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The Thermodynamic Properties of Silicon Oxynitride

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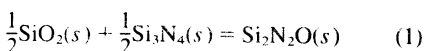
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A critical assessment of thermal and equilibrium data for silicon oxynitride ($\text{Si}_2\text{N}_2\text{O}$) is presented. Selected values for the heat of formation of $\text{Si}_2\text{N}_2\text{O}$ from the elements and the absolute entropy of $\text{Si}_2\text{N}_2\text{O}$ at 298.15 K are $\Delta H_{f,298}^\circ = -947.7 \pm 5.4$ kJ/mol and $S_{298}^\circ = 45.35 \pm 0.4$ J/mol·K, respectively. A table of thermodynamic functions for $\text{Si}_2\text{N}_2\text{O}$ from 298 to 2500 K, which has been calculated from the analysis of the literature data, is also presented.

LACK of thermodynamic data has hindered research on $\text{Si}_2\text{N}_2\text{O}$; the purpose of this communication is to present an internally consistent set of thermodynamic properties for this potentially important ceramic material.

Two measurements of the heat capacity (C_p) and one measurement of the heat content ($H_T - H_{298}$) of $\text{Si}_2\text{N}_2\text{O}$ are available. Guzman *et al.*¹ measured C_p from 55 to 310 K using adiabatic calorimetry; Ehlert² measured it from 296 to 738 K using differential scanning calorimetry. Washburn^{3,4} measured $H_T - H_{298}$ from 580 to 1027 K and presented the results as the mean heat capacity (\bar{C}_p). Although the experimental data extend to only 1000 K, C_p is already close to the classical value of ≈ 25 J/g/atom K (neglecting $C_p - C_v$, which is small) and extrapolation of the C_p data to higher temperatures should not lead to large errors.

Three methods, which are all applications of the Neumann-Kopp rule,⁵ have been used to extend the C_p data to higher temperatures. The first method involves the assumption that $\Delta C_p = 0$ for the reaction:



The second and third methods involve the assumption that the C_p (per g/atom) of $\text{Si}_2\text{N}_2\text{O}$ and of a compound with a similar effective Debye temperature (Θ_D) will be approximately equal. In this case, $\text{Si}_2\text{N}_2\text{O}$ ($\Theta_D = 1150$ K)¹ was compared with Si_3N_4 ($\Theta_D = 1130$ K)¹ and SiC ($\Theta_D = 1140$ K).¹ All three methods were used to calculate C_p values from 1500 to 3000 K. C_p data for α -SiC and SiO₂ (high cristobalite)⁶ and C_p data for Si_3N_4 ⁷ were used in the calcu-

lations. Each of the three sets of C_p values was then combined with all the C_p data points for $\text{Si}_2\text{N}_2\text{O}(c)^{2-4}$ and with $\text{Si}_2\text{N}_2\text{O}$ C_p data at 10 K intervals from 250 to 310 K from Guzman *et al.*¹ Each of the three resulting data sets was then fit to a Maier-Kelley polynomial⁸ by a least-squares analysis. All the data were converted to C_p per g/atom before fitting, and Washburn's data were corrected for the known amounts of Si_3N_4 and SiC impurities in his sample by using heat-capacity data from Kelley.⁸

The resulting C_p polynomials agreed with each other within $\pm 3\%$ over the range 298 to 2500 K, with the C_p data obtained from the comparison of $\text{Si}_2\text{N}_2\text{O}$ with Si_3N_4 being the median set. The thermal functions listed in Table I were calculated from the median C_p set and the $\text{Si}_2\text{N}_2\text{O}$ thermal functions at 298 K given by Guzman *et al.*¹

The thermal functions in Table I are

subject to two uncertainties. First, the $\text{Si}_2\text{N}_2\text{O}$ C_p data were extrapolated above 1000 K by using assumptions based on the Neumann-Kopp rule. Although these assumptions are crude approximations, the calculated thermal functions are probably reasonably accurate because (1) the $\text{Si}_2\text{N}_2\text{O}$, SiC, and Si_3N_4 C_p values were already near the classical value of ≈ 25 J/g/atom K and (2) tests on several nitride and carbide compounds indicate that the assumptions are accurate within $\pm 10\%$ from 1500 to 3000 K. Second, the least-squares fitting procedure smooths out the region of flat C_p versus T behavior reported by Ehlert.² However, the neglect of this apparent C_p anomaly should not significantly affect the calculated thermal functions.

