measured the vapor pressure by a

Langmuir method. At this temperature, the thermochemical calculations herein give a total vapor pressure of 6×10^{-10} atm. (see figure 4), a discrepancy by a factor of 180. However, it is shown in the following arguments that they have probably studied some other reaction, possibly the following:



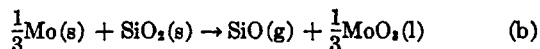
This reaction would tend to give a higher vapor pressure for SiO(g) than would be expected under neutral conditions. The presence of tungsten might also reduce silica, but it would not be expected to change the calculated pressure due to molybdenum by more than a small factor.

To obtain thermochemical data for the suspected

TABLE 9
Comparison of free energies based on mass-spectrometric data (56)

	P_{SiO}	P_{O_2}	$\Delta F^\circ_{\text{calcd.}}$	$\Delta F^\circ_{\text{(curve, figure 1)}}$
	atm.	atm.	cal./mole	cal./mole
1800°K.:				
Mass-spectrometric data, as is.....	6.8×10^{-6}	5.2×10^{-6}	72,400	76,000
Same data, corrected.....	2.68×10^{-6}	2.05×10^{-7}	65,100	
1900°K.:				
Same data, as is.....	3.4×10^{-6}	8.2×10^{-6}	69,595	71,000
Same data, corrected.....	1.34×10^{-6}	32.4×10^{-6}	61,800	

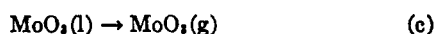
reaction with molybdenum, the free-energy data of Coughlin (18) are first used for the reaction to give liquid MoO_3 ,⁴ instead of the gaseous product.



The free energy of this reaction is then

$$\begin{aligned} \Delta F_{1473}^\circ &= \Delta F_{\text{SiO}}^\circ + \frac{1}{3}\Delta F_{\text{MoO}_3}^\circ - \Delta F_{\text{SiO}_2}^\circ \\ &= 63,000 \text{ cal./mole} \end{aligned}$$

Now it is necessary to estimate the free energy of vaporizing liquid molybdenum(VI) oxide:



It can be estimated that $\Delta F_{1530}^\circ = 0$ for the above vaporization process from the fact that the normal boiling point of MoO_3 is 1530°K ., according to Brewer (10). This assumption is probably conservative because Berkowitz, Inghram, and Chupka (4) have shown that, at the boiling point, the species $(\text{MoO}_3)_3$, $(\text{MoO}_3)_4$, and $(\text{MoO}_3)_5$ are probably most important. They indicate that the monomer is present in an amount less than a few per cent at the temperature of their measurements (near 900°K .). On the other hand, other authors (6, 10, 12) indicate that the monomer is probably the most important species. For the present calculation, the simplifying assumption is made that only the monomer is important. Therefore, it is assumed that $\Delta F_{1530}^\circ = 0$. Actually, if polymers of MoO_3 do exist at the normal boiling point, then $\Delta F_{1530}^\circ > 0$ for the above reaction.

The free-energy change for vaporization can now be estimated by assuming Trouton's constant to be 21. Therefore, $\Delta F_{1473}^\circ = 400$ cal./mole.

Now combining the last two reactions (b and c), it is found that, for the overall desired reaction (reaction a):

$$\Delta F_{1473}^\circ = +63,000 + 400 = 63,400 \text{ cal./mole}$$

Since

$$\begin{aligned} p_{\text{SiO}} \cdot p_{\text{MoO}_3}^{1/3} &= e^{-\Delta F^\circ/RT} \\ p_{\text{SiO}} &= 1.24 \times 10^{-7} \text{ atm.} \\ p_{\text{MoO}_3} &= 0.4 \times 10^{-7} \text{ atm.} \end{aligned}$$

and

$$p_{\text{total}} = 1.65 \times 10^{-7} \text{ atm.}$$

The pressure value of 1.65×10^{-7} atm. is in good agreement with the value of 1.1×10^{-7} atm. reported by Inuzuka and Ageha (43). The above discussion of their data shows that they have undoubtedly not been studying the vaporization of pure silica in a neutral atmosphere and gives additional strength to the data used herein. Since Coughlin (18) uses essentially the

same data for the heat of formation of SiO(g) as have been used earlier in this paper, a recalculation of the above results (43) further substantiates the present choice of data for the heat of formation of SiO(g) .

So far only one reaction has been considered in the decomposition of silica, as indicated in the title of this section. Because fairly good agreement is obtained with experimental data in this manner, it appears probable that this reaction is the most important. However, other additional competing or simultaneous reactions may also be important. They will now be considered in the following sections.

III. THERMOCHEMISTRY OF THE CONDENSATION REACTION OF SiO(g)

The equilibrium between gaseous SiO and its condensation product is of interest because of the possibility that formation of solid may limit the vapor pressure of SiO(g) to be expected from the reaction discussed in the previous sections. The nature of such a condensation product is subject to uncertainty. The two major possibilities are SiO(s) or a stoichiometric mixture of $\text{Si(s)} + \text{SiO}_2(\text{s})$. Data concerning the properties of solid SiO are very limited. According to Brewer and Edwards (11, 22) and Hoch and Johnston (34), SiO(s) is unstable relative to Si(s) and $\text{SiO}_2(\text{s})$ below 1450° and 1573°K ., respectively. However, above these temperatures the solid phase SiO(s) is considered the stable phase. Later work (7, 13) suggests that SiO(s) may not be stable for any portion of the temperature range.

With these uncertainties in mind, condensation effects have been calculated assuming that SiO(s) is the stable, condensed phase. The limited amount of thermodynamic data available for SiO(s) are quite uncertain. Brewer and Edwards (11) have interpreted the results of Tombs and Welch (68), which have been obtained over a mixture of silicon and silica, as referring to the reaction of $\text{SiO(s)} \rightleftharpoons \text{SiO(g)}$ in the temperature range from 1573° to 1920°K . They state that for this temperature range $\Delta H^\circ = 58,550$ cal./mole and $\Delta S^\circ = 25.45$ e. u., although they point out that the entropy data may be incorrect. If these data are used, as stated, for the free energy of reaction versus temperature, the approximate relation

$$\Delta F^\circ = 58,550 - 25.45T$$

is obtained. Thus, one obtains $p = 1$ atm. ($\Delta F^\circ = 0$) at $T = 2300^\circ\text{K}$.

Additional vapor-pressure data calculated from this relation are plotted in figure 6 by extrapolating to temperatures above 2000°K . This extrapolation is not considered too good in view of the uncertainty in the entropy.

One can also utilize the above data in another, more correct extrapolation above 2000°K . For this purpose,

⁴ Coughlin gives 1068°K . as the melting point of MoO_3 .

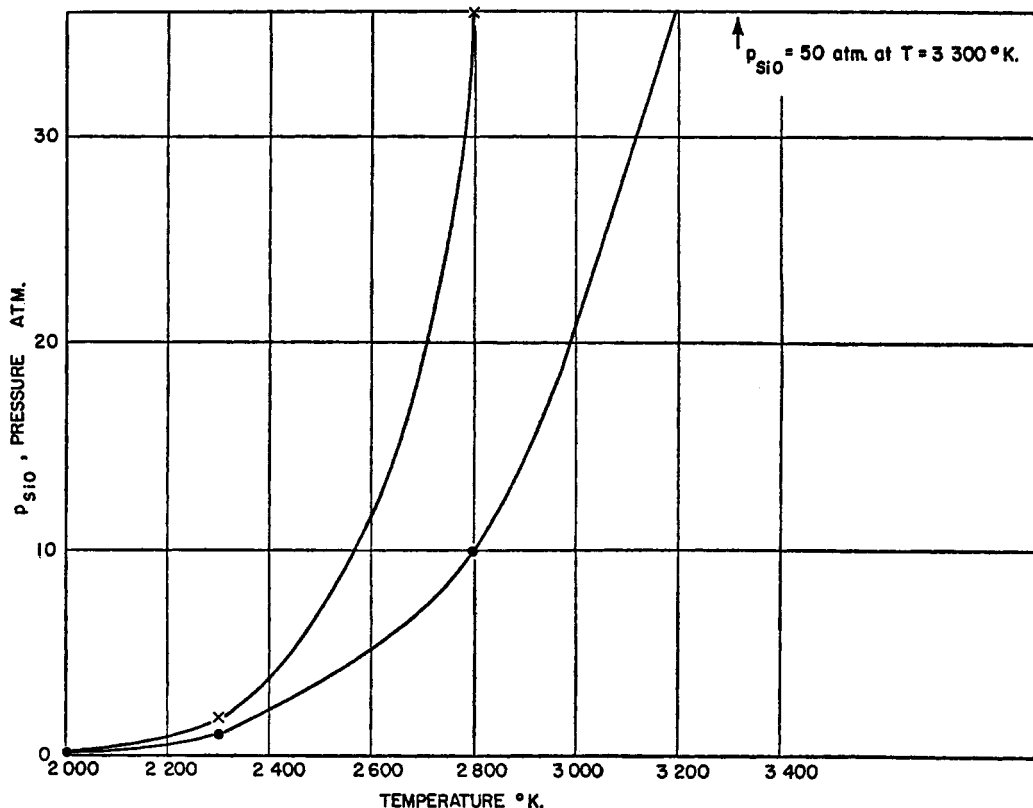


Fig. 6. Condensation effects of $\text{SiO}(\text{g})$, calculated by assuming that $\text{SiO}(\text{s})$ is the stable phase (see text). p_{SiO} for the reaction $\text{SiO}(\text{s}) \rightleftharpoons \text{SiO}(\text{g})$. ●, using the relation $\Delta F = 58,550 - T \times 25.45$ (probably inaccurate above 2000°K .; discussed by Brewer and Edwards (*J. Phys. Chem.* **58**, 355 (1954))). ×, using $\Delta F = 77,530 - 34.94T$.

the following data are taken from Brewer and Edwards (11, 22):

$$C_p^{\circ} \text{SiO (crystalline)} = 10.57 + 2.98 \times 10^{-3}T - 2.72 \times 10^{-6}T^{-2}$$

$$S_{298}^{\circ} \text{SiO (crystalline)} = 6.4 \text{ e.u.}$$

and

$$S_{298}^{\circ} \text{SiO (amorphous)} = 7.3 \text{ e.u.}$$

With these data,

$$S_{2000}^{\circ} \text{SiO (amorphous)} = 31.1 \pm 3.0 \text{ e.u.}$$

Using the earlier result that

$$S_{2000}^{\circ} \text{SiO}(\text{g}) = 66.04 \text{ e.u.}$$

then for the present reaction, $\Delta S^{\circ} = 34.94 \text{ e.u.}$

If it is now assumed that the earlier relation, $\Delta F^{\circ} = 58,550 - 25.45T$ is valid at $T = 2000^\circ\text{K}$., the equation at 2000°K . can be fitted with better entropy values to extrapolate to higher temperatures.