The Gibbs energy functions from Table I and data from the literature were used to analyze several $\text{Si}_2\text{N}_2\text{O}$ equilibrium studies⁹⁻¹⁴ by the second- and third-law methods.¹⁵ The second- and third-law heats of reaction ΔH_{298}° were calculated from Eqs. (2), (3), and (4), respectively:

$$-R \ln K_{eq} = \Delta H_T^\circ/T - \Delta S_T^\circ \quad (2)$$

$$\Delta H_{298}^\circ = \Delta H_T^\circ - \Delta(H_T^\circ - H_{298}^\circ) \quad (3)$$

$$\Delta H_{298}^\circ = -RT \ln K_{eq} - T\{\Delta[(G_T^\circ - H_{298}^\circ)/T]\} \quad (4)$$

where R is the gas constant, K_{eq} the equilibrium constant for the reaction being studied, T' the mean temperature, T is a temperature point, $\Delta(H_T^\circ - H_{298}^\circ)$ is the heat content of the products minus that of the reactants, and $\Delta[(G_T^\circ - H_{298}^\circ)/T]$ is the sum of the Gibbs energy functions of the products minus that of the reactants. The entropy change δS , or drift, required to bring the second- and third-law ΔH_{298}° values into agreement was also calculated from the relation:

$$\delta S = [(\Delta H_{298}^\circ)_{2nd \text{ law}} - (\Delta H_{298}^\circ)_{3rd \text{ law}}]/T' \quad (5)$$

Table I. Thermodynamic Properties of $\text{Si}_2\text{N}_2\text{O}(s)$

T/(K)	C_p° (J/mol·K)	S° (J/mol·K)	$(G^\circ - H_{298}^\circ)/T$ (J/mol·K)	$H^\circ - H_{298}^\circ$ (kJ/mol)	ΔH_T° (kJ/mol)	ΔG_T° (kJ/mol)	$\log K_f$
298	65.56	45.35	-45.35	.00	-947.70	-862.34	151.050
400	90.09	68.92	-48.37	8.22	-948.28	-833.04	108.764
500	100.53	90.26	-54.65	17.80	-947.73	-804.28	84.007
600	106.75	109.18	-62.19	28.19	-946.65	-775.69	67.517
700	110.99	125.97	-70.13	39.09	-945.32	-747.30	55.754
800	114.16	141.00	-78.06	50.35	-943.85	-719.11	46.944
900	116.72	154.60	-85.82	61.90	-942.31	-691.10	40.103
1000	118.89	167.01	-93.33	73.68	-940.72	-663.28	34.640
1100	120.82	178.44	-100.56	85.67	-939.09	-635.61	30.177
1200	122.57	189.03	-107.49	97.84	-937.44	-608.10	26.465
1300	124.21	198.90	-114.15	110.18	-935.77	-580.72	23.329
1400	125.76	208.17	-120.54	122.68	-934.07	-553.47	20.646
1500	127.24	216.89	-126.67	135.33	-932.37	-526.34	18.326
1600	128.68	225.15	-132.57	148.13	-930.63	-499.33	16.298
1700	130.07	232.99	-138.25	161.06	-1029.23	-471.53	14.486
1800	131.44	240.47	-143.72	174.14	-1027.01	-438.79	12.731
1900	132.79	247.61	-149.00	187.35	-1024.67	-406.18	11.165
2000	134.11	254.46	-154.11	200.70	-1022.24	-373.69	9.758
2100	135.42	261.03	-159.04	214.17	-1019.70	-341.33	8.489
2200	136.72	267.36	-163.82	227.78	-1017.06	-309.09	7.337
2300	138.00	273.47	-168.46	241.52	-1014.31	-276.97	6.289
2400	139.28	279.37	-172.96	255.38	-1011.47	-244.97	5.331
2500	140.55	285.08	-177.33	269.37	-1008.49	-213.09	4.452