By using more realistic entropy values,

$$\Delta F^{\circ} = 77,530 - 34.94T \quad (\text{d})$$

The above relationship corresponds to a heat of reaction of $\Delta H = 77,530 \text{ cal./mole}$ in the temperature range near 2000°K . These data are plotted in figure 1. The line is dashed above 2000°K . because of the uncertainty in the data.

Using the data of Brewer (10) on the heat of formation of $\text{SiO}(\text{s})$, $\Delta H_{298}^{\circ} = -104,600 \text{ cal./mole}$, the heat of the reaction $\text{SiO}(\text{s}) \rightarrow \text{SiO}(\text{g})$ can be estimated as follows:

$$\begin{aligned} \Delta H_{298}^{\circ} &= \Delta H_{f, \text{SiO}(\text{g})}^{\circ} - \Delta H_{f, \text{SiO}(\text{s})}^{\circ} \\ &= -21,800 - (-104,600) \text{ cal./mole} \\ &= +82,800 \text{ cal./mole} \end{aligned}$$

Also,

$$\begin{aligned} \Delta H_T^{\circ} &= \Delta H_{298}^{\circ} + \int_{298}^T \Delta C_p^{\circ} dT \\ \Delta H_T^{\circ} &= \Delta H_{298}^{\circ} + (H_T^{\circ} - H_{298}^{\circ})_{\text{SiO}(\text{g})} - (H_T^{\circ} - H_{298}^{\circ})_{\text{SiO}(\text{s})} \\ \Delta H_T^{\circ} &= \Delta H_{298}^{\circ} + (H_T^{\circ} - H_0^{\circ})_{\text{SiO}(\text{g})} - (H_{298}^{\circ} - H_0^{\circ})_{\text{SiO}(\text{g})} \\ &\quad - (H_T^{\circ} - H_{298}^{\circ})_{\text{SiO}(\text{s})} \end{aligned}$$

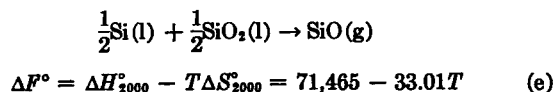
Therefore,

$$\begin{aligned} \Delta H_{2000}^{\circ} &= 82,800 + 8.18 \times 2000 - 6.955 \times 298 \\ &\quad - \int_{298}^{2000} [10.57 + 2.98 \times 10^{-3}T - 2.72 \times 10^{-6}T^{-2}] dT \\ &= 82,800 + 16,360 - 2070 - 23,090 \\ &= 74,000 \text{ cal./mole} \end{aligned}$$

This value agrees well with the value of $77,530 \text{ cal./mole}$ given above and thus makes the relation seem more reliable. Accordingly, the data for the relation $\Delta F =$

77,530 – 34.94*T* have been taken as the best and have been plotted in figure 6.

These data lead to a larger vapor pressure of SiO(g) in equilibrium with SiO(s) than that predicted by the first expression, $\Delta F = 58,500 - 25.45T$. However, the data show that the vapor pressure of SiO(s), which is based on either expression, is much greater than the vapor pressure of SiO(g) in equilibrium with SiO₂(s) under neutral conditions. It would, therefore, not be expected that SiO(s) could be formed from SiO₂(s) under neutral conditions. Furthermore, even if the assumption that SiO(s) is the stable, condensed phase is incorrect, so that the stoichiometric mixture of silicon and silica should be considered, similar conclusions would be obtained. The free-energy change of such a reaction can very easily be calculated near 2000°K., using the earlier heat of formation and entropy data in addition to entropy data for Si(l) from Stull and Sinke. Then, for the reaction:



This expression (e) is quite similar to the relation (d) for the vaporization of SiO(s) and leads to the same conclusion as above. Neither SiO(s) nor the stoichiometric mixture of silicon and silica would result from the vaporization of silica; i. e., the formation of SiO(g) is preferred.

IV. ASSOCIATION REACTIONS OF THE TYPE



Very little information is available regarding the formation of dimers and trimers of SiO(g). The paper of Porter, Chupka, and Inghram (56) gives one measurement of the pressure of Si₂O₂ in equilibrium with SiO(g). These pressures are 4.5×10^{-8} atm., and 1.1×10^{-4} atm., respectively, at 1463°K. For the reaction $2\text{SiO}(g) \rightleftharpoons \text{Si}_2\text{O}_2(g)$ it follows that

$$K_{eq} = \frac{p_{\text{Si}_2\text{O}_2}}{p_{\text{SiO}}^2} = 3.72 \text{ at } 1463^\circ\text{K.}$$

From the above equilibrium constant, the free-energy change for dimerization is $\Delta F_{1463}^\circ = -3820$ cal./mole of Si₂O₂(g). To get a very rough estimate of the degree of dimerization at higher temperatures, it is necessary to estimate the entropy change for the above reaction. Data are already available for the entropy of the monomer, SiO(g). For the dimer, however, no molecular data are available, and its entropy must be estimated by approximation methods.

The empirical equation of Kubaschewski and Evans (48) can be used to estimate $S_{298}^\circ = 64.1$ e. u. for Si₂O₂(g). Assuming that Si₂O₂(g) has about the same entropy increment as another four-atom molecule,

ClF₃, whose entropy increment is $S_{1500}^\circ - S_{298}^\circ = 29.5$ e. u. (55), then $S_{1500}^\circ = 93.6 \pm 5.0$ e. u. for Si₂O₂(g), where the uncertainty is only estimated.

The empirical data used in this calculation are preferred, since no detailed structural information concerning the Si₂O₂ molecule is available from spectroscopic or other sources. However, to illustrate that choice of a particular structure for the Si₂O₂ molecule leads to an entropy value in fair agreement with the above empirical values, a trial calculation has been performed assuming Si₂O₂ to be a linear molecule of the form:



The silicon-silicon distance, l_1 , was taken to be 2.25 Å., the same distance as for the Si₂ molecule (19, 20, 21). The silicon-oxygen distance, l_2 , was taken from Herzberg (32, p. 570) to be 1.51 Å. To make the vibrational frequency assignments, the valence force field theory which was discussed by Herzberg (31, p. 180) was used. For the force constant of the silicon-silicon bond, a value of 2.1×10^5 dynes/cm. was chosen (20, 21); that of the silicon-oxygen bond was taken as 9.25×10^5 dynes/cm. from Herzberg (32); and the bending force constant (31, p. 180)

$$\frac{k_g}{l_1 l_2} = 0.19 \times 10^6 \text{ dynes/cm.}$$

was taken to be the same as for cyanogen. Using Herzberg's formulas (31) the five fundamental frequencies which were obtained are: $\omega_1 = 1270$ cm.⁻¹; $\omega_2 = 380$ cm.⁻¹; $\omega_3 = 1230$ cm.⁻¹; $\omega_4 = 350$ cm.⁻¹ (doubly degenerate); and $\omega_5 = 219$ cm.⁻¹ (doubly degenerate). With the above assumptions, the entropy of gaseous Si₂O₂ in its standard state at 1500°K. was found to be $S_{1500}^\circ = 98.96$ e. u. This value compares favorably with the empirical value that was used. From the tables of Edwards (22),

$$S_{1500}^\circ; \text{SiO}(g) = 63.5 \text{ e.u.}$$

hence, for the reaction as given,

$$\Delta S^\circ = 93.6 - 2(63.5) = -33.4 \text{ e.u.}$$

Assuming that $\Delta S_{1500}^\circ = \Delta S_{1463}^\circ$ (the small temperature difference would contribute only a small change as compared to the accuracy of the data), and using the relation

$$\Delta F_T^\circ = \Delta H_{1463}^\circ - T \times \Delta S_{1463}^\circ$$

then $\Delta H_{1463}^\circ = -52,500$ cal./mole Si₂O₂(g), and also

$$\Delta F_T^\circ = -52,500 + 33.4T \quad (11)$$

This latter relation (equation 11) is, of course, very rough, and at an extrapolated temperature of 3000°K. the uncertainty may be at least ± 5000 cal./mole or more. The free-energy change for the reverse reaction is shown in figure 1.

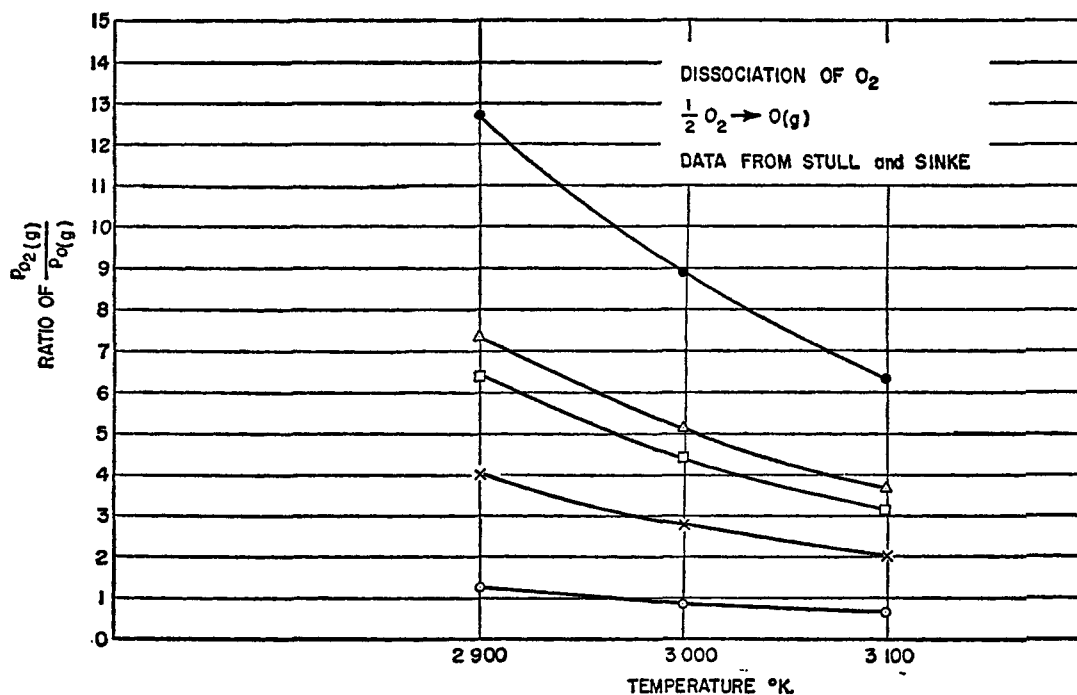


Fig. 7. Dissociation pressure ratios of oxygen near 3000°K. ●, $p_{O_2} = 1$ atm.; △, $p_{O_2} = 0.333$ atm.; □, $p_{O_2} = 0.25$ atm.; ×, $p_{O_2} = 0.1$ atm.; ○, $p_{O_2} = 0.01$ atm.