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Table II. Equilibrium Data for $\text{Si}_2\text{N}_2\text{O}(s)$

Ref.	Temp. range (K)	No. of points	Reaction [*]	$\Delta H_{f,298}^\circ$ (kJ/mol)		δS^\ddagger (J/mol · K)	$\text{Si}_2\text{N}_2\text{O}(s)$ ΔH_f° (298)
				2nd law	3rd law [†]		
Blegen 9	1775–1893	5 [§]	A	-929.3	-990.8 ± 15.9	33.5	-948.1 ± 11.3
Blegen 10	1480–1620	8	C	1475.3	1616.3 ± 4.6	-92.0	-901.6 ± 8.8
Colquhoun							
11, 18	1473–1623	3 [†]	B	-1411.7	-874.9 ± 26.8	-347.0	-874.9 ± 26.8
Ehlert 12	1260–1529	9 ^{**}	C ^{††}	1760.2	1779.9 ± 9.2	-14.2	-956.5 ± 10.0
Ehlert 12	1260–1581	33	C ^{††}	1730.1	1733.8 ± 0.2	-2.5	-941.0 ± 8.4
Ryall 13	1673–1773	2	D	881.2	862.7 ± 0.8	10.9	-948.1 ± 2.5
Ryall 13	1673–1773	2	A	-854.4	-915.4 ± 2.9	35.6	-910.4 ± 2.5
Wild 14	1557–1569	2	B		-890.4 ± 4.6		-890.4 ± 4.6

*Reactions: A: $3\text{Si}(s, l) + \text{SiO}_2(s) + 2\text{N}_2(g) = 2\text{Si}_2\text{N}_2\text{O}(s)$; B: $2\text{Si}(s) + \frac{1}{2}\text{O}_2(g) + \text{N}_2(g) = \text{Si}_2\text{N}_2\text{O}(s)$; C: $3\text{Si}_2\text{N}_2\text{O}(s) = 3\text{SiO}(g) + \text{N}_2(g) + \text{Si}_3\text{N}_4(s)$; D: $2\text{SiO}_2(s) + \text{N}_2(g) = \text{Si}_2\text{N}_2\text{O}(s) + \text{SiO}_2(g)$. Uncertainties are ± 1 standard deviation. $\delta S^\ddagger = (\Delta S_f^\ddagger)_{2\text{nd law}} - (\Delta S_f^\ddagger)_{3\text{rd law}}$. [§]One point at 1893 K excluded. [†]One point at 1573 K excluded. ^{**}One point at 1353 K excluded. ^{††} Al_2O_3 effusion cell. [‡] CaO -stabilized ZrO_2 effusion cell.

The drift indicates errors in either the equilibrium data or in the Gibbs energy functions used in the analysis. The results of the second- and third-law analyses are summarized in Table II and are discussed below.

Blegen⁹ studied the equilibrium between $\text{Si}_2\text{N}_2\text{O}$ and a mixture of SiO_2 and Si (in Fe–Si alloys) in N_2 atmosphere. Her results were recalculated using activity coefficient data for Si in Fe–Si alloys from Chart¹⁶ who has critically assessed thermodynamic data for the system Fe–Si. His results are in good agreement with the more recent evaluation of Schmid,¹⁷ and Chart's data were also used in Hendry's recalculation of equilibria in the system Si–N–O.¹⁸ JANAF⁶ data for SiO_2 (high cristobalite), $\text{Si}(s, l)$, and $\text{N}_2(g)$ were also used in the second- and third-law calculations. The first analysis of Blegen's data indicated that the 1893 K point was poor, so this point was dropped in the second analysis resulting in significantly better agreement between the second- and third-law heats of reaction.

Blegen¹⁰ also used a vacuum microbalance to study the decomposition of $\text{Si}_2\text{N}_2\text{O}$ by the Knudsen effusion method. Although Blegen was unable to determine the mechanism of decomposition from her results, later work by Ehlert *et al.*¹² (and references therein) has established that $\text{Si}_2\text{N}_2\text{O}$ decomposes to Si_3N_4 , $\text{SiO}(g)$, and $\text{N}_2(g)$. The second- and third-law analyses of Blegen's data for this decomposition mechanism are given in Table II.

Colquhoun *et al.*¹¹ studied the equilibrium between $\text{Si}_2\text{N}_2\text{O}$ and Si in Fe–Si alloys in an atmosphere with controlled O_2 and N_2 fugacities. Hendry¹⁸ recalculated their data using Chart's¹⁶ Si activity coefficient values and Hendry's points were analyzed. The first analysis indicated that the 1573 K point was poor and this point was dropped in the second analysis. However there is still a large disagreement between the second- and third-law heats of reaction which indicates either (1) that equilibrium was not reached in Colquhoun's study, or (2) that the Gibbs energy functions for $\text{Si}_2\text{N}_2\text{O}$ are seriously in error. Since the estimated uncertainty in the $\text{Si}_2\text{N}_2\text{O}$ Gibbs energy functions is, at most, equal to ± 4.2 J/mol · K, the large discrepancy between the second- and third-law heats of reaction

cannot be due solely to error in these functions. Furthermore, combined second- and third-law analyses of Colquhoun's equilibrium data¹¹ for Si_3N_4 formation, which are from the same study, also show large disagreements between the second- and third-law heats of reaction. These analyses, which use Gibbs energy functions for Si_3N_4 from Glushko *et al.*⁷ in combination with the analyses of the $\text{Si}_2\text{N}_2\text{O}$ equilibrium data indicate that equilibrium was apparently not attained in Colquhoun's study. Hendry¹⁸ has suggested that loss of Si from the Fe–Si alloy due to volatilization of $\text{SiO}(g)$ is responsible for Colquhoun's apparent failure to reach equilibrium.

Ehlert *et al.*¹² used mass spectrometry to study the decomposition of $\text{Si}_2\text{N}_2\text{O}$ to Si_3N_4 , $\text{SiO}(g)$, and $\text{N}_2(g)$ and did two sets of runs in two different effusion cell assemblies— Al_2O_3 and CaO —stabilized ZrO_2 . Their results were analyzed by the second- and third-law methods. JANAF⁶ data for $\text{SiO}(g)$ and $\text{N}_2(g)$ and Glushko *et al.*⁷ data for Si_3N_4 were used in the analyses. The first analysis of the data taken with the Al_2O_3 effusion cell indicated that the 1353 K point was poor and this point was dropped in the second analysis. The results in Table II indicate that the second- and third-law $\Delta H_{f,298}^\circ$ values are in good agreement and that the calculated $\text{Si}_2\text{N}_2\text{O}$ $\Delta H_{f,298}^\circ$ values are in good agreement with Blegen's heat of formation value from her Fe–Si equilibration work. However, the agreement between the ΔH_f° values from Ehlert's and Blegen's effusion studies is poor. The ΔH_f° values from Ehlert's study are assumed to be more reliable because the small entropy drifts indicate a close approach to equilibrium, while the large entropy drift in Blegen's effusion study suggests a failure to attain equilibrium.