At 3000°K., a free-energy change of +47,700 cal./mole is obtained from equation 11, corresponding to an equilibrium constant of 3.46×10^{-4} . The expected pressure of Si_2O_2 as a function of the pressure of SiO is presented.

Pressures of $\text{Si}_2\text{O}_2(\text{g})$ in equilibrium with SiO(g) at 3000°K.

p_{SiO}	$p_{\text{Si}_2\text{O}_2}$
atm.	atm.
0.4	5.55×10^{-5}
1	3.46×10^{-4}
10	3.46×10^{-2}
100	3.46

The data show that the dimerization effect is probably not too important for the case where the boiling point is above 3000°K. and the ambient pressures are less than 50 atm. However, the dimerization phenomenon would be more important (for a given pressure of SiO) at lower temperatures. Again, it should be emphasized that these data do not have high accuracy.

V. DISSOCIATION OF OXYGEN

Because the dissociation of oxygen may lead to a higher effective pressure in an equilibrium mixture of silica which is decomposing to form SiO(g) and $\text{O}_2(\text{g})$, the dissociation of oxygen in the temperature range from 2900° to 3100°K. has been reviewed briefly. The data of Stull and Sinke (65) have been used in the present case. It has been necessary to extrapolate the free-energy data from 3000° to 3100°K. to obtain an

equilibrium constant at the higher temperature. The extrapolated data agree with the earlier data given in Series III of the National Bureau of Standards (55). The values of the equilibrium constants which have been obtained are shown below:

Equilibrium constants for the reaction $\frac{1}{2}\text{O}_2(\text{g}) \rightleftharpoons \text{O}(\text{g})$

Temperature	$K = p_{\text{O}}/p_{\text{O}_2}^{1/2}$
°K.	
2900	0.079
3000	0.112
3100	0.157

From the equilibrium constants shown, values of the $p_{\text{O}_2}/p_{\text{O}}$ ratio have been obtained for various selected oxygen pressures. The results of these calculations are plotted in figure 7, where it is seen that, at an oxygen pressure of 0.01 atm. at 2960°K., the pressure of oxygen atoms, in equilibrium, is also about 0.01 atm. For the case of 0.333 atm. of oxygen at 3100°K., there will be an atomic oxygen pressure of $p_{\text{O}(\text{g})} = 0.09$ atm. The dissociation of $\text{O}(\text{g})$ will contribute a significant (although smaller) amount to the total pressure in the case of the decomposition of silica to SiO(g) and oxygen near 3100°K.

To cover an even wider temperature range, the data of Stull and Sinke below 3000°K. and of the National Bureau of Standards above 3000°K. have been used to obtain the free-energy change and equilibrium constants for the dissociation reaction. To get an approxi-

mate linear relation for the free-energy change of the reaction at 3000°K., the data of Stull and Sinke (65) have been used. From their heat of reaction and entropy data, the following relation is obtained: $\Delta F^\circ = 61,348 - 16.11T$. This relationship gives a free-energy change of 29,129 cal./mole at 2000°K., whereas their original tabulation (65) gives 29,091 cal./mole. The above free-energy relation and the corresponding equilibrium constants are plotted in figures 1 and 2.

The data on the dissociation of oxygen are well known and provide a test of the reliability of the data for the decomposition data of silica reported by Porter, Chupka, and Inghram (56), since their mass-spectrometric measurements have included both O₂ and O. At 1900°K. they give

$$p_o = 2.2 \times 10^{-7} \text{ atm. and } p_{o_2} = 8.2 \times 10^{-8} \text{ atm.}$$

for the reaction $\frac{1}{2}O_2 \rightarrow O(g)$, which corresponds to

$$K_{1900} = 7.7 \times 10^{-4} = p_o/p_{o_2}^{1/2}$$

Hence, $\Delta F_{1900}^\circ = 27,065$ cal./mole. For the same dissociation reaction, Stull and Sinke (65) give

Temperature	$\log_{10} K$	ΔF°
°K.		cal./mole
1900	-3.529	30,678
2000	-3.178	29,091
2100	-2.859	27,477

Thus, the free-energy value of 27,065 cal./mole, which is based on mass-spectrometric pressure measurements (56), is low by 3613 cal./mole at 1900°K.

If the mass-spectrometric vapor pressures had been corrected by using the more recent vapor-pressure data for gold, then the pressures would have been increased by a factor of 3.95. This would have raised the equilibrium constant at 1900°K. to a value of $\log_{10} K = -2.815$, thus making the standard free-energy change $\Delta F_{1900}^\circ = 24,400$ cal./mole.

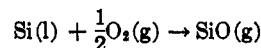
However, this value is in error by 6300 cal. at 1900°K., whereas the actual value which has been reported (56) is in error by only 3600 cal./mole. Therefore, it seems that there may have been compensating errors in the reported data, in the choice of cross sections, or the newer vapor-pressure data for gold may be in error. In any case, at this time it appears more logical to accept the tabulated pressure data (56) as being correct, because they yield free-energy values in better agreement with the known values on the dissociation of oxygen.

VI. THERMOCHEMISTRY OF THE REACTION

$$SiO(g) \rightarrow Si(g) + \frac{1}{2}O_2(g)$$

To estimate the importance of the dissociation of SiO to yield Si(g), the following free-energy and entropy of

formation data at 3000°K. can be used: For Si(g), $\Delta F_{3000}^\circ = 10,618$ cal./mole (65), using Si(l) as the reference state; for O₂(g), $\Delta F_{3000}^\circ = 0$, since O₂ is the reference state; for the formation of SiO(g), i. e., for the reaction,



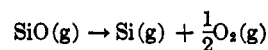
$$\Delta F_{3000}^\circ = \Delta H_{3000}^\circ - T\Delta S_{3000}^\circ = -38,954 - 3000(\Delta S_{3000}^\circ) \text{ cal./mole}$$

$$\Delta S_{3000}^\circ = S_{SiO}^\circ - \frac{1}{2}S_{O_2(g)}^\circ - S_{Si(l)}^\circ = 10.17 \text{ e.u.}$$

and

$$\Delta F_{3000}^\circ = 69,464 \text{ cal./mole for the formation of SiO(g)}$$

where the entropies of Si(l) and O₂ are from Stull and Sinke (65) and that of SiO(g) from the calculations. Assuming that ΔH° and ΔS° do not depend upon temperature, then $\Delta F^\circ = -38,954 - 10.17T$ for this reaction in the temperature range from 2000° to 3000°K. From these data for the first reaction given above, i. e.,



$$\Delta F_{3000}^\circ = +80,082 \text{ cal./mole}$$

and

$$\Delta S_{3000}^\circ = \frac{1}{2}S_{O_2(g)}^\circ + S_{Si(g)}^\circ - S_{SiO(g)}^\circ = 16.31 \text{ e.u.}$$

Hence, $\Delta F^\circ = 129,000 - 16.31T$ near $T = 3000^\circ\text{K.}$

Now, the equilibrium constant at 3000°K. can be calculated:

$$\Delta F_{3000}^\circ = -RT \ln K = 80,082$$

or

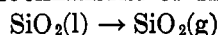
$$K = 1.45 \times 10^{-6} = p_{Si}p_{O_2}^{1/2}/p_{SiO}$$

If the case where $p_{SiO} = 0.4$ atm. and $p_{O_2} = 0.2$ atm. is considered, i. e., the approximate vapor pressures under neutral conditions at 3000°K. from figure 3, then

$$p_{Si} = 1.30 \times 10^{-6} \text{ atm.}$$

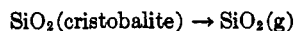
It can be seen that a negligible amount of monomeric Si(g) vapor exists under these conditions. Dimers and larger aggregates of silicon would also be negligible under these conditions, since the equilibrium studies of Honig (36) show the monomer to be the most important species, even when the condensed phase of silicon is present. The calculated partial pressure of silicon is far removed from such saturation conditions, since Stull and Sinke (65) report a boiling point for silicon of 2950°K. and Honig (37) gives 3060°K.

VII. THERMOCHEMISTRY OF THE REACTION



A. GENERAL

For the estimation of thermochemical quantities involved in the vaporization of liquid silica to gaseous silica, the most pertinent available data are those of Porter, Chupka, and Inghram (56). They have made a mass-spectrometric study of the decomposition of cristobalite at 1800° and 1900°K.



They found that $\Delta H_{298}^\circ = 136 \pm 8$ kcal./mole, from slopes of their $\log \Sigma$ vs. $1/T$ data. However, more

ture, it has been assumed that the $\text{SiO}_2(\text{g})$ molecule is also linear. In estimating the interatomic distances the following data have been considered:

Molecule	r_0	Reference
	A.	
SiO.....	1.510	Herzberg (32)
CO.....	1.1284	Herzberg (31)
CO ₂ ($r_{\text{O-O}}$).....	1.1615	Herzberg (31)

From these data, the interatomic distance (silicon-oxygen) in linear SiO_2 is estimated to be 1.54 Å.

The estimation of the vibrational frequencies for the

TABLE 10

Vibrational frequency data estimated for $\text{SiO}_2(\text{g})$

Mode or Frequency	CO ₂	CS ₂	Ratio $\nu_{\text{CS}_2}/\nu_{\text{CO}_2}$	Reference
	cm. ⁻¹	cm. ⁻¹		
Stretching, ν_1	1342	656.5	0.49	Herzberg (31)
Bending, ν_2 (degenerate).....	667	396	0.59	Herzberg (31)
Stretching, ν_3	2349	1523	0.65	Herzberg (31)
Mode or Frequency	CO	CS	Ratio $\nu_{\text{CS}}/\nu_{\text{CO}}$	Reference
	cm. ⁻¹	cm. ⁻¹		
ν_1	2170	1285	0.59	Herzberg (32)
Mode or Frequency	CO	SiO	Ratio $\nu_{\text{SiO}}/\nu_{\text{CO}}$	Reference
	cm. ⁻¹	cm. ⁻¹		
ν_1	2170	1242	0.572	Herzberg (32)
Mode or Frequency	CO ₂	SiO ₂ (calculated)	Ratio $\nu_{\text{SiO}_2}/\nu_{\text{CO}_2}$ (assumed)	
	cm. ⁻¹	cm. ⁻¹		
ν_1	1342	767	0.572	
ν_2	667	382	0.572	
ν_3	2349	1340	0.572	

accurate heat of reaction data (and hence, free-energy data) could be obtained for the above reaction with a suitable estimate of the entropy change in combination with their published pressures. Brewer and Searcy (15) have also discussed the value of this type of calculation.

B. ESTIMATE OF ENTROPY FOR $\text{SiO}_2(\text{g})$

Since there is little published information about $\text{SiO}_2(\text{g})$, it has been necessary to make some assumptions about the configuration of the molecule. Knowledge of the carbon dioxide molecule is used as the basis for estimating properties of the $\text{SiO}_2(\text{g})$ molecule.

Since the carbon dioxide molecule has a linear struc-

linear SiO_2 molecule has also been done by analogy with carbon dioxide. In table 10 some vibrational frequency data are shown for carbon dioxide, carbon disulfide, carbon monoxide, and carbon sulfide molecules. It is seen that for the diatomic molecules the ratio of the vibrational frequencies, $\nu_{\text{CS}}/\nu_{\text{CO}} = 0.59$, a value that agrees qualitatively (maximum error = 17 per cent) with the corresponding ratios for the triatomic molecules carbon dioxide and carbon disulfide. The corresponding ratio of vibrational frequencies for the diatomic molecules SiO and CO was obtained from Herzberg's book (32): $\nu_{\text{SiO}}/\nu_{\text{CO}} = 0.572$. This ratio was then used to calculate the vibrational frequencies of $\text{SiO}_2(\text{g})$ from the corresponding frequencies for carbon dioxide. This calculation was approximate, and the

TABLE 11

Heat capacity, enthalpy, and entropy data for the assumed linear SiO₂(g) molecule

Temperature	C_p°	$\frac{(H^\circ - H_0^\circ)}{T}$	$H^\circ - H_0^\circ$	$H^\circ - H_{298}^\circ$	S°
°K.	cal./mole °K.	cal./mole °K.	cal./mole	cal./mole	e. u.
298	10.80	8.53	2,542	0	54.65
500	12.55	9.83	4,915	2,373	
1000	14.10	11.66	11,660	9,118	
1500	14.50	12.57	18,855	16,313	
1800		12.90	23,220	20,678	78.57
1900		12.99	24,681	22,139	79.37
2000	14.67	13.06	26,120	23,578	80.06
2500	14.73	13.40	33,500	30,958	83.37
3000	14.79	13.62	40,860	38,318	85.96

calculated vibrational frequencies might be in error by as much as 15 to 20 per cent.

For the moment of inertia of the SiO₂ molecule, the relation given by Herzberg (31) for the moment of inertia of a symmetrical molecule has been used.

$$I_B = 2M_O r_{\text{Si-O}}^2$$

where M_O is the mass of the oxygen atom and $r_{\text{Si-O}}$ is the interatomic distance:

$$M_O = 16 \times 1.66 \times 10^{-24} \text{ g.}$$

$$r_{\text{Si-O}} = 1.54 \text{ \AA.} = 1.54 \times 10^{-8} \text{ cm.}$$

Hence, for SiO₂,

$$I_B = 1.26 \times 10^{-38} \text{ g.-cm.}^2$$

For the temperature ranges of possible interest in this calculation ($T < 5000^\circ\text{K.}$), electronic contributions are assumed to be negligible. It is assumed that only a single electronic ground state is occupied, because the SiO₂(g) molecule has an even number of electrons. Thus, the electronic-partition function will be considered to be unity. Further discussion of this point may be found in Glasstone (27, pp. 108 and 116).

The calculation of the entropy for SiO₂(g) is made with the statistical mechanical formula given by Kelley (47) for linear polyatomic molecules.

$$S = \frac{3}{2}R \ln M + \frac{7}{2}R \ln T - R \ln P + R \ln I - R \ln \sigma \\ + \Sigma S(\text{Einstein}) + S_{\text{el}}^\circ + 175.385$$

The present calculation is for atmospheric pressure; hence the third term above does not contribute to S . The symmetry number σ has the value of 2 for the SiO₂(g) molecule. Evaluation of the ΣS (Einstein) contribution must be made for the four vibrational degrees of freedom for a linear triatomic molecule.

Terms for ν_1 and ν_3 contribute once each to this sum, whereas those for ν_2 (the bending vibration) contribute twice. The tables of Taylor and Glasstone (66) have facilitated evaluation of the vibrational terms.

No attempt has been made to incorporate refinements such as Fermi resonance which apply to the carbon dioxide molecule.

Enthalpy calculations have been made with the relation

$$\left(\frac{H^\circ - H_0^\circ}{T}\right)_{\text{Translation + rotation + electronic}} = \frac{7}{2}R = 6.954$$

The terms due to vibration can again be added from Taylor and Glasstone's tables (66).

In table 11 the resulting heat-capacity, enthalpy, and entropy data calculated for the linear SiO₂(g) molecule are listed. The heat-capacity data in table 11 are plotted in figure 8. For comparison purposes, the heat capacity of CO₂(g) has been included. It is seen that above 2500°K. the heat capacity of carbon dioxide exceeds the estimated heat capacity for SiO₂(g). This result probably occurs because such complicating factors in carbon dioxide as the Fermi resonance (or accidental degeneracy) and other refinements have not been considered in the present calculation.

From Porter, Chupka, and Inghram's paper (56), for the reaction SiO₂(crist.) → SiO₂(g), the vapor-pressure data shown in table 12 are obtained. The free energies shown are calculated from their vapor-pressure data.

To convert the data for the heat of reaction at 1800° and 1900°K. to data for the heat of reaction at 298°K., the values from table 11 can be used for the heat content of SiO₂(g) and those from Kelley (46) for that of cristobalite at 1800°K. In this way, one obtains

$$\Delta H_{298}^\circ = \Delta H_T^\circ - (H_T^\circ - H_{298}^\circ)_{\text{SiO}_2(\text{g})} + (H_T^\circ - H_{298}^\circ)_{\text{SiO}_2(\text{crist.})} \\ \Delta H_{298}^\circ = 140,822 \text{ cal./mole}$$

Also, from data at 1900°K.,

$$\Delta H_{298}^\circ = 141,516 \text{ cal./mole}$$

The average of these two results is $\Delta H_{298}^\circ = 141,169$ cal./mole. This value is somewhat higher than the original value reported by Porter, Chupka, and Inghram (56) of $136,000 \pm 8000$ cal./mole but falls

TABLE 12
Data for SiO₂(crist.) → SiO₂(g)

	1800°K.	1900°K.
p_{SiO_2} (atm.)	1.6×10^{-8}	1.0×10^{-7}
$\Delta F^\circ = -RT \ln p_{SiO_2}$ (cal./mole)	64,214	60,860
$S^\circ_{SiO_2(g)}$ (from table 11) (e. u.)	78.57	79.37
$S^\circ_{SiO_2(crist.)}$ (from Kelley (46, 47)) (e. u.)	38.15	39.12
ΔS° (e. u.)	40.42	40.25
$T\Delta S^\circ$ (cal./mole)	72,756	76,475
$\Delta H_T^\circ = \Delta F^\circ + T\Delta S^\circ$ (cal./mole)	136,970	137,335

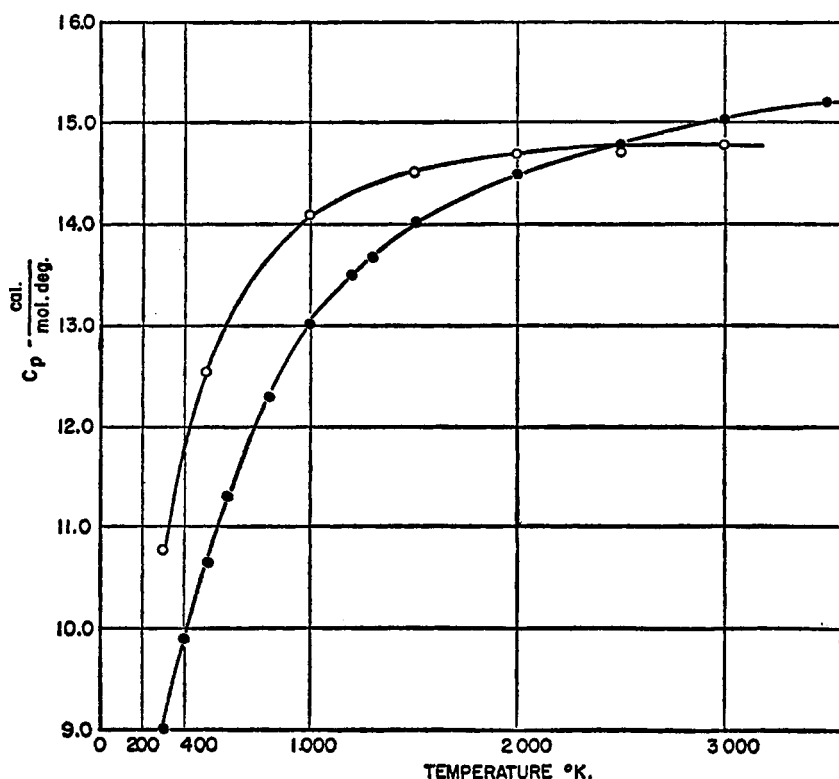


FIG. 8. Heat capacity of SiO₂(g) versus temperature. ●, C_p for carbon dioxide (tables of the National Bureau of Standards); ○, C_p (calculated) for SiO₂(g).

within their range of uncertainty. ΔH_{2000}° for the reaction SiO₂(crist.) → SiO₂(g) is calculated as follows:

$$\Delta H_{2000}^\circ = \Delta H_{298}^\circ + (H_T^\circ - H_{298}^\circ)_{SiO_2(g)} - (H_T^\circ - H_{298}^\circ)_{crist.}$$

$$\Delta H_{2000}^\circ = 136,627 \text{ cal./mole}$$

By taking into account the heat of fusion of cristobalite (2500 cal./mole), the heat of vaporization of liquid silica can be calculated

$$SiO_2(l) \rightarrow SiO_2(g) \quad \Delta H_{2000}^\circ = 134,127 \text{ cal./mole}$$

from the above.

For the heat of this reaction at higher temperatures,

$$\Delta H_T^\circ = \Delta H_{2000}^\circ + (H_T^\circ - H_{2000}^\circ)_{SiO_2(g)} - (H_T^\circ - H_{2000}^\circ)_{SiO_2(l)}$$

The additional necessary data for calculations of ΔH_T° are in tables 1 and 11. Results of such a calculation are summarized in table 13.