Ryall and Muan¹³ studied two different $\text{Si}_2\text{N}_2\text{O}$ equilibria and their results were analyzed by both the second- and third-law methods. Their original data for one reaction (reaction A in Table II) appear to be in error since the N_2 pressure at 1500°C from their second table does not correspond with the N_2 pressure calculated at this temperature for the N_2 buffer which they used (Cr_2N –Cr). Furthermore, a combined second- and third-law analysis of their original data for reaction A shows a large

discrepancy between the second- and third-law heats of reaction (-595.0 versus -931.8 kJ/mol, respectively). Thus, the N_2 pressures at 1400° and 1500°C have been recalculated using the Cr_2N –Cr equilibrium data from Seybolt and Oriani,¹⁹ which is the reference cited by Ryall and Muan. The recalculated and original N_2 pressures are 0.06 and 0.05 atm, respectively, at 1400°C and 0.13 and 0.05 atm, respectively, at 1500°C. The second- and third-law heats of reaction in Table II, which are from the analysis of the recalculated data for Ryall and Muan's reaction A, show significantly better agreement than the heats of reaction calculated from the original data.

Finally, Wild *et al.*¹⁴ studied the same $\text{Si}_2\text{N}_2\text{O}$ equilibrium reaction as Colquhoun *et al.*¹¹ studied. Wild's data, which are at two closely spaced temperatures, were analyzed by the third-law method only and thus temperature dependent drifts could not be assessed. However, the third-law analysis of Wild's one data point for Si_3N_4 formation yields a heat of formation in fairly good agreement with the second- and third-law heats calculated from Blegen's data⁹ for Si_3N_4 . Furthermore Hendry's¹⁸ calculation of the Gibbs energy of formation for silica from Wild's data is in good agreement with values tabulated by JANAF. Thus, it appears that unlike Colquhoun's study, equilibrium was attained in Wild's study.

The selected $\Delta H_{f,298}^\circ$ value for $\text{Si}_2\text{N}_2\text{O}$ was calculated from three of the eight $\Delta H_{f,298}^\circ$ values listed in Table II. The $\Delta H_{f,298}^\circ$ values calculated from the studies by Blegen⁹ and Ehlert *et al.*¹² were used because these two studies showed small entropy drifts and comprised the large majority of the data points analyzed. The selected $\text{Si}_2\text{N}_2\text{O}$ $\Delta H_{f,298}^\circ$ value, which is the weighted average of these three values, is -947.7 ± 5.4 kJ/mol. The $\Delta H_{f,298}^\circ$ values from Blegen's effusion study¹⁰ and Colquhoun's study¹¹ were not used in the calculation because of the apparent failures to attain equilibrium in these two studies. Also, the three heats of formation from the investigations by Ryall and Muan¹³ and Wild *et al.*¹⁴ were not considered because only two experimental points were studied for each reaction, thus the uncertainties due to random and systematic errors were not

considered to be adequately established in these investigations. Therefore it was not thought desirable to include these results in a weighted average since the small uncertainties would disproportionately influence the calculated average. However, it should be noted that Ryall and Muan's $\Delta H_{f,298}^{\circ}$ value from reaction D is in excellent agreement with the selected heat of formation calculated above. Nevertheless, the discrepancies among the selected $\Delta H_{f,298}^{\circ}$ value, Ryall and Muan's $\Delta H_{f,298}^{\circ}$ value from reaction A, and Wild's $\Delta H_{f,298}^{\circ}$ value are disturbing and require exploration by further experimental work. Thus it may be desirable to determine the $\Delta H_{f,298}^{\circ}$ for $\text{Si}_2\text{N}_2\text{O}$ by fluorine bomb calorimetry, which has been applied to SiO_2 , SiC , and Si_3N_4 , or by other calorimetric methods.

The selected $\Delta H_{f,298}^{\circ}$ value, thermal functions for $\text{Si}_2\text{N}_2\text{O}$, and thermal functions for Si , O_2 , and N_2 in their reference states⁶ were then used to calculate the ΔH° , ΔG° , and $\log K$ values from 298 to 2500 K which are listed in Table I. Until further experimental work is done, it is believed that the functions listed in Table I represent the best available set of thermodynamic

data for $\text{Si}_2\text{N}_2\text{O}$ and it is hoped that these data will prove useful for thermodynamic calculations involving $\text{Si}_2\text{N}_2\text{O}$.

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