TABLE 13
Heat of vaporization of liquid silica: SiO₂(l) → SiO₂(g)

	2000°K.	2500°K.	3000°K.
	cal./mole	cal./mole	cal./mole
$(H_T^\circ - H_{2000}^\circ)_{SiO_2(l)}$	0	10,830	21,660
$(H_T^\circ - H_{2000}^\circ)_{SiO_2(g)}$	0	7,380	14,740
ΔH_T°	134,127	130,677	127,207

TABLE 14
Entropy change for vaporization of liquid silica: $\text{SiO}_2(\text{l}) \rightarrow \text{SiO}_2(\text{g})$

	2000°K.	2500°K.	3000°K.
$S_{\text{SiO}_2(\text{g})}^{\circ}$ (e. u.)	80.06	83.37	85.96
$S_{\text{SiO}_2(\text{l})}^{\circ}$ (e. u.)	41.07 ± 0.6	46.13 ± 0.8	50.03 ± 1.0
ΔS° (e. u.)	38.99	37.24	35.93
$T\Delta S^{\circ}$ (cal./mole)	77,980	93,100	107,791
ΔH° (cal./mole)	134,127	130,677	127,207
$\Delta F^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$ (cal./mole)	56,147	37,577	19,416

Likewise, to calculate the entropy change for the last reaction, the data of table 7 and table 11 can be used as shown in table 14.

The free-energy data given in table 14 have been plotted in figure 1, where it can be seen that $\Delta F^{\circ} = 0$ ($p_{\text{SiO}_2} = 1$ atm.) at $T = 3540^{\circ}\text{K}$. These data show that at 3000°K ., $\Delta F^{\circ} = 19,416$ cal./mole and

$$p_{\text{SiO}_2} = e^{-19,416/R \times 3000} = 0.039 \text{ atm.}$$

Pressures of $\text{SiO}_2(\text{g})$ as a function of $1/T$ are shown in figure 2. In this case, the equilibrium constant is equal to the partial pressure of $\text{SiO}_2(\text{g})$ in atmospheres.

If silica vaporizes according to the above reaction at 3000°K ., then the total amount of heat absorbed, including the sensible heat of solid and liquid silica from 298° to 3000°K ., is

$$\Delta H_{\text{total}; 3000} = (H_{3000} - H_{298})_{\text{SiO}_2(\text{l})} + \Delta H_{\text{vaporization}; 3000} \quad (12)$$

$$= (H_{2000} - H_{298})_{\text{SiO}_2(\text{glass})} + (H_{3000} - H_{2000})_{\text{SiO}_2(\text{l})} + \Delta H_{\text{vaporization}; 3000} \quad (13)$$

$$= 177,877 \text{ cal./mole} \quad (14)$$

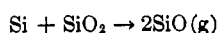
The sensible heat (the first two terms in equation 13) contributes 50,670 cal./mole, and the vaporization contributes 127,207 cal./mole. It should be noted that simple vaporization of $\text{SiO}_2(\text{g})$ at 3000°K . gives a total heat absorption of only 177,877 cal./mole as against the value of 222,183 cal./mole found for the case of the formation of $\text{SiO}(\text{g})$ and $\text{O}_2(\text{g})$.

VIII. SILICA IN REDUCING ATMOSPHERES

A. SILICON AS REDUCING AGENT

In a reducing atmosphere, decomposition of silica to produce $\text{SiO}(\text{g})$ occurs at a much lower temperature than under neutral or oxidizing conditions. Three typical reducing agents, for which data are available, include elemental silicon, carbon, and hydrogen. Since the reducing reactions occur at lower temperatures, they are of considerable interest.

The reaction between stoichiometric amounts of silicon and silica leads to the reaction:

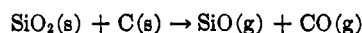


Although a mixture of silicon and silica in a closed system will decompose at a lower temperature than pure silica, one cannot conclude that the reaction is independent of oxygen pressure. This deduction arises from the fact that the simultaneous reaction, $\text{Si} + \text{O}_2$, must be considered. Hence, if one is discussing an equilibrium case where an unlimited amount of oxygen is available, then the process reverts to a decomposition of silica in an oxidizing atmosphere.

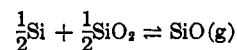
Some typical vapor-pressure data for the silicon-silica reaction which have been taken from a Bureau of Mines Bulletin (41) are plotted in the lower curve of figure 9.

B. CARBON AS REDUCING AGENT

For the reducing reaction between carbon and silica, one of the possible reactions is that for the formation of $\text{SiO}(\text{g})$ and $\text{CO}(\text{g})$.



The data for this reaction have also been taken from published tables (41) and are plotted in figure 9. The upper curve gives the pressure of carbon monoxide, while the lower curve is again assumed to represent the actual pressure of SiO in the system because of disproportionation to $\text{Si}(\text{s})$ and $\text{SiO}_2(\text{s})$. Reference to these data would indicate that a pressure of 1 atm. ($p_{\text{CO}} = 0.89$ atm., $p_{\text{SiO}} = 0.11$ atm.) is reached at a temperature of 1845°K . The assumption that the pressure of SiO is fixed by the Si-SiO_2 equilibrium appears to be quite valid, since if it had been ignored higher SiO pressures would have been obtained by calculation. It is probable that such a stoichiometric mixture of silicon and silica is formed rather than $\text{SiO}(\text{s})$, as discussed in Section III. However, even if the $\text{SiO}(\text{s}) \rightleftharpoons \text{SiO}(\text{g})$ equilibrium is the important one rather than the equilibrium



similar results may be expected near 1700°K . This follows if it is assumed that $\text{SiO}(\text{s})$ becomes stable at about 1500°K . (see Section III).

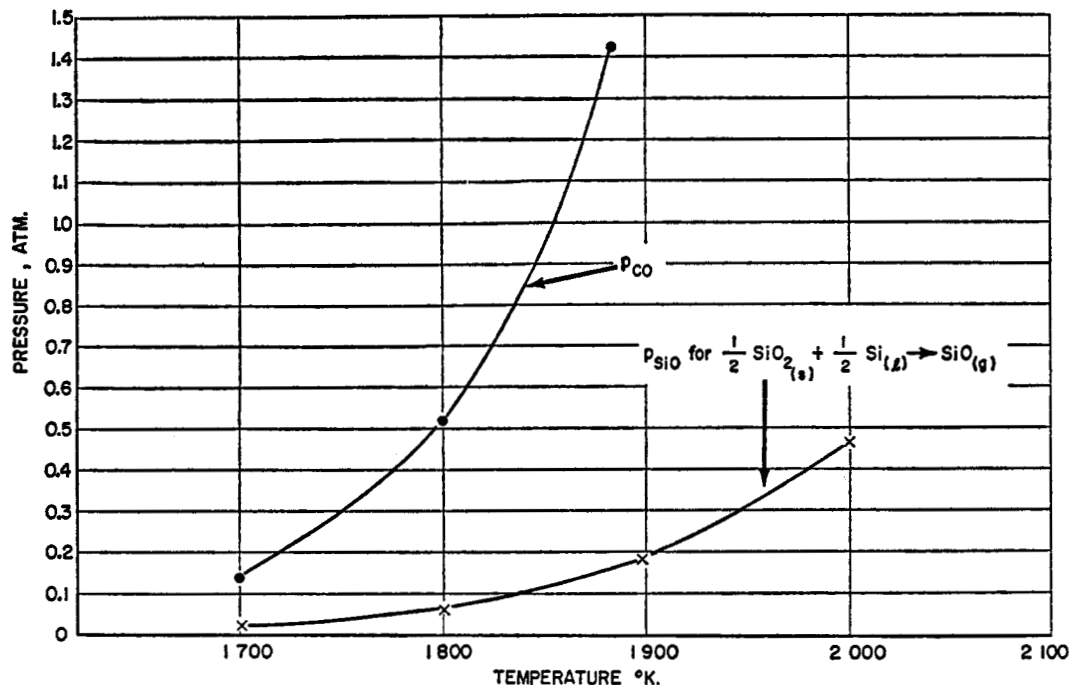
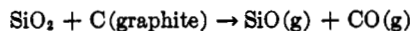


FIG. 9. Partial pressures of important species when silica is decomposed by carbon or silicon. $\times = p_{\text{SiO}}$ for the reaction



●, pressure of $\text{CO}(\text{g})$ for the reaction



where $p_{\text{SiO}(\text{g})}$ is assumed fixed by the reaction



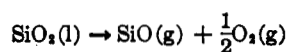
From Humphrey and coworkers.

C. HYDROGEN AS REDUCING AGENT

Another reducing reaction of interest is that of silica with hydrogen. The applicable experimental data of Grube and Speidel (28), as given by Edwards (22), have been plotted in figure 10. Here it can be seen that their tabulated vapor-pressure data for $\text{SiO}(\text{g})$ are in agreement with those determined by Tombs and Welch (68). Figure 10 also shows the expected vapor pressures of $\text{SiO}(\text{g})$ corresponding to the vaporization of $\text{SiO}(\text{s})$ or $\text{Si}(\text{s}) + \text{SiO}_2(\text{s})$. It should be noted that in an atmosphere of hydrogen, the pressure of $\text{SiO}(\text{g})$ is less than either of these equilibria would predict; hence $\text{SiO}(\text{g})$ will be formed rather than a solid phase. These results show that decomposition of silica under these conditions occurs at much lower temperatures than under oxidizing or neutral conditions.

IX. SUMMARY OF CALCULATED VAPORIZATION DATA FOR $\text{SiO}_2(\text{l})$ AND COMPARISON WITH PUBLISHED VALUES

In the preceding sections various equilibria involving SiO_2 have been considered. The data show that the first reaction,



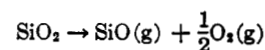
is most important for neutral conditions. However, the reaction $\text{SiO}_2(\text{l}) \rightarrow \text{SiO}_2(\text{g})$ makes a significant contribution to the vapor pressure. It becomes even more important under oxidizing conditions.

For each of the reactions which have been considered, a standard free energy of reaction has been obtained. Simple approximate formulas have been developed to express these free energies as functions of temperature. The resulting formulas are summarized in table 15. From these approximate relations or the somewhat more accurate data obtained earlier in this paper for a few of the reactions, equilibrium constants have been calculated by means of the relation:

$$K = e^{-\Delta F^\circ/RT}$$

The results are plotted in figure 2.

Although vaporization phenomena have been discussed in terms of the single reaction



it is now possible to consider an additional reaction, the dissociation of oxygen. The effect of the latter can be evaluated both for the case of neutral conditions and for the case of oxidizing conditions.

TABLE 15
Free-energy relations for various reactions

Reaction	Free-energy Change	Estimated Uncertainty	Temperature Range	Remarks and Sources of Data
	<i>cal./mole</i>	<i>cal./mole</i>	<i>°K.</i>	
SiO ₂ (crist.) → SiO(g) + ½O ₂ (g)...	ΔF° = 180,800 - 58.11T	± 3000	1800-2000	Data based on work of Schafer and Hornle (60)
SiO ₂ (l) → SiO(g) + ½O ₂ (g).....	ΔF° = 173,000 - 54.2T	± 4000	2000-4000	
SiO(s) → SiO(g)*.....	ΔF° = 77,530 - 34.9T	± 8000	1800-2000	May be used at higher temperatures. Melting point of SiO(s) is unknown; uncertainty is a guess.
Si ₂ O ₂ (g) → 2SiO(g).....	ΔF° = 52,500 - 33.4T	± 10,000	1500-3000	Data based on work of Porter, Chupka, and Inghram (56)
½O ₂ (g) → O(g).....	ΔF° = 61,348 - 16.11T	± 400	2000-4000	For tabulated data, see Stull and Sinke (65) (ΔH° = 58,980) or older tables of the National Bureau of Standards (ΔH° = 58,586)
SiO ₂ (l) → SiO ₂ (g).....	ΔF° = 127,200 - 36.0T	± 6000	2000-4000	Data based on work of Porter, Chupka, and Inghram (56)
Si(l) + O ₂ (g) → SiO(g).....	ΔF° = -38,954 - 10.17T	± 3000	1700-2950	
SiO(g) → Si(g) + ½O ₂ (g).....	ΔF° = 129,000 - 16.31T	± 3000	Near 3000	

* It is likely that this equilibrium should be replaced by ½Si(l) + ½SiO₂(l) → SiO(g), giving an expression ΔF° = 71,465 - 33.01T (see Section III).

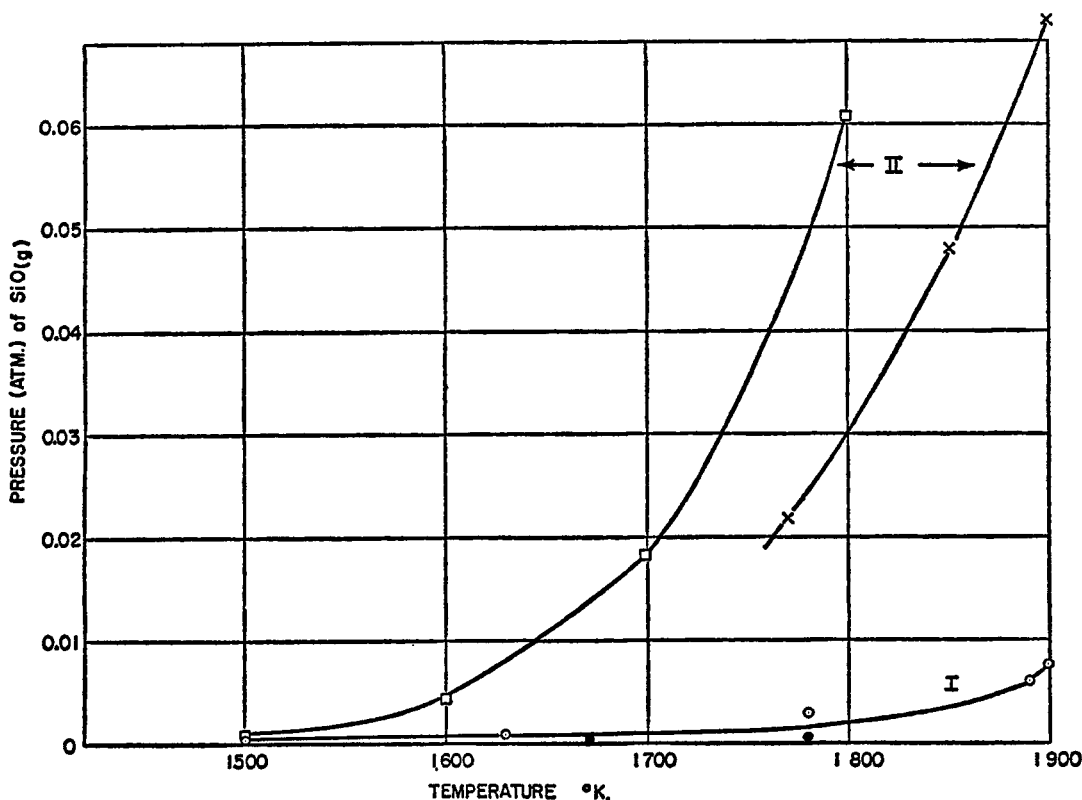
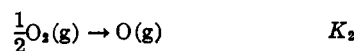
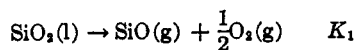


FIG. 10. Partial pressure of SiO(g) when silica is decomposed by hydrogen or silicon. Reaction I: H₂(g) + SiO₂ → SiO(g) + H₂O(g). O, Tombs and Welch; ●, Grube and Speidel. Reaction II: Si + SiO₂ → SiO(g). □, Humphrey *et al.*; ×, Tombs and Welch. Since p_{SiO} for reaction I < p_{SiO} for reaction II, no solid SiO or Si + SiO₂ can form.

A. NEUTRAL CONDITIONS

For the case of neutral conditions,



and

p_{SiO} = partial pressure of SiO

p_{O_2} = partial pressure of O₂

p_{O} = partial pressure of O

Under the assumed conditions,

$$p_{\text{O}_2} + \frac{1}{2}p_{\text{O}} = \frac{1}{2}p_{\text{SiO}} \quad (15)$$

$$K_1 = p_{\text{SiO}} \cdot p_{\text{O}_2}^{1/2} \quad (16)$$

and

$$K_2 = p_{\text{O}}/p_{\text{O}_2}^{1/2} \quad (17)$$

Equations 15, 16, and 17 are sufficient to determine the three unknowns p_{SiO} , p_{O_2} , and p_{O} in terms of the two equilibrium constants K_1 and K_2 .

Rearranging equation 17 to

$$p_o = K_2 p_{O_2}^{1/2} \tag{18}$$

and substituting into equation 15,

$$2p_{O_2} + K_2 p_{O_2}^{1/2} = p_{SiO} \tag{19}$$

Finally, substituting equation 19 into equation 16,

$$2p_{O_2}^{3/2} + K_2 p_{O_2} - K_1 = 0 \tag{20}$$

for p_{O_2} in terms of K_1 and K_2 .

For the case where K_2 is small, i. e., where the dissociation of oxygen is negligible, solving equation 20 gives:

$$p_{O_2} \cong (K_1/2)^{2/3} \quad (K_1 \ll K_2 p_{O_2}) \tag{21}$$

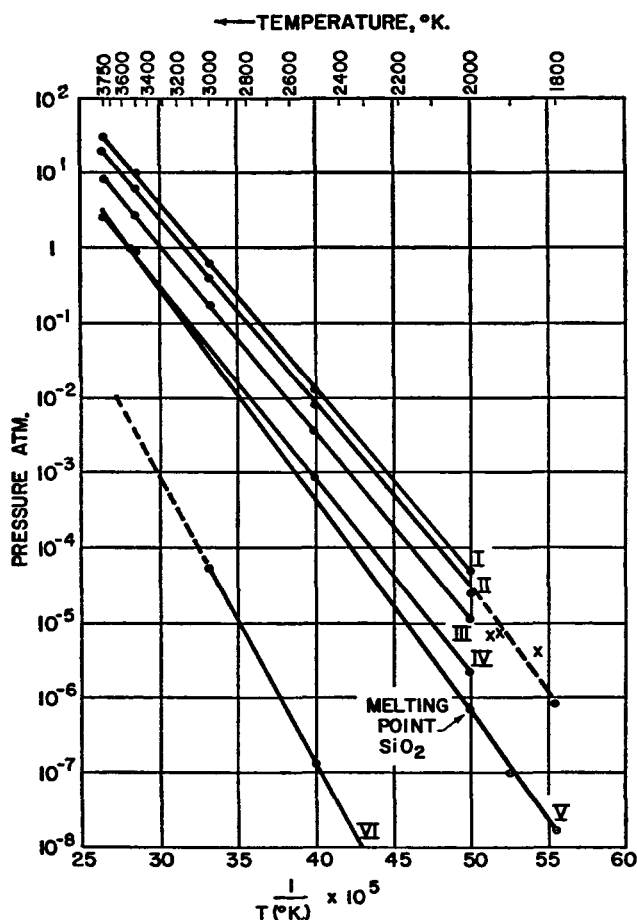


FIG. 11. Partial pressure of product when silica decomposes under neutral conditions and the dissociation of oxygen is included. \circ , experimental points of Porter, Chupka, and Inghram for $p_{SiO(g)}$; \times , experimental points of Brewer and Mastick for $p_{SiO(g)}$. I, p_{total} ; II, p_{SiO} ; III, p_{O_2} ; IV, p_o ; V, p_{SiO_2} ; VI, $p_{Si_2O_2}$.

Reactions considered:

1. $SiO_2(l) \rightarrow SiO(g) + \frac{1}{2}O_2(g)$
2. $\frac{1}{2}O_2(g) \rightarrow O(g)$
3. $SiO_2(l) \rightarrow SiO_2(g) \quad T > 2000^\circ K.$
4. $2SiO(g) \rightarrow Si_2O_2(g)$

For the case where the dissociation of oxygen cannot be neglected, equation 20 must be solved.

After solving equation 20 for p_{O_2} , p_o can be obtained from equation 18 and p_{SiO} from equation 15.

From selected values of the equilibrium constants K_1 and K_2 at 2000° , 2500° , 3000° , 3500° , and $3750^\circ K.$, it has been possible to calculate corresponding values of the partial pressures of SiO , O_2 , and O as described above. The resulting calculated partial pressures, which are based on neutral conditions and include the dissociation of oxygen, have been plotted in figure 11.

Referring to the data in figure 11, one can see that a total pressure of 1 atm. is obtained at $3070^\circ K.$ This temperature corresponds to the normal boiling point of silica. By reading partial pressures of the various components from the graph at $3070^\circ K.$, one obtains the following:

$p_{SiO} = 0.62 \text{ atm.}$	(+0.6 or -0.2)
$p_{O_2} = 0.26 \text{ atm.}$	(+0.25 or -0.08)
$p_o = 0.074 \text{ atm.}$	(+0.07 or -0.002)
$p_{SiO_2} = 0.058 \text{ atm.}$	(+0.12 or -0.002)
$p_{Si_2O_2} = 0.0001 \text{ atm.}$	(+0.0003 or -0.00003)

$$p_{total} = 1.012 \text{ atm.} \quad (+1.04 \text{ atm. or } -0.28 \text{ atm.})$$

The uncertainties in the partial pressures are indicated in parentheses. For example, p_{SiO} may possibly have values from 0.42 to 1.22 at $3070^\circ K.$

It is seen that within the accuracy of these data, a total pressure of 1 atm. is obtained at $3070^\circ \pm 75^\circ K.$ for a neutral equilibrium mixture. The accuracy of this boiling point can be determined from the fact that the free-energy function of importance here is

$$\Delta F^\circ = 173,000 - 54.2T$$

where ΔF° is accurate to $\pm 4000 \text{ cal./mole}$ near $3000^\circ K.$ Using this uncertainty in ΔF° , then $d(\Delta F^\circ)/dT = 54.2$, from which it follows that $\Delta T = \pm 75^\circ K.$

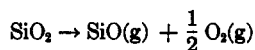
A more complete analysis of the expected equilibrium gaseous species at $3000^\circ K.$ is as follows:

Species	Pressure
	atm.
SiO.....	0.43
SiO ₂	0.04
Si ₂ O ₂	5×10^{-6}
(SiO) ₂	Unknown*
O ₂	0.18
O.....	0.05
Si.....	1.3×10^{-6}
p_{total}.....	0.70

* But likely to be less than that of the dimer.

The results tabulated above show that SiO and O_2 are the predominant species. In the neutral equilibrium mixture Si and Si_2O_2 are present in minor amounts. However, significant amounts of SiO_2 and O are also present.

As has just been seen, a normal boiling point of 3070°K. is predicted for silica. If all the other reactions had been neglected and only the decomposition reaction



had been considered, then a boiling point of 3085°K. would have been predicted, as discussed earlier. Thus, the other reactions have only a small effect on the predicted boiling point. The possibility of reactions other than those already discussed should not be completely overlooked, but they are not likely to be important. In the absence of further information and in view of the fact that the observed reactions predict vaporization phenomena in agreement with experiments at lower temperatures, it does seem likely that the present calculations should give a reasonable boiling-point

TABLE 16

Tabulated boiling points for silica

Temperature °C.	Original Reference	Date	Quoted by
2230	Ruff and Schmidt (59)	1921	Lange, <i>Handbook of Chemistry</i> (49) <i>Handbook of Chemistry and Physics</i> (30) International Critical Tables (42)
2590	Ruff and Kenschak (58)	1926	<i>Handbook of Chemistry and Physics</i> (30) Sidgwich (63) Eitel (23)
2800	Present work		
2950	Ruff (57)	1935	Silverman (64) Campbell (16)
3500	Mott (53)	1918	

temperature. Hence it is concluded that the boiling temperature is $3070^\circ \pm 75^\circ\text{K}$.

Table 16 contains values of boiling points which are given in the literature and which can be compared with the present calculations.

In reviewing the above data, it was found that Brewer (10) rightfully criticized the boiling-point data of Ruff and Schmidt (59) because the measurements were carried out in an atmosphere of carbon vapor (reducing). The original paper by Ruff and Kenschak (58) also shows uncertainty of the same type. Although they used an iridium container, it was inside a graphite vessel. Under such conditions, they observed rapid attack of the iridium container and were able to obtain only a single measurement at 2060°C. They used this measurement to obtain their extrapolated boiling point. In view of the fact that their container was subject to such rapid attack, it appears possible that a reducing atmosphere (of iridium or carbon) was actually present. This would lead to observation of a higher vapor pressure, and hence a lower boiling point than the true one.

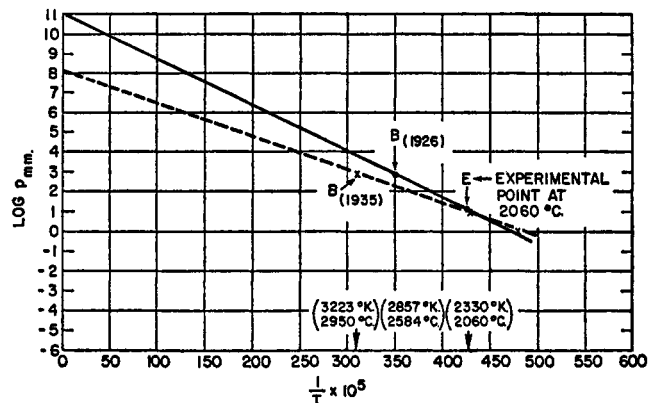


FIG. 12. Repeat of Ruff's extrapolation for the boiling point of silica. —, extrapolation performed according to Ruff in 1926; ---, apparent extrapolation used by Ruff in 1935. ● ← E, single actual experimental point given by Ruff in 1926 and 1935; X, calculated points given by Ruff in 1935; B₍₁₉₂₆₎ → X, boiling point reported by Ruff in 1935; B₍₁₉₂₆₎ → ●, boiling point reported by Ruff in 1926.

Other container materials tried by Ruff and Kenschak (58) without success included tantalum, tungsten, molybdenum, and zirconium oxide. Ruff and Kenschak (58) further stated that their calculated boiling point of 2590°C. was only a minimum value.

The boiling point of 2950°C. given by Ruff (57) in 1935 was simply a restatement of his earlier work with Kenschak in 1926. In 1935 he stated that the original boiling point of 2590°C. was a misprint and that the measured 11.0 mm. pressure at 2060°C. should extrapolate to a boiling point of 2950°C. However, in repeating his extrapolation, the boiling point of 2590°C. appears more reasonable. In figure 12, for example, the extrapolation through the ordinate 11.1 at $1/T = 0$, as recommended by Ruff and Kenschak in 1926, leads to $\log_{10} 760 \text{ mm.} = 2.88$ at 2590°C., as they had reported at that time.

If the three calculated figures for the vapor pressure as given by Ruff in 1935 are plotted, and the dashed line which is shown in the graph (figure 12) is drawn, an intercept of 8.15 at $1/T = 0$ is obtained. Since

$$p_{\text{mm.}} = p_{\text{atm.}} \times 760$$

and

$$\log_{10} p_{\text{mm.}} = \log_{10} p_{\text{atm.}} + \log_{10} 760$$

the intercepts for the different pressure units are therefore

$$[\log_{10} p_{\text{mm.}}]_{1/T=0} = 11.03$$

$$[\log_{10} p_{\text{atm.}}]_{1/T=0} = 8.15$$

A value of 8.15 for the intercept at $1/T = 0$ would appear reasonable if the ordinate were given as $\log_{10} p_{\text{atm.}}$ instead of the $\log_{10} p_{\text{mm.}}$ which was actually used.

It thus would appear that Ruff might have mistakenly used 8.15 as an intercept when $\log_{10} p_{\text{mm.}}$ was plotted as the ordinate. Actually, to be correct, it would be necessary to plot $\log_{10} p_{\text{atm.}}$ in conjunction with the 8.15 intercept.

In view of the uncertainties in the analysis just given above, it is desirable to present some independent data supporting Ruff and Kenschak's extrapolation in 1926 to an intercept of 11.1 at $1/T = 0$. It has already been shown in Section II,E that

$$p_t \text{ (atm.)} = \frac{3}{2} e^{18.41(1-3160/T)} \quad (22)$$

or

$$p_t \text{ (mm.)} = \frac{3}{2} \times 760 e^{18.41(1-3160/T)} \quad (23)$$

Equation 23 can be rearranged to the form

$$\log_{10} p_t \text{ (mm.)} = 11.1 - 25,200/T \quad (24)$$

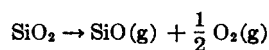
in which it is obvious that the intercept is 11.1.

Therefore, it is concluded that the boiling point of 2950°C. given by Ruff in 1935 is too high. On the other hand, the value of 2590°C. is only a lower limit, since his measurements were performed under reducing conditions.

The high boiling-point temperature of 3500°C. given by Mott (53) in 1918 was obtained by decomposing silica in an arc. The temperature measurements were very rough; hence the figure is quite uncertain.

Summarizing then, the boiling points recorded for silica in the literature are spread over a considerable range. The lower values of 2230° and 2590°C. must be considered as lower limits. The value of 2950°C. is apparently a mistake, and the value of 3500°C. is only an approximation. Thus, the calculated value of 2800°C. appears to be reasonable and is probably more reliable than the values in the literature. A measurement from this laboratory, based on the surface temperature of ablating quartz, has led to a boiling point of 2950° ± 125°K. (2680°C.) (62). This value agrees within the possible errors with the calculated value herein.

Additional vapor-pressure data for the decomposition of silica, under so-called neutral conditions, have been given by Brewer and Mastick (14), Inuzuka and Ageha (43), and Porter, Chupka, and Inghram (56). The data of Brewer and Mastick have been shown to agree with the calculations which are based on the first reaction



Since it has been found that consideration of all the other possible reactions has only changed the predicted boiling point from 3085° to 3070°K., it can be seen that the first reaction is of primary importance. The present calculated vapor-pressure data at low

temperatures are compared with the data of Brewer and Mastick (14) in figure 5. The agreement is good and, if anything, Brewer and Mastick's extrapolated data may indicate an even higher boiling point than the one calculated here.

The data of Porter, Chupka, and Inghram (56) are seen to be too high relative to the vapor pressures in figure 5. However, they were apparently not operating under strictly neutral conditions. Thus, for 1900°K. they gave $p_{\text{SiO}} = 3.4 \times 10^{-5}$ and $p_{\text{O}_2} = 8.2 \times 10^{-8}$ atm. It follows that

$$p_{\text{SiO}} p_{\text{O}_2}^{1/2} = 9.7 \times 10^{-9} \text{ atm.}^{3/2}$$

and that

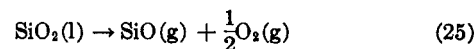
$$\Delta F_{1900}^\circ = +69,595 \text{ cal./mole}$$

As seen in table 9, this free-energy value agrees closely with the thermochemical value of 71,000 cal./mole.

The data of Inuzuka and Ageha (43) were discussed earlier, and it was shown that their reported high data for the vapor pressure could be accounted for by a reducing reaction involving the molybdenum wire.

B. OXIDIZING CONDITIONS

Just as in the case of neutral conditions, the same two reactions are considered for the case of oxidizing conditions in air. That is, other possible reactions are neglected. It is possible that excess oxygen or nitrogen may lead to new species which are not considered here, but until experimental data clarify this point, the assumption is made that other reactions are negligible.



It is assumed that silica decomposes in the presence of air at various total pressures, p_t . For the present case, nitrogen is assumed to be inert. A further approximation is made by assuming that normal air contains 80 per cent nitrogen and 20 per cent oxygen. Then,

$$p_t = p_{\text{N}_2} + p_{\text{O}_2} + p_{\text{SiO}} + p_{\text{O}} \quad (27)$$

$$p_{\text{N}_2} = 4(p_{\text{O}_2} + \frac{1}{2}p_{\text{O}} - \frac{1}{2}p_{\text{SiO}}) \quad (28)$$

$$K_1 = p_{\text{SiO}} p_{\text{O}_2}^{1/2} \quad (29)$$

$$K_2 = p_{\text{O}} / p_{\text{O}_2}^{1/2} \quad (30)$$

Equations 27, 28, 29, and 30 can be solved for the four unknowns p_{N_2} , p_{O_2} , p_{O} , and p_{SiO} , in terms of p_t , K_1 , and K_2 as known parameters. Combining equations 27 and 28,

$$p_t = 5p_{\text{O}_2} + 3p_{\text{O}} - p_{\text{SiO}} \quad (31)$$

But from equation 30, $p_{\text{O}} = K_2 p_{\text{O}_2}^{1/2}$, and equation 31 becomes

$$p_t = 5p_{\text{O}_2} + 3K_2 p_{\text{O}_2}^{1/2} - p_{\text{SiO}} \quad (32)$$

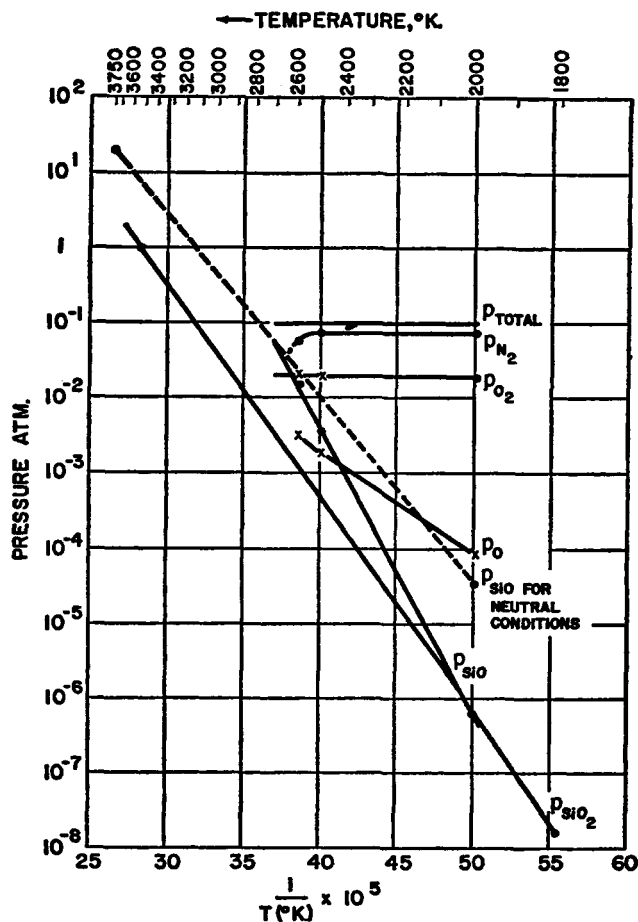


FIG. 13. Decomposition of silica in air at 0.1 atm. Nitrogen assumed to be inert; dissociation of oxygen included.

or

$$p_{\text{SiO}} = 5p_{\text{O}_2} + 3K_2 p_{\text{O}_2}^{1/2} - p_i \quad (33)$$

Also, from equation 29,

$$p_{\text{SiO}} = \frac{K_1}{p_{\text{O}_2}^{1/2}} \quad (34)$$

Combining this with equation 33,

$$5p_{\text{O}_2}^{3/2} + 3K_2 p_{\text{O}_2} - p_i p_{\text{O}_2}^{1/2} - K_1 = 0 \quad (35)$$

After the cubic equation (equation 35) has been solved for p_{O_2} , the other unknowns can be evaluated from equations 28, 30, and 34.

Solutions for this set of equations were obtained for values of $p_i = 0.1, 1, 10,$ and 50 atm. Calculations were made in the range from 2000° to 3750°K . The resulting data have been plotted in figures 13, 14, 15, and 16, which show the partial pressures of SiO, O_2 , SiO_2 , and N_2 as functions of $1/T$.

It is seen that at temperatures well below the boiling point, the formation of $\text{SiO}(\text{g})$ is markedly repressed. Thus from figure 13 at $p_i = 0.1$ atm. and $T = 2000^\circ\text{K}$, the partial pressure of SiO is essentially equal to the partial pressure of SiO_2 . However, in this case a boiling

point is not reached until about 2700°K . At all higher temperatures, formation of $\text{SiO}(\text{g})$ becomes more important than formation of $\text{SiO}_2(\text{g})$. For reference purposes in figures 13 through 16, the vaporization curve for SiO under neutral conditions is also given. The curves given in each of the figures extend up to the boiling point. At higher temperatures, total pressures are obtained in excess of the postulated pressure. At the boiling point and higher temperatures, the nitrogen pressure is zero. Also, at the higher temperatures the partial pressures of SiO, O_2 , and O are the same as for the neutral conditions already discussed. However, these data are not repeated in figures 13 through 16. The rapid variation in the partial pressure of nitrogen has not been indicated with much precision, but an approximate indication is given in the figures.

The data presented in figures 13 through 16 show that under some conditions the oxygen present in air is sufficient to repress the formation of $\text{SiO}(\text{g})$ significantly. Although the effect decreases near the boiling point, it becomes very pronounced at lower temperatures.

Consequently in any proposed application of fused silica, the conditions of the high-temperature exposure

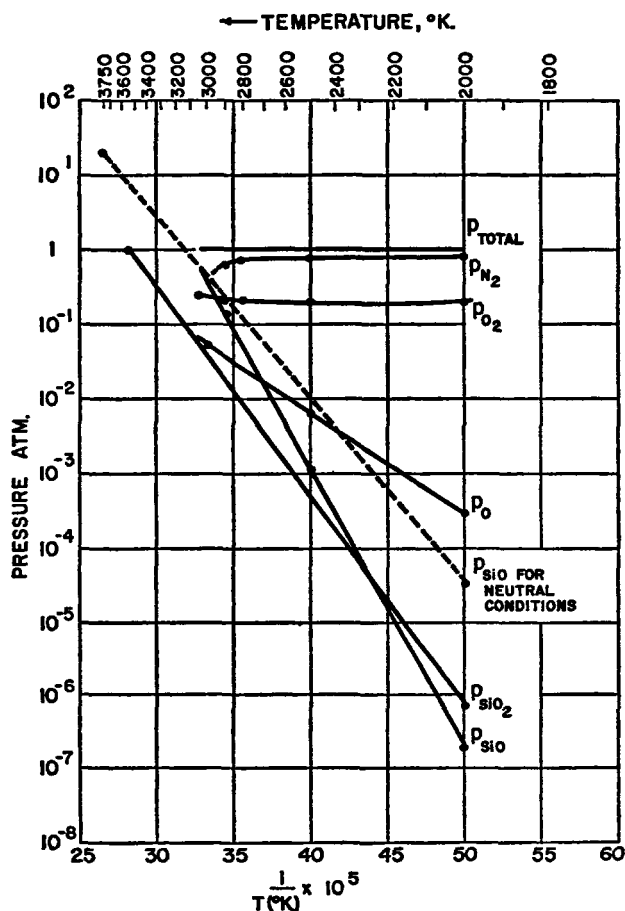


FIG. 14. Decomposition of silica in air at 1.0 atm. Nitrogen assumed to be inert; dissociation of oxygen included.

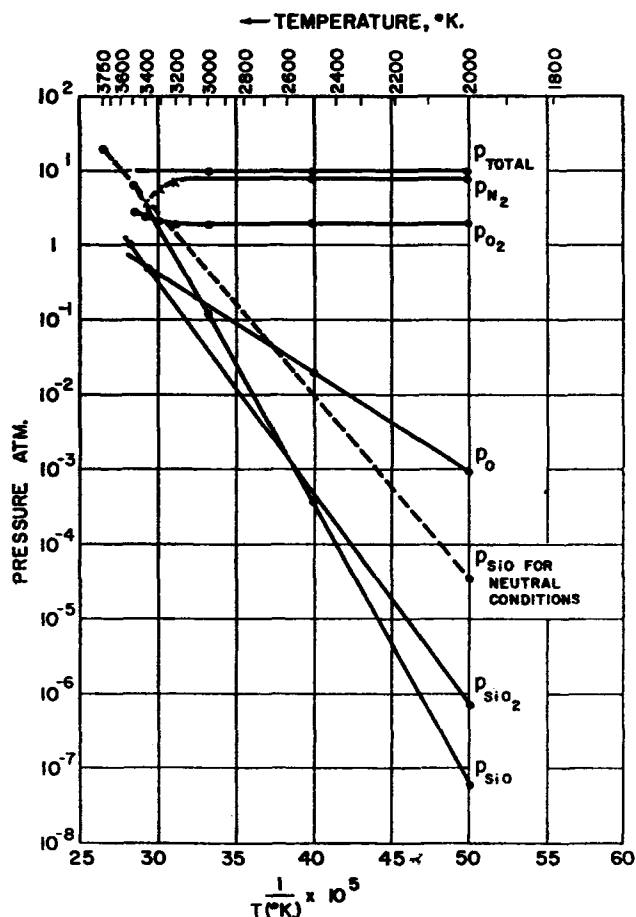


FIG. 15. Decomposition of silica in air at 10 atm. Nitrogen assumed to be inert; dissociation of oxygen included.

must be known before the equilibrium gas species can be estimated.

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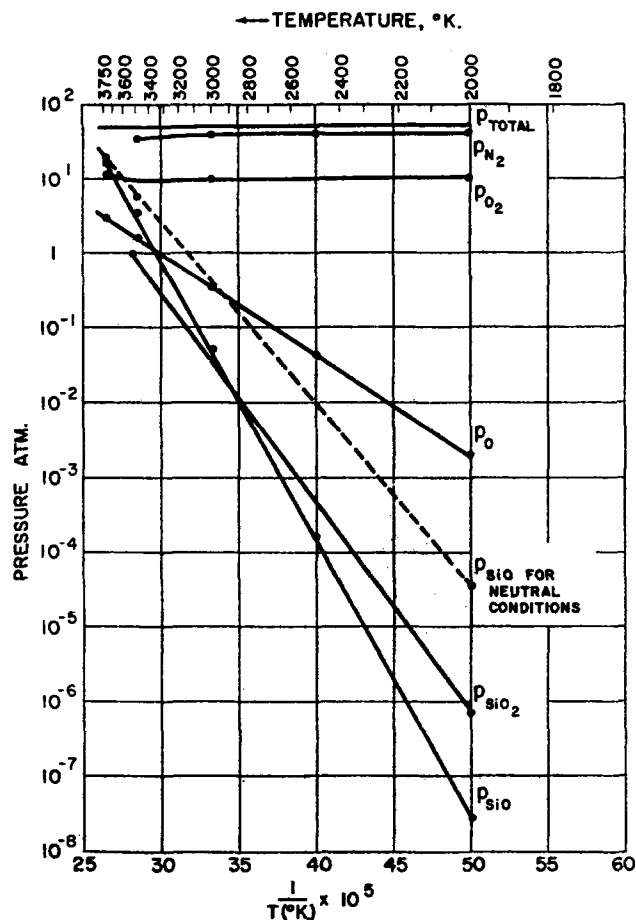


FIG. 16. Decomposition of silica in air at 50 atm. Nitrogen assumed to be inert; dissociation of oxygen included.

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